

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 9963-1:1995
	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	ISO 6058:1984
	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 7980:2000
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtrated sample [0.45 µm]	0.5 mg Mg/l	EN ISO 11885:2009
	since 2009	IC	Analysing of the filtrated sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg Mg/l	EN ISO 14911:1999
Potassium, K ⁺	until 1989	AAS	Direct air-acetylene flame method of the filtrated sample [0.45 µm]	0.05 mg K/l	EN ISO 7980:2009
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtrated sample [0.45 µm]	0.1 mg K/l	EN ISO 11885:2009
	2009 - 2012 (July)	IC	Analysing of the filtrated 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 spektrometry (contrAA 700 Analytik Jena)	0.05 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 7980:2000
	1990 - 2008	ICP-AES	Inductively coupled plasma atomic emission spectrometry of the filtrated sample [0.45 µm]	0.5 mg Na/l	EN ISO 11885:2009
	since 2009	IC	Analysing of the filtrated sample [0.45µm] with a cation-exchange column and detection by conductivity	0.5 mg Na/l	EN ISO 14911:1999
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 10304-1:2007
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 10304-1:2007
	1987 - 1989	Methylthymol blue method (FIA, photometric)	Precipitation of BaSO ₄ in the filtrated sample [0.45µm]. Photometric detection of the remaining MTB-barium complexe 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 10304-1:2007
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	EN ISO 16264:2004
	since 002	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 16264:2004

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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 10304-1:2007
	since 2005	IC	Analysing of the filtrated sample [0.45µm] with a anion-exchange column and detection by conductivity		0.2 mg N/l
photometric		Samples with concentrations under 0.2 mg N/l: spiked with sodiumsalicylat and analysed at 420 nm		0.005 mg N/l	ISO 7980: 1986
Ammonium	until 1986	CFA, photometric	Spiked with isocyanurat and salicylat ammonium forms indophenol, which is analysed by CFA	0.02 mg N/l	ISO 7150-1:1985 EN ISO 11732:2005
Nitrite	until 1986	CFA, photometric	The NO ₂ is diazotizing with sulfanilamide and detected by photometry.	0.005 mg N/l	ISO 13395:1996
Kjeldahl-Nitrogen	until 1986		Distilling and analysing ammonium after oxidation under acidic digestion	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 12260:2003
	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 12260:2003
	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 12260:2003
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	EN ISO DIS 15681:2004
Orthophosphate o-P (until 2010)	since 2001	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 2008 0.003 mg P/l until 2009 0.001 mg P/l	EN ISO 6874:2004

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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 8245:1999 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 8245:1999 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 8245:1999 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 8245:1999 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 8245:1999
	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 8245:1999
	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 8245:1999
	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 8245:1999
	2001 - 2006	Combustion-infrared method	Combustion with synthetic air at 950°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
	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 8245:1999 EN 1484:1997

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Zinc, Zn ¹	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/l	ISO 17294:2003
Copper, Cu ¹	until 1980	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	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 ₃)	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 ₃)	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 ₃)	0.05 µg Cu/l until 2000 0.1 µg Cu/l until 2006 0.5 µg Cu/l	ISO 17294:2003
Lead, Pb ¹	until 1980	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	1 µg Pb/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 ₃)	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 ₃) 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 ₃)	0.1 µg Pb/l	ISO 17294:2003
Cadmium, Cd ¹	until 1980	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	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 ₃)	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 ₃) 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 ₃)	0.01 µg Cd/l until 2000 0.02 µg Cd/l	ISO 17294:2003
Chromium, Cr ¹	1985 - 1994	ET AAS 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 15586:2003
	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 17294:2003
	2001 - 2007	Et AAS	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO ₃)	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 ₃)	0.2 µg Cr/l	ISO 17294:2003

¹ 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.

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Nickel, Ni ²	1985 - 1994	ET AAS	Atomic absorption spectrometry with graphite furnace of the acidified sample (0.01 M HNO ₃)	0.5 µg Ni/l	ISO 15586:2003
	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 17294:2003
	2001 - 2007	Et AAS	Atomic absorption spectrometry with graphite furnace of the acidified and evaporated sample (0.01 M HNO ₃)	0.5 µg Ni/l	ISO 15586:2003
	since 2008	ICP-MS	Inductively coupled plasma mass spectrometry of the acidified and decanted sample (0.01 M HNO ₃)	0.5 µg Ni/l	ISO 17294:2003
Iron, Fe ¹	until 1989	AAS	Direct air-acetylene flame absorption of the acidified sample (0.01 M HNO ₃)	25 µg Fe/l	ISO 8288:1986
Mercury, Hg ¹	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-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	

² 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.