Template for comments and secretariat observations	Date: 2006-06-30	Document: **CEN/BT/TF 151/TG 4 N0013**
Horizontal 4.27 BFR		
Author of comments: ALL; Replies: TG 4		

1	2	(3)	4	5	(6)	(7)
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NL			ge	This document is poorly attuned to the other documents within HORIZONTAL with respect to the layout, editorial as well as technical content. The compounds which are to be analyzed are comparable (when the physical properties are concerned) to those within the PCB standard.	In order to harmonize all documents within HORIZONTAL concerning the layout, editorial and technical content, this document needs revising.	This will be done.
DE			ge	This paper was kept very much in general. It was not clearly stated in the paper which PBDEs are covered by the scope and which PBDE-analytes are to be measured with high priority due to their environmental relevance and which can be measured definitely without interferences. The ISO FDIS 22032 of ISO/TC 147- Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge by extraction and GC-MS- was stated in the reference but it was not looked deeply into the matter so that there was no discussion and conclusion made on its applicability as well as on the limitations to be used as horizontal standard.		The PBDEs which will be included in the scope are the same as in ISO 22032, i.e. BDE-196, -197 and octaBDE For additional discussion about the ISO 22032 work, see observations on the comments made by Sabine Geiss in the ISO 22032 group.
AT			ge	At the moment two relevant papers are provided for consultation. The draft standard and a ruggedness report. The draft standard is a comprehensive review of the current state of PBDE analysis. Necessary analytic steps are listed and described well, especially the chromatographic part and the detection by mass spectrometry, but not in detail. As an example in the ruggedness report an analytic procedure using Soxhlet extraction or PLE, SPE Cleanup and NCI-MS detection is		Yes, more details will be given in the next round.

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				described in detail, comprising quality criteria for the described method. Other detection and clean-up methods which are mentioned in the draft standard are not described in the ruggedness report and no quality criteria from the ruggedness report are deducted for the draft standard. For the next round of consultation a detailed description of all mentioned methods including quality criteria which have to be met during analysis should be given.		
DK			Ge	The desk study as well as the report is named Brominated Flame Retardants, however, only Polybrominated Diphenyl Ethers (PBDEs) are mentioned in the report. This comment is primarily related to the desk study report.	Include a description of BFR as such and of the analysis of other BFR such as HBCD, TBBPA and PBB.	We suggest that "BFR" is changed to "PBDE", since BFR is a group of compounds with very different physicochemical properties. An extension on other BFR (see left column) is not accepted, because there either was no experience or no necessity for testing in soils and/or sludges.
DK			Ge	The method is not written as a draft method, more as a very general technical report.	Change the method to the CEN format with specified description of the method.	This will be done.
DK			Te	The ISO/DIS 22032 standard for PBDEs in sediment and sewage sludge is based on a extensive work by Sabine Geiss and coworkers from Freistaat Thüringen. This is not reflected in the draft horizontal standard.	Include the experiences from the German studies made for the ISO/DIS 22032.	The Desk study includes data from ISO/DIS 22032. Certainly, more experiences

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						from ISO/DIS 22032 will be added in the next round.
DK	1?		Te	The scope of the method with the exact list of analytes is missing.	Include a scope in the method. As for analytes use the list of congeners from ISO/DIS 22032.	See observation above
DK	3		Te	Other extraction methods should also be examined. Particularly shaking is widely used, and the method should allow other extraction techniques to be used, if they are shown to be equivalent with the prescribed technique.	Include other extraction techniques, if they are shown to be equivalent with the prescribed technique.	This will be done. Shaking and sonication will be added.
DK	3		Te	It is uncertain if recovery studies are based only on spiked values or on “real” content of the sludge.	Recovery studies could include measurement on PBDEs already on the sample. Comparisons on different techniques and conditions can be made.	Our recovery studies are all blank corrected. Reference materials are existing.
NL	3		te	This document needs to be attuned to the HORIZONTAL standards of PAH and PCB, concerning the extraction methods. In this way also other extraction solvents should be introduced next to dichloromethane which is currently prescribed (unwanted due to environmental concerns).	Tune the extraction methods with the methods used in the standards of PAH and PCB.	Shaking and sonication will be added. No other extraction solvents will be introduced.
DE	Clause 3	Extraction	te	*“A traditional extraction method used for PBDE applications is based on a centrifugation methodology.“* (also see Table 1). There is no extraction method based on centrifugation. Centrifugation is mainly used for separation of phases with different specific gravities e.g. liquid-solid separation. May be it is used in terms of “Sonication” i.e. extraction by using ultrasonic bath.		This will be clarified to mechanical shaking.

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NL	4		te	This document needs to be attuned to the HORIZONTAL standards of PAH and PCB, concerning the clean-up methods.	Tune the clean-up methods with the methods used in the standards of PAH and PCB	This will be done for PCB clean-up procedures. Except for gel permeation chromatography, no other PAH clean-up procedures are suitable for PBDEs.
NL			te	The sample volume of 0.5g or 1.0g of dry weight sample is not suitable for soil samples	The sample volume of soil samples should be tuned to the amounts used within the other Horizontal standards	Minimum requirements will be as for Soxhlet. In ISO 22032 5 g to 10 g material are used. For soils also up to 10 6 sems sufficient. For sludges 1 g to 2 g seem to be ok due to the fineness of substance.
FI	4 (page 5)	Line 17-18	ge	Automated cleanup system based on the pre-packed Teflon columns requires large sample sets to be economical and system is also tricky to use. System is expensive to purchase compared to open column glassware		In the standard we will suggest both alternatives, columns made in house and commercial pre-packed columns.
FI	5 (page 7)	Line 7	ge	Tandem MS is possible also with Q3 MS instruments		Yes, but this technique has not been used in PBDE analysis and Q3 MS instruments are more expensive compared to QIT-

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						MS instruments.
FI	5.2 (p 8)	Last line	te	Analysis of BDE-209 can occur together with other PBDE congeners, if the suitable technique is used	The use of the vacuum technique is recommended to analyse all PBDEs	Yes, analysis of triBDEs up to decaBDE can be preformed on one column e.g. non-polar GC column 15 m, 0.25 mm, 0.10 µm. However, to avoid co-elutions on tri- up to heptaBDEs, a longer GC column 30 m may be preferable. Mrs Eljarrat will check the risk for co-elution.
NL	5.3		te	Using the internal standard BDE-209 is not preferred, because of recoveries of 200%.	Use another internal standard instead of BDE-209.	New recoveries on the BDE-209 showed acceptable results (67% for Soxhlet 1 g sample and 5 g alumina. Like ISO/DIS 22032 standard for PBDEs in sediment and sewage sludge we will include BDE-77, BDE-181 and ^{13}C-BDE-209 as internal standards when NCI detection is used. Two additional ^{13}C-labelled PBDEs (compared to ISO/DIS 22032) i.e. ^{13}C-

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						BDE-197 and ^{13}C-BDE-207 will be added to the to the method based on EI detection to cover octa- and nonaBDEs. Fluorinated BDF are available as internal standards.
FI	6.1	2nd last line	te	GC-MS in the NCI mode: m/z 79, 81 proves only that the compound contains Br, not that it is a PBDE compound. See 6.3 interferences	Only GC-MS/MS in the EI mode is recommended	EI-LRMS and especially EI-HRMS are good for identification. However, PBDE analysis in NCI mode is accepted and the most commonly used detection method in scientific peer reviewed articles. At least one internal standard should be used per level of chlorination. If higher accurance is needed the use of more internal standards is recommended.
FR	4.27	Intro	Te	The scope refers to "Sludge, soil, contaminated sludge and treated biowaste". However the method has only be tested on a single material, HORIZONTAL SL 11, which is	This document would not go forward to phase II. So we think that it is not possible to forward it to phase III.	In case ruggedness results for waste can be achieved in time (soil is available but was

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				a sludge. The number of validation sample cannort support a horizontal scope.	Add ruggedness test on soil and waste.	not reported) , the scope may stay as presented. Otherwise a restriction of the method on soil and sludge is necessary.
FR	4.27			The results for HORIZONTAL SL 11 are claimed to be reported in the "completed experimental report", which cannot be found on the website ecn.nl. Another "report on phase II ruggedness (04/05)" is addressed: where has it been published?	The experts cannot express any opinion on the good adaptation of the method without access to these reports. Make them available.	Mrs Eljarrat agreed to submit the second ruggedness report to van der Sloot.
FR	4.27	Pretreatment	Te	Freeze drying as a pretreatment is acceptable. A surrogate standard is supposed to be added at this step: which one?	Give information	Surrogate will be deleted from the method.
FR	4.27	Extraction, Soxhlet	Te	No data were found on an azeotrope between DCM and hexane. What is the purpose of solvent mixture?	Give information	Will be aligned to ISO 22032.
FR	4.27	PLE	Te	Sulfur remopval by copper addition in extrcation cell: Ruggedness data?	Give information	Ruggedness report needs to be more detailed.
FR	4.27	Whole step	Te	Data in table 1 suggest that extraction efficiency is better for higher congener with 0,5 g of sample instead of 1 g.	As far as a separate analytical process is recommended for higher congeners, why not recommend a separate extraction process?	Extraction step is not critical, for ease of practicability one extraction should be enough.
FR	4.27	Clean-up	Te	An ISO method for purification of water extracts is already published. Why not adopt it, in order for the laboratories to treat the water or the soil and sludge extracts in the same way?	Give ruggedness data to explain.	The comment is in principle correct. However, for ruggedness testing different clean-ups have been tested. Clean-ups according to ISO

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						22032 should also be tested.
FR	4.27	GC-MS	Te	Though it does not appear as scientifically baseless, the need of 2 different GC process for either lower or higher congeners is not explained by ruggedness data. In the water standard the process is unique. Laboratories would appreciate a homogeneous analytical frame, if possible.	Give ruggedness data to explain.	Solved already.
FR	4.27		Te	Literature accredit the fact that the analytical step should be different and specific for congener 209. The "further measurements on recoveries of BDE-209" are lacking.	We would like to see ruggedness data for this congener.	Ruggedness report will be updated.
FR	4.27	Table 1, 2, 3	Te	There are 23 congeners in table 1, 8 congeners in table 2, 6 congeners in table 3: which congeners are validated, which are in the scope?	Give information.	Will be added.
FR	4.27	Table 3	Te	LOD and LOQ are calculated on a real sample: this is good	Have the same requirement on every method.	Noted.
FR	4.27	6.1	Ed	ISO 22032 is now published.		Noted.
FR	4.27	2, last line	Te	The affirmation on the comparability of starting material is very interesting. Unfortunately, no information is given. 25 % of water seems too high content.	Give more information on recommended way to achieve comparability. Show ruggedness test.	Will be added in revised draft.
FR	4.27	3, last-1 line	Te	The use of SPME is proposed which is a nonsense in a solid matrix, even in headspace mode, regarding the volatility of analytes!		To be reconsidered.
FR	4.27	General	Ge	No ruggedness data is provided. What is the connection between these two papers?		Noted.

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