

– Report –

**CEN/TC 230/WG 1 – M/424
Interlaboratory comparison
for validation of CEN/TS 16692**

**Water quality — Determination of
tributyl tin (TBT) in
whole water samples using
solid phase extraction (SPE)
and gas chromatography with
triple quadrupole mass spectrometry**

provided by
OD Nature
3^e en 23^e Linierégimentsplein
8400 Oostende
Belgium

October 2014

Organisation/responsibility:	WG 1 within CEN/TC 230/WG 1
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ACKNOWLEDGEMENTS

This study was financed by the European Commission.

OD Nature wishes to thank EC-JRC-IRMM, particularly Håkan Emteborg and Saioa Elordui, for the cooperation and the efforts made to prepare and send out samples.

Many thanks to Gerhild Donnevert for the statistical evaluation of the interlaboratory results.

1. General

This document contains the results of the interlaboratory trial to validate the method described in CEN/TS 16692 "Water quality — Determination of tributyl tin (TBT) in whole water samples using solid phase extraction (SPE) and gas chromatography with triple quadrupole mass spectrometry". The interlaboratory trial was designed to serve as a validation exercise and not a proficiency testing trial. Therefore, it was mandatory for all participants to be included in the evaluation process to strictly follow the procedure as prescribed in the draft standard (prEN 16693) that had been made available to each participant.

2. Samples

Each participant received the following 4 samples of 1 L in duplicate:

- Sample 1: Low level sample containing 20 mg/L SPM
- Sample 2: High level sample containing 200 mg/L SPM
- Sample 3: Blank sample for spiking by the participant with TBT⁺ (ampoule supplied)
- Sample 4: Blank sample

The samples were prepared as described below. VITO (Mol, Belgium) pre-cleaned the bottles, IRMM (Geel, Belgium) performed additional cleaning steps with nitric acid, triton-x and hexane. The bottles were then filled, prepared and shipped the samples to the participants. The spike was prepared and sent by OD Nature (Ostend, Belgium) and ampouled at IRMM.

Cleaning of bottles

New borosilicate bottles were cleaned in a dishwasher and rinsed with deionized water and acetone. Screw-caps and PTFE inserts were rinsed with acetone. The bottles were dried in a clean cell and filled with 6.7 % HNO₃ solution. The bottles were left overnight and then rinsed with Type-1 water (18 MΩ cm, 0.056 μS/cm, <10 μg/L TOC, Millipore N.V., Belgium) and filled with 0.2% Triton X-100 solution. Then the materials were rinsed with Type-1 water, dried and rinsed with hexane suprasolv. Thereafter the bottles were left to dry in a clean cell equipped with a HEPA filter to avoid any contamination by air-borne dust.

Preparation of spiking solution

A spiking solution containing TBTCI was prepared by dissolving an appropriate quantity of pure tributyltin monochloride (Quasimeme office, Aberdeen) in iso-propanol. 2.7 mL of the spiking solutions were filled manually into 3 mL amber glass ampoules using a glass-syringe and the ampoules were sealed. The participating laboratories added 500 μL of the spiking solution to sample 3 before analysis.

Preparation of samples

The cleaned bottles were filled with SPA[®] mineral water. Mineral water was selected for practical reasons: it is easy to obtain, free of significant levels of contaminants and the ionic strength is representative for surface water. The use of natural waters directly from a lake or a river would imply a pre-treatment of the water like filtration, an exhaustive analysis of blanks and in case of needing extra water the repetition of the whole process. The SPA[®] was first poured into a (perfluoroalkyloxy)polymer) PFA-lined tank and continuously mixed using an inert bellow-pump and thereafter the bottles were filled using a custom-made system based on displacement of the water by an inert gas.

A model SPM containing TBT similar to natural SPM, was prepared by IRMM. Model-SPM-ENV08-TBT was prepared by fine milling and homogenization of BCR646 sediment. In addition blank model SPM was prepared by IRMM by fine milling soil not containing TBT. The top particle size of this model-SPM was in the range from 9 to 12.5 μm which corresponds to natural SPM in many respects. Homogeneous

SPM containing slurries were prepared by adding an appropriate amount of model-SPM-ENV08-TBT to high purity water (reverse osmosis type) and the mixture was stirred with a glass-coated magnetic stir bar. Under constant mixing defined aliquots of the slurries were taken and added reproducibly to Sample-1 and Sample-2 bottles. Table 1 shows the amount of SPM added to samples 1 and 2.

Table 1: SPM amounts added to sample, n= 6

Sample Nr	Model SPM (mg)	Blank SPM (mg)
Sample 1	7.86 ± 0.17	13.60 ± 0.56
Sample 2	7.07 ± 0.22	187.87 ± 0.83

Homogeneity test and stability test

Conceptual proof has been collected within IRMM with respect to homogeneity and stability of the final water samples. Samples have been checked with respect to stability for a period of 1 month at +18 and +4 °C, respectively. The conclusion was that all samples should be shipped with overnight courier and stored at +4 °C until analysis. Under such conditions the samples were deemed stable for the lifetime of the intercomparison (4 weeks).

Since the addition of target analytes was based on slurry addition it was important to assess if there was a change in the density in the constantly mixed slurry over time. Therefore, aliquots of the slurry were placed on pre-weighed Petri dishes at different times. No trend or difference was observed for the added SPM amounts between the beginning and the end of the preparation sequence.

3. Participating laboratories

10 laboratories were selected for participation in the interlaboratory trial, whereof 2 laboratories that used another method than described in FprEN/TS 16692 as an independent check. The laboratories are given in Table 2. One laboratory did not submit any results due to technical problems. All samples were shipped to the laboratories on June, 3rd 2014. A total of 9 labs reported results.

Table 2: Participating laboratories

Nr	Participant	Country	Adress	
1	BAM Federal Institute for Materials Research and Testing	D	Richard-Willstaetter-Str 11	12489 Berlin
2	VMM (Vlaamse Milieu Maatschappij)	B	Raymond de Larochelaan 1	9051 Sint Denijs Westrem
3	Scottishwater	UK	Avenue North	Edinburgh EH14 4AP
4	SGS Belgium N.V.	B	Polderdijkweg 16 (Haven 407)	B-2030 Antwerpen
5	Laboratorios Technologicos de Levante	SP	C/Benjamin Franklin 16	46890 Paterna (Valenci-Espana)
6	INERIS	Fr	Parc technologique Alata, BP 2	F-60550 Verneuil en Halatte
7	Cefas, Juniper House, Heriot Watt research park	UK	Pakefield Road	Lowesoft, Suffolk, NR33 0HT
8	University of Oviédo, Facultad de Quimica, Departamento Quimica Analytica	SP	Julian Claveria 8	33006 Oviedo
9	Provinciaal Instituut voor Hygiéne	B	Kronenburgstraat 45	2000 Antwerpen
10	Operational Directorate Natural Environment	B	3e en 23e Linieregimentsplein	8400 Oostende

4. Results of the data evaluation according to ISO 5725-2

The statistical evaluation of the analytical data reported by the laboratories was conducted by Ing. Gerhild Donnevert from the Technische Hochschule Mittelhessen (D). The results are summarized for the resp. samples in Table 3. Graphical presentations of the results are given in figure 1, 2 and 3.

Remark:

- The physio-chemical interactions taking place when adding model SPM to pre-filled water bottles are not known in detail. In addition, no characterisation of the final samples took place due to time-restraints coupled with potential stability issues when extending the necessary life-time for the prepared samples. Therefore all concentrations in the final water samples based on slurry addition are estimated.
- Recoveries (η) were calculated relative to an estimated assigned value (X), not a certified value. X is an estimated concentration based on the added mass of model SPM (Table 1) and the certified value of TBT in BCR-646 measurements of TBT in the finely milled model SPM were well within the uncertainty of the certified value).

Sample 1: Low SPM, Matrix: Mineral water spiked with 20 mg SPM
 Sample 2: High SPM, Matrix: Mineral water spiked with 200 mg SPM
 Sample 3: Spike, Matrix: Mineral Water spiked with TBT
 Sample 4: Blank, Matrix: Mineral Water

Table 3: results of the interlaboratory comparison for validation of TS 16692

Sample	l	n	o %	X ng/l	\bar{x} ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
1	7	14	0.0	3.8	4.21	110.8	2.25	53.4	1.05	24.9
2	7	14	0.0	3.4	3.51	103.2	1.10	31.3	0.42	12.0
3	6	12	14.3	17	17.4	102.5	2.18	12.5	1.12	6.4
4	7	13	0.0	-	0.32	-	0.20	62.5	0.10	31.3

Explanation of symbols:

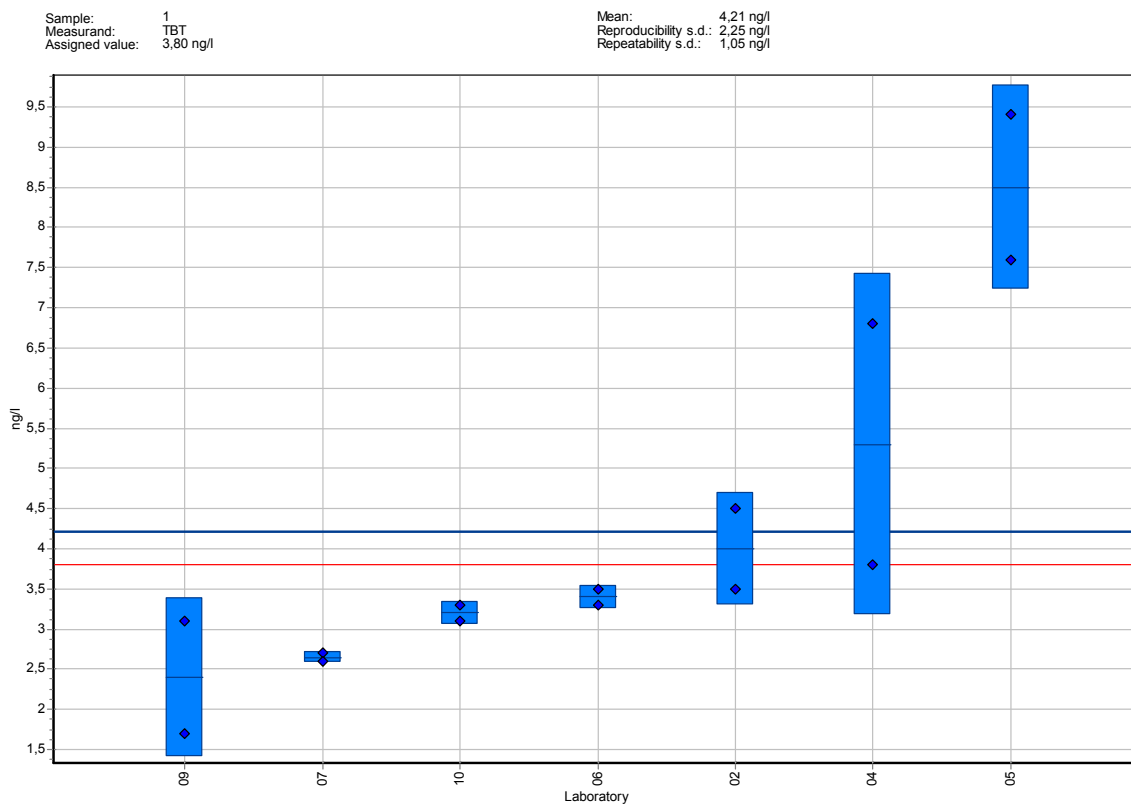
- l number of laboratories after outlier rejection
- n number of individual test results after outlier rejection
- o percentage of outliers
- X assigned value (estimated)
- \bar{x} overall mean of results (without outliers)
- η recovery rate
- s_R reproducibility standard deviation
- $C_{V,R}$ coefficient of variation of reproducibility
- s_r repeatability standard deviation
- $C_{V,r}$ coefficient of variation of repeatability

Graphical presentation of the results of the Interlaboratory Trial for the validation of CEN/TS 16692 *Determination of tributyl tin (TBT) in whole water samples using solid phase extraction (SPE) and gas chromatography with triple quadrupole mass spectrometry*

- Sample 1: Low SPM, Matrix: Mineral water spiked with 20 mg SPM
- Sample 2: High SPM, Matrix: Mineral water spiked with 200 mg SPM
- Sample 3: Spike, Matrix: Mineral Water spiked with TBT
- Sample 4: Blank, Matrix: Mineral Water

Legend: — assigned value
— overall mean

- Outliers: A outlying single result of one laboratory (not detectable in duplicate analysis),
 B outlying laboratory mean,
 C outlying within-laboratory variance



PROLab Smart for ISO 5725-2

Figure 1: TBT, sample 1



Figure 2: TBT, sample 2

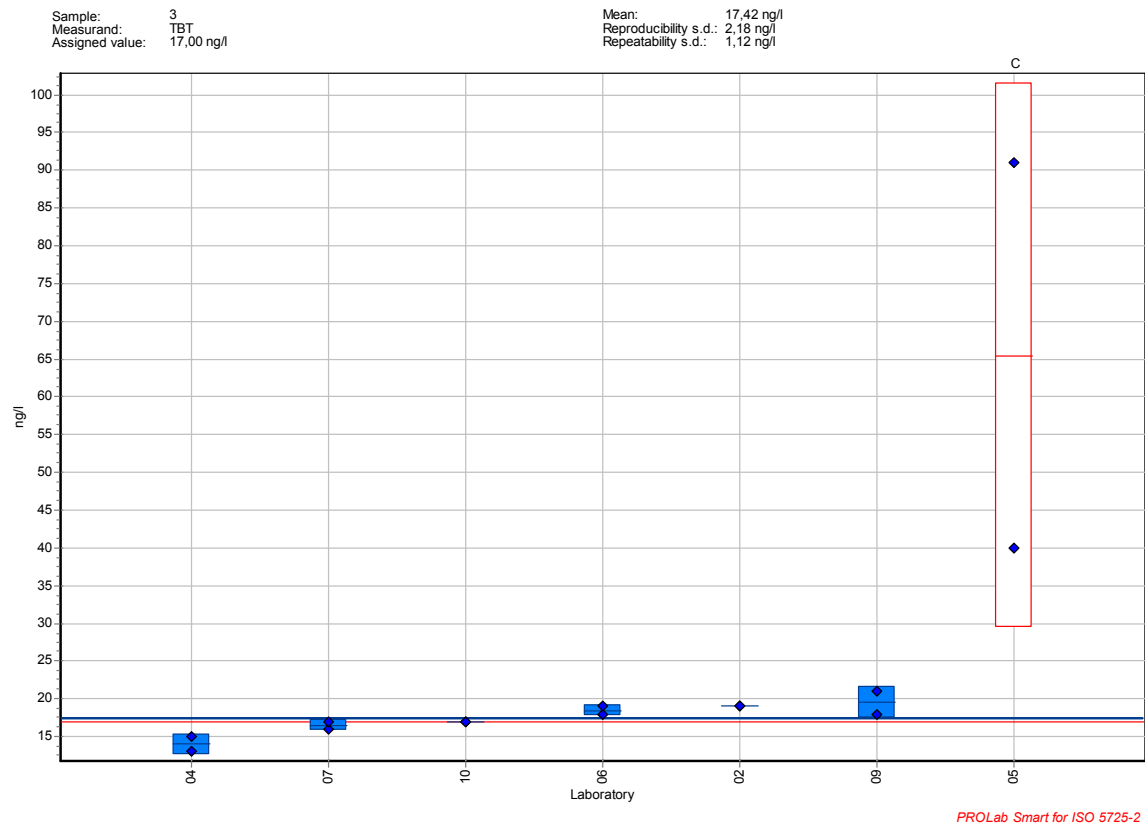


Figure 3: TBT, sample 3

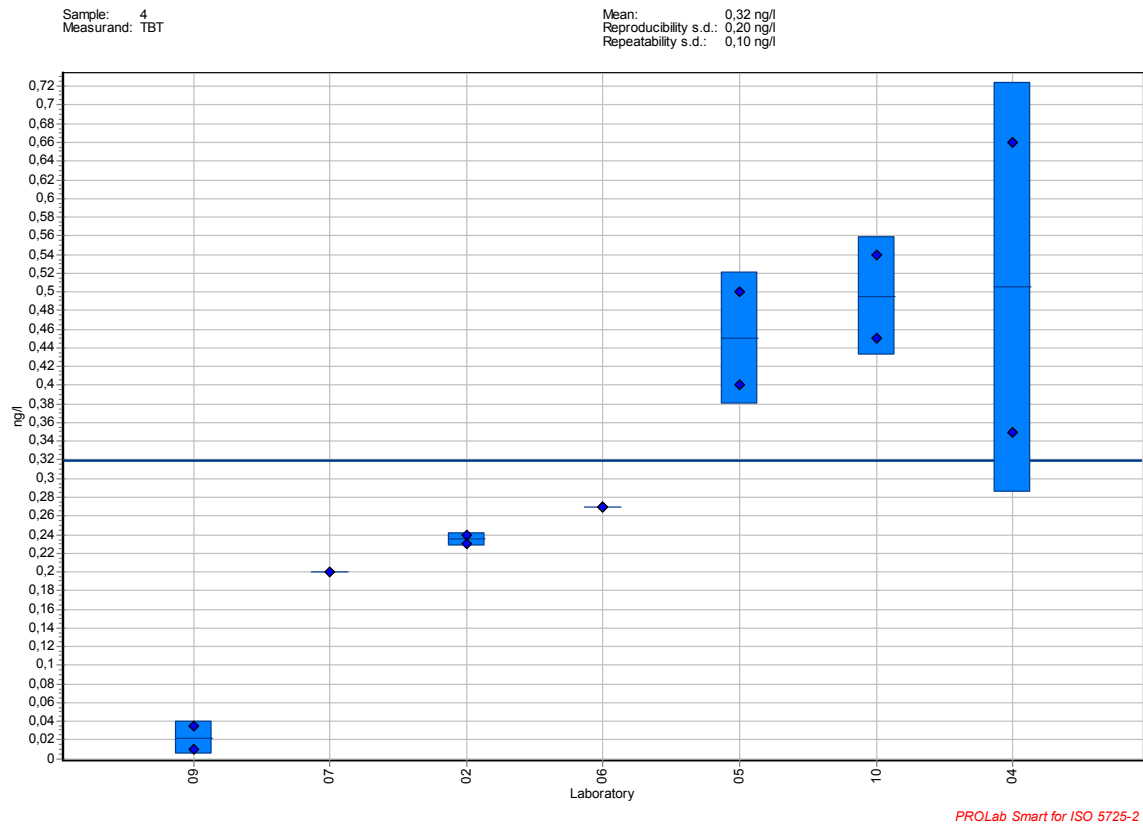


Figure 4: TBT, sample 4