Validation of prEN 17813

Environmental solid matrices – Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography

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VITO
Boeretang 200
2400 MOL
Belgium
VAT No: BE0244.195.916
vito@vito.be – www.vito.be
IBAN BE34 3751 1173 5490 BBRUBEBB

Chris Vanhoof
Senior Researcher
T+32 14 33 50 38/
Christine.vanhoof@vito.be

AUTHORS

Chris Vanhoof, VITO, Belgium

SUMMARY

The European Standard prEN 17183 *Environmental solid matrices – Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography* was prepared by the experts of CEN/TC 444 'Environmental characterization of solid matrices' in working group 3 'Inorganic analysis'.

Before finalising the drafted European standard prEN 17813, the performance characteristics of the analytical method need to be defined. Therefore, an interlaboratory validation trial was organised in 2022-2023.

A method for the determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography in environmental solid matrices was developed within CEN/TC444/WG3 and successfully validated.

The method performance characteristics were assessed in a collaborative trial with 15 participating laboratories from 5 EU and 2 International countries on five different samples. The validated samples included a soil sample, a wood sample, a polymer sample, a sludge sample and a solid recovered fuel (SRF).

Based on the statistical evaluation of the results from the collaborative trial, it is concluded that the proposed method is suitable for the determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography in environmental solid matrices.

The tables with the method performance characteristics are presented in §4.2 on page 10.

The graphical presentation of the results are per parameter and per sample presented in Annex D. The distribution of the individual results (with 4 replicates) of the participating laboratories is shown.

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1 INTRODUCTION

The European Standard prEN 17183 *Environmental solid matrices – Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography* was prepared by the experts of CEN/TC 444 'Environmental characterization of solid matrices' in working group 3 'Inorganic analysis'.

Before finalising the drafted European standard prEN 17813, the performance characteristics of the analytical method need to be defined. Therefore, an interlaboratory validation trial was organised in 2022-2023.

The following timeframe was followed for the validation of the prEN 17813 standard:

Call for participation of laboratories	July 2022
Preparation of ILT samples	August - September 2022
Homogeneity testing	October 2022
Stability testing	October – November 2022
Distribution of the samples	End of October 2022
Reporting of the ILT results	December 9th, 2022
Statistical evaluation	January 2023
Presentation of the ILT results in CEN/TC444/WG3	February 7th, 2023
Finalizing performance data and incorporating data in prEN 17183	End of February 2023
Finalizing validation report	End of March 2023

2 METHOD DESCRIPTION

The analytical method is described in the European Standard prEN 17183 *Environmental solid matrices – Determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography*.

2.1 Scope

This European Standard prEN 17813 specifies an empirical method for the simultaneous direct determination of the fluorine, chlorine, bromine, and sulfur content in environmental solid matrices by oxidative pyrohydrolytic combustion at (1050 ± 50) °C, followed by ion chromatography.

The method is applicable for the determination of concentrations ≥ 10 mg/kg of each element based on dry matter. The upper limit and exact concentration range covered depends on the blank levels of the instrumentation and the capacity of the chromatographic separation column used for determination.

2.2 Principle

The homogenized sample is combusted under oxidative conditions. For the determination of fluorine the combustion is performed under pyrohydrolytic conditions. The combustion gases are absorbed in an aqueous solution. For the determination of sulfur the absorption solution contains an oxidizing agent to ensure complete conversion to sulfate. Changes in the volume of the absorption solution are considered for concentration calculations.

The anions of interest (bromide, chloride, fluoride, and sulfate) are separated by ion chromatography, and detected with a conductivity detector. To reduce the total conductivity caused by the eluent a suppressor unit (cation exchange unit) is used.

3 ORGANISATION OF THE ILT

The coordination of the ILT, the preparation and distribution of the samples, the compilation and finalization of the performance data of the method was carried out by VITO (Flemish Institute for Technological Research, Belgium).

The homogeneity and stability tests were conducted by Mitsubishi Chemical Europe – Analytical Instruments (Düsseldorf, Germany).

The statistical evaluation was carried out by THM University of applied sciences (Giessen, Germany).

3.1 Participating laboratories

In July 2022 a call for tender to ask for laboratories to participate to the ILT was launched (see Annex A).

At first 18 laboratories confirmed their participation. Beginning of October 2022, these laboratories received the confirmation for their participation to the ILT, and simultaneously the final standard prEN 17813 which should be applied in the ILT, was sent to them.

Finally, 15 laboratories reported results. These 15 participating laboratories were located in Belgium, France, Germany, Netherlands, Switzerland, China and United States of America, as show in Table 1.

Table 1 Participating laboratories

Country	Organization
Belgium	Metrohm Belgium
Belgium	Solvay R&I Centre Brussels
China	Metrohm China
France	Metrohm France
France	BRGM, Service Géologic National
France	NQAC, Nestlé Quality Assurance Center Vittel
Germany	a1-environsciences
Germany	Agrolab Labor GmbH
Netherlands	TLR International Laboratories
Netherlands	Eurofins Materials Science (Eindhoven)
Netherlands	TE Instruments Application Lab
Netherlands	AVR
Netherlands	Shell Global Solutions International

Country	Organization
Switzerland	Metrohm International Headquarters
USA	Metrohm USA

3.2 Preparation and distribution of the ILT samples

For the ILT 5 samples were prepared for distribution. The selected samples were homogenized, spiked if needed, dried at 105°C, and grinded to a particle size of < 250 µm or < 500 µm, depending on the matrix.

The following samples were prepared to determine the performance characteristics of the method:

- Soil sample (sandy loam, Flanders, Belgium), spiked with the various parameters, dried at 105°C, grinded to a particle size < 250 µm;
- Wood samples, dried at 105°C, grinded to a particle size < 250 µm;
- Polymer sample (certified material, ERM EC 681m, polyethylene), cryogenic milling to a particle size < 500 µm;
- Sludge sample, dried at 105°C, grinded to a particle size < 250 µm;
- Solid recovered fuel (SRF), proficiency test sample of DCC Delta Coal Control GmbH (Germany), cryogenic milling to a particle size < 500 µm.

Note that in the prEN 17813 it is described to reduce the particle size < 250 µm, unless not feasible for e.g. plastics and solid recovered fuels.

Plastic HDPE bottles (50 ml) were filled with about 2.5 g of sample. Samples were foreseen for distribution to the participating laboratories, and also for homogeneity (5 bottles) and stability (5 bottles) tests.

Pictures of the prepared samples are shown in Figure 1 until Figure 3.

Figure 1 (Left) Soil sample < 250 µm – (Right) Wood sample < 250 µm

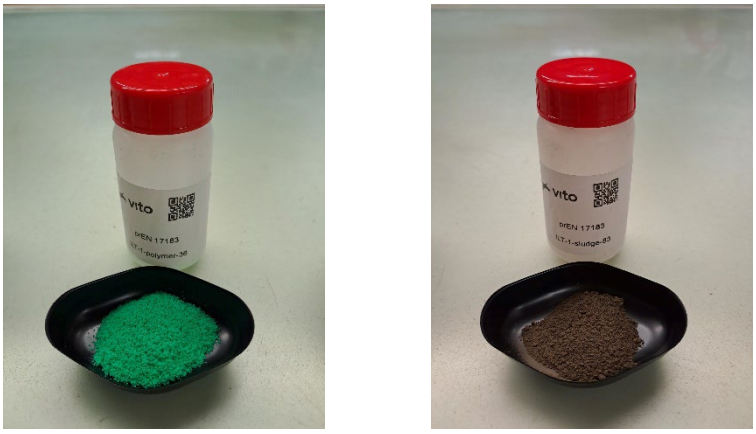

Figure 2 (Left) Polymer sample < 500 µm – (Right) Sludge sample < 250 µm

Figure 3 (Left) original SRF – (right) SRF < 500 µm after cryogenic milling

The samples were distributed on October 26th, 2022 to the participating laboratories. All of them received by email practical information (see Annex B) how to perform the analyses. Besides that an excel template was delivered to report the results, which also included a request for additional information (Annex C) related to the applied techniques and instrumental details.

3.3 Homogeneity and stability tests of the ILT samples

The homogeneity and stability tests were performed using the combustion-IC technique and analysed according to prEN 17813 for the determination of F, Cl, Br and S.

For the homogeneity tests 5 bottles per sample were delivered. From each bottle at least 2 duplicate analyses (often with different intakes) were conducted. For the stability tests 5 additional bottles per sample were delivered and each bottle was analysed once or several times.

The homogeneity tests were conducted in October 2022, prior to the distribution of the ILT samples. The stability tests were conducted 6-8 weeks later.

The homogeneity results of the 5 ILT samples are presented in Table 2, whereby the mean concentration, the standard deviation and the relative standard deviation (RSD) is shown. For fluorine in the polymer sample no data are presented as the content is below 10 mg/kg dm. In general it can be stated that the obtained results are within acceptable ranges. For fluorine and bromine in wood, the obtained % RSD are higher, 50% and 17% respectively, due to the low concentration range. For chlorine in sludge also a higher %RSD is observed, namely 23%. Nevertheless, these samples are suitable to be distributed for the ILT.

Table 2 Homogeneity results for the 5 ILT samples (5 bottles)

Parameter	Matrix	Mean concentration (mg/kg dm)	Stand. Deviation (mg/kg dm)	RSD (%)
Fluorine	Soil	585	31,3	5%
	Wood	20,8	10,5	50%
	Sludge	243	10,5	4%
	SRF	90,1	6,80	8%
Chlorine	Soil	784	27,8	4%
	Wood	517	38,6	7%
	Polymer	382	45,9	12%
	Sludge	3370	776	23%
	SRF	6390	724	11%
Bromine	Soil	345	15,1	4%
	Wood	23,1	3,90	17%
	Polymer	1330	27,6	2%
	Sludge	44,2	1,90	4%
	SRF	327	48,7	15%
Sulfur	Soil	234	9,80	4%
	Wood	634	22,2	4%
	Polymer	593	13,9	2%
	Sludge	8750	199	2%
	SRF	1260	72,8	6%

The results of the 5 ILT samples, measured to verify the stability, are presented in Table 3, whereby the mean concentration, the standard deviation and the relative standard deviation (RSD) is shown. For fluorine in the polymer and the wood sample no data are presented. The stability test samples were measured 6-8 weeks later than the homogeneity samples.

Table 3 Stability results for the 5 ILT samples, measured after 6-8 weeks (5 bottles)

Parameter	Matrix	Mean concentration (mg/kg dm)	Stand. Deviation (mg/kg dm)	RSD (%)
Fluorine	Soil	627	16,7	3%
	Wood	14,0	1,00	7%
	Sludge	242	8,70	4%
	SRF	97,6	17,7	18%
Chlorine	Soil	866	28,5	3%
	Wood	595	41,9	7%

Parameter	Matrix	Mean concentration (mg/kg dm)	Stand. Deviation (mg/kg dm)	RSD (%)
	Polymer	383	14,3	4%
	Sludge	3260	110	3%
	SRF	9005	1310	15%
Bromine	Soil	375	8,20	2%
	Polymer	1560	44,2	3%
	Sludge	33,9	0,80	2%
	SRF	330	87,5	27%
Sulfur	Soil	265	7,70	3%
	Wood	739	13,9	2%
	Polymer	698	19,2	3%
	Sludge	4430	227	5%
	SRF	1320	87,4	7%

To verify the stability of the samples the ratio between the mean results obtained from the homogeneity test results (Time = 0) and the stability test results (Time = 6-8 weeks) was calculated and is presented in Figure 4. The figure show that for Cl in SRF and S in sludge deviated results are obtained. For Cl in SRF the deviation can be attributed to the heterogeneity of the sample. For the S in sludge the reduced recovery could later be attributed to wrong preparation of the absorption solution. Nevertheless, the obtained data of the ILT were critically evaluated. The overall mean of results (without outliers) of the ILT is 8900 mg/kg dm (see §4.2 on page 10), which corresponds to the results at Time = 0. There are some outliers detected for the parameter S in sludge, but probably associated with the execution of the method rather than to the stability of the sample.

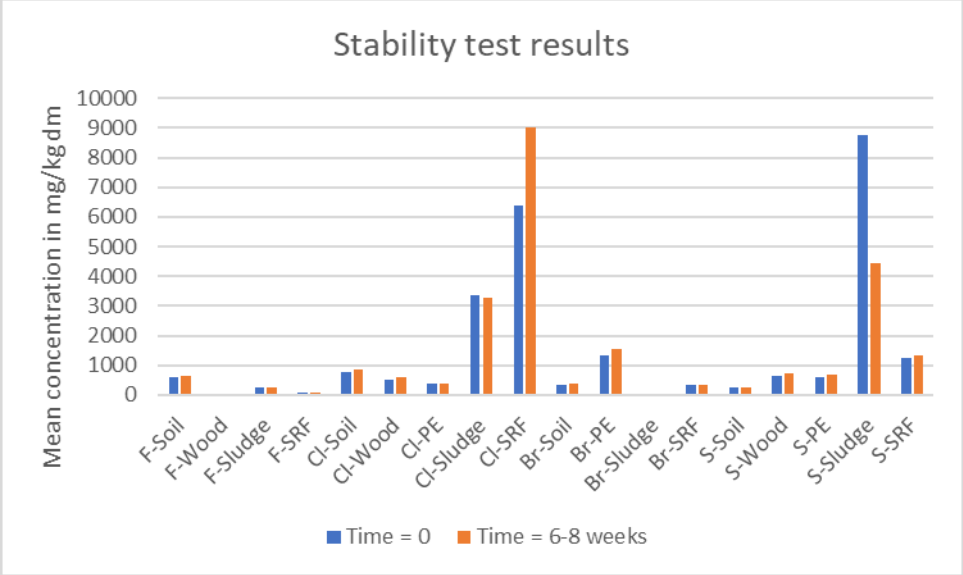

Figure 4 Stability test results for all samples (comparison results Time = 0/Time = 6-8 weeks later)

In Figure 5 a graphical overview of the homogeneity and stability test results is given.

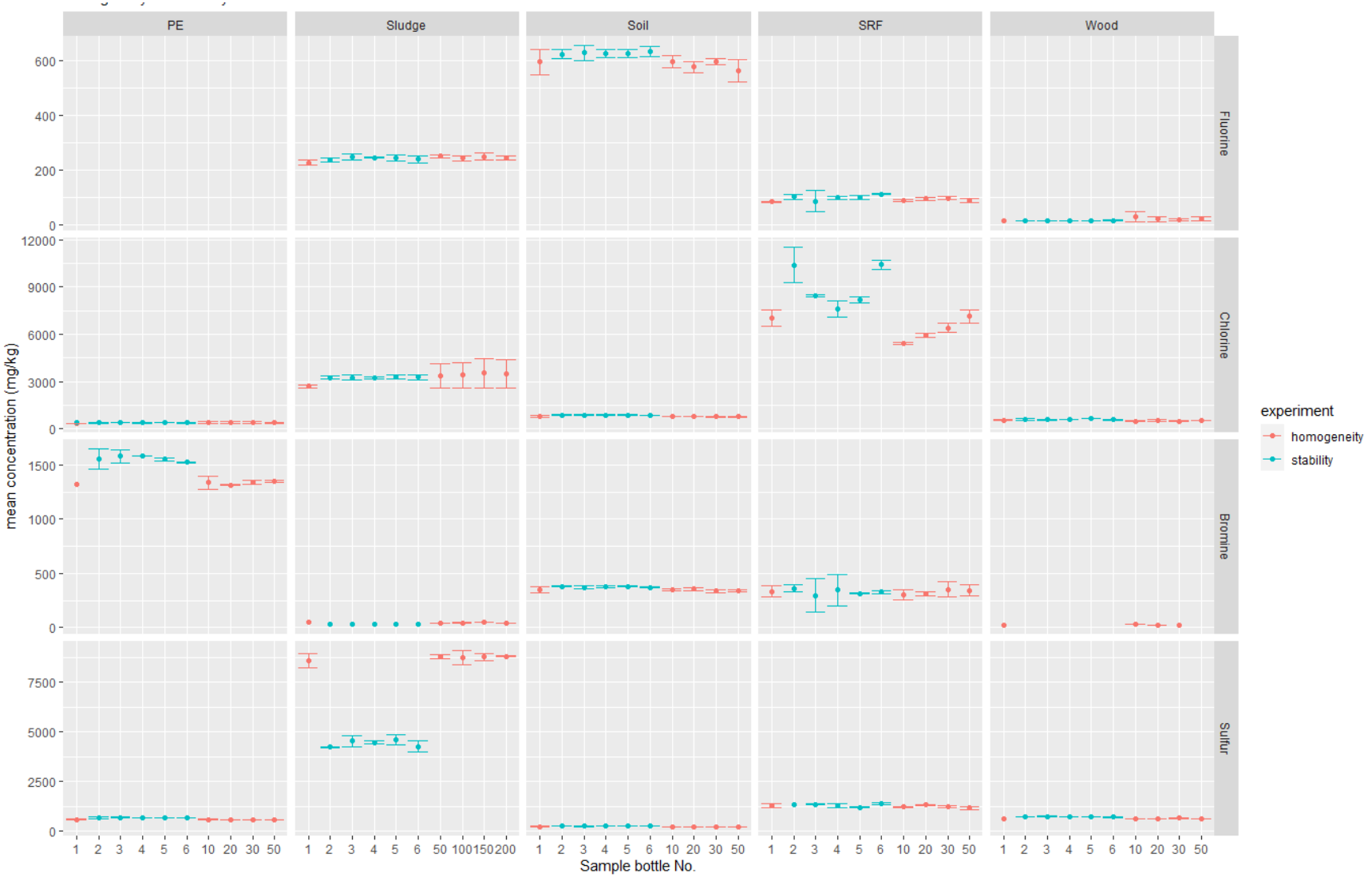

Figure 5 Graphical overview of the homogeneity and stability results

3.4 Statistical evaluation

The statistical evaluation was carried out by THM University of applied sciences (Giessen, Germany) using a validated software based on the mathematical algorithms prescribed by ISO 5725-2 *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

Exclusion of the outlying results: First step was to identify outliers (1% confidence level) and stragglers (5% confidence level) by the Cochran and Grubbs tests.

Performance characteristics: The remaining measurements were used to evaluate the basic performance characteristics of the methods:

- Number of laboratories after outlier rejection
- Number of individual test results after outlier rejection
- Percentage of outliers [%]
- Overall mean of results without outliers
- Reproducibility standard deviation, s_R
- Coefficient of variation of reproducibility $C_{V,R}$
- Repeatability standard deviation s_r
- Coefficient of variation of repeatability $C_{V,r}$

For assessment of the statistical evaluation ISO DTS 7013 *Water quality — Guidance document on designing an interlaboratory trial for validation of analytical methods* (Clause 6) can be applied. Generally the validation of the analytical method is successful if the following criteria are fulfilled:

- for each sample remain at least eight valid data sets (l = 8) after elimination of outliers;
- the percentage of outliers is less than 20 %;
- the variation coefficient of reproducibility $CV_{,R}$ is acceptable. In any case $CV_{,R}$ > 40 % is not acceptable;
- the recovery rate η lies within acceptable limits (e.g. ±30 %).

4 RESULTS AND STATISTICAL EVALUATION

4.1 Results

The results were reported by email using a template excel file. All participating laboratories filled in the requested information.

A variety of instruments and analytical conditions were used, but the retained data used to calculate the performance characteristics are conform to the quality parameters specified in the method. From each sample 4 replicates were measured.

From Lab 11 the results for the element S were not included in the dataset because no oxidizing agents was used in the absorption solution, as prescribed in the prEN standard. This results in a significant underestimation of the sulfur content present.

In Table 4 a summary is given of the applied instrument and measurement conditions.

Table 4 Applied instrument and measurement conditions

Item	Condition	Remark
Combustion unit	3 different manufacturers	
Ion chromatograph unit	2 different manufacturers	
Mode	13 online / 2 offline	
Intake sample	10-100 mg	Sample and parameter dependent
Combustion temperature	900 – 1100°C	
Time of combustion	5 -15 min	
Composition absorption solution	H_2O with H_2O_2	
Volume absorption solution	3 – 11 ml	
IC injection volume	10 – 200 µl	

The statistical evaluation of the obtained data was carried out according to § 3.4.

The graphical presentation of the results are per parameter and per sample presented in Annex D. The distribution of the individual results (with 4 replicates) of the participating laboratories is shown.

4.2 Method performance characteristics for the parameters F, Cl, Br and S

The method performance characteristics for the parameters F, Cl, Br and S are summarized in Table 5 up to Table 8. These data are included in Annex A of the European standard prEN 17813.

For the parameter F the coefficient of reproducibility $CV_{,R}$ fluctuates around 20%, except for the wood sample. For the wood sample a $CV_{,R}$ of 36% was obtained, but the concentration level is very low (i.e. 10 mg/kg), close to the reporting limit.

Table 5 Method performance data for the parameter fluorine

Sample	*l*	*n*	*o* %	$\bar{\bar{x}}$ mg/kg	s_R mg/kg	$C_{V,R}$ %	s_r mg/kg	$C_{V,r}$ %
Soil	12	48	20,0	540	110	20	13	2,4
Wood	14	53	7,02	12	4,2	36	1,09	9,3
Polymer	-	-	-	<10	-	-	-	-
Sludge	15	60	0,0	240	50	21	11	4,7
SRF	14	56	6,70	96	17	18	8,4	8,7

Key

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
$\bar{\bar{x}}$	overall mean of results (without outliers)
sR	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

For the parameter Cl the coefficient of reproducibility $CV,_R$ is within acceptable ranges. For the SRF sample the $CV,_R$ is higher compared to the other samples, but note that no outliers were removed for the SRF sample.

Table 6 Method performance data for the parameter chlorine

Sample	*l*	*n*	*o* %	$\bar{\bar{x}}$ mg/kg	s_R mg/kg	$C_{V,R}$ %	s_r mg/kg	$C_{V,r}$ %	η %
Soil	14	56	6,7	760	94	12	40	5,3	-
Wood	14	56	6,7	550	110	19	63	11	-
Polymer	13	51	15	340	47	14	13	3,8	90
Sludge	11	44	27	3200	300	9,5	54	1,7	-
SRF	15	60	0,0	6500	1800	28	1200	18	-

Key

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
$\bar{\bar{x}}$	overall mean of results (without outliers)
sR	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

For the parameter Br the coefficient of reproducibility $CV_{,R}$ varies between 10 - 20% for the soil, polymer and sludge sample. For the wood sample a $CV_{,R}$ of 42% was obtained, but the concentration level is very low (i.e. 7.7 mg/kg), for some labs below the reporting limit. For the SRF sample the $CV_{,R}$ is higher compared to the other samples, but note that no outliers were removed for the SRF sample.

Table 7 Method performance data for the parameter bromine

Sample	*l*	*n*	*o*	$\bar{\bar{x}}$	s_R	$C_{V,R}$	s_r	$C_{V,r}$	η
			%	mg/kg	mg/kg	%	mg/kg	%	%
Soil	13	52	13	310	47	15	9,7	3,1	-
Wood	9	36	18	7,7	3,3	42	0,68	8,9	-
Polymer	11	44	27	1400	150	10	21	1,4	101
Sludge	13	51	15	38	7,9	21	3,02	8,1	-
SRF	15	60	0,0	340	120	35	72	21	-

Key

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
$\bar{\bar{x}}$	overall mean of results (without outliers)
sR	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

For the parameter S the coefficient of reproducibility $CV_{,R}$ is within acceptable ranges. For the sludge sample the $CV_{,R}$ is low (7.9%), but the % outlier (33%) is high.

Table 8 Method performance data for the parameter sulfur

Sample	*l*	*n*	*o*	$\bar{\bar{x}}$	s_R	$C_{V,R}$	s_r	$C_{V,r}$	η
			%	mg/kg	mg/kg	%	mg/kg	%	%
Soil	12	48	7,7	180	33	18	10	5,7	-
Wood	10	40	23	570	140	25	19	3,3	-
Polymer	12	48	7,7	580	73	13	14	2,4	91
Sludge	9	35	33	8900	700	7,9	120	1,3	-
SRF	10	40	23	920	260	28	52	5,7	-

Key

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
$\bar{\bar{x}}$	overall mean of results (without outliers)
sR	reproducibility standard deviation

$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

5 COMPARISON WITH EN 14582

Within CEN/TC444/WG3 there are 2 EN standards developed for the determination of halogens and sulfur is solid environmental matrices.

Besides de standard prEN 17813, discussed in this document, also EN 14582:2016 *Characterization of waste – Halogen and sulfur content – Oxygen combustion in closed systems and determination methods* is available. The EN 14582 standard specifies a combustion method for the determination of halogen and sulphur contents in materials by combustion in a closed system containing oxygen (calorimetric bomb), and the subsequent analysis of the combustion product using different analytical techniques.

Therefore it is useful to compare the data obtained by both methods.

The samples of the ILT of prEN 17183 were also analysed according to EN 14582 by 1 laboratory. NaOH-H_2O_2 was as absorption solution and the laboratory indicated that, according to EN 14582, this is not the appropriate solution for bromide. Results obtained for bromide were therefore not evaluated. The soil sample didn't burn in the calorimetric bomb, so no results could be reported for this sample. For analysing these type of materials a combustion enhancer has to be used. The 4 other samples (wood, polymer, sludge and SRF) were analysed in duplo and the results are presented below.

		prEN 17183		EN 14582		Ratio EN14582/ prEN 17183
Parameter	**Matrix**	**n**	$\bar{\bar{x}}$ **mg/kg dm**	**n**	$\bar{\bar{x}}$ **mg/kg dm**	
Fluorine	Wood	53	12	2	< 30	-
	Sludge	60	240	2	144	0.60
	SRF	56	96	2	87	0.91
Chlorine	Wood	56	550	2	540	0.98
	Polymer	51	340	2	350	1.01
	Sludge	44	3200	2	3000	0.93
	SRF	60	6500	2	5400	0.84
Sulfur	Wood	40	570	2	630	1.10
	Polymer	48	580	2	640	1.09
	Sludge	35	8900	2	8800	0.99
	SRF	40	920	2	1040	1.12

n number of individual test results
$\bar{\bar{x}}$ overall mean of results (without outliers)

For the obtained values there is a good correspondence between the results of both methods. All the results according to EN 14582 are situated between the ($\bar{\bar{x}}$ ± 2*$C_{V,R}$) interval obtained by prEN 17183.

6 CONCLUSION

A method for the determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography in environmental solid matrices was developed within CEN/TC444/WG3 and successfully validated.

The method performance characteristics were assessed in a collaborative trial with 15 participating laboratories from 5 EU and 2 International countries on five different samples. The validated samples included a soil sample, a wood sample, a polymer sample, a sludge sample and a solid recovered fuel (SRF).

Based on the statistical evaluation of the results from the collaborative trial, it is concluded that the proposed method is suitable for the determination of halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography in environmental solid matrices.

Acknowledgement

The author wants to thank the following organizations for their financial or analytical support, which allowed the organisation of this validation study:

- Metrohm AG
- Mitsubishi Chemical Europe – Analytical Instruments
- Thermo Fisher Scientific GmbH
- OVAM (Flemish Waste Agency, Belgium)

The author would like to express thanks to all participants for taking part in the validation study. The input of the active members of CEN/TC444/WG3 and support from the chairman and the secretariat is also gratefully acknowledged.

ANNEX A CALL FOR TENDER – LABORATORIES FOR INTERLABORATORY STUDY OF PREN 17813

prEN 17813:2022 Environmental matrices — Halogens and sulfur by oxidative pyrohydrolytic combustion followed by ion chromatography detection and complementary determination methods

For the validation of the prEN 17813 standard an interlaboratory trial (ILT) is scheduled in October-December 2022. Interested participants are kindly requested to indicate their interest by returning a completely filled application form as soon as possible, but no later than September 15th, 2022, per email to christine.vanhoof@vito.be

A draft method of prEN 17813 will be distributed to the participating laboratories in the beginning of October 2022.

Brief description of the method
The homogenized sample is combusted under oxidative conditions. For the determination of fluorine the combustion is performed under pyrohydrolytic conditions. The combustion gases are absorbed in an aqueous solution. For the determination of sulfur the absorption solution contains an oxidizing agent to ensure complete conversion to sulfate. Changes in the volume of the absorption solution are considered for concentration calculations.
The anions of interest (bromide, chloride, fluoride, and sulfate) are separated by ion chromatography, and detected with a conductivity detector. To reduce total conductivity caused by the eluent a suppressor unit (cation exchange unit) is used.

Note: The IC system can directly be coupled to the combustion apparatus or be used for an offline determination of the absorption solution. In order to reduce the risk of contamination, and to facilitate trace analytical determinations, it is recommended to work in a closed system, thus directly coupling the combustion device and the ion chromatograph.

Participation conditions / requirements:

Laboratories with suitable instrumentation and analytical experience in the determination of halogens and sulfur by combustion-IC can participate in the interlaboratory trial.

Participation is at no charge under the following conditions:
The participant must follow the requirements and procedures defined in the test protocol.
Any modification, e.g., of reagent concentrations or application of alternative reagents, acids or mixtures etc. is not permitted.
Participants will receive a report with their results. All laboratory-related data and results will be treated confidential, and results will be presented anonymised.

ILT samples
About 5 solid samples, dried and fine grinded, will be distributed tot he participating laboratories. Before start of the analyses samples need to be pre-dried at 105°C during 2 hours. Per sample 4 independent replicate determinations have to be performed and 4 results have to be reported.

The ILT sample concentrations will range for:
- Fluoride: from 10 - 1000 mg/kg dm
- Chloride: from 50 – 15000 mg/kg dm

- Bromide: from 10 – 2000 mg/kg dm
- Sulfur: from 50 – 10000 mg/kg dm

Additional information (e.g., presentation of results form) will be distributed with the ILT samples.

Important dates
Expected sample dispatch: 24.10.2022.
Results reporting deadline: 09.12.2022.

Interested participants are kindly requested to indicate their interest by returning a completely filled application form as soon as possible, but no later than September 15th, 2022, per email to christine.vanhoof@vito.be . It is necessary to fill in the attached application form.

The organisers reserve the right to limit the number of participants.

APPLICATION FORM: Interlaboratory trial prEN 17813

General information	
Lab Manager	
Laboratory	
Adress (Distribution address)	
Country	
Phone	
Email	

Instrument information	
Combustion-IC manufacturer	
Combustion-IC Instrument type – online?	
Combustion-IC Instrument type – offline?	
Remarks/additional information	
Years of experience with combustion-IC?	

ANNEX B INFORMATION DISTRIBUTED TO THE PARTICIPANTS

An excel template was sent to the participating laboratories with the following instructions:

The ILT consists of 5 samples, already dried, homogenised and milled:

- ILT-1-Soil-xx < 250 µm
- ILT-1-wood-xx < 250 µm
- ILT-1-polymer-xx < 500 µm
- ILT-1-sludge-xx < 250 µm
- ILT-1-SRF-xx < 500 µm

The samples are already pretreated and dried, but please pre-dry the samples at 105°C for 2 hours before use.

The following parameters need to be determined: F, Cl, Br and S.

It is mandatory that four replicates of each sample are performed.

When analyzing the samples the procedure of prEN 17813 must be applied exactly so that your data can be used for the validation.

Please report any deviations.

Please complete the other worksheets:

- 2_Requested information
- 3_Parameter 1 - F
- 4_Parameter 2 - Cl
- 5_Parameter 3 - Br
- 6_Parameter 4 – S

Deadline reporting date: December 9th, 2022

Please send this file after completion to: christine.vanhoof@vito.be

ANNEX C REQUESTED INFORMATION FROM THE PARTICIPANTS

The participants were requested to fill in the following questionnaire, included in the excel template.

General information

Laboratory lab code		**1**
Laboratory address		
Contact person lab		
	Phone	
	Email	
Date of receipt of samples		
Date of analysis		

Technical information

Combustion unit - Instrument type	
Ion chromatograph - Instrument type	
Online or offline IC measurements	
Combustion conditions	*Describe here to which sample/parameter it is*

	applicable
Sample weight	
Combustion temperature	
Introduction speed	
Time of combustion	

Absorption solution

Composition	
Volume	

IC conditions

Eluens/concentration	
Analytical column	
Sample size	

Blanc values

F (mg/kg dm)	
Cl (mg/kg dm)	
Br (mg/kg dm)	
S (mg/kg dm)	

General remarks

ANNEX D GRAPHICAL PRESENTATION OF THE RESULTS OF THE EN VALIDATION STUDY PREN 17813

Legend:
- Laboratory specific standard deviation
- Outlier
- Measured value
- Mean line (overall mean)

Outlier types
- A outlying single result of one laboratory,
- B outlying laboratory mean (Grubbs),
- C outlying within-laboratory variance (Cochran),
- L outlying laboratory means (Grubbs for two).

D.1 Determination of fluorine content

In Figure 6 up to Figure 9 the graphical results are presented for the fluorine content for the 5 ILT samples.

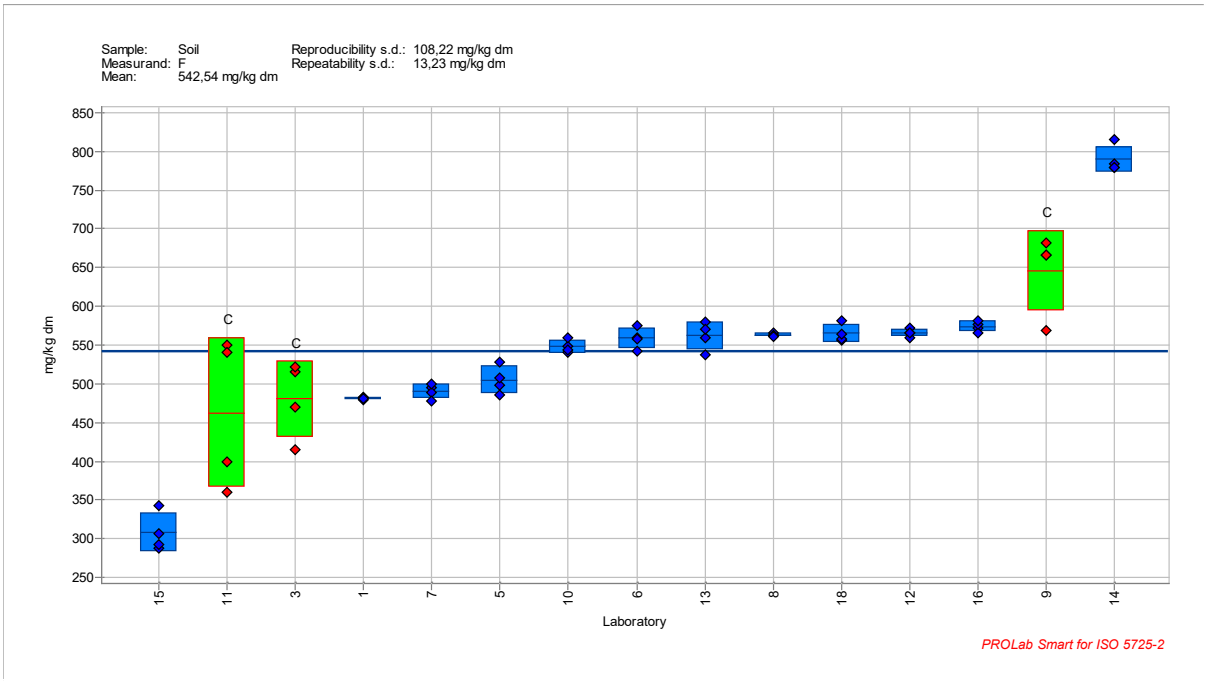

Figure 6 Results for fluorine content of soil sample

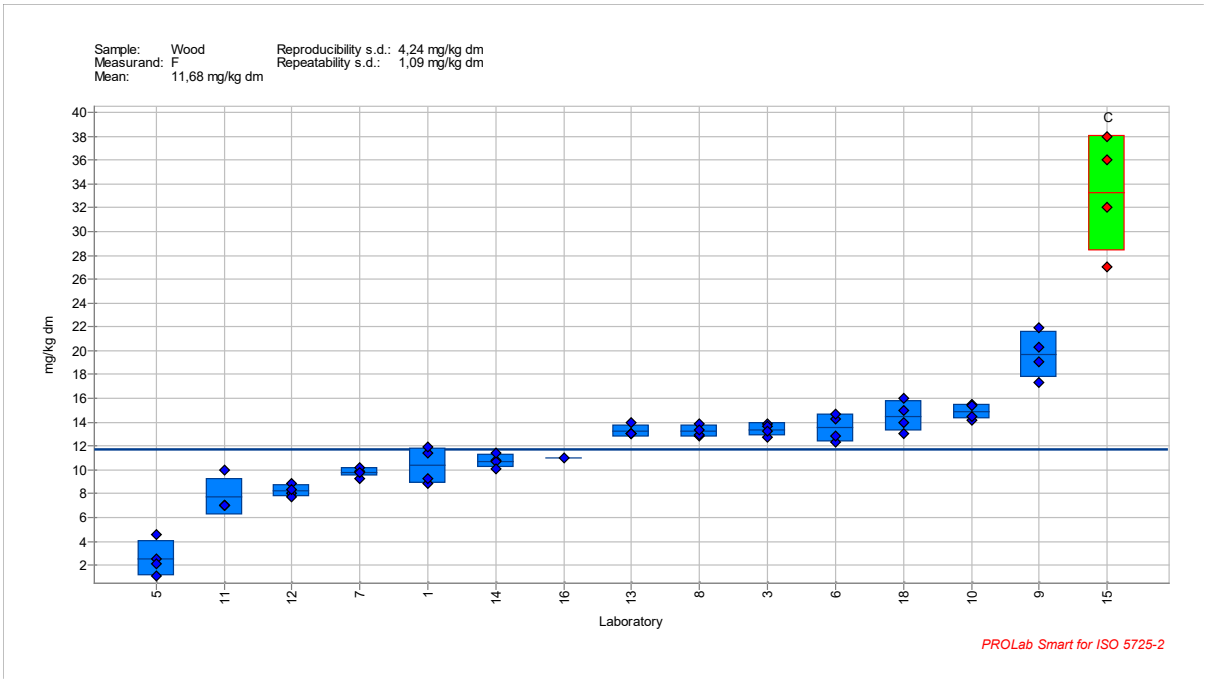

Figure 7 Results for fluorine content of wood sample

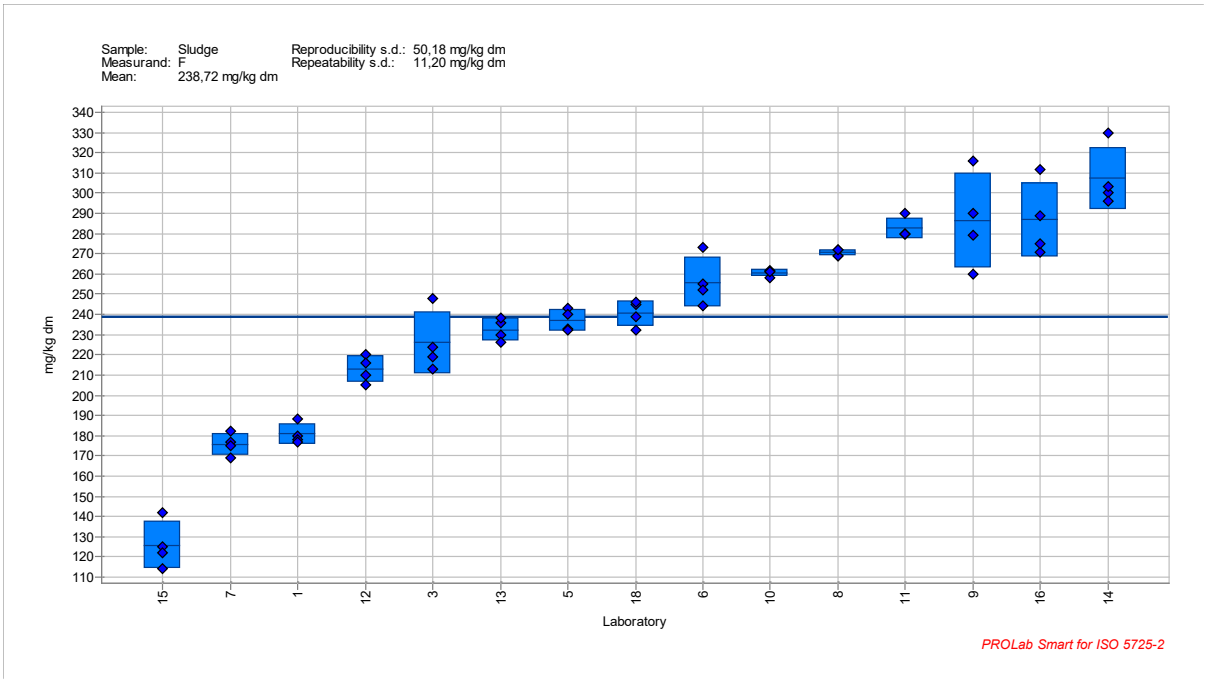

Figure 8 Results for fluorine content of sludge sample

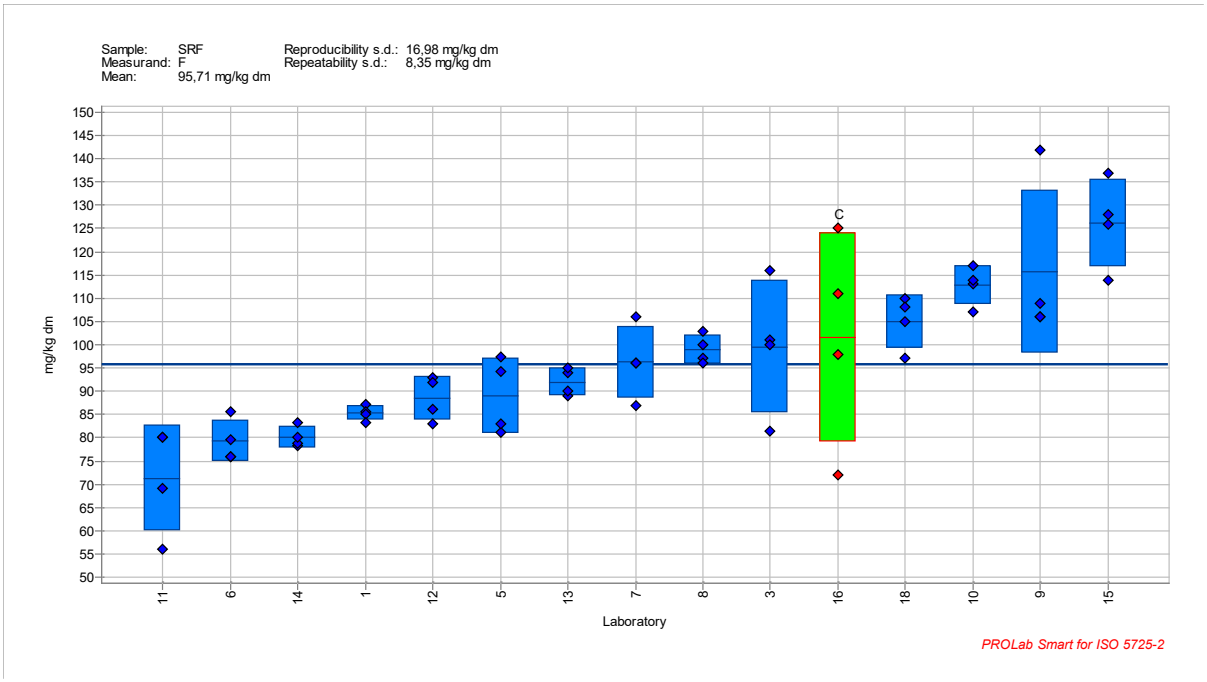

Figure 9 Results for fluorine content of SRF sample

D.2 Determination of chlorine content

In Figure 10 up to Figure 9 the graphical results are presented for the chlorine content for the 5 ILT samples.

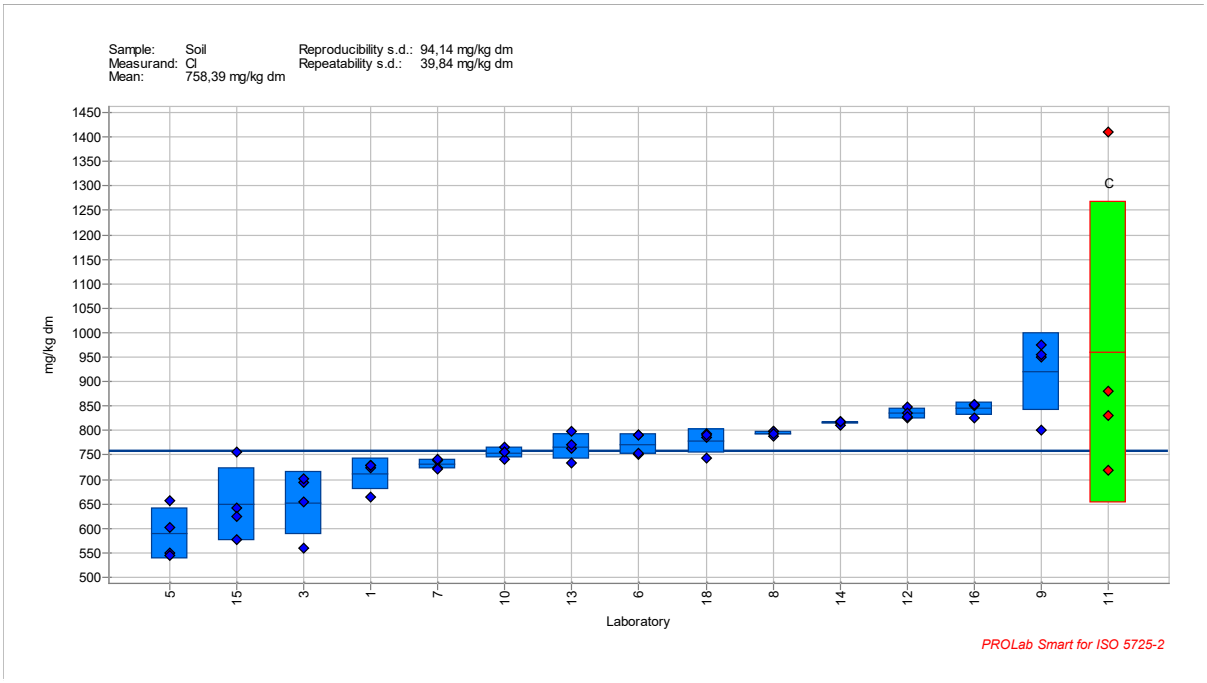

Figure 10 Results for chlorine content of soil sample

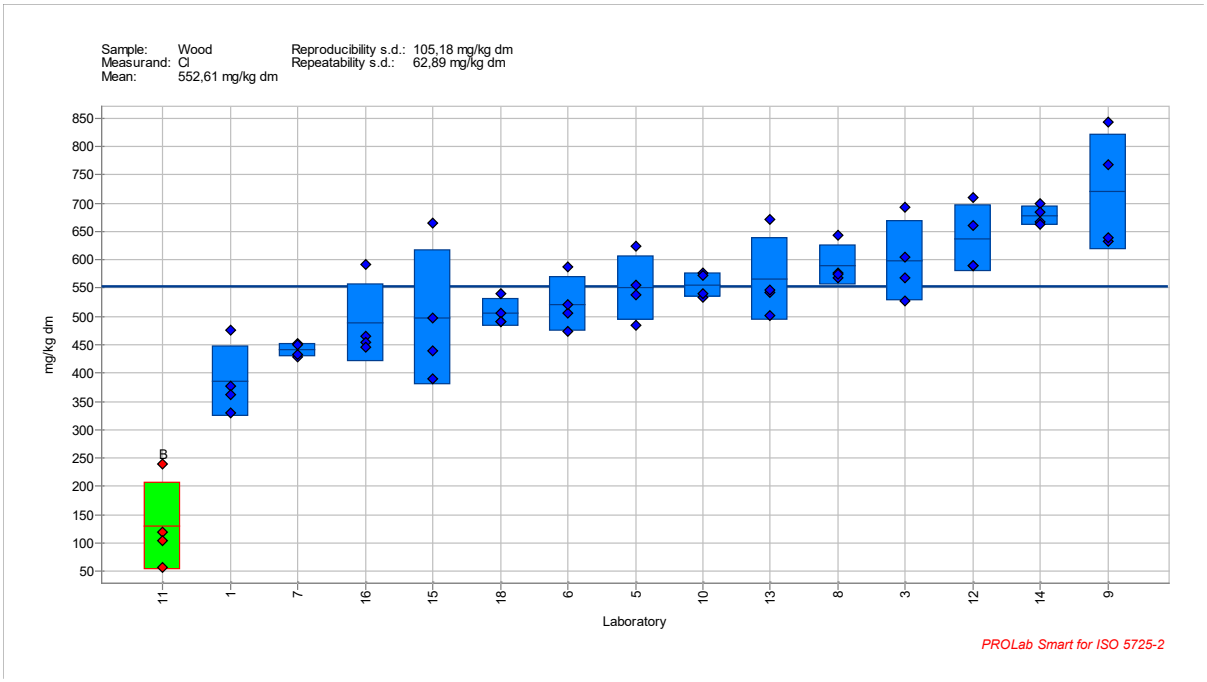

Figure 11 Results for chlorine content of wood sample

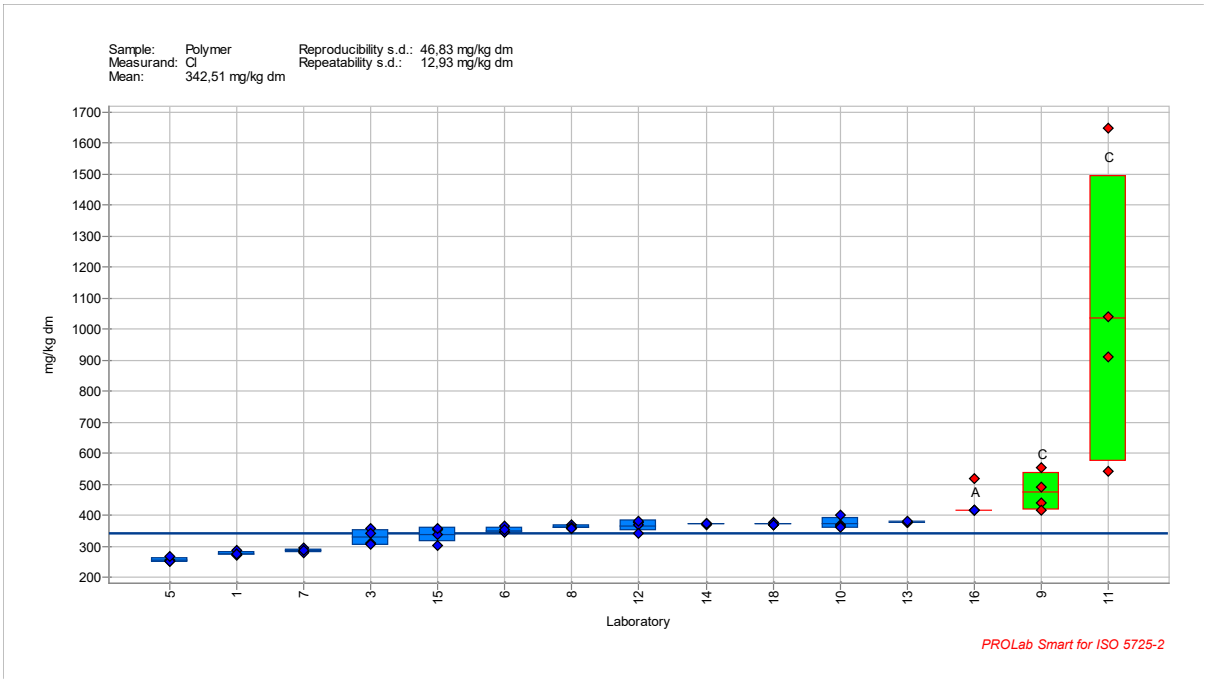

Figure 12 Results for chlorine content of polymer sample

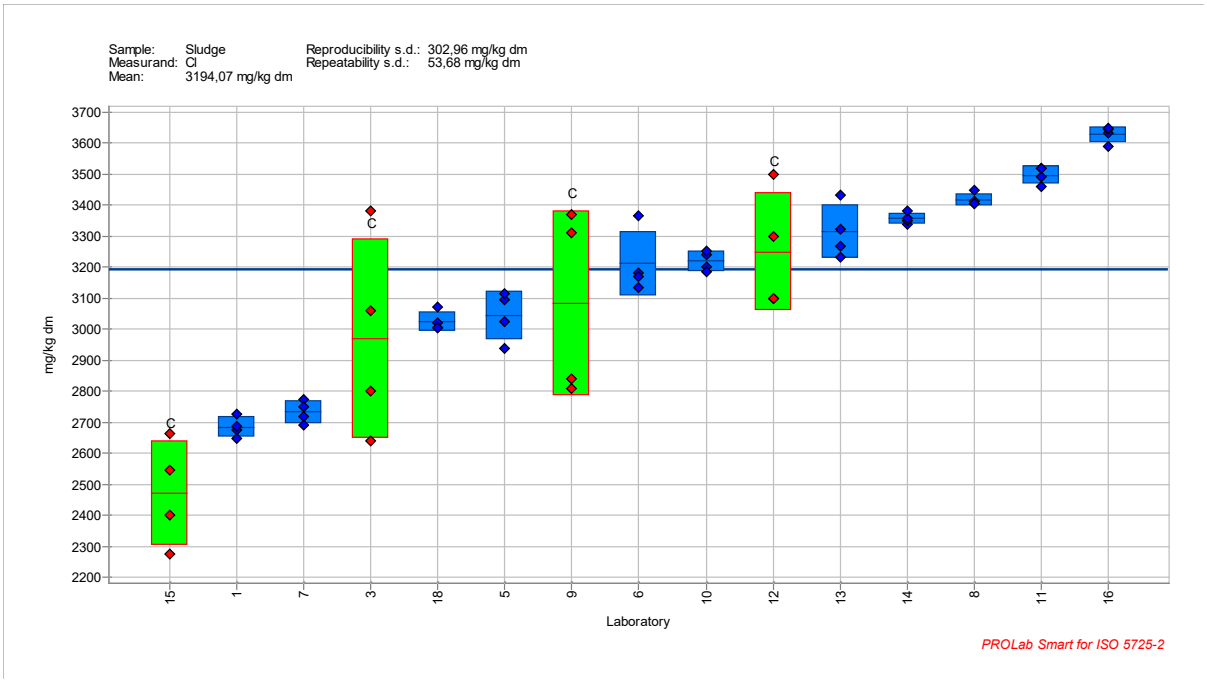

Figure 13 Results for chlorine content of sludge sample

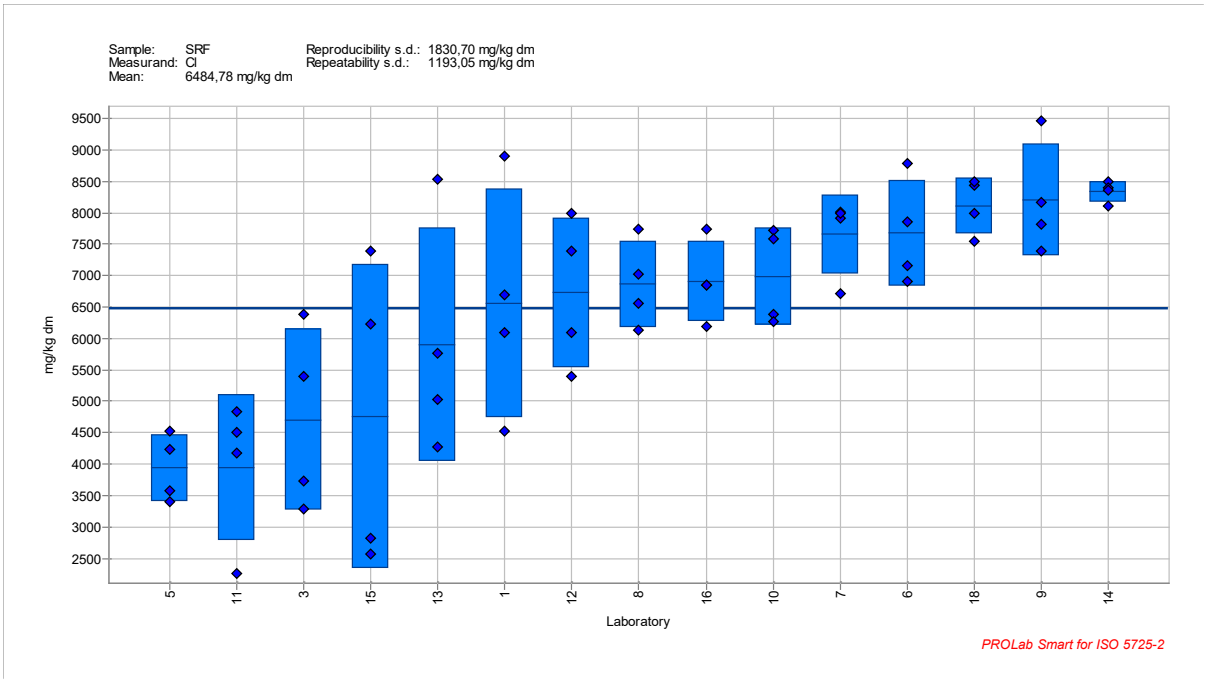

Figure 14 Results for chlorine content of SRF sample

D.3 Determination of bromine content

In Figure 15 up to Figure 20 the graphical results are presented for the bromine content for the 5 ILT samples.

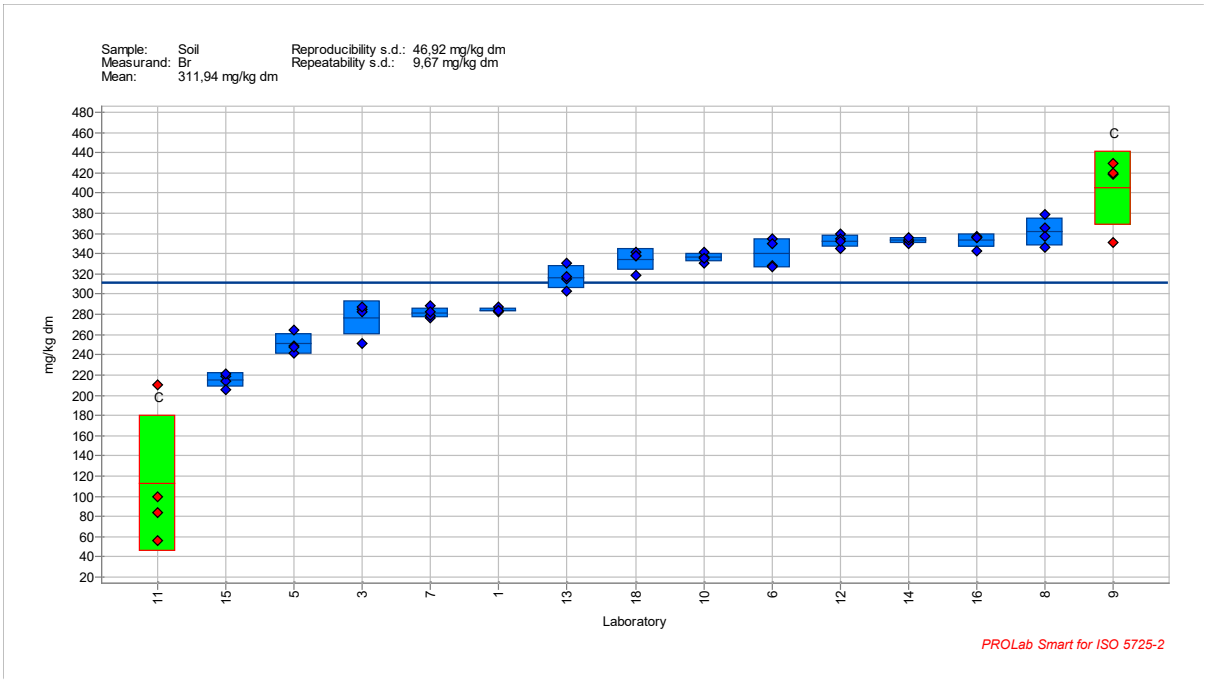

Figure 15 Results for bromine content of soil sample

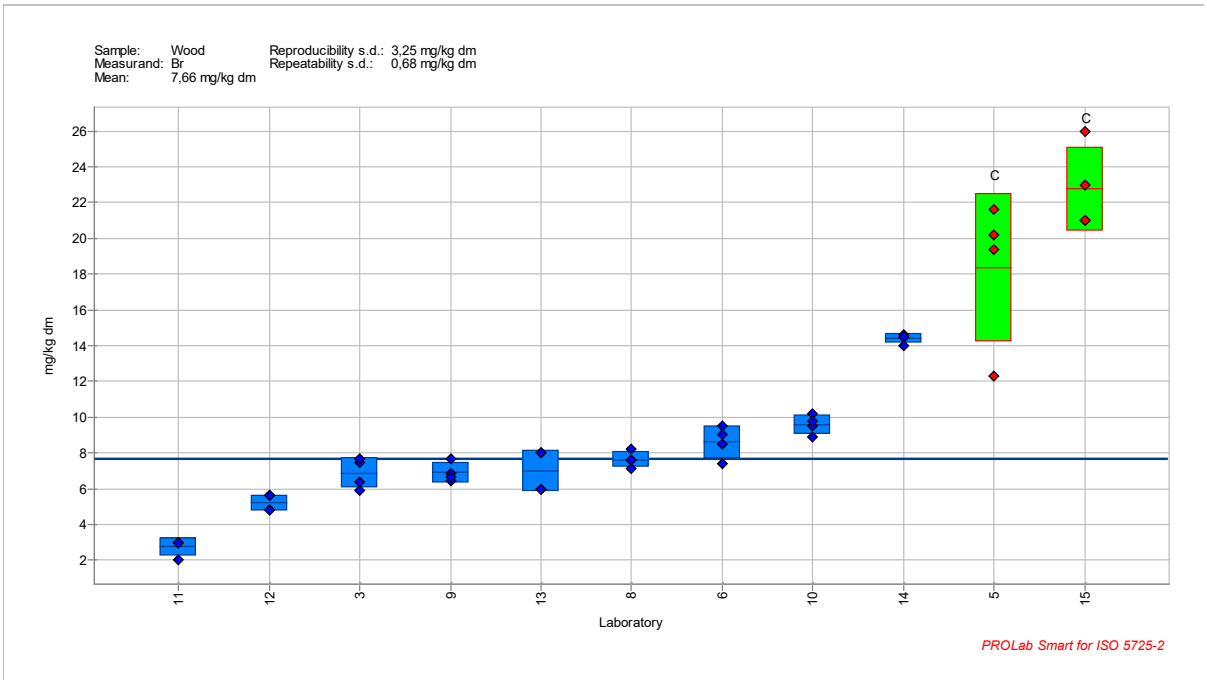

Figure 16 Results for bromine content of wood sample

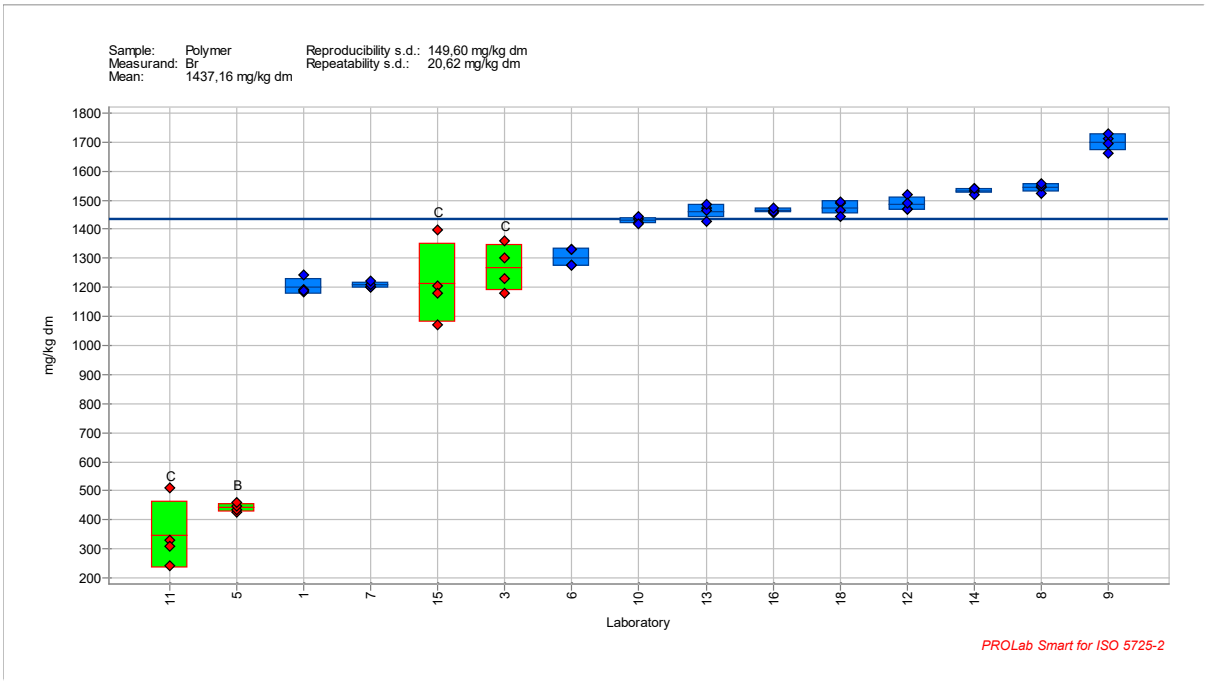

Figure 17 Results for bromine content of polymer sample

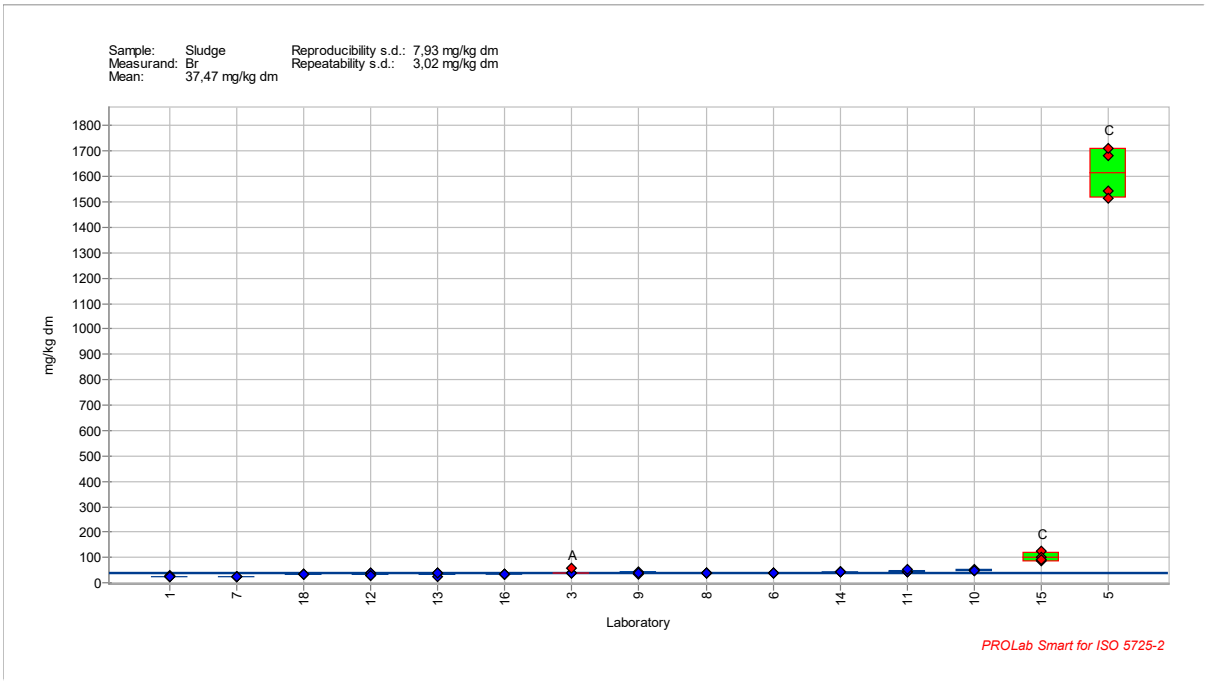

Figure 18 Results for bromine content of sludge sample

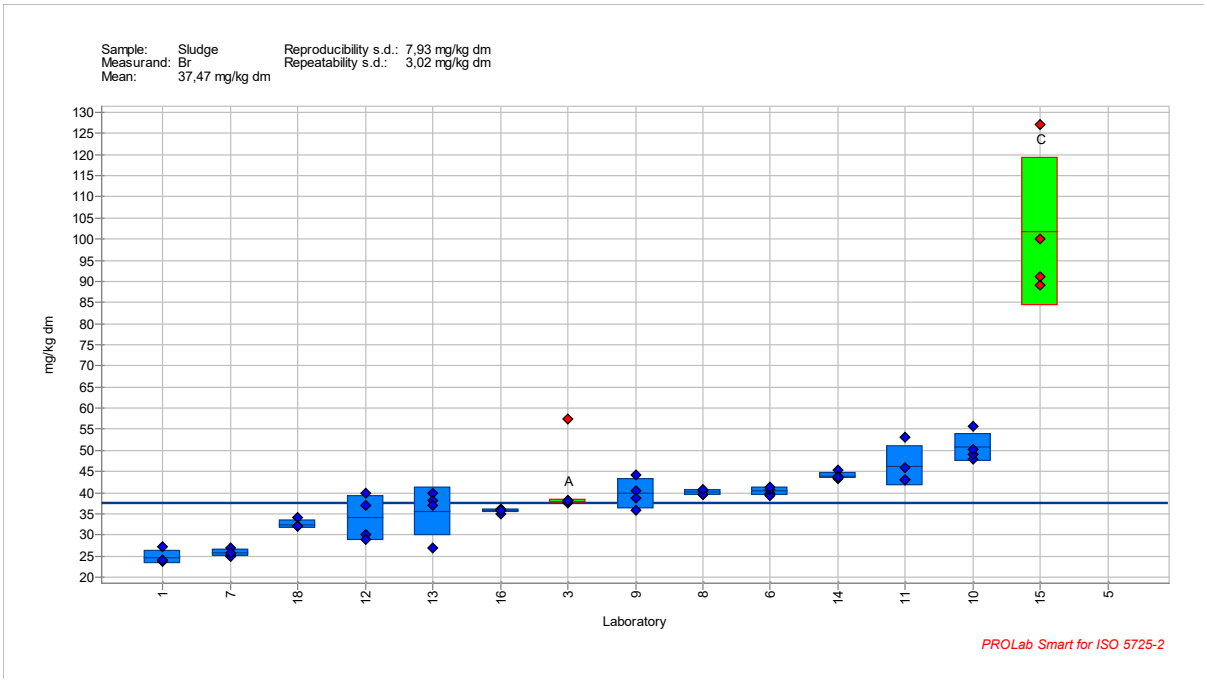

Figure 19 Results for bromine content of sludge sample without results of laboratory n°5

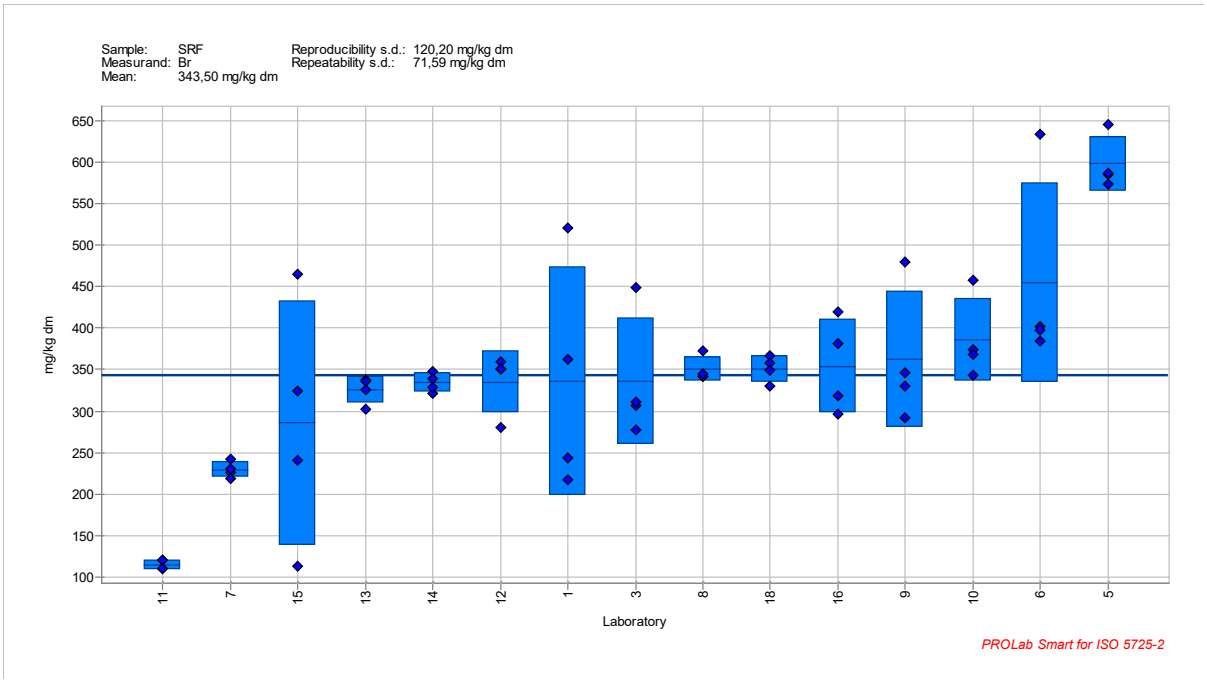

Figure 20 Results for bromine content of SRF sample

D.4 Determination of sulfur content

In Figure 21 up to Figure 25 the graphical results are presented for the sulfur content for the 5 ILT samples.

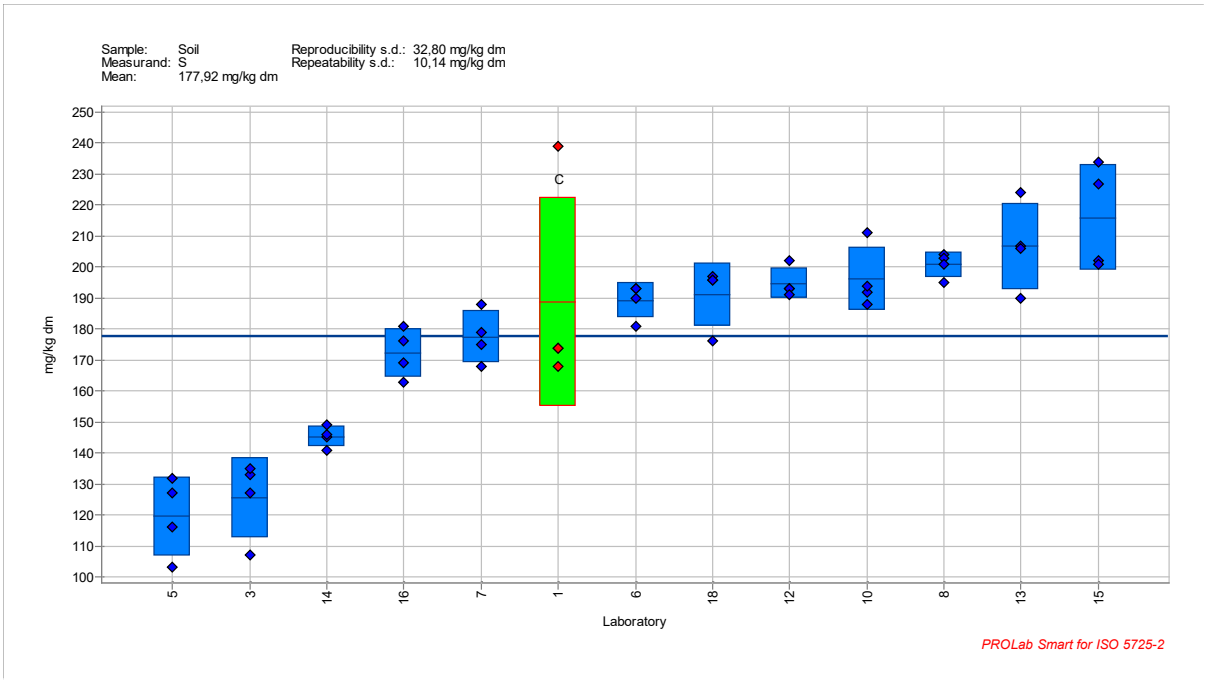

Figure 21 Results for sulfur content of soil sample

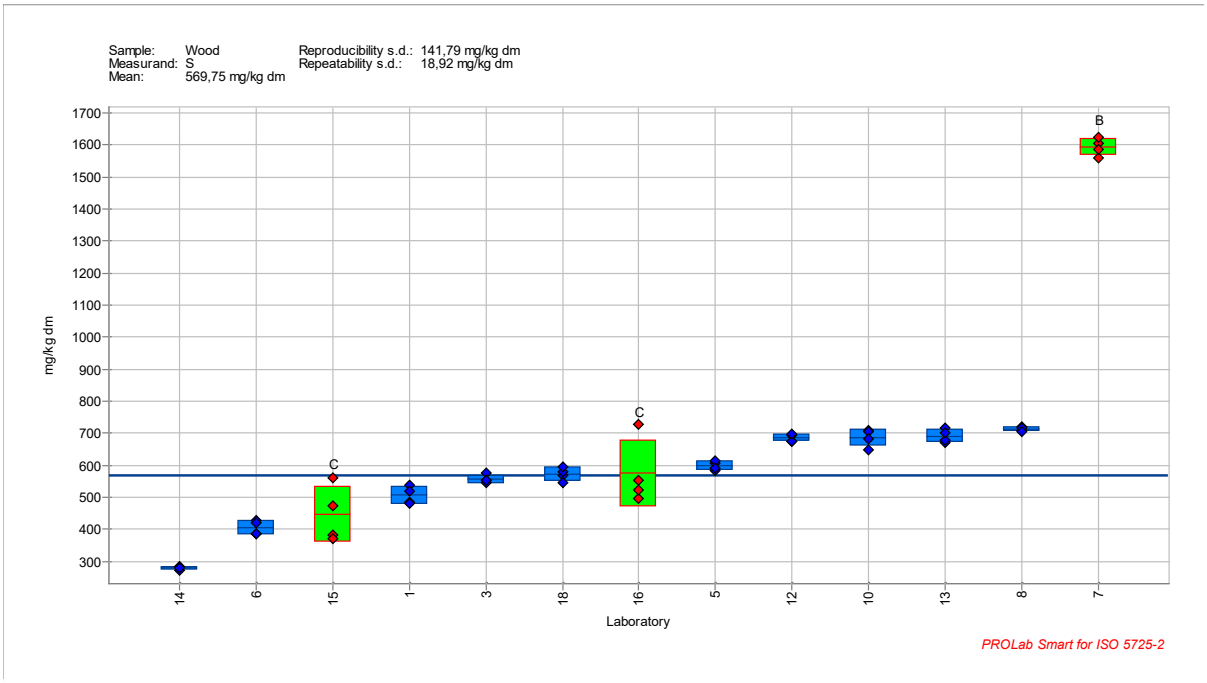

Figure 22 Results for sulfur content of wood sample

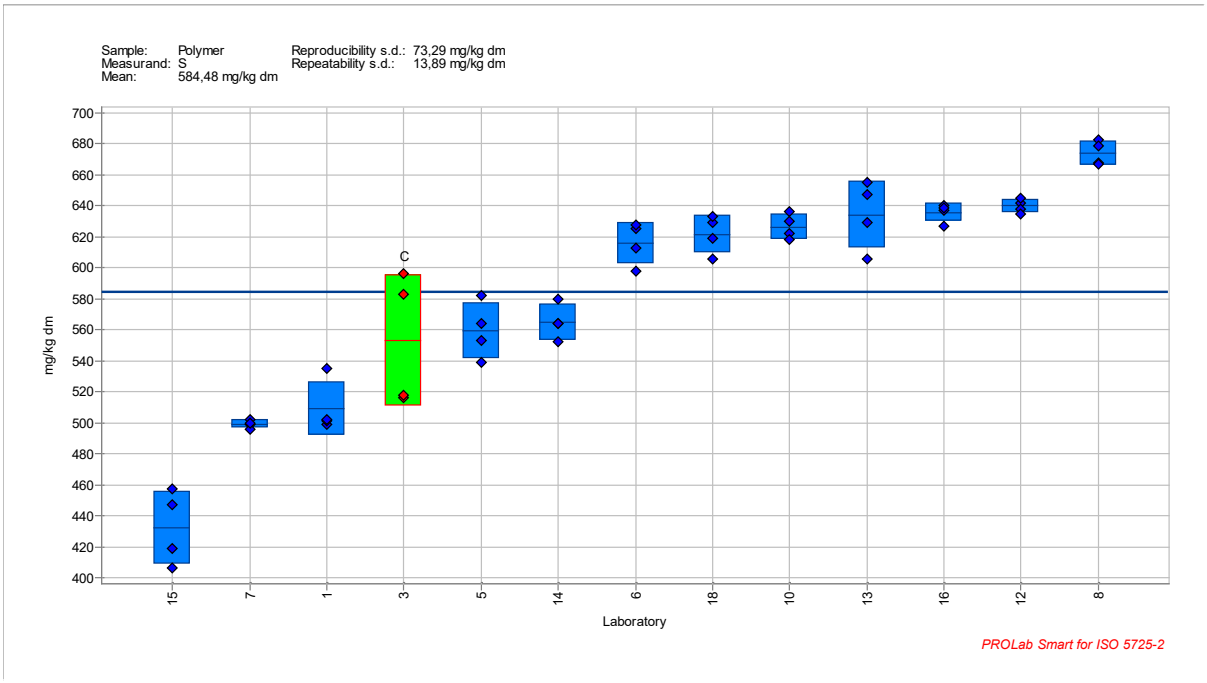

Figure 23 Results for sulfur content of polymer sample

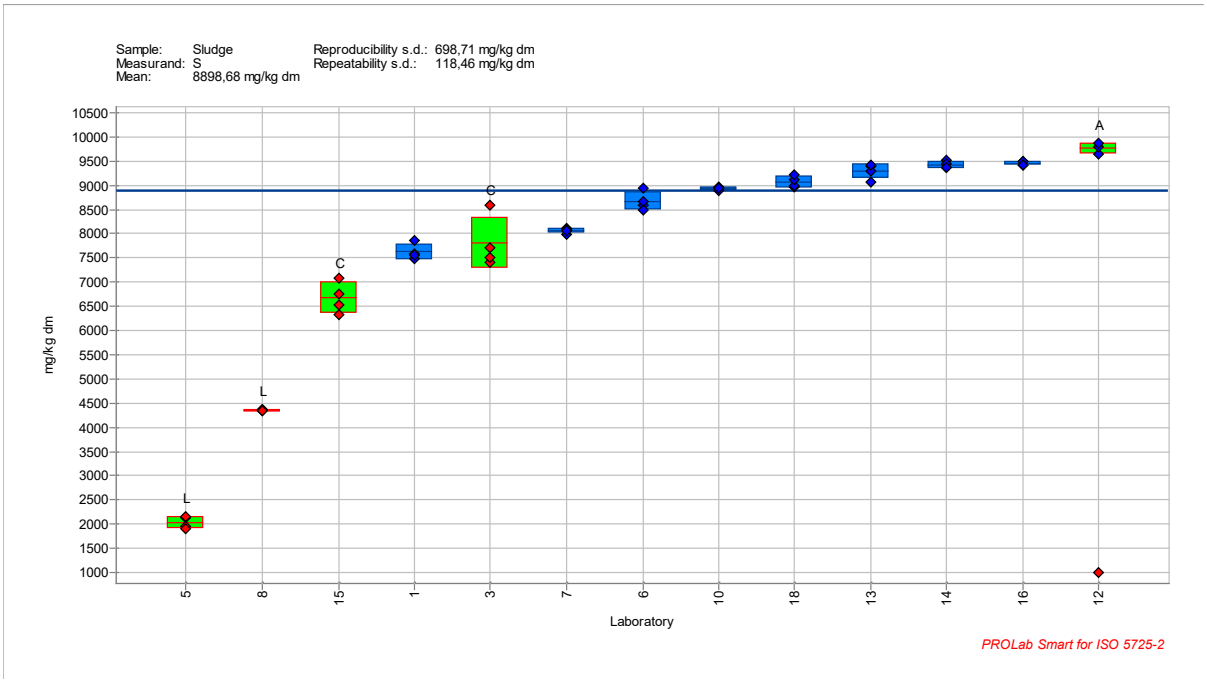

Figure 24 Results for sulfur content of sludge sample

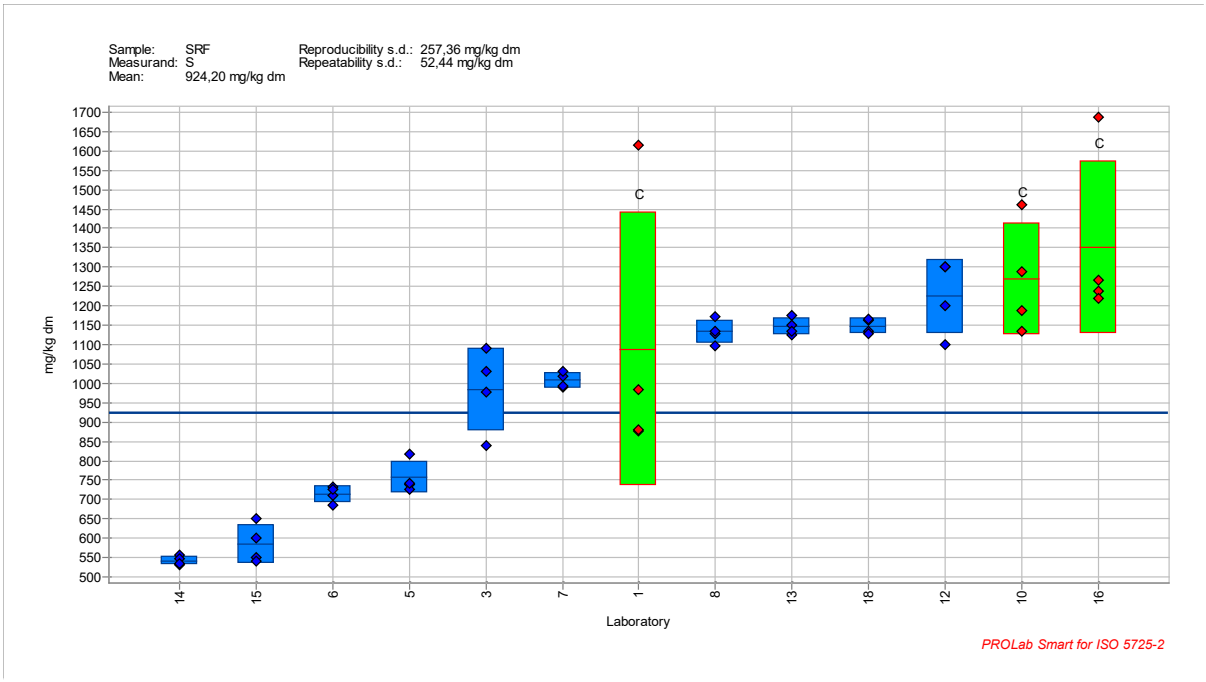

Figure 25 Results for sulfur content of SRF sample

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