

Results of Proficiency Test
TCEP in Foam
February 2014

Organised by: Institute for Interlaboratory Studies
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1 INTRODUCTION

The substance tris(2-chloroethyl)phosphate (TCEP) is an alkyl phosphate ester used as a Flame-retardant plasticiser and viscosity regulator in polyurethanes, polyester resins, polyacrylates and other polymers. The main industrial branches in which TCEP has been used are the building industry, the furniture and the textile industry.

However, production and use has been in decline since the 1980s, when TCEP has been progressively replaced by other flame retardants. TCEP was comprehensively evaluated under the EU existing substances regulation (EEC) 793/93 in 2009. TCEP is classified under Regulation (EC) No 1272/2008 as a carcinogenic, mutagenic and toxic substance. In March 2012, the European Union decided to lower the limit of TCEP in toys (5 mg/kg). Regrettably, no certified reference materials (CRMs) for TCEP are available to optimise the determination of TCEP. As an alternative, participation in a proficiency test may enable the laboratories to check their performance and thus to increase this comparability. Therefore, a proficiency testing scheme (laboratory-evaluating interlaboratory study) for the determination of TCEP was started by the Institute for Interlaboratory Studies.

In the international interlaboratory study of February 2014, 25 laboratories from 11 different countries participated (See appendix 3). In this report the results of the proficiency test are presented and discussed.

2 SET UP

The Institute for Interlaboratory Studies in Spijkenisse was the organizer of this proficiency test. It was decided to send 1 foam sample (approximately 3 gram), positive on TCEP, and labelled #14007. Participants were requested to report rounded and unrounded test results. These unrounded test results were preferably used for statistical evaluation. The participants were asked to report the analytical results using the indicated units on the report form.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Also customer's satisfaction is measured on a regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organization was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organization, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

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 suitable foam, positive on TCEP, was obtained from the market via a third party laboratory. Samples of approx. 3 gram were prepared, by cutting it. Eight stratified randomly selected samples were tested using an in house test method to check the homogeneity of the batch. See the following table for the test results.

	<i>TCEP in mg/kg</i>
sample #14007-1	1022
sample #14007-2	987
sample #14007-3	1020
sample #14007-4	941
sample #14007-5	1001
sample #14007-6	1028
sample #14007-7	1058
sample #14007-8	1052

table 1: homogeneity test results of subsamples #14007

From the test results of table 1, the repeatabilities were calculated and compared with 0.3 times the corresponding estimated target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	<i>TCEP in mg/kg</i>
r (observed)	71
reference method	EN71-11:2005
0.3*R (reference method)	67

table 2: evaluation of the precision data of subsamples #14007

The repeatability of the results of homogeneity test for TCEP was in agreement with the 0.3 times the estimated reproducibility limit of the respective test method.

Therefore, homogeneity of the subsamples was assumed.

Approx. 3 grams of sample #14007 was sent to each of the participating laboratories on January 29, 2014.

2.5 ANALYSES

The participants were requested to determine the concentration of TCEP, applying the analysis procedure that is routinely used in the laboratory. To get comparable results a detailed report form, on which the unit was prescribed, was sent together with the sample. Also, a letter of instructions was added to the package. The laboratories were also requested to report some of the test conditions that the laboratory has used.

3 RESULTS

During four weeks after sample despatch, the results of the individual laboratories were gathered. The original data are tabulated in the appendices of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder fax was sent to those laboratories that had not yet reported. Shortly after the deadline, the available results were screened for suspect data. A result was called suspect in case the Huber Elimination Rule (a robust outlier test, see lit.5) found it to be an outlier. The laboratories that produced these suspect data were asked to check the results. Additional or corrected data are placed under 'Remarks' in the result tables in appendix 1. A list of abbreviations used in the tables can be found in appendix 5.

3.1 STATISTICS

The protocol followed in the organisation of this proficiency test is described in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of January 2010 (iis-protocol, version 3.2).

For the statistical evaluation the *unrounded* (when available) figures were used instead of the rounded results. 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. After removal of outliers this check was repeated. In case a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

In accordance with ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon and Grubbs outlier tests. Outliers are marked by D(0.01) for the Dixon test and by G(0.01) or DG(0.01) for the Grubbs test. Stragglers are marked by D(0.05) for the Dixon test and by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test (ref. 14). Both outliers and stragglers were not included in the calculations of the averages and the 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. When the uncertainty passed the evaluation no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have consequences for the evaluation of the test results.

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

3.2 GRAPHICS

In order to visualise 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 analysis results are plotted. The corresponding laboratory numbers are under 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 standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. The Kernel Density Graph 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 was projected over the Kernel Density Graph for reference.

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, e.g. EN reproducibility, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the spread of this interlaboratory study. The target standard deviation was calculated from the literature reproducibility by division with 2.8.

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 the fit-for-useness of the reported test result.

In case no literature reproducibility was available, other target values were used. In some cases literature repeatability is available; in other cases a reproducibility of a former iis proficiency test could be used and also the Horwitz equation can be used to estimate target reproducibility.

The z-scores were calculated according to:

$$Z_{(\text{target})} = (\text{result} - \text{average of PT}) / \text{target standard deviation}$$

Absolute values for $z < 2$ are very common and absolute values for $z > 3$ are very rare. 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

During the execution of this proficiency test no reporting problems occurred. Twenty three participants reported a test result of which five participants after the deadline. Two participants did not report any test results. Finally, the 23 participants did report 23 numerical results. Observed was 1 outlying result, which is 4.3% of the numerical results. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

The data set of TCEP does not show a Gaussian distribution.

Regretfully in EN71-11:2005, no reproducibility requirements for TCEP are mentioned, but only the standard deviation for the repeatability.

The target reproducibility is estimated as follows: the standard deviation was multiplied with 2.8 to get the target repeatability. And this was multiplied with 3 to get an estimate of the target reproducibility.

4.1 EVALUATION PER COMPONENT

In this section, the results are discussed per sample. All statistical results reported on the foam sample are summarised in appendix 1 and analytical details are summarised in appendix 2.

TCEP: The determination of this flame retardant at a concentration level of 900 mg/kg was problematic. The test results reported by the participants vary from 455.6 – 2930 mg/kg. Only one statistical outlier was observed. However, the observed reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility of EN71-11:2005.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the relevant standard method and the reproducibility as found for the group of participating laboratories.

The number of significant test results, the average result, the calculated reproducibility (standard deviation*2.8) and the target reproducibility, calculated using the Horwitz equation are presented in the next table.

Parameter	unit	n	Average	2.8 * sd	R(target)
TCEP	mg/kg	23	899.4	579.2	196.4

table 3: reproducibility of TCEP in sample #14007

Without further statistical calculations, it can be concluded that the group of participating laboratories have problems with the analysis of TCEP in foam at this level.

See also the discussion in paragraphs 4.1 and 5.

4.3 EVALUATION OF THE TEST METHODS USED

Most participants reported to have used an 'in house' test method. It is remarkable that only three participants reported to have used the EN71-11 method.

The reported details of the methods that were used by the participants are listed in appendix 2.

5 DISCUSSION

A number of different test methods were reported to have been used. Most often "in house" (17 laboratories) was mentioned as test method used, followed by EN71 (3 laboratories). From the details it can be noticed that several different extraction solvents were used. It is remarkable to see that when only the reported results were evaluated of the laboratories that used Acetonitrile (as prescribed in EN71), the calculated reproducibility of the group is in good agreement with the estimated target reproducibility of EN71-11:2005.

The average of the Acetonitrile test results is high in comparison with the consensus value, while the average of the test results using ethylacetate:hexane=1:1 for extraction (average is 871 mg/kg, st.dev is 102.6 mg/kg), is low in comparison with the consensus value.

Not surprisingly, the choice of solvent used is of utmost importance.

It can be concluded that the observed spread in this interlaboratory study may not be caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary.

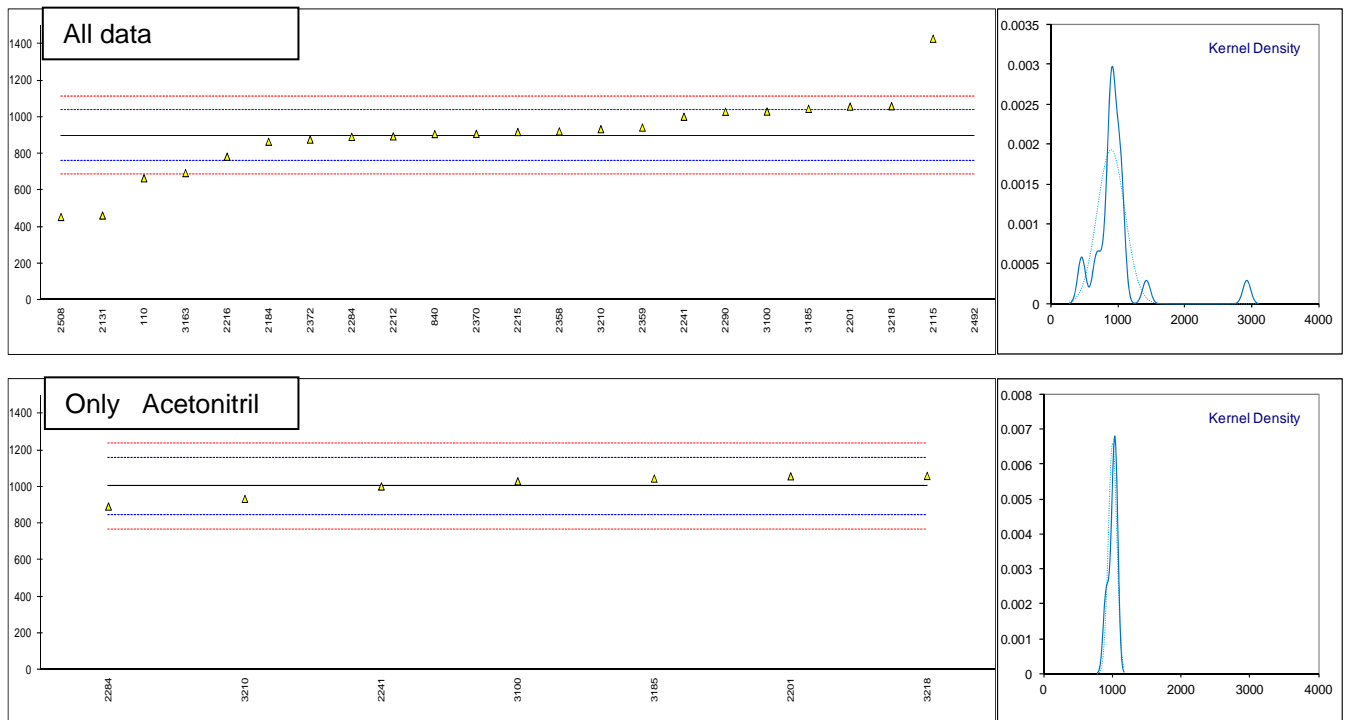
APPENDIX 1

Determination of Tris(2-chloro-ethyl)phosphate (TCEP) in sample #14007; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	INH-221	666.36		-3.32	
840	in house	907.95		0.12	
2115	Oeko-Tex	1428		7.54	
2131	in house	463.48		-6.21	
2184	in house	866		-0.48	
2201	in house	1057.5		2.25	
2212	in house	895.1		-0.06	
2215	in house	918.9		0.28	
2216	INH-82	784.33		-1.64	
2241	in house	1002.4		1.47	
2284	EN71	892.8		-0.09	
2290	in house	1029.48		1.85	
2358	in house	922.48		0.33	
2359	in house	943.4		0.63	
2370	in house	909		0.14	
2372	EPA3550C	877.8		-0.31	
2492	in house	2930	R(0.05)	28.95	
2508	EN15777	455.6		-6.33	
2571		----		----	
3100	EN71	1030.5		1.87	
3163	in house	695	C	-2.91	First reported 195
3185	EN71	1045.5		2.08	
3210	in house	934.4		0.50	
3218	in house	1060		2.29	
3220		----		----	

Only Laboratories that used Acetonitril:

normality	not OK	OK
n	22	7
outliers	1	0
mean (n)	899.36	1003.30
st.dev. (n)	206.843	65.360
R(calc.)	579.16	183.01
R(EN71-11:05)	196.42	219.12



APPENDIX 2

Analytical details

lab	grinded/cut	Size (mm)	extraction solvent	time	detection technique	recovery
110	Cut	3*3	Ethylacetate:hexane (1:1)	1 hr	GC/MS	Yes, 93%
840	Cut	3*3	Ethylacetate:hexane (1:1)	1 hr, Ultrasonic	--	Yes, 87%
2115	Cut	0.5*0.5	Hexane	20min, ASE	GC/MS	Yes, 99%
2131	Cut	--	Hexane	3.5 hrs	GC/MS	No
2184	--	--	Acetone/hexane/MTBE	3 hrs	GC/MS	No
2201	Cut	2*2	Acetonitril	1 hr, Ultrasonic	--	No
2212	--	<2	THF	1 hr	GC/MS	Yes, 89%
2215	--	1*1	Toluene	2 hrs	GC/MS	No
2216	Cut	small pieces	THF	1 hr	GC/MS	Yes, 90%
2241	--	5*5*5	Acetonitril	1 hr, Ultrasonic	--	Yes, 95%
2284	--	5*5	Acetonitril	1 hr	LC/MS	Yes, 105%
2290	--	--	Chlorobenzene	30 min	GC/MS	Yes, 95%
2358	--	5*5	Ethylacetate:hexane (1:1)	1.5 hrs	GC/MS	Yes, 95%
2359	Cut	3*3	Ethylacetate:hexane (1:1)	1 hr	GC/MS	Yes, 108%
2370	Cut	3*3	Ethylacetate:hexane (1:1)	1.5 hrs	GC/MS	Yes, 92.7%
2372	Cut	0.5*0.5	Ethylacetate:hexane (1:1)	1 hr, sonication	GC/MS	Yes, --
2492	Cut	5	hexane	3 hrs	GC/MS/MS	No
2508	--	--	--	--	--	--
2571	--	--	--	--	--	--
3100	--	--	Acetonitril	1 hr	GC/MS	No
3163	--	--	--	thermal desorption	GC/MS	--
3185	--	--	Acetonitril	1 hr	GC/MS	No
3210	Cut	<4	Acetonitril	1.5 hrs, ultrasonic	LC/MS/MS	--
3218	Cut	3*3	Acetonitril	1 hr, ultrasonic	GC/MS	No
3220	--	--	--	--	--	--

APPENDIX 3

Number of participants per country

1 lab in	FRANCE
1 lab in	GERMANY
5 labs in	HONG KONG
1 lab in	INDIA
1 lab in	ITALY
8 labs in	P.R. of CHINA
1 lab in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
1 lab in	THE NETHERLANDS
2 labs in	U.S.A.
2 labs in	VIETNAM

APPENDIX 4

Abbreviations:

C	= final result after checking of first reported suspect 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
R(0.05)	= straggler in Rosner's outlier test
DG(0.01)	= outlier in Double Grubbs' outlier test
DG(0.05)	= straggler in Double Grubbs' outlier test
n.e.	= not evaluated
n.d.	= not detected

Literature:

- 1 DIN 53316
- 2 ISO 17234:2010
- 3 EN71-11:2005
- 4 EN71-10:2005
- 5 iis-Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation, January 2010
- 6 XP G 08-014:97
- 7 P.L. Davies, *Fr Z. Anal. Chem.*, 351, 513, (1988)
- 8 W.J. Conover, *Practical; Nonparametric Statistics*, J. Wiley&Sons, NY, p.302, (1971)
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- 11 M. Thompson and R. Wood, *J. AOAC Int.*, 76, 926, (1993)
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- 13 OEKO-TEX Std 100, p19, (ed. 04/2013)
- 14 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, *Technometrics*, 25(2), pp. 165-172, (1983)