HORIZONTAL

Secrétariat Horizontal – Task Group 3

Task Group 3 "Organic parameters – AOX – PAH – PCB – LAS – NP – selected phtalates"

Responsable : Monique POTTEVIN
ligne directe : +33 (0)1 41 62 84 98
monique.pottevin@afnor.org

Secrétaire : Elisabeth DERCHE
ligne directe : +33 (0)1 41 62 80 32
elisabeth.derche@afnor.org

TG 3 N 20

June 2006

Le comité membre français :

Association

Française de

Normalisation

11 avenue Francis de Pressensé

93571 Saint-Denis La Plaine Cedex

France

Tél. : +33 (0)1 41 62 80 00

Fax : +33 (0)1 49 17 90 00

http://www.afnor.fr

Subject :	**HORIZONTAL – TG 3 "Organic parameters – AOX – PAH – PCB – LAS – NP – selected phtalates"**
Comments :	**Soils, sludges and treated bio-waste – Organic constituents – Nonylphenols (NP) and nonylphenol-mono- and diethoxylates by gas chromatography with mass selective detection (GC-MS) - Comments -**
For action :	For information

Association reconnue

d'utilité publique

Comité membre français

du CEN et de l'ISO

Siret 775 724 818 00015

Code NAF 751 E

Template for comments and secretariat observations
Horizontal 3.13.1 Nonylphenols (NP)

Date: 2006-03-24	Document: **2006-XX**

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
AFNOR				NP : the studies comply with the requirements of phase II. The ruggedness tests are relevant. The matrices were well chosen. This method may go forward to phase III.		No comment.
AFNOR	Whole doc		ge	Very consistent study : 10 samples covering all fields of HORIZONTAL scope were used to investigate every step of the proposed analytical process. One would hope to find the same consistency in every phase II final report.		No comment.
NL			ge	The quality assurance of this standard is to low. The use of 13C labeled standards is good but more information has to be obtained from these compounds. This can be done by adding an inert /extractable internal standard to the internal standard solution (7.10). With this internal standard it is possible to demand minimal recoveries of these standards for the whole procedure (from extraction up to analysis). Within this method a derivatization is obligatory. However there is no guarantee that the available nonylphenols are derivatized, extracted and/or lost due to adsorption during the extraction.	Add a inert internal standard which can be used to quantify the recovery of the 13C labeled standards. Add the option, that if the limit of determination is feasible, no derivatization is needed.	Not agree. The addition of an inert compound will not help to calculate the recovery of the internal standards. Add note in chapter 11: "Recovery of internal standards can be checked by comparing the amount of added and found internal standard, e.g. by comparing the areas." Leave the acceptance criteria to the internal QC of the laboratory. Agreed by TG3. To be discussed at the Task Group 3 meeting. The derivatization efficiency has been proved to be ≈100%. The derivatization is

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)
2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial
NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
				Within ISO 17495 there is no derivatization, is this taken into account within HORIZONTAL? In general: is a derivatization of the extract always necessary?	Add an extractable internal standard which can be used to test the extraction / derivatization efficiency.	necessary, when the NP1EO and NP2EO are included. TG 3 recommends that the derivatization should be mandatory. In ISO 18857 (not 17495) the ethoxylates are not included, and a derivatization is therefore not necessary.
NL			ge	In general it can be concluded that large parts of the standard are not normative, rephrase. E.g. 10.4 “The derivatization can be carried out….”. Many other examples can be found.	Make normative	Agree. Has been corrected, where found. Agreed by TG3
AFNOR	2.3		Te	The change from 4D labelled internal standard to 13C ones is a positive proposal, 4D labelled standards having shown instability in some configurations.	We would not accept any draw back to 4D labelled IS.	We have used D4-labelled NP for the experimental work, and we have not experienced instability of this internal standard. No correction made. TG 3 suggests to add a note on ^{13}C labeled standards for the use of ion trap.
AFNOR	7.10		ge	For the CAS number, I am nearly sure that the 4-nonylphenol is 25 154-52-3 I think NP1EO is 104-35-8. Apparently, there are some problems to find CAS numbers. I hope it is easy to purchase the labelled compounds and it has good quality without too many impurities.	We consider that this method is applicable to all three matrices. The calculation of the recovery rates is missing. This method may go forward to phase III.	There are much confusion about the CAS numbers. The CAS number for NP is corrected to 84852-15-3, which is the branched NP in para position. The CAS number for NP2EO is corrected to 20427-84-3.

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)

2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial

NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
						The chromatogram can be used to ensure that the correct standard substance is used. Agreed by TG3.
NL	8		Te	"All equipment that gets into contact with the sample or extract shall be free from nonylphenols and nonylphenol ethoxylates. Glassware may be cleaned by ignition, at least for 2 hours at 450°C." This should be checked by using a blank for example for every series of samples.		Agree, that is one of the reasons to prepare a blank. No correction made. Ignition replaced by heating.
UK	8.2		ed	horisontal	Horizontal	Yes, text will be changed accordingly. Agreed by TG3
UK	8.6	2nd para	ed	tne	The	Yes, text will be changed accordingly. Agreed by TG3
NL	8.6		te	"The first two peaks of …". The selection of the first two peaks as a critical pair is not normative. Which compounds get of the column depends on conditions and the type of column used. It is also doubtful if the stated criterion can be reached (base line separated) and if it is necessary.	Rephrase GC criterion.	A good separation on the GC-column is necessary in order to obtain a sufficiently high selectivity and detect interferences. This is most important for NP2EO. No correction made. TG 3 suggests to show this on a chromatogram in an annex.

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)
2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial
NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
UK	9.1	2nd para	ed	….in according to…	..in accordance with…	Yes, text will be changed accordingly. Agreed by TG3
NL	9.2		te	"Samples shall be pre-treated as soon as possible after sampling." This phrase is not normative.	Make normative	Agree. Add after the phrase: "Samples shall be stored in the dark at a temperature of 4°C ± 3°C no longer than 7 days. " TG 3 agrees this change provided 7 days will be confirmed by the stability test. This report shall be made available on the homepage of Horizontal. website
NL	10.1.1		te	Is 10 ml of Acetone enough for the samples which contain 5%-50% of dry matter content (no filtration). Also the recovery of the 13C labeled compounds might be to low when a filtration is done (<5w% dry mater content) but this is currently not tested with the described standard.	Change the amount of acetone for samples with an intermediate dry matter content.	Yes. The amount of acetone is sufficient. In the draft for consultation no filtration is used. The recoveries of the internal standards have been tested. No corrections made. Agreed by TG3
NL	10.1.1 / 10.1.2		Te	"shake for at least 2 h / resp. 1 h" why is the shaking time different for these two extraction methods.	Make shaking time the same for both extraction procedures or change to at least.	No. 2 hours necessary for all extractions except 10.1.2. No corrections made. May be discussed at the Task Group 3 meeting. TG 3 decides to keep as it is.

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)
2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial
NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
NL	10.2		Te	"Concentrate the extract on a rotary evaporator or by the use of a gentle stream of nitrogen at room temperature." Can you also use nitrogen or are other gases or air also allowed. Define room temperature. Define the recoveries of the concentration procedure.	Also allow other gasses. Define room temperature. Define minimal recoveries of the concentration procedure.	No other gases allowed. TG 3 decides to include a note to allow other inert gases. Room temperature is not defined, since the actual temperature of the extract is lower and depends on the evaporation speed. TG 3 decides not to define the room temperature. The evaporation step is not critical for the recovery, when no heating is used. No corrections made. Agreed by TG3
UK	10.3	3rd para	ed	The cleaned are now ready..	The cleaned extract is now ready…	Yes, text will be changed accordingly. Agreed by TG3.
UK	10.3	Note	te	There is no recovery standard added to the extract following extraction and clean-up, and recovery is therefore not calculated. How do you check the clean-up recovery for individual sample matrices?	Delete note or add additional recovery standard to extract.	Agree. Add to the note: "This can be done by adding an additional standard to the extract after clean-up. If e.g. phenanthrene-D10 is added, the recoveries of the two internal standards can be calculated and thereby used as recovery standards."

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)
2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial
NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
						Agreed by TG3
NL	10.4		Te	"The derivatization can be carried…" is the described derivatization procedure optional or mandatory.	Make the text normative.	Agree. New text: "The derivatization shall be ….." Agreed by TG3
UK	10.5		ed	..and clean-up (optional).	This should state that if the clean-up has been used, then the blank should also be taken through the C/U procedure. This is not optional.	Agree. New text in 10.5 1st para: "Perform a blank determination following the procedure as described. Prepare the blank exactly as by the analysis of the sample, including the clean-up if the clean-up has been used for the samples." Agreed by TG3
NL	10.5		Te	"The blank value shall not be above 10% of the lowest value of interest". This statement is unclear and not normative, in the Netherlands it is common procedure to allow a blank value of 50% of the reporting limit.	Make normative and change the maximal blanc value.	The blank can be kept low for the actual analytes. New text in 10.5 2nd para: "The blank value shall be lower than 50% of the limit of detection." TG 3 agrees that the limit of detection is changed to the lowest reporting limit.
NL	10.6		Ed	"…. must fulfill the requirements described in 8.5." Change 8.5 to 8.6. Other internal references are also incorrect (e.g. within 10.7 there is a reference to 9.7.1 and 9.7.2 these should be 10.7.1 respectively 10.7.2).	Change 8.5 to 8.6.	Yes, text will be changed accordingly. Other references had been changed in the draft for consultation. Agreed by TG3
AE			Te	There is no recovery calculation.		That is correct, however, there is a correction for

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)

2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial

NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
						recovery of the internal standard. No correction made. Agreed by TG3
UK	10.7.2		te	Other horizontal standards (PAH and PCB) follow a similar procedure but include a comment that the standards at 20 and 80% of calibration should fall inside the 95% confidence limits for the calibration curve.	Bring re-calibration procedure in-line with PAH and PCB horizontal standards.	Yes. Add to the text in 10.7.2: " If the straight line falls within the 95% confidence limits of the initial calibration line, the initial calibration line is assumed to be valid. If not, a new calibration line has to be established according to 10.7.1." Agreed by TG3.
NL	10.7.2		Te	"Inject at least two calibration standards (after derivatization) with concentrations of 20 ± 10 % and 80 ± 10 % of the established linear range and calculate the straight line from these measurements." There should be a criterion on the found values when compared to the initial calibration.	Add criterion.	Yes. See comment above. Agreed by TG3
NL	10.7.3		Te	"If the concentration of one of the analytes is out of the calibration range (higher than the upper calibration limit), the final extract is diluted with isooctane and injected again." There is no guarantee that the amount of derivatization agents was enough for high concentrations	Add criterion	Agree. New text in 10.7.3 last para: "If the concentration of one of the analytes is out of the calibration range (higher than the upper calibration limit), the final extract is diluted with 5% MSTFA in isooctane (7.7). Wait minimum 15 min for the reaction to occur and inject again."

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)
2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial
NOTE Columns 1, 2, 4, 5 are compulsory.

1	2	(3)	4	5	(6)	(7)
MB[1]	**Clause No./ Subclause No./ Annex** (e.g. 3.1)	**Paragraph/ Figure/Table/ Note** (e.g. Table 1)	**Type of com-ment**[2]	**Comment (justification for change) by the MB**	**Proposed change by the MB**	**Project Horizontal observations** on each comment submitted
						TG 3 recommends to write : "A dilution of the extract of 10 times is allowed. The linearity of the internal standard shall be checked" .
AFNOR	5 Table 12		Te	Acetone/pentane NP recovery : is it 98 +/- 33 or 98 +/-3.3 ?	Correct or confirm.	Recoveries in Table 12 are confirmed. Agreed by TG3
AFNOR	Table 11		Te	The detection limits were es tablished on the analytical step of standard solutions. It is sufficient for the purpose of comparison of derivatization agents efficiency, but not to establish the application range of the method.	Give data on the LOD/LOQ of spiked matrices.	Results will be presented at the Task Group 3 meeting. TG 3 recommends that the working range of the method is checked after the interlaboratory trial. TG 3 expresses the need to include one sample of each matrix with a content near the quantification limit.

1 **MB** = Member body (enter the ISO 3166 two-letter country code, e.g. CN for China; comments from the ISO/CS editing unit are identified by ******)
2 **Type of comment:** **ge** = general **te** = technical **ed** = editorial
NOTE Columns 1, 2, 4, 5 are compulsory.