TEXTE
42/2015

Validation of analytical procedures developed within the project HORIZONTAL

Summary

For our Environment

Umwelt Bundesamt

TEXTE 42/2015

Environmental Research of the
Federal Ministry for the
Environment, Nature Conservation,
Building and Nuclear Safety

Project No. (FKZ) 3711 26 325
Report No. (UBA-FB) 002060

Validation of analytical procedures developed within the project HORIZONTAL

Summary

by

Dr. Holger Scharf, Dr. Detlef Lück, Dr. Ute Kalbe, Dr. Petra Lehnik-Habrink, Dr.
Nicole Bandow, Dr. Wolfgang Berger, Andreas Buchholz
BAM Federal Institute for Materials Reseach and Testing, Berlin , Germany

On behalf of the Federal Environment Agency (Germany)

Imprint

Publisher:
Umweltbundesamt
Wörlitzer Platz 1
06844 Dessau-Roßlau
Tel: +49 340-2103-0
Fax: +49 340-2103-2285
info@umweltbundesamt.de
Internet: www.umweltbundesamt.de

f /umweltbundesamt.de
🐦 /umweltbundesamt

Study performed by:
BAM Federal Institute for Materials Research and Testing
12200 Berlin, Germany

Study completed in:
December 2014

Edited by:
Section III 2.5 Monitoring Methods, Waste Water Management
Dr. Andrea Roskosch

Publication as pdf:
http://www.umweltbundesamt.de/publikationen/validierung-von-analyseverfahren-die-im-rahmen-des

ISSN 1862-4804

Dessau-Roßlau, May 2015

The Project underlying this report was supported with funding from the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear safety under project number FKZ 3711 26 325. The responsibility for the content of this publication lies with the author(s).

List of Tables

Abbreviations

CEN	European Committee for Standardization, Comité Européen de Normalisation
CV-AAS	Cold-vapour atomic absorption spectrometry
CV-AFS	Cold-vapour atomic fluorescence spectrometry
DIN	German Standardization Organization
dl-PCB	Dioxin-like polychlorinated biphenyls
GC-ECD	Gas chromatography with electron-capture detection
GC-MS	Gas chromatography with mass selective detection
GF-AAS	Graphite furnace atomic absorption spectrometry
HPLC	High performance liquid chromatography
HR GC-MS	Gas chromatography with high resolution mass selective detection
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma optical emission spectrometry
ISO	International Standardization Organization
PAK	Polycyclic aromatic hydrocarbons
16 EPA PAK	Sum of the 16 PAH substances selected by US EPA as priority pollutants
15 EPA PAK	Sum 16 EPA PAH excluding acenaphthylene
PCB	Polychlorinated biphenyls
Summe 7 PCB	Sum 6 PCB according to Ballschmiter, PCB 118 added
TOC	Total organic carbon

Abbreviations for samples and analytes for the project part „Organic parameters“

SOPAH	Soil contaminated with PAH
COPAH	Compost contaminated with PAH
SLPAH	Sewage sludge contaminated with PAH
SOPCB	Soil contaminated with PCB
COPCB	Compost contaminated with PCB
SLPCB	Sewage sludge contaminated with PAH
SODIO	Soil contaminated with dioxins, furans and dl-PCB
CODIO	Compost contaminated with dioxins, furans and dl-PCB
SLDIO	Sewage sludge contaminated with dioxins, furans and dl-PCB
NAPHTHA	Naphthaline
ACENYLEN	Acenaphthylene
ACENTHEN	Acenaphthene
FLUOREN	Fluorene
PHENANTH	Phenanthrene
ANTHRAC	Anthracene
FLUORANT	Fluoranthene
PYREN	Pyrene
BENZAANT	Benz[*a*]anthracene
CHRYSEN	Chrysene
BENZBFLU	Benzo[*b*]fluoranthene
BENZKFLU	Benzo[*k*]fluoranthene
SUMBKFLU	Sum Benzo[*b*+*k*]fluoranthene
BENZAPYR	Benzo[*a*]pyrene
BENZGHIP	Benzo[*ghi*]perylene
DIBENZAH	Dibenz[*ah*]anthracene
IND123CD	Indeno[1,2,3*cd*]pyrene

Summary

The presented research and development project was included in the environmental research program of the German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety. The aim of this project was the provision of validation data for analytical procedures developed in the framework of the EU project HORIZONTAL. According to the description of tasks of the Federal Environment Agency (UBA) from 29th September 2011 the following Technical Specifications for the determination of environmental relevant pollutants in sludge, treated biowaste and soil had to be validated:

Sub-project “inorganic parameters”

- CEN/TS 16170 (elements, ICP-OES)
- CEN/TS 16171 (elements, ICP-MS)
- CEN/TS 16172 (elements, GF-AAS)
- CEN/TS 16175-2 (mercury, CV-AFS)

Sub-project “organic parameters”

- FprCEN/TS 16181(PAH, GC-MS and HPLC)
- EN 16167(PCB, GC-MS and GC-ECD)
- CEN/TS 16190 (dioxins, furans und dl-PCB, HR GC-MS)

For both sub-projects inter-laboratory comparisons were organized separately including the acquisition and processing of suitable materials with relevant content of all analytes for all three matrices (sludge, treated biowaste and soil) as a first task.

Concerning the analysis of inorganic parameters numerous potential test materials were tested. The results showed extremely low contents for certain environmentally relevant elements as Mo, Sb and Tl especially for sludge and treated biowaste. Therefore these elements had not been included in the list of elements which had to be determined in the framework of this inter-laboratory test, for minimizing the risk of concentrations below the limit of quantification. Thus, the list was limited to Ag, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Sn, V and Zn.

Sludge with suitable PAH and dioxin content as well as biowaste with suitable PAH content was available for the sub-project considering organic parameters. In contrast to that it was necessary to dilute the soils containing PAH and PCB and the sludge containing PCB with non-polluted soil or sludge, respectively. For all other analyte-matrix combinations the respective matrix was spiked either by single substances or by suitable contaminated soil-like material.

All sample batches prepared as described above were homogenized according to a so called cross-riffling procedure and divided into sub-samples using a rotating sample divider. Sub-samples were chosen randomly and used for the homogeneity test based on content analysis of the analytes of interest. The results were evaluated using one-way analysis of variance (ANOVA) or f-test respectively. For all analyte-matrix combinations sufficient homogeneity for the inter-laboratory comparisons was proven.

In total 54 laboratories from 13 European and 2 Asian countries participated in the inter-laboratory validation trials. The percentage of international participants was comparable for

both sub-projects: 34% of 29 laboratories within the tests for “inorganic parameters” and 38% of 34 laboratories within the sub-project “organic parameters”. The evaluation of the results was performed according to DIN ISO 5725-2 using the software ProLab Plus (QuoData, GmbH Dresden, Germany).

In addition to the samples (sludge, treated biowaste and soil), quality control samples (reference solutions) were prepared and had to be analyzed by the participants in order to assess the contribution of the analysis itself to results for the sample materials.

The quality control samples were sent together with the portioned sub-samples of sludge, biowaste and soil to the participating laboratories. Furthermore all relevant standards, standard drafts or further specifications for the analytical methods as well as data sheets for submission of the results were provided.

Inorganic Parameters

All participants of the validation trial were requested to perform the digestion and the subsequent analysis of the extracts on three sub-samples of sludge, biowaste and soil each using nitric acid according to EN 16173 and using aqua regia according to EN 16174, which includes two methods: method A (digestion in an open vessels under reflux conditions) and method B (micro wave assisted digestion). For evaluation of accuracy of the matrix matched calibration curves of the participating laboratories a synthetic extraction solution with known elemental concentrations has to be analyzed by the participants.

The following numbers of registrations were received from the participants: ICP-OES (27), ICP-MS (17), CV-AFS (11) and GF-AAS (2). The low resonance related to GF-AAS may indicate that this analytical method is hardly used for routine testing of environmental relevant samples in particular by commercial test laboratories. Therefore the primary intension to provide validation data for CEN/TS 16172 had to be dismissed.

Results submitted by the participants show that some laboratories did not conduct all analyses in its entirety. Either not all three requested options of digestion were applied or not all three matrices were included. Furthermore for some elements only the limit of quantification was submitted as the performance of the measurement devices was not sufficient.

Concerning the determination of mercury it has to be noted that only six laboratories used CV-AFS as requested. Contrary to consent during the registration three laboratories submitted results, which were obtained by CV-AAS; two laboratories used solid matter analyzers based on atomic absorption. These data sets have been eliminated from further evaluation.

Furthermore results of single participants, which determined concentrations in the control sample differing more than 30 % from the nominal value were not considered for the respective analytes. This deviation was considered as evidence for poor quality of calibration caused by missing control of calibration standards or a non-suitable matrix match of calibration solutions. All remaining results were included in the statistical evaluation comprising 225 different combinations of analytes, matrices, digestion and measurement methods.

Results of the validation trial are presented in detail in tabular and graphical form in Annex 1 of this report. The following four tables (Table 1 to 4) summarize the performance characteristics of the sub-project “inorganic parameters”. Thereby the following abbreviations are used:

$\bar{x}$	Total mean (after elimination of outliers)
CV_R	Variation coefficient of reproducibility
CV_r	Variation coefficient of repeatability
N_{Lab}	Number of participationf labs

Table 1: Performance characteristics for the determination of mercury using CV-AFS (CEN/TS 16175-2)

Sample	**Extraction method**	$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}
Sewage sludge	EN 16173	0.579	19.7	10.1	6
	EN 16174, method A	0.653	15.3	8.7	6
	EN 16174, method B	0.608	17.6	12.4	6
Compost	EN 16173	0.0784	30.1	8.6	6
	EN 16174, method A	0.0897	34.2	10.7	6
	EN 16174, method B	0.0836	23.4	12.2	6
Soil	EN 16173	0.878	12.8	4.2	6
	EN 16174, method A	0.871	4.9	2.1	6
	EN 16174, method B	0.883	11.2	3.0	6

Table 2 Performance characteristics for the investigation of sewage sludge following CEN/TS 16170 und CEN/TS 16171

Element	Extraktions methode	ICP-OES (CEN/TS 16170)				ICP-MS (CEN/TS 16171)			
		$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}	$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}
Ag	EN 16173	5.439	17.6	5.8	22	4.968	39.1	7.9	16
	EN 16174 A	6.070	10.7	2.1	23	6.137	10.0	2.4	13
	EN 16174 B	6.146	15.1	3.9	24	6.256	14.2	6.8	16
As	EN 16173	4.381	19.9	11.7	20	3.778	22.3	3.4	16
	EN 16174 A	4.373	31.7	7.7	20	3.397	14.8	3.6	13
	EN 16174 B	4.213	23.8	14.0	21	3.901	25.6	4.3	16
Cd	EN 16173	1.007	18.0	5.7	20	0.972	16.4	4.6	16
	EN 16174 A	1.002	14.0	4.1	19	0.991	22.5	4.0	13
	EN 16174 B	0.976	19.7	4.3	22	1.007	17.4	5.4	16
Co	EN 16173	2.555	22.5	4.6	24	2.681	11.0	3.6	16
	EN 16174 A	2.329	15.0	4.9	22	2.337	12.6	2.8	13
	EN 16174 B	2.838	24.8	9.9	25	2.820	13.6	7.3	16
Cr	EN 16173	18.60	14.2	3.5	25	18.38	12.9	3.7	16
	EN 16174 A	18.99	10.3	3.4	23	18.86	8.9	4.0	13
	EN 16174 B	19.86	13.6	3.7	26	19.51	11.8	6.1	16
Cu	EN 16173	967.4	10.3	2.6	25	944.4	11.4	2.4	15
	EN 16174 A	959.7	8.3	1.4	23	953.5	8.3	2.3	12
	EN 16174 B	978.3	10.6	1.9	26	952.5	10.9	3.8	15
Hg	EN 16173	n.b.	n.b.	n.b.	n.b.	0.582	24.6	11.7	12
	EN 16174 A	n.b.	n.b.	n.b.	n.b.	0.605	24.8	9.2	10
	EN 16174 B	n.b.	n.b.	n.b.	n.b.	0.633	29.0	12.1	12
Ni	EN 16173	18.23	12.9	3.7	25	18.66	8.9	3.7	16
	EN 16174 A	18.30	11.3	2.6	23	18.94	6.3	3.7	13
	EN 16174 B	18.97	13.4	3.9	26	19.09	11.1	4.4	16
Pb	EN 16173	27.98	13.1	3.3	23	27.99	13.0	3.4	16
	EN 16174 A	27.30	12.1	2.5	21	28.26	9.9	2.5	13
	EN 16174 B	29.20	15.2	3.8	24	28.04	11.4	4.1	16
Se	EN 16173	n.b.	n.b.	n.b.	n.b.	1.883	18.3	7.9	13
	EN 16174 A	n.b.	n.b.	n.b.	n.b.	1.811	10.8	1.8	11
	EN 16174 B	n.b.	n.b.	n.b.	n.b.	1.861	15.7	9.5	13
Sn	EN 16173	11.57	70.3	19.1	22	12.20	73.7	18.7	16
	EN 16174 A	33.85	21.3	2.2	20	34.75	9.5	2.9	13
	EN 16174 B	35.05	10.3	3.7	23	36.69	15.8	6.9	16
V	EN 16173	5.564	11.0	4.0	25	5.642	12.5	3.1	13
	EN 16174 A	5.365	11.2	1.9	23	5.440	11.0	3.6	12
	EN 16174 B	5.971	14.8	4.2	26	6.132	12.8	2.3	12
Zn	EN 16173	1035	12.0	2.4	25	1025	13.1	2.6	15
	EN 16174 A	1017	9.8	2.2	23	1052	9.4	2.0	13
	EN 16174 B	1044	12.2	2.3	25	1045	11.2	2.1	15

Table 3: Performance characteristics for the investigation of compost following CEN/TS 16170 and CEN/TS 16171

Element	**Extraktions methode**	**ICP-OES (CEN/TS 16170)**				**ICP-MS (CEN/TS 16171)**			
		$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}	$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}
Ag	EN 16173	0.229	81.4	13.7	10	0.180	41.4	12.8	12
	EN 16174 A	0.318	83.8	19.8	11	0.212	27.3	8.8	10
	EN 16174 B	0.175	24.6	10.5	10	0.238	40.0	15.1	12
As	EN 16173	5.395	23.8	7.7	20	5.041	13.9	3.2	16
	EN 16174 A	5.322	21.6	7.3	20	5.101	14.3	3.4	13
	EN 16174 B	5.482	22.0	5.7	21	5.483	19.5	4.4	16
Cd	EN 16173	0.550	24.0	7.3	19	0.554	9.2	4.3	16
	EN 16174 A	0.554	23.0	4.6	19	0.572	7.3	4.1	13
	EN 16174 B	0.504	27.2	8.0	21	0.583	11.2	5.9	16
Co	EN 16173	6.679	13.9	3.4	25	6.934	8.9	3.1	16
	EN 16174 A	6.613	16.4	5.3	22	6.898	9.1	2.7	13
	EN 16174 B	7.184	18.4	3.8	26	7.041	12.7	2.7	16
Cr	EN 16173	29.33	23.7	6.3	25	29.46	21.4	6.3	16
	EN 16174 A	28.60	18.1	5.3	23	29.73	10.2	3.8	13
	EN 16174 B	34.13	22.9	5.9	26	34.35	21.3	7.1	16
Cu	EN 16173	45.13	10.2	2.6	25	43.68	12.0	2.7	15
	EN 16174 A	45.48	10.4	6.1	23	43.86	10.1	3.0	12
	EN 16174 B	45.81	14.9	4.5	26	44.34	9.8	2.8	15
Hg	EN 16173	n.b.	n.b.	n.b.	n.b.	0.0911	28.5	12.6	10
	EN 16174 A	n.b.	n.b.	n.b.	n.b.	0.0867	26.0	23.4	8
	EN 16174 B	n.b.	n.b.	n.b.	n.b.	0.0891	28.5	26.3	11
Ni	EN 16173	22.49	13.5	3.8	25	23.56	14.5	4.2	16
	EN 16174 A	22.36	14.0	3.0	23	23.31	13.2	1.8	13
	EN 16174 B	23.50	16.8	2.5	26	24.64	16.2	5.1	16
Pb	EN 16173	32.04	11.9	4.9	23	34.42	8.2	5.8	16
	EN 16174 A	32.18	11.5	5.3	21	34.06	8.7	3.8	13
	EN 16174 B	33.18	9.9	4.1	24	33.51	11.5	4.2	16
Se	EN 16173	n.b.	n.b.	n.b.	n.b.	0.458	70.8	11.5	11
	EN 16174 A	n.b.	n.b.	n.b.	n.b.	0.364	48.3	12.9	11
	EN 16174 B	n.b.	n.b.	n.b.	n.b.	0.495	75.7	15.3	12
Sn	EN 16173	1.678	65.5	9.0	14	1.339	63.4	20.9	15
	EN 16174 A	2.596	29.4	8.3	19	2.713	14.5	5.5	13
	EN 16174 B	2.886	38.9	25.5	21	3.019	21.2	13.3	16
V	EN 16173	24.19	28.6	6.6	25	23.86	27.5	4.7	13
	EN 16174 A	24.74	19.6	3.3	23	25.82	11.2	2.2	12
	EN 16174 B	29.84	27.3	5.6	26	30.95	24.3	6.9	13
Zn	EN 16173	168.3	9.9	2.6	25	168.4	12.0	3.2	15
	EN 16174 A	162.1	11.8	2.7	23	166.6	10.8	1.9	13
	EN 16174 B	164.4	13.2	2.6	25	167.7	11.6	2.8	15

Table 4: Performance characteristics for the investigation of soil following CEN/TS 16170 and CEN/TS 16171

Element	Extraktions methode	ICP-OES (CEN/TS 16170)				ICP-MS (CEN/TS 16171)			
		$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}	$\bar{x}$ (mg/kg)	CV_R (%)	CV_r (%)	N_{Lab}
Ag	EN 16173	0.635	25.4	4.9	13	0.620	32.2	6.9	15
	EN 16174 A	0.629	29.8	6.2	16	0.614	5.8	4.2	13
	EN 16174 B	0.824	52.0	6.5	16	0.688	26.9	9.0	15
As	EN 16173	45.13	7.0	2.1	23	44.95	9.7	2.5	16
	EN 16174 A	46.93	8.5	1.7	22	46.01	6.2	2.6	13
	EN 16174 B	47.90	10.5	2.8	24	45.25	7.7	2.8	16
Cd	EN 16173	13.26	13.4	3.4	25	13.06	12.5	3.9	16
	EN 16174 A	12.89	10.1	2.3	23	13.44	6.2	4.2	13
	EN 16174 B	13.06	11.0	4.1	26	13.40	6.9	3.7	16
Co	EN 16173	3.790	9.7	3.0	24	3.881	6.4	2.6	16
	EN 16174 A	3.989	10.7	2.2	22	3.792	8.5	2.3	13
	EN 16174 B	4.195	15.3	2.6	25	3.908	7.2	3.3	16
Cr	EN 16173	21.79	8.1	3.3	25	21.18	9.2	3.8	16
	EN 16174 A	21.86	7.6	1.8	23	21.09	8.7	3.5	13
	EN 16174 B	22.70	13.1	2.7	26	21.78	8.7	5.0	16
Cu	EN 16173	35.50	7.6	3.4	25	34.37	10.5	4.0	15
	EN 16174 A	35.82	7.4	1.7	23	34.35	10.1	4.3	12
	EN 16174 B	36.35	8.6	3.6	26	35.54	6.3	4.2	15
Hg	EN 16173	n.b.	n.b.	n.b.	n.b.	0.771	21.5	7.1	12
	EN 16174 A	n.b.	n.b.	n.b.	n.b.	0.851	12.3	6.5	10
	EN 16174 B	n.b.	n.b.	n.b.	n.b.	0.876	12.1	3.4	12
Ni	EN 16173	7.013	12.7	3.3	25	6.767	11.9	6.8	16
	EN 16174 A	7.050	12.4	2.5	23	7.004	9.4	4.9	13
	EN 16174 B	7.423	15.2	2.3	26	7.094	7.6	5.2	16
Pb	EN 16173	74.01	8.5	4.6	23	75.25	7.5	4.8	16
	EN 16174 A	74.94	10.4	3.2	21	74.74	9.2	4.1	13
	EN 16174 B	77.53	15.2	5.8	24	74.60	7.2	5.4	16
Se	EN 16173	n.b.	n.b.	n.b.	n.b.	0.484	44.0	13.9	12
	EN 16174 A	n.b.	n.b.	n.b.	n.b.	0.531	20.7	15.0	12
	EN 16174 B	n.b.	n.b.	n.b.	n.b.	0.577	41.2	11.6	12
Sn	EN 16173	3.153	59.3	23.9	19	2.538	55.7	32.5	16
	EN 16174 A	10.86	18.5	7.9	20	10.58	12.6	7.9	13
	EN 16174 B	11.49	17.2	14.2	23	11.38	22.8	20.9	16
V	EN 16173	6.225	15.7	4.8	25	6.021	13.9	4.5	13
	EN 16174 A	6.977	11.4	2.6	23	6.467	11.2	4.1	12
	EN 16174 B	7.682	16.0	4.0	26	7.443	16.4	6.2	13
Zn	EN 16173	178.6	9.4	1.8	25	170.3	11.4	1.4	15
	EN 16174 A	176.8	11.1	2.3	23	173.45	9.1	3.3	13
	EN 16174 B	185.5	15.8	1.9	25	174.1	9.5	1.6	15

As expected, the lowest variation coefficients of repeatability were obtained with few exceptions for the analyses after digestion of samples with aqua regia in open vessels under reflux conditions (EN 16174, method A). This is certainly caused by the higher sample mass used in the open digestion in comparison to both methods assisted by microwave (EN 16173 and EN 16174, method B). This reduces the influence of possible sample inhomogeneity on the results and also provides higher elemental concentrations in the extracts to be measured.

Variation coefficients of repeatability for the analyses using ICP-OES and ICP-MS were in most cases below 5 % and thus on an excellent level. Higher values, as determined for some elements, correlate mostly with very low analyte concentrations in the extracts. Only for tin the variance of the results was unacceptable. It is a known fact that Sn is oxidized gradually to insoluble SnO_2 in nitric solutions. This reaction influences the reproducibility seriously and has a higher impact if only nitric acid (EN 16173) is used for digestion than for aqua regia (EN 16174).

Overall the variation coefficients of reproducibility of determination of mercury using CV-AFS are satisfying (in all cases below 13%). However, it should be noted that the variation coefficients are clearly higher for the sludge and biowaste samples in comparison to the soil samples. This is possibly caused by the higher organic content of samples resulting in a higher risk for the presence of inferring organic compounds in the extraction solution.

In general the variation coefficients of reproducibility have to be evaluated in the same manner as for the repeatability: The influence of digestion method has also to be taken into account. Variation coefficients of reproducibility below 20% as observed for most of the results can be accepted unconditionally. Possibly reasons for higher coefficients are besides partly very low elemental concentrations in the extracts also factors such as the internal implementation of instructions by the laboratories and differences in the performance of the spectrometers used. Furthermore inadequate compensation of spectral interferences for ICP-OES or isobaric interferences for ICP-MS, respectively, maybe sources of errors.

The comparison of results obtained by ICP-OES and ICP-MS does not reveal a significant dependency of results on the extraction method or measurement method used. However, it was observed that usage of ICP-MS tends to result in lower variation coefficients of reproducibility in comparison to ICP-OES. Apparently the lower limit of quantification is responsible, which allows higher dilution of samples. Higher dilution reduces matrix caused interferences more efficiently.

Results of mercury determination using CV-AFS and ICP-MS are almost in agreement. This is valid for all three matrices for the mercury content and for the variation coefficients of repeatability and reproducibility.

Comparative evaluation of the three extraction methods was not part of this validation project. Nevertheless the results cannot be evaluated independent of sample preparation as a possible influence of this step on the results in the analytical practice has to be considered in any case.

Regarding the variation coefficients of reproducibility only for Sn a significant influence of the used extraction method on the results can be observed. Even if the results of the validation trial do not indicate a clear proof of the influence of the extraction method on the results of the other elements, it cannot be assumed that the three extraction methods are equivalent in all cases. For example numerous inter-laboratory studies conducted by BAM show that microwave assisted digestion with aqua regia (EN 16174, method B) delivers higher contents for certain samples especially for Cr and V in comparison to the open digestion (EN 16174, method A). The results of the actual trial also reveal this tendency.

Organic Parameters:

Considering the organic parameters the inter-laboratory comparisons were based on the procedures FprCEN/TS 16181 for the analysis of PAH using GC-MS or HPLC (status March 2012), EN 16167 for the analysis of PCB using GC-MS or GC-ECD (status August 2012) and CEN/TS 16190 for the analysis of dioxins, furans and dl-PCB using HR GC-MS (status February 2012). Comments to the specifications which received the responsible standardization committee (CEN/TC 400/WG 3 and the mirror committee ISO TC 190/SC3/WG6) between March 2012 and the start of the validation trial in October 2013 had been included to the documents and provided to the participants.

In contrast to the procedures for the determination of the inorganic parameters, the Technical Specifications for the analysis of organic substance groups comprise instructions on the sample preparation steps (extraction and clean-up of the extract) as well as on the analytical measurement. There are several options available to choose for both the extraction and the clean-up of the extract. In the course of the validation trial not all options and their possible combinations, respectively, could be evaluated.

During the registration of the participants attention was paid on the likewise representation of both analytical methods for the determination of PAH (HPLC and GC-MS) and PCB (GC-MS and GC-ECD) in order to enable a reliable statistical evaluation. For the analysis of PAH in the samples nine participants registered for HPLC and 17 for GC-MS whereas the PCB results were obtained using GC-ECD by eight participants and using GC-MS by 17 participants. Twelve participants took part in the validation trial for the determination of dioxins, furans and dl-PCB.

Detailed results of the inter-laboratory comparisons are given as tables and graphs in Annex 2 of this report. Within this summary only the sum parameters of the substance groups are considered in the following (Table 5-7). Thereby the following abbreviations are used:

l_0	Number of participating laboratories
l	Number of participating laboratories after elimination of outliers
n_0	Number of single values
n	Number of single values after elimination of outliers
$\bar{x}$	Total mean after elimination of outliers
S_R	Standard deviation of reproducibility
CV_R	Variation coefficient of reproducibility
S_r	Standard deviation of repeatability
CV_r	Variation coefficient of repeatability

Table 5: Performance characteristics for the analysis of PAH following FprCEN/TS 16181 (sum parameters)

Parameter	**Matrix**	l_o	l	n_o	n	$\bar{x}$ mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
Summe 15 EPA PAK	SOPAH	29	27	87	81	2.242	0.672	29.99	0.160	7.16
	COPAH	29	27	87	81	2.782	0.723	25.98	0.138	4.96
	SLPAH	29	28	87	84	2.726	0.95	34.84	0.163	5.98

Table 6: Performance characteristics for the analysis of PCB following EN 16167 (sum parameters)

Parameter	**Matrix**	l_o	l	n_o	n	$\bar{x}$ mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
Summe 7 PCB	SOPCB	27	27	81	81	3.14	0.641	20.41	0.185	5.89
	COPCB	27	25	81	75	2.81	0.545	19.42	0.120	4.28
	SLPCB	27	26	81	78	2.91	0.666	22.89	0.178	6.13

Table 7: Performance characteristics for the analysis of dioxins. furans und dl-PCB following CEN/TS 16190 (sum parameters)

Parameter	**Matrix**	l_o	l	n_o	n	$\bar{x}$ mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
NATO/CCMS-TEQ	SODIO	12	12	35	35	480.0	74.51	15.52	36.31	7.56
	CODIO	12	12	35	35	1321	142.9	10.82	91.99	6.97
	SLDIO	12	12	35	35	166.6	28.45	17.08	9.34	5.60
WHO-TEQ 2005	SODIO	11	11	32	32	382.0	63.86	16.72	27.05	7.08
	CODIO	11	11	32	32	1162	116.1	10.00	72.72	6.26
	SLDIO	11	10	31	29	533	39.11	7.34	16.59	3.11

The variation coefficient of reproducibility for the three substance groups and three matrices demonstrate higher differences between the substance groups than between the matrices (sewage sludge, treated biowaste and soil). The highest coefficient of reproducibility was found for the analysis of PAH which was between 26 and 35% depending on the matrix. For the sum 7 PCB the variation coefficient of reproducibility ranged between 19 and 23%. The lowest variation coefficient of reproducibility were determined for the calculated toxicity equivalents comprising dioxins, furans and dl-PCB (7 -17%). Overall the variation coefficients of reproducibility were in the usual range for the analysis of organic substances 25 – 50%. The higher variation for PAH and PCB might be attributed to the different admitted analytical methods in each case. Probably the variance of measured values is enhanced by this factor. However, it has to be recognized that only the sum parameters are considered.

The concentrations of the single substances varied for several orders of magnitude. Usually the variation coefficients for substances with low concentrations are higher. Thus, their contribution to the sum parameter may be small and the sum parameter may exhibit a better variation coefficient than the single substances.

The variation coefficients of repeatability range between 3.1 % and 7.6 % and show no trend considering the substance groups or matrices.

Overall the results confirm that the procedures described in the Technical Specifications are comparably applicable for all three matrices and thereby the feasibility of the HORIZONTAL approach.

Conclusions

Based on the obtained results of the inter-laboratory comparison it can be acknowledged that the Technical Specifications developed within the EU project HORIZONTAL CEN/TS 16170 (ICP-OES), CEN/TS 16171 (ICP-MS) und CEN/TS 16175-2 (CV-AFS) are appropriate for the analysis of the matrices sludge, treated biowaste and soil. Validation data that meet the requirements of standards could be derived for most of the elements included in the evaluation. It can be assumed that the results of the inter-laboratory comparison represent a realistic impression of the currently feasible performance of the analytical protocols evaluated. This applies also to the elements where the performance data are less sufficient.

Similarly, the results of the inter-laboratory comparisons for the analysis of organic substances based on CEN/TS 16181 (PAK using HPLC and GC), CEN/TS 16167 (PCB using GC-MS and GC-ECD) and CEN/TS 16190 (dioxins, furans and dl-PCB using HRGC-MS) deliver sufficient performance data and confirm the suitability of the Technical Specifications for the analytes and matrices considered.

The results were presented to the German Federal Environment Agency as the funding authority. Furthermore, the results have been discussed within the responsible standardization committee. The obtained performance data have been confirmed to be appropriate for the validation of the considered Technical Specifications. Further actions to implement the data to the standards have been started.

Between May and September 2014 the official voting for the revised prEN 16170, prEN 16171, prEN 16175-2 regarding the inorganic parameters had passed. Their publication as full standards can be expected in spring 2015 as far as the voting results are published with a positive outcome. In addition it has been decided by CEN/TC 400 to keep the status of a Technical Specification for the procedure CEN/TS 16172 “Sludge, treated biowaste and soil – Determination of elements using graphite furnace atomic absorption spectrometry (GF-AAS)“ and to postpone the decision on its withdrawal up to the next regularly systematic review in 2016.

In case of the organic substances new work item proposals (NWIP) for FprCEN/TS 16181 (PAK), EN 16167(PCB) und CEN/TS 16190 (dioxins, furans and dl-PCB) are being in preparation under the assistance of BAM. After the official confirmation of CEN the slightly revised procedures including the new validation data are planned to be submitted to Unique Acceptance Procedures (UAP) in February. The publication of the full standards can then be assumed by the end of 2015.

Overall the results of the inter-laboratory validation trials confirm that the procedures described in all considered procedures are comparably applicable for all three matrices. Thereby feasibility of the HORIZONTAL approach can be acknowledged.