Results of Proficiency Test
SCCP in Textile
November 2021

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis21T21

February 2022

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1 INTRODUCTION

Commercially produced Chlorinated Paraffins (CPs) are classified according to their carbon chain length into Short Chain CPs (SCCP C_{10}-C_{13}), Medium Chain CPs (MCCP C_{14}-C_{17}) and Long Chain CPs (LCCP >C_{17}). The Chlorine content of these mixtures can vary from 30-70% depending on the application. Technical CPs are used as plasticizers or fire retardants. CPs are classified as persistent and non-biodegradable and they accumulate in the food chain. SCCPs were categorized in group 2B as possibly carcinogenic to humans from the International Agency for Research on Cancer (IARC). SCCPs (chlorine content >48%) are listed by the Stockholm Convention on Persistent Organic Pollutants. In Europe SCCPs as constituents of articles are prohibited according to regulation 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants. Articles containing SCCPs in concentrations lower than 0.15% by weight are allowed. Furthermore, it became industrial practice to restrict MCCPs as well.

For the determination of SCCPs and MCCPs it may be that there is a large variation in test results between the different laboratories and thus with the comparability of laboratory results. Participation in a proficiency test (laboratory-evaluating interlaboratory study) may enable laboratories to check their performance. Therefore, a proficiency test for the determination of SCCP and MCCP compounds in textile was organized for the first time by the Institute for Interlaboratory Studies (iis) in November 2021 on request of many participants.

In this new interlaboratory study 12 laboratories in 8 different countries registered for participation. See appendix 3 for the number of participants per country. In this report the results of the proficiency test on SCCP in Textile are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory.
It was decided to send one cotton sample positive on SCCP and MCCP of approximately 3 grams labelled #21905.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

A batch of approximately 300 grams lilac colored cotton textile was selected which was made positive on SCCP and MCCP. After homogenization 30 small plastic bags were filled with approximately 3 grams each and labelled #21905.
The homogeneity of the subsamples was checked by determination of the total SCCP content according to ISO18219 on 9 stratified randomly selected subsamples.

	total SCCP in mg/kg
sample #21905-1	118.1
sample #21905-2	116.7
sample #21905-3	120.0
sample #21905-4	107.9
sample #21905-5	104.1
sample #21905-6	99.6
sample #21905-7	108.6
sample #21905-8	99.0
sample #21905-9	116.6

Table 1: homogeneity test results of subsamples #21905

From the above test results the repeatability was calculated and compared with 0.3 times the estimated reproducibility calculated with the Horwitz equation in agreement with the procedure of ISO13528, Annex B2 in the next table.

	total SCCP in mg/kg
r (observed)	22.7
reference method	Horwitz (n=9)
0.3 x R (reference method)	21.9

Table 2: evaluation of the repeatability of subsamples #21905

The calculated repeatability is in agreement with 0.3 times the estimated reproducibility calculated with the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one textile sample labelled #21905 was sent on October 6, 2021.

2.5 ANALYZES

The participants were requested to determine: SCCP and MCCP. It was also requested to report if the laboratory was accredited for the requested components and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample and to report the test results using the indicated units on the report form and not to round the test results, but report as much significant figures as possible. It was also requested not to report ‘less than’ test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis/. The reported test results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment. Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results (no reanalyzes). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organization of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5).
For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as '<…' or '>…' were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either 'unknown', 'OK', 'suspect' or 'not OK'. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1. was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data is shown as a triangle.

Furthermore, Kernel Density Graphs were made. This is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

3.3 z-scores

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements (derived from e.g. ISO or ASTM test methods), the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.
The z-scores were calculated according to:

$z_{(target)}$ = (test result - average of PT) / target standard deviation

The $z_{(target)}$ scores are listed in the test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

	|z|	< 1	good
1 <	|z|	< 2	satisfactory
2 <	|z|	< 3	questionable
3 <	|z|		unsatisfactory

4 Evaluation

In this proficiency test no problems were encountered with the dispatch of the samples. All participants reported test results before the final reporting date except one other participant who did not report any test results.
In total 11 participants reported 21 numerical test results. There were no outlying test results observed. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

Not all data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER COMPONENT

In this section the reported test results are discussed per component. The test methods which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the tables together in appendix 1 with the original data. The abbreviations, used in these tables, are explained in appendix 4.

Since early 2021 test method ISO22818 is available for the determination of total SCCP and total MCCP in textile products out of different matrices, especially in polymer of the coated fabrics, prints made of polymer and buttons made of polymer (e.g. PVC).
Unfortunately, the reliability in this test method, expressed as relative standard deviations (RSD), are mentioned for two specific type of coated fabrics only. For uncoated cotton samples, as in this PT, it is not clear which RSD to use from table C.1 in ISO22818:21 for the evaluation of results. Therefore, for the evaluation in this PT the calculated reproducibility was compared against the estimated reproducibility calculated with the Horwitz equation.

SCCP: This determination may not be problematic. No statistical outliers were observed. The calculated reproducibility is in full agreement with the estimated reproducibility calculated with the Horwitz equation (n=9) but not with the requirements of ISO22818:21.

MCCP: This determination may be problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the estimated reproducibility calculated with the Horwitz equation (n=9) nor with the requirements of ISO22818:21.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the estimated target reproducibilities and the reproducibilities as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility estimated with the Horwitz equation are compared in the next table.

Component	unit	n	average	2.8 * sd	R(target)
SCCP	mg/kg	10	82.0	53.8	56.8
MCCP	mg/kg	11	366	398	202

Table 3: reproducibilities of components on sample #21905

Without further statistical calculations, it can be concluded that for SCCP there is a good compliance of the group of participating laboratories with the reference method but may have difficulties with the analyzes of MCCP. See also the discussion in paragraphs 4.1 and 5.

4.3 PERFORMANCE OF THE PROFICIENCY TEST OF NOVEMBER 2021

	November 2021
Number of reporting laboratories	11
Number of test results	21
Number of statistical outliers	0
Percentage of statistical outliers	0%

Table 4: overview of the proficiency test

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency test was compared, expressed as relative standard deviation (RSD), see next table.

Component	November 2021	ISO22818	Horwitz (n=9)
SCCP	23%	18.7%	25%
MCCP	39%	16.1%	20%

Table 5: comparison of the uncertainties in this PT with reference method

The observed uncertainties in this PT for both SCCP and MCCP are higher than the relative standard deviations mentioned in ISO22818:21, especially for MCCP. Compared to the estimated reproducibility from the Horwitz equation the observed reproducibility for SCCP is in line but the observed reproducibility for MCCP is much higher.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The test method ISO22818 is used by the majority of the reporting participants.
For this PT some analytical details were requested which are given in appendix 2. Based on the answers given by the 11 participants the following can be summarized:

- 8 participants mentioned that they are accredited to determine the reported component(s).
- 8 participants used the sample as received and 3 participants did further cut the sample prior to analysis.
- 10 participants used 0.5 grams of sample intake, 1 participant used 1 grams.
- 8 participants have used Toluene as extraction solvent, 3 participants used Hexane or a Hexane mixture
- Almost all participants used an extraction time of 60 minutes and an extraction temperature of 60°C.

Since the majority of the laboratories used the same method (ISO22818) to extract and determine SCCP and MCCP and mentioned the same analytical details, no further analyzes are performed.

5 DISCUSSION

All reporting participants were able to detect SCCP and MCCP in the sample.

In Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutant it is mentioned that articles containing SCCPs in concentrations lower than 0.15% by weight are allowed. When the results of this interlaboratory study were compared to this regulation, it was noticed that all participants would accept both SCCP and MCCP levels in the sample.

6 CONCLUSION

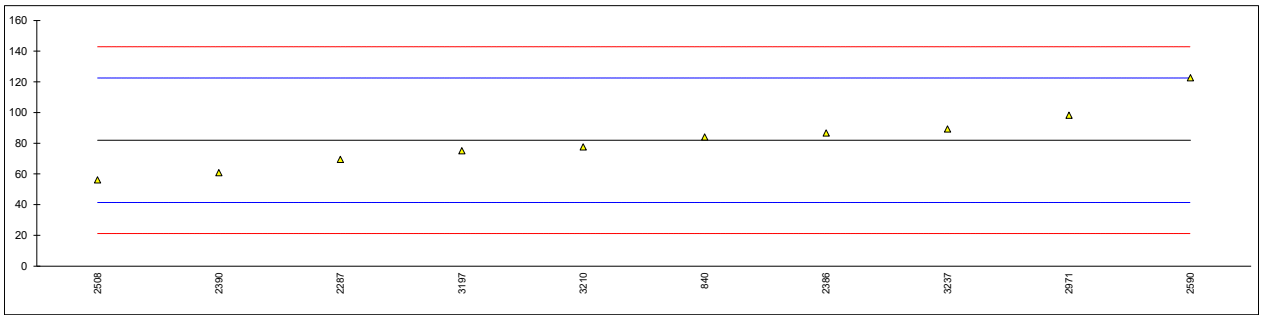
Although it can be concluded that most of the participants have no problem with the determination of SCCP and/or MCCP in this PT, each laboratory will have to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

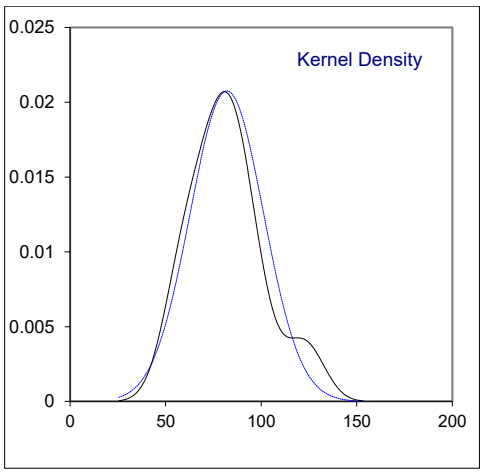
APPENDIX 1

Determination of SCCPs, CAS No. 85535-84-8 on sample #21905; results in mg/kg

lab	method	value	mark	z(targ)	remarks
840	ISO22818	84		0.10	
2287	ISO22818	69.52		-0.61	
2295		-----		-----	
2386	ISO22818	86.64		0.23	
2390	ISO18219	60.8		-1.05	
2508	ISO22818	56.19		-1.27	
2590	ISO22818	122.59		2.00	
2826	ISO18219-1	<200		-----	
2971	ISO22818	98.2		0.80	
3197	ISO22818	75.1		-0.34	
3210	ISO22818	77.635		-0.21	
3237	ISO17881-2	89.21		0.36	

	normality	suspect
	n	10
	outliers	0
	mean (n)	81.989
	st.dev. (n)	19.2224
	R(calc.)	53.823
	st.dev.(Horwitz n=9)	20.2743
	R(Horwitz n=9)	56.768
Compare		
	R(ISO22818:21)	42.929

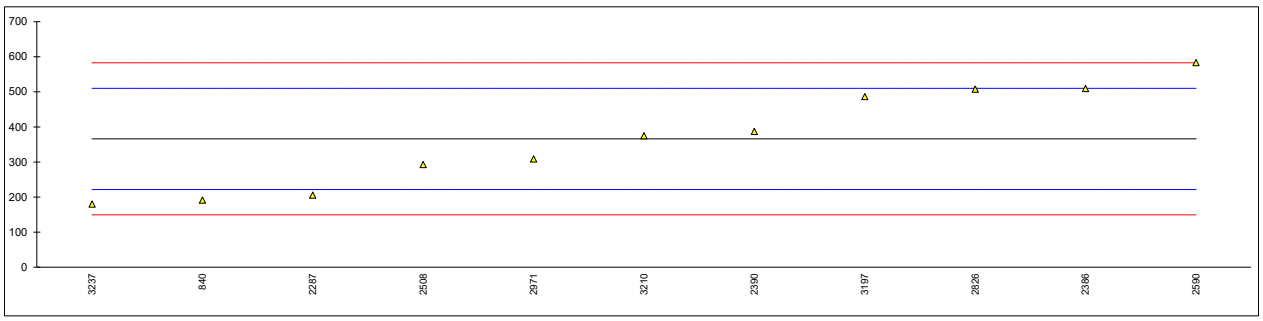


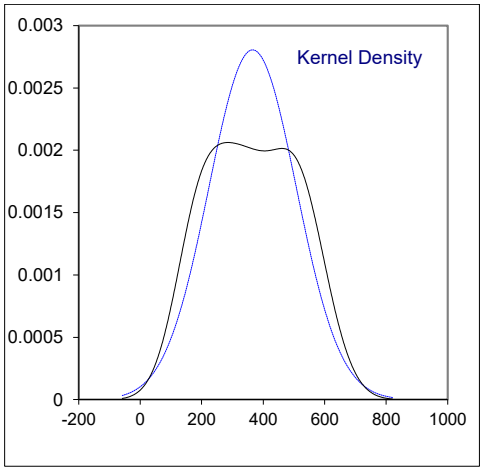


Determination of MCCPs, CAS No. 85535-85-9 on sample #21905; results in mg/kg

lab	method	value	mark	z(targ)	remarks
840	ISO22818	191		-2.42	
2287	ISO22818	205.3		-2.22	
2295		-----		-----	
2386	ISO22818	508.90		1.98	
2390	ISO18219	387.3		0.30	
2508	ISO22818	292.32		-1.02	
2590	ISO22818	583.02	C	3.01	first reported 1166.03
2826	ISO18219-2	507.336		1.96	
2971	ISO22818	308.4		-0.79	
3197	ISO22818	485.9		1.66	
3210	ISO22818	374.351		0.12	
3237	ISO17881-3	179.6		-2.58	

	normality	OK
	n	11
	outliers	0
	mean (n)	365.766
	st.dev. (n)	142.2441
	R(calc.)	398.283
	st.dev.(Horwitz n=9)	72.2178
	R(Horwitz n=9)	202.210
Compare		
	R(ISO22818:21)	164.887





APPENDIX 2 Analytical details

lab	ISO/IEC17025 accredited	sample preparation before use	sample intake (g)	extraction solvent	extraction time (minutes)	extraction temp. (°C)
840	Yes	Used as received	0.5031	Toluene	60	60
2287	No	Used as received	0.5g	Hexane	60 min	60 ℃
2295	---	---				
2386	Yes	Used as received	0,7	Toluene	60	60
2390	Yes	Further cut	0.5 g	Toluene	60 minute	60 °C
2508	Yes	Used as received	0.5	Toluene	60	60
2590	No	Used as received	0.5g	toluene	60 min	60°C
2826	Yes	Used as received	0.5g	Toluene	60 minutes	60°C
2971	Yes	Used as received	0.5	toluene	60	60
3197	Yes	Further cut	0,5	toluene/n-hexane	60 min (1.process) 15 min (2.process)	60
3210	No	Further cut	1 g	Toluene	60 minutes	60°C
3237	Yes	Used as received	0,5	Hexane/acetone	45	Room Temp.

APPENDIX 3

Number of participants per country

1 lab in	FRANCE
2 labs in	GERMANY
1 lab in	HONG KONG
1 lab in	ITALY
1 lab in	JAPAN
1 lab in	PAKISTAN
3 labs in	TURKEY
2 labs in	VIETNAM

APPENDIX 4

Abbreviations

C	= final test result after checking of first reported suspect test result
D(0.01)	= outlier in Dixon's outlier test
D(0.05)	= straggler in Dixon's outlier test
G(0.01)	= outlier in Grubbs' outlier test
G(0.05)	= straggler in Grubbs' outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
R(0.01)	= outlier in Rosner's outlier test
R(0.05)	= straggler in Rosner's outlier test
E	= calculation difference between reported test result and result calculated by iis
W	= test result withdrawn on request of participant
ex	= test result excluded from statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

Literature

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