Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Hardness (Ca <sup>2+</sup> + Mg <sup>2+)</sup> EAWAG	until 1974	EDTA Titration (manual)	Titration with EDTA (0.05 M) at pH 10 (buffer: ammoniac) and visual detection of the end point of the filtered sample $[0.45 \mu m]$	0.05 mmol/l	ISO 6059:1984
	1975 - 1976	EDTA Titration (automated)	Titration with EDTA (0.05 M) at pH 10 (buffer: ammoniac) and photometric detection of the end point of the filtered sample [0.45 $\mu$ m]	0.02 mmol/l	
	1977 - 2006	EDTA Titration (automated)	Titration with EDTA (0.05 M) at pH 10 (buffer: borate) and photometric detection of the end point Since 1991: detection of the end point with ion-selective electrode of the filtered sample $[0.45 \ \mu m]$	0.2 mmol/l	
	since 2007	EDTA Titration (automated)	Titration with EDTA (0.025 M) at pH 10 (buffer: borate) and detection of the end point with ion-selective electrode of the filtered sample $[0.45 \mu m]$	0.2 mmol/l	
Hardness (Ca <sup>2+</sup> + Mg <sup>2+)</sup> AUE	2006 - 2010	EDTA Titration (automated)	Titration with Triplex R (Merck 1.09895, 0.0178mol/l an EDTA-Na <sub>2</sub> ) at pH 10 (buffer: borate) and potentiometric detection of the filtered sample [0.45 μm]	0.2 mmol/l	
	2011	EDTA Titration (automated)	Titration with Titriplex III – solvent (c(Na <sub>2</sub> -EDTA 2xH <sub>2</sub> O)=0.1 mol/I – Titrisol 1.09992.0001) with 10 % NH <sub>3</sub> and Eriochrome Black T, detection with Phototrode of the filtered sample [0.45 $\mu$ m]	0.09 mmol/l	
	since 2012	EDTA Titration (automated)	Titration with Triplex R (Merck 1.09895, 0.0178mol/l an EDTA-Na <sub>2</sub> ) at pH 10 (buffer: borate) and potentiometric detection of the filtered sample [0.45 µm]	0.089 mmol/l	
Alkalinity (H+-eq) EAWAG	until 1974	Acidimetric Titration (manual)	Titration of the filtered sample [0.45 $\mu$ m] with 0.1M HCl to the colour change of methyl orange	0.05 mmol/l	EN ISO 9963-1:1995
	1975 - 1989	Acidimetric Titration (automated)	Titration of the filtered sample $[0.45\mu m]$ with 0.1M HCl to pH 4.3 (m-value), potentiometric detection of the end point	0.02 mmol/l	
	since 1990	Acidimetric Titration (automated)	Titration of the filtered sample $[0.45\mu m]$ with 0.1M HCl to pH 4.5 (m-value), potentiometric detection of the end point	0.2 mmol/l	
Alkalinity (H+-eq) AUE	since 2006	Acidimetric Titration (automated)	Titration of the filtered sample $[0.45\mu m]$ with 0.1M HCl to pH 4.5 (m-value), potentiometric detection of the end point	2.0 mmol/l until 2008 0.2 mmol/l until 2010 0.05 mmol/l	
Calcium, Ca <sup>2+</sup>	until 1975	EDTA Titration (manual)	Titration with EDTA after precipitation of Mg <sup>2+</sup>	5 mg Ca/l	ISO 6058:1984
	since 1976	Calculation	Hardness minus magnesium	8 mg Ca/l	
Magnesium, Mg²+ EAWAG	until 1975 1976 - 1989	Calculation AAS	Hardness minus calcium  Direct air-acetylene flame method of the filtered sample [0.45 $\mu$ m]	1 mg Mg/l 0.05 mg Mg/l	EN ISO 7980:2000
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtered sample [0.45 $\mu$ m]	0.5 mg Mg/l	EN ISO 11885:2009
	since 2009	IC	Analysing of the filtered sample [0.45µm] with a cation-exchange column	0.5 mg Mg/l until 2017 1.0 mg Mg/l	EN ISO 14911:1999
Magnesium, Mg <sup>2+</sup> AUE	since 2006	IC	and detection by conductivity  Analysing of the filtered sample [0.45µm] with a cation-exchange column and detection by conductivity	1.0 mg Mg/l	
Potassium, K+ EAWAG	until 1989	AAS	Direct air-acetylene flame method of the filtered sample [0.45 $\mu$ m]	0.05 mg K/l	EN ISO 7980:2009
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtered sample [0.45 $\mu$ m]	0.1 mg K/l	EN ISO 11885:2009
	2009 - 2012 (July)	IC	Analysing of the filtered sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg K/l	EN ISO 14911:1999
	since 2012 (July)	AAS	Atom absorption spectrometry (contrAA 700 Analytik Jena)	0.05 mg K/l	
Potassium, K+ AUE	since 2006	IC	Analysing of the filtered sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg K/l	

Parameter	Year	Method	Details	Limit	s of determination	Method applied corresponding to
Sodium, Na+ EAWAG	until 1989	AAS	Direct air-acetylene flame method of the filtered sample [0.45 $\mu$ m]	0.05	mg Na/l	EN ISO 7980:2000
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtered sample [0.45 µm]	0.5	mg Na/l	EN ISO 11885:2009
	since 2009	IC	Analysing of the filtered sample $[0.45\mu m]$ with a cation-exchange column and detection by conductivity	0.5 1.0	mg Na/l until 2017 mg Na/l	EN ISO 14911:1999
odium, Na+ JUE	since 2006	IC	Analysing of the filtered sample [0.45 $\mu$ m] with a cation-exchange column and detection by conductivity	2.0	mg Na/l	
hloride, Cl <sup>-</sup> AWAG	until 1993	Ferricyanide method (CFA, photometric)	In the filtered sample [0.45µm] SCN <sup>-</sup> is liberated from Hg (SCN) <sub>2</sub> by the formation of soluble mercuric chloride. Free SCN <sup>-</sup> forms a highly coloured ferric thiocyanate (480nm).	0.5	mg Cl/l	EN ISO 15682:2001
	since 1994	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.5	mg Cl/l	EN ISO 10304-1:2007
Chloride, Cl <sup>-</sup> NUE	since 2006	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	1.5	mg CI/I	
luoride, F <sup>-</sup> AWAG	since 2020	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.05	mg F/I	
luoride, F <sup>-</sup> JUE	since 2017	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.03	mg F/I	
romide, Br <sup>-</sup> AWAG	since 2020	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.05	mg Br/l	
Bromide, Br- AUE	since 2017	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.01	mg Br/l	
oulfate, SO₄²- AWAG	until 1981	Indirect complexometric Titration	In the filtered sample $[0.45\mu m]$ two-valence cations are separated. Precipitation of $SO_4^{2-}$ with barium and titration of the surplus barium.	5	mg SO <sub>4</sub> /I	
	1982 - 1986	IC	Analysing of the filtered sample [0.45 $\mu$ m] with a anion-exchange column and detection by conductivity	1	mg SO <sub>4</sub> /I	EN ISO 10304-1:2007
	1987 - 1989	Methylthymol blue method (FIA, photometric)	Precipitation of BaSO <sub>4</sub> in the filtered sample [0.45 $\mu$ m]. Photometric detection of the remaining MTB-barium complex at 630 nm.	1	mg SO <sub>4</sub> /I	
	since 1990	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	1 5	mg SO <sub>4</sub> /l until 2000 mg SO <sub>4</sub> /l	EN ISO 10304-1:2007
ulfate, SO <sub>4</sub> <sup>2-</sup> JUE	since 2006	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	2.5	mg SO <sub>4</sub> /I	
Silicic acid H <sub>4</sub> SiO <sub>4</sub> EAWAG	1976 - 2001	Molybdosilicate method (CFA, photometric)	In the filtered sample [0.45µm] molybdate forms yellow molybdosilicic acids at pH 1.5, which is reduced by ascorbic acid to form blue molybdosilicic acid (660 nm). Oxalic acid is added to destroy the molybdophosphoric acid.	0.5	mg H <sub>4</sub> SiO <sub>4</sub> /l until 2000 mg H <sub>4</sub> SiO <sub>4</sub> /l	EN ISO 16264:2004
	since 2002	Molybdosilicate method (CFA, photometric)	In the filtered sample [0.45µm] molybdate forms yellow molybdosilicic acids at pH 1.5, which is reduced by ascorbic acid to form blue molybdosilicic acid (810 nm). Oxalic acid is added to destroy the molybdophosphoric acid.	1.0 0.5	mg H <sub>4</sub> SiO <sub>4</sub> /I until 2009 mg H <sub>4</sub> SiO <sub>4</sub> /I	ISO 16264:2004
illicic acid H <sub>4</sub> SiO <sub>4</sub> AUE	since 2006	Molybdosilicate method (CFA, photometric)	In the filtered sample [0.45µm] molybdate forms yellow molybdosilicic acids at pH 1.5, which is reduced by ascorbic acid to form blue molybdosilicic acid (820 nm). Oxalic acid is added to destroy the molybdophosphoric acid.	1.0 0.1 0.35	mg H <sub>4</sub> SiO <sub>4</sub> /l until 2010 mg H <sub>4</sub> SiO <sub>4</sub> /l until 2018 mg H <sub>4</sub> SiO <sub>4</sub> /l	

Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Nitrate, NO₃ <sup>-</sup> EAWAG	until 1993	Cadmium reduction method (CFA, photometric)	The $NO_3$ of the filtered sample [0.45 $\mu$ m] is reduced to $NO_2$ in the presence of Cd (Cd/Cu-alloy) at pH 8.5. The $NO_2$ is diazotizing with sulfanilamide and detected by photometry.	0.05 mg N/I	EN ISO 13395:1996
	1994 - 2004	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.1 mg N/l until 2000 0.2 mg N/l	EN ISO 10304-1:2007
	since 2005	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.2 mg N/l until 2017 0.25 mg N/l until 2019 0.1 mg N/l	EN ISO 10304-1:2007
		photometric	Samples with concentrations under 0.25 mg N/I: spiked with sodiumsalicylat and analysed at 420 nm	0.005 mg N/I until 2017 0.010 mg N/I until 2019 0.050 mg N/I	ISO 7980: 1986
Nitrate, NO₃ <sup>-</sup> AUE	2006 - 2009	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity	0.06 mg N/I	
		photometric	Samples with concentrations under 0.25 mg N/I: spiked with sodiumsalicylat and analysed at 420 nm	0.005 mg N/I	
	since 2010	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity and UV (215 nm)	0.060 mg N/I	
Ammonium, NH <sub>4</sub> + EAWAG	until 1986	CFA, photometric	Spiked with isocyanurat and salicylat ammonium forms indophenol, which is analysed by CFA	0.02 mg N/I	ISO 7150-1:1985 EN ISO 11732:2005
	since 2011	photometric	photometric detection (Berthelot'sche reaction)	0.005 mg N/I	
Ammonium, NH <sub>4</sub> + AUE	since 2006	photometric		0.01 mg N/l	
Nitrite, NO₂ <sup>-</sup> EAWAG	until 1986	CFA, photometric	The NO <sub>2</sub> is diazotizing with sulfanilamide and detected by photometry.	0.005 mg N/I	ISO 13395:1996
Nitrite, NO₂⁻ AUE	since 2006	IC	Analysing of the filtered sample [0.45µm] with an anion-exchange column and detection by conductivity and UV (215 nm)	0.004 mg N/I	
Kjeldahl-Nitrogen	until 1986		Distilling and analysing ammonium after oxidation under acidic digestion	0.1 mg N/I	
Total nitrogen N-tot EAWAG	1987 - 1997	Persulfate digestion method	Oxidation of all N-compounds in the unfiltered sample with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (pH 12.7, 120 °C, 1.1 bar). Norg+NH <sub>4</sub> +NO <sub>3</sub> is measured as NO <sub>3</sub>	0.1 mg N/I	EN ISO 11905-1:1998
	1998 - 2000	Combustion- chemiluminescence method	Combustion of the unfiltered sample with synthetic air at 680°C. NO <sub>2</sub> -is detected by chemiluminescence (Shimadzu)	0.1 mg N/I	pr EN 12260:2003
	2001 - 2006	Combustion- chemiluminescence method	Combustion of the unfiltered sample with synthetic air at 950°C. NO <sub>2</sub> -is detected by chemiluminescence (Elementar)	0.5 mg N/I	pr EN 12260:2003
	since 2007	Combustion- chemiluminescence method	Combustion of the unfiltered sample with synthetic air at 720°C. NO <sub>2</sub> -is detected by chemiluminescence (Shimadzu)	0.5 mg N/I	pr EN 12260:2003
Total nitrogen N-tot AUE	2006 - 2016	Combustion- chemiluminescence method	Combustion of the unfiltered sample with synthetic air at 720°C. NO <sub>2</sub> -is detected by chemiluminescence (Shimadzu)	0.45 mg N/l	
	since 2017	Combustion- chemiluminescence method	Combustion of the unfiltered sample with synthetic air at 720°C. NO <sub>2</sub> -is detected by chemiluminescence (Analytik Jena)	0.45 mg N/l until 2018 0.20 mg N/l	

## NADUF: Methods of the chemical Analysis (EAWAG and AUE)

Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Total phosphorus P- tot	until 1981	hydrogen peroxide digestion method	Oxidation of organic P with hydrogen peroxide in sulfuric acid	0.02 mg P/I	
EAWAG	since 1982	Persulfate digestion method	Oxidation of all P-comounds with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (pH 2, 120 °C, 1.1 bar). Porg+Ppoly+o-P is measured as o-P	0.01 mg P/l until 2000 0.005 mg P/l until 2008 0.003 mg P/l	EN 1189:2002
Total phosphorus P-tot AUE	since 2006	Persulfate digestion method	Oxidation of all P compounds in the unfiltered sample with $K_2S_2O_8$ (pH 2, 120 °C, 1.1 bar). Porg+Ppoly+o-P is measured as o-P	0.005 mg P/l until 2010 0.003 mg P/l	
Dissolved Reactive Phosphorus DRP Orthophosphate o-P EAWAG	until 2000	Ascorbic acid method (CFA, photometric)	In the filtered sample [0.45µm] molybdate forms yellow molybdophosphoric acids at pH 1, which is reduced by ascorbic acid to form blue molybdophosphoric acid (660 nm).	0.010 mg P/l until 1976 0.005 mg P/l until 1981 0.001 mg P/l until 1989 0.003 mg P/l	EN ISO DIS 15681:2004
	since 2001	photometric	In the filtered sample [0.45µm] molybdate forms yellow molybdophosphoric acids at pH 1, which is reduced by ascorbic acid to form blue molybdophosphoric acid (885 nm).	0.005 mg P/l until 2008 0.003 mg P/l until 2009 0.001 mg P/l	EN ISO 6874:2004
Dissolved Reactive Phosphorus DRP Orthophosphate o-P AUE	since 2006	photometric	In the filtered sample [0.45µm] molybdate forms yellow molybdophosphoric acids at pH 1, which is reduced by ascorbic acid to form blue molybdophosphoric acid (885 nm).	0.005 mg P/l until 2010 0.003 mg P/l	
Total phosphorus P-tot filtered	until 1981	hydrogen peroxide digestion method	Oxidation of organic P compounds in the filtered sample with hydrogen peroxide in sulfuric acid	0.02 mg P/I	
	since 2012	Persulfate digestion method	Oxidation of all P compounds in the filtered sample with $K_2S_2O_8$ (pH 2, 120 °C, 1.1 bar). Porg+Ppoly+o-P is measured as o-P	0.003 mg P/I	EN 1189:2002

## NADUF: Methods of the chemical Analysis (EAWAG and AUE)

Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Total suspended solids		Filtration and weighing	Filtration through a membrane filter [0,45 $\mu$ m]. After drying at 105 $^{\circ}$ C the membrane is weighted	1 mg/l	
Total organic carbon TOC EAWAG	until 1990	Combustion-infrared method	Combustion of the unfiltered sample with synthetic air at 950°C. CO <sub>2</sub> is measured in the gas stream by infrared (Beckman)	0.5 mg C/I	ISO 8245:1999 EN 1484:1997
	1991 - 2000	Combustion-infrared method	Combustion of the unfiltered sample with synthetic air at 680°C. CO <sub>2</sub> is measured in the gas stream by infrared (Shimadzu)	0.5 mg C/I	ISO 8245:1999 EN 1484:1997
	2001 - 2006	Combustion-infrared method	Combustion of the unfiltered sample with synthetic air at 950°C. CO <sub>2</sub> is measured in the gas stream by infrared (Elementar)	0.5 mg C/I	ISO 8245:1999 EN 1484:1997
	since 2007	Combustion-infrared method	Combustion of the unfiltered sample with synthetic air at 720°C. CO <sub>2</sub> is measured in the gas stream by infrared (Shimadzu)	0.5 mg C/I	ISO 8245:1999 EN 1484:1997
Total organic carbon TOC AUE	since 2006	Combustion-infrared method	Combustion of the unfiltered sample with synthetic air at 720°C. CO <sub>2</sub> is measured in the gas stream by infrared (Shimadzu)	0.1 mg C/l until 2015 0.25 mg C/l	
Dissolved organic carbon DOC EAWAG	until 1974	Combustion-infrared method	Combustion of the filtered sample [0.45µm] with synthetic air at 950°C. CO <sub>2</sub> is measured in the gas stream by infrared (Beckman)	0.5 mg C/I	ISO 8245:1999
	1975 - 1981	Combustion-infrared method	Combustion of the filtered sample $[0.45\mu m]$ with $O_2/N_2$ at $850^{\circ}$ C. $CO_2$ is measured in the gas stream by infrared (UNOR)	0.1 mg C/l	ISO 8245:1999
	1982 - 1991	Wet-oxidation- infrared method	Wet oxidation with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /UV (650 ° C) of the filtered sample [0.45µm]. CO <sub>2</sub> -CO <sub>2</sub> is measured in the gas stream by infrared (Dohrmann)	0.2 mg C/I	ISO 8245:1999
	1991 -2000	Combustion-infrared method	Combustion with synthetic air at 680°C of the filtered sample [0.45µm]. CO <sub>2</sub> is measured in the gas stream by infrared (Shimadzu)	0.2 mg C/I	ISO 8245:1999
	2001 - 2006	Combustion-infrared method	Combustion with synthetic air at 950°C of the filtered sample [0.45µm]. CO <sub>2</sub> is measured in the gas stream by infrared (Elementar)	0.5 mg C/I	ISO 8245:1999
	since 2007	Combustion-infrared method	Combustion with synthetic air at 720°C of the filtered sample [0.45µm]. CO <sub>2</sub> is measured in the gas stream by infrared (Shimadzu)	0.5 mg C/I	ISO 8245:1999 EN 1484:1997
Dissolved organic carbon DOC AUE	since 2006	Combustion-infrared method	Combustion with synthetic air at $720^{\circ}$ C of the filtered sample [0.45 $\mu$ m]. CO <sub>2</sub> is measured in the gas stream by infrared (Shimadzu)	0.1 mg C/l until 2015 0.25 mg C/l	

Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Zinc, Zn¹	until 1980	AAS	Direct air-acetylene flame absorption of the acidified sample (0.01 M HNO <sub>3</sub> )	10 μg Zn/l until Feb. 1978 1 μg Zn/l	ISO 8288:1986
	1981 - 1990	AAS after enrichment	Direct air-acetylene flame absorption of the acidified (0.01 M HNO <sub>3</sub> ) and evaporated sample	1 μg Zn/l	ISO 8288:1986
	1991 - 1994	AAS after enrichment	Enrichment by extraction with APDC-DDC of the acidified (0.01 M HNO <sub>3</sub> ) sample followed by air-acetylene flame absorption	1 μg Zn/l	
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.1 μg Zn/l until 2000 1.0 μg Zn/	ISO 17294:2003
Copper, Cu <sup>1</sup>	until 1980	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO <sub>3</sub> )	1 μg Cu/l	ISO 15586:2003
	1981 - 1982	ET AAS after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO <sub>3</sub> )	0.5 μg Cu/l	ISO 15586:2003
	1983 - 1994	ET AAS after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO <sub>3</sub> )	0.5 μg Cu/l	ISO 15586:2003
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.05 μg Cu/l until 2000 0.1 μg Cu/l until 2006 0.5 μg Cu/l	ISO 17294:2003
Lead, Pb¹	until 1980	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO <sub>3</sub> )	1 μg Pb/I	ISO 15586:2003
	1981 - 1990	ET AAS after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO <sub>3</sub> )	0.2 μg Pb/l	ISO 15586:2003
	1991 - 1994	ET AAS after enrichment	Enrichment by extraction with APDC-DDC of the acidified (0.01 M HNO <sub>3</sub> ) sample followed by atomic absorption spectrometry with graphite furnace	0.2 μg Pb/l	ISO 15586:2003
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.1 μg Pb/l	ISO 17294:2003
Cadmium, Cd <sup>1</sup>	until 1980	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO <sub>3</sub> )	0.2 μg Cd/l	ISO 15586:2003
	1981 - 1990	ET AAS after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO <sub>3</sub> )	0.02 μg Cd/l	ISO 15586:2003
	1991 - 1994	ET AAS after enrichment	Enrichment by extraction with APDC-DDC of the acidified (0.01 M HNO <sub>3</sub> ) followed by atomic absorption spectrometry with graphite furnace	0.02 μg Cd/l	ISO 15586:2003
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.01 μg Cd/l until 2000 0.02 μg Cd/l	ISO 17294:2003
Chromium, Cr <sup>1</sup>	1985 - 1994	ET AAS after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO <sub>3</sub> )	0.5 μg Cr/l	ISO 15586:2003
	1995 - 2000	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.1 μg Cr/l	ISO 17294:2003
	2001 - 2007	Et AAS	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO <sub>3</sub> )	0.2 μg Cr/l	ISO 15586:2003
	since 2008	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.2 μg Cr/l	ISO 17294:2003
Mangan, Mn¹	since 2021	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	1.0 μg Mn/l	ISO 17294:2003

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<sup>&</sup>lt;sup>1</sup> These are acid-soluble concentrations corresponding closely to total concentrations, apart from small proportions of certain elements that are more firmly attached to suspended material.

Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Nickel, Ni <sup>1</sup>	1985 - 1994	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO <sub>3</sub> )	0.5 μg Ni/I	ISO 15586:2003
	1995 - 2000	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.1 μg Ni/l	ISO 17294:2003
	2001 - 2007	Et AAS	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO <sub>3</sub> )	0.5 μg Ni/I	ISO 15586:2003
	since 2008	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO <sub>3</sub> )	0.5 μg Ni/I	ISO 17294:2003
Iron, Fe <sup>1</sup> EAWAG	until 1989	AAS	Direct air-acetylene flame absorption of the acidified sample (0.01 M HNO <sub>3</sub> )	25 μg Fe/l	ISO 8288:1986
Iron, Fe <sup>1</sup> AUE	since 2020	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO3)	10 μg Fe/l	ISO 17294:2003
Mercury, Hg <sup>1</sup>	until 1989	Cold-vapour-AAS	Atomic absorption spectrometry with cold vapour after digestion with permanganate/peroxydisulfate	0.05 μg Hg/l	ISO 5666-1:1983
	1990 - 1998	Cold-vapour-AAS after enrichment	Atomic absorption spectrometry with cold vapour of the acidified (K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /H <sub>2</sub> SO <sub>4</sub> ) and with amalgam enriched sample	0.01 μg Hg/l	EN 12338:1998
	1999 - 2001	Cold-vapour-AAS after enrichment	Atomic absorption spectrometry with cold vapour of the acidified (K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /H <sub>2</sub> SO <sub>4</sub> ) and with amalgam enriched sample. Three times enlarged injection quantity	0.002 μg Hg/l until 2000 0.01 μg Hg/l	EN 12338:1998
	2001 - Aug 2008	Cold-vapour-AAS	Atomic absorption spectrometry with cold vapour of the with SnCl <sub>2</sub> reduced sample.  Pretreatment: oxidation with CrVI and HNO <sub>3</sub>	0.01 μg Hg/l	
	Sept 2008 - Oct 2011	Cold-vapour-AAS	Atomic absorption spectrometry with cold vapour of the with SnCl <sub>2</sub> reduced sample.  Pretreatment: oxidation with H <sub>2</sub> O <sub>2</sub> and UV irradiation	0.01 μg Hg/l	
	since Nov 2011	Cold-vapour-AAS	Atomic absorption spectrometry with cold vapour of the with SnCl <sub>2</sub> reduced sample.  Pretreatment: oxidation Br <sup>-</sup> /BrO <sub>3</sub> <sup>-</sup>	0.005 μg Hg/l	ISO 17294:2003
Barium, Ba <sup>1</sup>	since 2017	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO3)	0.5 μg Ba/l	ISO 17294:2003
Strontium, Sr <sup>1</sup>	since 2017	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO3)	5 μg Sr/l	ISO 17294:2003
Arsenic, As <sup>1</sup>	since 2008	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO3)	0.5 μg As/l	ISO 17294:2003
4-Nonylphenol, NP	1983-1998	HPLC	HPLC with hexane/isopropanol and fluorescence detection	0.09 μg /l	
4-Nonylphenol- monoethoxylate, NP1EO	1983-1998	HPLC	HPLC with hexane/isopropanol and fluorescence detection	0.08 μg /l	
4-Nonylphenoldi- ethoxylate, NP2EO	1983-1998	HPLC	HPLC with hexane/isopropanol and fluorescence detection	0.08 μg /l	
4-Nonylphenoltri- ethoxylat, NP3EO	1983-1998	HPLC	HPLC with hexane/isopropanol and fluorescence detection	0.08 μg /l	

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<sup>&</sup>lt;sup>1</sup> These are acid-soluble concentrations corresponding closely to total concentrations, apart from small proportions of certain elements that are more firmly attached to suspended material.