

NADUF: Methods of the chemical Analysis (EAWAG)

Parameter	Year	Method	Details	Limits of determination	Method applied corresponding to
Hardness (Ca ²⁺ + Mg ²⁺)	until 1974	EDTA Titration (manual)	Titration with EDTA (0.05 M) at pH 10 (buffer: ammoniac) and visual detection of the end point	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	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	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	0.2 mmol/l	
Alkalinity (H ⁺ -eq)	until 1974	Acidimetric Titration (manual)	Titration of the filtrated sample [0.45µm] with 0.1M HCl to the colour change of methyl orange	0.05 mmol/l	EN ISO 9963-1:1994
	1975 - 1989	Acidimetric Titration (automated)	Titration of the filtrated sample [0.45µm] 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 filtrated sample [0.45µm] with 0.1M HCl to pH 4.5 (m-value), potentiometric detection of the end point	0.2 mmol/l	
Calcium, Ca ²⁺	until 1975	EDTA Titration (manual)	Titration with EDTA after precipitation of Mg ²⁺	5 mg Ca/l	
	since 1976	Calculation	Hardness minus magnesium	1 mg Ca/l	
Magnesium, Mg ²⁺	until 1975	Calculation	Hardness minus calcium	1 mg Mg/l	
	1976 - 1989	AAS	Direct air-acetylene flame method of the filtrated sample [0.45 µm]	0.05 mg Mg/l	EN ISO 7890:1988
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtrated sample [0.45 µm]	0.5 mg Mg/l	EN ISO 11885:1998
	since 2009	IC	Analysing of the filtrated sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg Mg/l	
Potassium, K ⁺	until 1989	AAS	Direct air-acetylene flame method of the filtrated sample [0.45 µm]	0.05 mg K/l	EN ISO 7890:1988
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtrated sample [0.45 µm]	0.1 mg K/l	EN ISO 11885:1998
	since 2009	IC	Analysing of the filtrated sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg K/l	
Sodium, Na ⁺	until 1989	AAS	Direct air-acetylene flame method of the filtrated sample [0.45 µm]	0.05 mg Na/l	EN ISO 7890:1988
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtrated sample [0.45 µm]	0.5 mg Na/l	EN ISO 11885:1998
	since 2009	IC	Analysing of the filtrated sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg Na/l	
Chloride, Cl ⁻	until 1993	Ferricyanide method (CFA, photometric)	In the filtrated sample [0.45µm] SCN ⁻ is liberated from Hg(SCN) ₂ by the formation of soluble mercuric chloride. Free SCN ⁻ forms a highly coloured ferric thiocyanate (480nm).	0.5 mg Cl/l	EN ISO 15682:2001
	since 1994	IC	Analysing of the filtrated sample [0.45µm] with a anion-exchange column and detection by conductivity	0.5 mg Cl/l	EN ISO 10304-1:1995
Sulfate, SO ₄ ²⁻	until 1981	Indirect complexometric Titration	In the filtrated sample [0.45µm] two-valence cations are separated. Precipitation of SO ₄ ²⁻ with barium and titration of the surplus barium.	5 mg SO ₄ /l	
	1982 - 1986	IC	Analysing of the filtrated sample [0.45µm] with a anion-exchange column and detection by conductivity	1 mg SO ₄ /l	EN ISO 10304-1:1995
	1987 - 1989	Methylthymol blue method (FIA, photometric)	Precipitation of BaSO ₄ in the filtrated sample [0.45µm]. Photometric detection of the remaining MTB-barium complex at 630 nm.	1 mg SO ₄ /l	
	since 1990	IC	Analysing of the filtrated sample [0.45µm] with a anion-exchange column and detection by conductivity	1 mg SO ₄ /l until 2000 5 mg SO ₄ /l	EN ISO 10304-1:1995
Silicic acid H ₄ SiO ₄	1976 - 2001	Molybdosilicate method (CFA, photometric)	In the filtrated 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 ₄ SiO ₄ /l until 2000 1 mg H ₄ SiO ₄ /l	ISO 16264:2002
	since 2002	Molybdosilicate method (CFA, photometric)	In the filtrated 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 mg H ₄ SiO ₄ /l until 2009 0.5 mg H ₄ SiO ₄ /l	ISO 16264:2002

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Nitrate, NO ₃ ⁻	until 1993	Cadmium reduction method (CFA, photometric)	The NO ₃ of the filtrated sample [0.45µm] 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/l	EN ISO 13395:1996
	1994 - 2004	IC	Analysing of the filtrated sample [0.45µm] with a anion-exchange column and detection by conductivity	0.1 mg N/l until 2000 0.2 mg N/l	EN ISO 10304-1:1995
	since 2005	IC	Analysing of the filtrated sample [0.45µm] with a anion-exchange column and detection by conductivity	0.2 mg N/l	EN ISO 10304-1:1995
		photometric	Spiked with sodiumsalicylat and analysed at 420 nm	0.005 mg N/l	DIN 38 405-29
Ammonium	until 1985	CFA, photometric	Spiked with isocyanurat and salicylat ammonium forms indophenol, which is analysed by CFA	0.02 mg N/l	ISO 7150-2:1988 EN ISO 11732:2005
Nitrite	until 1985	CFA, photometric	The NO ₂ is diazotizing with sulfanilamide and detected by photometry.	0.005 mg N/l	ISO 13395:1996
Kjeldahl-Nitrogen	until 1985		Distilling and analysing ammonium after oxidation under acidic pulping	0.1 mg N/l	
Total nitrogen N-tot	1987 - 1997	Persulfate digestion method	Oxidation of all N-compounds with K ₂ S ₂ O ₈ (pH 12.7, 120 °C, 1.1 bar). Norg+NH ₄ +NO ₃ is measured as NO ₃	0.1 mg N/l	EN ISO 11905-1:1998
	1998 - 2000	Combustion-chemoluminescence method	Combustion with synthetic air at 680°C. NO ₂ -is detected by chemoluminescence (Shimadzu)	0.1 mg N/l	pr EN 12260:2002
	2001 - 2006	Combustion-chemoluminescence method	Combustion with synthetic air at 950°C. NO ₂ -is detected by chemoluminescence (Elementar)	0.5 mg N/l	pr EN 12260:2002
	since 2007	Combustion-chemoluminescence method	Combustion with synthetic air at 720°C. NO ₂ -is detected by chemoluminescence (Shimatsu)	0.5 mg N/l	pr EN 12260:2002
Total phosphorus P-tot	until 1981	hydrogen peroxide digestion method	Oxidation of organic P with hydrogen peroxide in sulfuric acid	0.02 mg P/l	
	since 1982	Persulfate digestion method	Oxidation of all P-compounds with K ₂ S ₂ O ₈ (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
Dissolved Reactive Phosphorus DRP (since 2010)	until 2000	Ascorbic acid method (CFA, photometric)	In the filtrated sample [0.45µm] molybdate forms yellow molybdosilicic acids at pH 1, which is reduced by ascorbic acid to form blue molybdosilicic acid (660 nm).	0.005 mg P/l until 1981 0.001 mg P/l until 1989 0.003 mg P/l	ISO DIS:15681
Orthophosphate o-P (until 2010)	since 2001	Ascorbic acid method (manual, photometric)	In the filtrated sample [0.45µm] molybdate forms yellow molybdosilicic acids at pH 1, which is reduced by ascorbic acid to form blue molybdosilicic acid (885 nm).	0.005 mg P/l until 2009 0.003 mg P/l until 2010 0.001 mg P/l	EN 1189:1996
Total suspended solids		Filtration and weighing	Filtration through a membrane filter [0,45 µm]. After drying at 105 ° C the membrane is weighted	1 mg/l	
Total organic carbon TOC	until 1990	Combustion-infrared method	Combustion with synthetic air at 950°C. CO ₂ is measured in the gas stream by infrared (Beckman)	0.5 mg C/l	ISO 8245:1987 EN 1484:1997
	1991 - 2000	Combustion-infrared method	Combustion with synthetic air at 680°C. CO ₂ is measured in the gas stream by infrared (Shimadzu)	0.5 mg C/l	ISO 8245:1987 EN 1484:1997
	2001 - 2006	Combustion-infrared method	Combustion with synthetic air at 950°C. CO ₂ is measured in the gas stream by infrared (Elementar)	0.5 mg C/l	ISO 8245:1987 EN 1484:1997
	since 2007	Combustion-infrared method	Combustion with synthetic air at 720°C. CO ₂ is measured in the gas stream by infrared (Shimatsu)	0.5 mg C/l	ISO 8245:1987 EN 1484:1997
Dissolved organic carbon DOC	until 1974	Combustion-infrared method	Combustion of the filtrated sample [0.45µm] with synthetic air at 950°C. CO ₂ is measured in the gas stream by infrared (Beckman)	0.5 mg C/l	ISO 8245:1987
	1975 - 1981	Combustion-infrared method	Combustion of the filtrated sample [0.45µm] with O ₂ /N ₂ at 850°C. CO ₂ is measured in the gas stream by infrared (UNOR)	0.1 mg C/l	ISO 8245:1987
	1982 - 1991	Wet-oxidation-infrared method	Wet oxidation with K ₂ S ₂ O ₈ /UV (650 ° C) of the filtrated sample [0.45µm]. CO ₂ -CO ₂ is measured in the gas stream by infrared (Dohrmann)	0.2 mg C/l	ISO 8245:1987
	1991 -2000	Combustion-infrared method	Combustion with synthetic air at 680°C of the filtrated sample [0.45µm]. CO ₂ is measured in the gas stream by infrared (Shimadzu)	0.2 mg C/l	ISO 8245:1987
	since 2001	Combustion-infrared method	Combustion with synthetic air at 690°C of the filtrated sample [0.45µm]. CO ₂ is measured in the gas stream by infrared (Elementar)	0.5 mg C/l	ISO 8245:1999

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Zinc, Zn	until 1980	AAS	Direct air-acetylene flame absorption of the acidified sample (0.01 M HNO ₃)	10 µg Zn/l until 1976 1 µg Zn/l	ISO 8288:1986
	1981 - 1990	AAS after enrichment	Direct air-acetylene flame absorption of the acidified (0.01 M HNO ₃) 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 ₃) 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 ₃)	0.1 µg Zn/l until 2000 1.0 µg Zn/	ISO DIS 17294:2001
Copper, Cu	until 1980	AAS-GF	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	1 µg Cu/l	ISO DIS 15586:2001
	1981 - 1982	AAS-GF after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO ₃)	0.5 µg Cu/l	ISO DIS 15586:2001
	1983 - 1994	AAS-GF after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	0.5 µg Cu/l	ISO DIS 15586:2001
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample(0.01 M HNO ₃)	0.05 µg Cu/l until 2000 0.1 µg Cu/l until 2006 0.5 µg Cu/l	ISO DIS 17294:2001
Lead, Pb	until 1980	AAS-GF	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	1 µg Pb/l	ISO DIS 15586:2001
	1981 - 1990	AAS-GF after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO ₃)	0.2 µg Pb/l	ISO DIS 15586:2001
	1991 - 1994	AAS-GF after enrichment	Enrichment by extraction with APDC-DDC of the acidified (0.01 M HNO ₃) sample followed by atomic absorption spectrometry with graphite furnace	0.2 µg Pb/l	ISO DIS 15586:2001
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample(0.01 M HNO ₃)	0.1 µg Pb/l	ISO DIS 17294:2001
Cadmium, Cd	until 1980	AAS-GF	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	0.2 µg Cd/l	ISO DIS 15586:2001
	1981 - 1990	AAS-GF after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO ₃)	0.02 µg Cd/l	ISO DIS 15586:2001
	1991 - 1994	AAS-GF after enrichment	Enrichment by extraction with APDC-DDC of the acidified (0.01 M HNO ₃) followed by atomic absorption spectrometry with graphite furnace	0.02 µg Cd/l	ISO DIS 15586:2001
	since 1995	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample(0.01 M HNO ₃)	0.01 µg Cd/l until 2000 0.02 µg Cd/l	ISO DIS 17294:2001
Chromium, Cr (total)	1985 - 1994	AAS-GF after enrichment	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO ₃)	0.5 µg Cr/l	ISO DIS 15586:2001
	1995 - 2000	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample(0.01 M HNO ₃)	0.1 µg Cr/l	ISO DIS 17294:2001
	2001 - 2006	AAS-GF		0.2 µg Cr/l	
	since 2007	EtAAS		0.2 µg Cr/l	
Nickel, Ni	1985 - 1994	AAS-GF	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	0.5 µg Ni/l	ISO DIS 15586:2001
	1995 - 2000	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample(0.01 M HNO ₃)	0.1 µg Ni/l	ISO DIS 17294:2001
	2001 - 2006	AAS-GF		0.5 µg Ni/l	
	since 2007	EtAAS		0.5 µg Ni/l	
Iron, Fe	until 1988	AAS	Direct air-acetylene flame absorption of the acidified sample (0.01 M HNO ₃)	25 µg Fe/l	ISO 8288:1986

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Mercury, Hg	until 1989	Cold-vapour-AAS	Atomic absorption spectrometry with cold vapour after digestion with permanganate/peroxodisulfate	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 ₂ S ₂ O ₈ /H ₂ SO ₄) and with amalgam enriched sample	0.01 µg Hg/l	EN 12338:1998
	since 1999	Cold-vapour-AAS after enrichment	Atomic absorption spectrometry with cold vapour of the acidified (K ₂ S ₂ O ₈ /H ₂ SO ₄) 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
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-Nonylphenoldiethoxylate, NP2EO	1983-1998	HPLC	HPLC with hexane/isopropanol and fluorescence detection	0.08 µg /l	
4-Nonylphenoltriethoxylat, NP3EO	1983-1998	HPLC	HPLC with hexane/isopropanol and fluorescence detection	0.08 µg /l	