



**New Method Code
for ICP Forests
Ringtests and QA forms
(Nils König, Alfred Fürst)**





Necessity of a new method code:

1. Different codes for the ringtests and the QA-forms (database)
2. Method codes for deposition and soil solution must be harmonized with soil and foliage
3. Unclear codes for some methods
4. Harmonisation of the code structure (e.g. sieving/milling, pretreatment, determination)
5. Simplification of the code



Timetable

- Extra QA/QC Group Meeting in Vienna - First Draft elaborated from Nils König & Alfred Fürst in June 2014
- Submitted a first draft to the Chairs of the EP Depo, Soil Solution, Soil, Foliage and Litterfall and all ringtest providers
- Feedback was included in the final version
- Final version was finished in September 2014

What is new?

- Codes for **sample preparation**
 - Soil
 - Deposition & Soil Solution
- Codes for **pretreatment**
 - Soil
 - Foliage and Litterfall
- Codes for **determination**
 - Soil
 - Deposition & Soil Solution
 - Foliage and Litterfall

Meeting of the Working Group QA/QC in Labs 22. April, Göttingen (Germany)



Old structure of the method code:

Sieving/Milling Method	Code Removal Compounds	Digestion/Extraction Method (Pretreatment)			Determination Method			
SO	SO	SO	DE	FO/LI/GB	SO	DE	SS	FO/LI/GB

New structure of the method code:

Sample preparation		Pretreatment		Determination		
SO	DE/SS	FO/LF/GB	SO	FO/LF/GB	SO	DE/SS



Structure of the code

- Character 4 byte long (as it was in the past)
- First letter
 - M = Sample preparation
 - P = Pretreatment
 - D = Determination
- Second letter A-Z (groups of similar methods)
 - PD = Microwave pressure digestion methods
 - DA = Element analyzer
- Third & fourth are serially numbered
 - PD01 = Microwave pressure digestion HNO₃
 - PD02 = Microwave pressure digestion HNO₃/H₂O₂
 - PD99 = Other microwave pressure digestion method

Benefits of the new code system

- Useable for all surveys and ringtests (soil, soil solution, deposition, foliage and litterfall)
- Fade in or fade out code numbers
- Add new method groups
- Delete or fade out method groups
- Shorten the code list dramatically

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New method code sample preparation:

		SO	DE/SS
	Sieving and Milling		
MA01	No sieving and milling	X	
MA02	Sieving and/or crushing mesh size < 2 mm	X	
MA03	Sieving and/or crushing other mesh size	X	
MA04	Milling to 150 micrometer	X	
MA05	Milling as fine as possible	X	
MA99	Other sieving and milling method	X	
	Filtration		
MB01	No filtration		X
MB02	Filtration with membrane filter 0,45 µm		X
MB03	Filtration with membrane filter 0,45 µm and prefiltration with glass fibre filter		X
MB04	Filtration with paper filters (Schwarzband)		X
MB99	Other filtration method		X

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New method code pretreatment (1):

		FO/LF/GB	SO
	Extraction methods		
PA01	Extraction H ₂ O		X
PA02	Extraction CaCl ₂		X
PA03	Extraction single BaCl ₂		X
PA04	Extraction triple BaCl ₂		X
PA05	Extraction with Acid Ammonium Oxalate		X
PA06	Extraction with diluted HNO ₃	X	
PA99	Other extraction method	X	X

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New method code pretreatment (2):

		FO/LF/GB	SO
	Digestion methods (open system)		
PB01	Aqua regia (HCl/HNO ₃ ; 3/1) extract		X
PB02	Open digestion with H ₂ SO ₄ /H ₂ O ₂	X	
PB03	Open digestion with HNO ₃	X	
PB04	Open digestion with HNO ₃ /H ₂ SO ₄	X	
PB05	Open digestion with HNO ₃ /H ₂ O ₂	X	
PB06	Open digestion with HNO ₃ /HClO ₄	X	
PB07	Kjeldahl H ₂ SO ₄ with Se or Cu catalyst	X	
PB08	Modified Kjeldahl H ₂ SO ₄ with Ti/Cu catalyst	X	X
PB09	Total digestion with HF/HClO ₄		X
PB10	Total digestion with LiBO ₂		X
PB99	Other digestion method (open system)	X	X

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New method code pretreatment (3):

		FO/LF/GB	SO
	Digestion methods (open system)		
PB01	Aqua regia (HCl/HNO ₃ ; 3/1) extract		X
PB02	Open digestion with H ₂ SO ₄ /H ₂ O ₂	X	
PB03	Open digestion with HNO ₃	X	
PB04	Open digestion with HNO ₃ /H ₂ SO ₄	X	
PB05	Open digestion with HNO ₃ /H ₂ O ₂	X	
PB06	Open digestion with HNO ₃ /HClO ₄	X	
PB07	Kjeldahl H ₂ SO ₄ with Se or Cu catalyst	X	
PB08	Modified Kjeldahl H ₂ SO ₄ with Ti/Cu catalyst	X	X
PB09	Total digestion with HF/HClO ₄		X
PB10	Total digestion with LiBO ₂		X
PB99	Other digestion method (open system)	X	X

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New method code pretreatment (4):

		FO/LF/GB	SO
	Dry ashing digestion methods		
PE01	Oxygen ashing (Schöniger)	X	
PE99	Other dry ashing methods	X	
	Other methods		
PZ01	Material melted and formed (tablet) for XRF methods	X	X
PZ02	Material pressed (pellet) for XRF methods	X	X
PZ98	No pretreatment	X	X
PZ99	Pretreatment method not in this list	X	X

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New method code determination (1):

		FO/LF/GB	SO	DE/SS
	Element analyzer			
DA01	Macro Elemental-analyzers for C, N or S for solids (Sample > 100mg)	X	X	
DA02	Micro Elemental-analyzers for C, N or S for solids (Sample ≤ 100mg) with an extra milling step	X	X	
DA03	TOC/TN Analyzers (total organic C/total N-Analyzer) for liquids			X
DA04	CO ₃ -Determination, Calcimeter (Scheibler unit)		X	
DA05	Hg-Analyzer	X	X	X
DA99	Other Element analyzers methods	X	X	X

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New method code determination (2):

		FO/LF/GB	SO	DE/SS
	Atomic Absorption or Emission Spectroscopy			
DB01	AAS-flame technique (C ₂ H ₂ /Air)	X	X	X
DB02	AAS-flame technique (C ₂ H ₂ /N ₂ O)	X	X	X
DB03	AAS-cold vapor technique	X	X	X
DB04	AAS-hydride technique	X	X	X
DB05	AAS-flameless (electrothermal technique)	X	X	X
DB06	AES-Flame technique (Flame photometry)	X	X	X
DB07	AES-hydride-technique	X	X	X
DB08	ICP-AES without Ultrasonic nebulisation	X	X	X
DB09	ICP-AES with Ultrasonic nebulisation	X	X	X
DB10	ICP-MS	X	X	X
DB99	Other Atomic Absorption or Emission Spectroscopy methods	X	X	X

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New method code determination (3):

		FO/LF/GB	SO	DE/SS
	Ionchromatographic methods			
DC01	Ion chromatography with eluent suppression			X
DC02	Ion chromatography without eluent suppression			X
DC03	Ion chromatography with UV detection			X
DC99	Other Ionchromatographic methods			X
	Physical techniques			
DD01	X-ray-energy dispersive	X	X	
DD02	X-ray-wavelength dispersive	X	X	
DD99	Other physical techniques	X	X	

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New method code determination (4):

		FO/LF/GB	SO	DE/SS
	UV-VIS Spectrophotometry techniques			
DE01	UV-VIS-spectrophotometry-techniques	X	X	X
DE02	UV-VIS-spectrophotometry-techniques after digestion pretreatment (e.g. K ₂ S ₂ O ₈ /H ₃ BO ₃ /NaOH, UV-digestion etc)			X
DE03	Continous flow UV-VIS-spectrophotometry-techniques	X	X	X
DE04	Continous flow UV-VIS-spectrophotometry-techniques with integrated digestion pretreatment (e.g. K ₂ S ₂ O ₈ /H ₃ BO ₃ /NaOH, UV-digestion etc)			X
DE05	Flow injection UV-VIS-spectrophotometry-techniques	X	X	X
DE06	Flow injection UV-VIS-spectrophotometry-techniques with integrated digestion pretreatment (e.g. K ₂ S ₂ O ₈ /H ₃ BO ₃ /NaOH, UV-digestion etc)			X
DE99	Other UV-VIS Spectrophotometry techniques	X	X	X



Intergration of pretreatment in the
determination code

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New method code determination (5):

		FO/LF/GB	SO	DE/SS
	Electrochemical methods			
DF01	pH-Electrode		X	X
DF02	pH-Electrode (Low ionic strength electrode)			X
DF03	Ion selective electrodes (except pH-Electrodes)	X	X	X
DF04	Potentiometric titration, Gran method for alkalinity			X
DF05	Potentiometric titration, extrapolation of the equivalent point two end-points			X
DF06	Potentiometric titration, single end-point pH end-point 4.5			X
DF07	Potentiometric titration, single end-point pH end-point 7.8		X	
DF08	Other Potentiometric titration	X		X
DF09	Conductometric Measurement (25 °C)			X
DF99	Other Electrochemical methods	X	X	X



New method code determination (6):

		FO/LF/GB	SO	DE/SS
	Particle size determination methods			
DG01	Particle size distribution determination, pipette method; without removal of compounds		X	
DG02	Particle size distribution determination, pipette method; after removal of OC		X	
DG03	Particle size distribution determination, pipette method, after removal of OC, CO3		X	
DG04	Particle size distribution determination, pipette method, after removal of OC, CO3, soluble salts and/or gypsum		X	
DG05	Particle size distribution determination, laser diffraction method; without removal of compounds		X	
DG06	Particle size distribution determination, laser diffraction method; after removal of OC		X	
DG07	Particle size distribution determination, laser diffraction method; after removal of OC, CO3		X	
DG08	Particle size distribution determination, laser diffraction method; after removal of OC, CO3, soluble salts and/or gypsum		X	
DG99	other Particle size distribution determination		X	
	Soil physics determination methods			
	?????			

Intergration of removal compounds in the determination code

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New method code determination (7):

		FO/LF/GB	SO	DE/SS
	Other methods			
DZ01	Calculation		X	
DZ02	N-Determination (after Kjeldahl digestion)	X	X	X
DZ99	Detection method not in this list	X	X	X

Conversion of submitted codes

- Codes of the submitted „old“ LQA-Files will be converted (a keylist was provided)
- Up from February 2015 only the new codes are valid for monitoring data, LQA data and ringtest data submission
- In case of data re-submission **only** the new codes are valid

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Code conversion list (1):

Pretreatment methods – old/new code numbers

Old Code	<u>Pretreatment methods</u>	New Code	Old Code	<u>Pretreatment methods</u>	New Code
0	No information	PZ99			
1	No pretreatment	PZ98	3	Wet ashings at room pressure (open system)	PB99
2	Extractions	PA99	3.1	Wet ashing HNO ₃	PB03
2.11	Single BaCl ₂ extraction	PA03	3.11	Wet ashing HNO ₃ /H ₂ SO ₄	PB04
2.12	Triple BaCl ₂ extraction	PA04	3.12	Wet ashing aqua regia (HCl/HNO ₃)	PB01
2.2	Extraction KCl	PA99	3.2	Wet ashing HNO ₃ /HF	PB99
2.3	Extraction aqua regia	PB01	3.21	Wet ashing HClO ₄ /H ₂ O ₂	PB99
2.4	Total extraction with HF/HClO ₄	PB09	3.22	Wet ashing HClO ₄ /H ₂ SO ₄	PB99
2.5	Total extraction with LiBO ₂	PB10	3.3	Wet ashing HNO ₃ /HClO ₄	PB06
2.6	Extraction with Acid ammonium oxalate	PA05	3.31	Wet ashing H ₂ SO ₄ /H ₂ O ₂	PB02
2.7	Extraction H ₂ O	PA01	3.32	Wet ashing H ₂ SO ₄ /K ₂ CrO ₇	PB99
2.8	Extraction HNO ₃	PA06	3.4	Wet ashing HNO ₃ /HClO ₄ /HF	PB99
2.9	Extraction CaCl ₂	PA02	3.5	Wet ashing HNO ₃ /H ₂ O	PB05

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Code conversion list (2):

Old Code	<u>Pretreatment methods</u>	New Code
3.51	Kjeldahl H ₂ SO ₄ / Se-catalyst	PB07
3.52	Kjeldahl H ₂ SO ₄ /Cu-catalyst	PB07
3.53	Kjeldahl H ₂ SO ₄ /Ti-Cu-catalyst	PB08
3.54	Kjeldahl H ₂ SO ₄ /Hg-catalyst	PB99
3.6	Wet ashing HNO ₃ /HClO ₄ /H ₂ SO ₄	PB99
3.7	Wet ashing HNO ₃ /HClO ₄ /CaCl ₂	PB99
3.8	Wet ashing HNO ₃ /HClO ₄ /H ₂ O ₂	PB99
3.9	Wet ashing HNO ₃ ,/HClO ₄ /HCl	PB99
4	Pressure digestions (closed system)	PC99
4.1	Pressure digestion HNO ₃	PC01
4.2	Pressure digestion HNO ₃ /HF	PC03
4.3	Pressure digestion HNO ₃ /HClO ₄	PC99
4.4	Pressure digestion HNO ₃ /HClO ₄ /HF	PC99
4.5	Pressure digestion HNO ₃ /H ₂ O ₂	PD02

Old Code	<u>Pretreatment methods</u>	New Code
5	Microwave pressure digestions (closed system)	PD99
5.1	Microwave digestion HNO ₃	PD01
5.2	Microwave digestion HNO ₃ /HF	PD05
5.3	Microwave digestion HNO ₃ /HClO ₄	PD04
5.4	Microwave digestion HNO ₃ /HClO ₄ /HF	PD99
5.5	Microwave digestion HNO ₃ /H ₂ O ₂	PD02
5.6	Microwave digestion HNO ₃ /H ₂ O ₂ /HF	PD99
5.7	Microwave digestion HNO ₃ /H ₂ O ₂ /HCl	PD03
5.8	Microwave aqua regia	PD99

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Code conversion list (3):

Old Code	<u>Pretreatment methods</u>	New Code
6	Dry ashings	PE99
6.1	Dry ashing dissolution with HNO ₃	PE99
6.2	Dry ashing dissolution with HNO ₃ /MgNO ₃	PE99
6.3	Dry ashing dissolution with HNO ₃ /HF	PE99
6.4	Dry ashing dissolution with HNO ₃ /HCl	PE99
6.5	Dry ashing dissolution with HCl	PE99
6.6	Dry ashing dissolution with HCl/HF	PE99
6.7	Dry ashing dissolution with H ₂ SO ₄	PE99

Old Code	<u>Pretreatment methods</u>	New Code
7	Oxygen ashings	PE99
7.1	Oxygen ashing Schöniger	PE01
7.2	Oxygen ashing Wickbold	PE99
7.3	Oxygen ashing calorimetric bomb	PE99
8.2	Hydrolysis with K ₂ S ₂ O ₈ + H ₃ BO ₃ + NaOH	See spezial list 1
8.3	Persulfate digestion (K ₂ S ₂ O ₈ + H ₂ SO ₄)	See spezial list 1
8.4	Persulfate digestion (K ₂ S ₂ O ₈ + NaOH)	See spezial list 1
8.7	Other deposition pretreatment (please specify per email)	See spezial list 1
9	X-ray-pretreatments and other pretreatments	PZ99
9.1	Material pressed (pellet)	PZ02
9.2	Material melted and formed (tablet)	PZ01
9.5	Melting (NaOH)	PZ99

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Code conversion list (4):

Determination methods – old/new code numbers

Old Code	<u>Determination method</u>	New code	Old Code	<u>Determination method</u>	New Code
0	No information	DZ99			
1	No detection	DZ99			
10	Elemental-analyzers	DA99			
11	Kjeldahl-apparatus	DZ02			
11.1	Kjeldahl-apparatus (Tecator)	DZ02			
11.2	Kjeldahl-apparatus (Gerhardt)	DZ02			
11.3	Kjeldahl-apparatus (Büchi)	DZ02			
12	N-Analyzer	DA99			
12.1	N-Analyzer (Heraeus/Elementar)	DA02			
12.2	N-Analyzer (Vario)	DA01			
12.3	N-Analyzer (Leco)	DA01			
			13	C-Analyzer	DA99
			13.1	C-Analyzer (Leco)	DA01
			13.2	TOC Analyzer	DA03
			13.3	C-Analyzer (Heraeus/Elementar)	DA02
			14	S-Analyzer	DA99
			14.1	S-Analyzer (Leco)x	DA01
			15	C/N-Analyzer	DA99
			15.1	C/N-Analyzer (Carlo-Erba=CE Instruments)	DA02
			15.2	C/N-Analyzer (Leco)	DA01
			15.3	C/N-Analyzer (Heraeus/Elementar)	DA02
			15.4	C/N-Analyzer (Vario)	DA01
			15.5	C/N-Analyzer (Hekatech)	DA02

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Code conversion list (5):

Old Code	<u>Pretreatment methods</u>	New Code
16	C/S-Analyzer	DA99
16.1	C/S-Analyzer (Leco)	DA01
17	C/N/S-Analyzer	DA99
17.1	C/N/S-Analyzer (Leco)	DA01
17.2	C/N/S-Analyzer (Heraeus/Elementar)	DA02
17.3	C/N/S-Analyzer (Thermo Electron)	DA02
17.4	C/N/S-Analyzer (Carlo-Erba=CE Instruments)	DA02
18	C/N/H-Analyzer	DA99
18.1	C/N/H-Analyzer (Leco)	DA02
18.2	C/H/N-Analyzer (Heraeus/Elementar)	DA02
19	C/H/N/S-Analyzer	DA99

New list C/N/S/TOC-Analyzers:

	Element analyzer
DA01	Macro Elemental-analyzers for C, N or S for solids (Sample > 100mg)
DA02	Micro Elemental-analyzers for C, N or S for solids (Sample ≤ 100mg) with an extra milling step
DA03	TOC/TN Analyzers (total organic C/total N-Analyzer) for liquids
DA04	CO ₃ -Determination, Calcimeter (Scheibler unit)
DA05	Hg-Analyzer
DA99	Other Element analyzers methods

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Code conversion list (6):

Old Code	<u>Pretreatment methods</u>	New Code
50	UV-VIS-spectrophotometry-techniques	DE99
51	Colorimetric N-Determination	See spezial list 1
51.1	Indophenol-blue-method	See spezial list 1
51.2	Flow Injection (FIAS)-NH3-Membrane-diffusion 566 nm	DE05
51.3	Continuous flow method, Indophenol blue	See spezial list 1
52	Colorimetric S-Determination	DE01
52.1	Nephelometry	DE99
52.2	Turbidimetry	DE99
53	Colorimetric P-Determination	See spezial list 1
53.1	Molybdene-blue-method	See spezial list 1
53.2	Vanadium-Mo-blue-method	See spezial list 1
53.3	Continuous flow method, Molybdene-blue	See spezial list 1
54	Colorimetric B-Determination	DE01
54.1	Azomethin – H	DE01
54.2	Carmin	DE01
55	Colorimetric C-Determination	See spezial list 1



Code conversion list (7):

Special list (1)

Old Code	<u>Determination Code</u> combined with	Old Pretreatment Code 8.2 or 8.3 or 8.4	Old Pretreatment Code 1 or 8.7
50	UV-VIS-spectrophotometry-techniques	DE02	DE01
51	Colorimetric N-Determination	DE02	DE01
51.1	Indophenol-blue-method	DE02	DE01
51.3	Continuous flow method, Indophenol blue	DE04	DE03
53	Colorimetric P-Determination	DE02	DE01
53.1	Molybdene-blue-method	DE02	DE01
53.2	Vanadium-Mo-blue-method	DE02	DE01
53.3	Continuous flow method, Molybdene-blue	DE04	DE03
55	Colorimetric C-Determination	DE02	DE01

UV-VIS Spectrophotometry techniques	
DE01	UV-VIS-spectrophotometry-techniques
DE02	UV-VIS-spectrophotometry-techniques after digestion pretreatment (e.g. K ₂ S ₂ O ₈ /H ₃ BO ₃ /NaOH, UV-digestion etc)
DE03	Continous flow UV-VIS-spectrophotometry-techniques
DE04	Continous flow UV-VIS-spectrophotometry-techniques with integrated digestion pretreatment (e.g. K ₂ S ₂ O ₈ /H ₃ BO ₃ /NaOH, UV-digestion etc)
DE05	Flow injection UV-VIS-spectrophotometry-techniques
DE06	Flow injection UV-VIS-spectrophotometry-techniques with integrated digestion pretreatment (e.g. K ₂ S ₂ O ₈ /H ₃ BO ₃ /NaOH, UV-digestion etc)
DE99	Other UV-VIS Spectrophotometry techniques



Intergration of pretreatment in the determination code

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Consequences:

- New code has to be used in all ringtests starting with foliar ringtest 2014/15 and deposition/soil solution ringtest 2014/15
- New code has to be used for the QA forms starting with 2015 (???)
- all QA form information in the ICP Forests database have to be changed using the code conversion list

LQA-File

Column	Description	Format
01 – 04	Sequence number (1 to 9999)	I 4
06 – 07	Country code (= 01, = 02, etc.)	I 2
09 – 12	Observation Plot number (maximum 9999)	I 4
14 – 19	start date	Date
21 – 26	end date	Date
28 – 29	Parameter Code (N, S, Ca etc.)	C 2
31 – 34	Pretreatment method (see reference list)	F 4
36 – 39	Determination method (see reference list)	F 4
41 – 46	Quantification limit (unit of parameter)	F 6
48 – 53	Mean of control chart	F 6
55 – 57	Relative Standard Deviation [%]	F 3
59	Participated at ring Test (yes = 1, no = 0)	I 1
61 – 63	ICP Forests Ring Test Number	C 3
65 – 67	ID of laboratory (e.g. H45, B78, etc.)	C 3
69 – 71	Percentage [%] of the results of the ring tests within tolerable limits for each ring test	I 3
73	Requalification information (yes = 1, no = 0)	I 1
75 – 77	Percentage [%] of the results of the ring tests within tolerable limits for each ring test in requalification	I 3 +

Improving the data quality of the LQA-File

- **LOQ-Files** **have to** submit with all monitoring results - this will be checked during data submission!
- **Ringtest results** as a part of the LQA-File are **coming from the ringtest organizers** (with a crosscheck of the method code numbers)