Guidelines for Non-Intentionally Added Substances (NIAS) evaluation in PET & rPET

Reference : NIAS_guidelines_document	Version : 1	Date : Nov. 07th 2019

Discussion:

This document explains the tests to be conducted to evaluate the (NIAS) in resins or bottle wall.

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1. PURPOSE & OBJECTIVES

This document is designed to explain general recommendations in methods to carry out a NIAS evaluation, from sampling, through analysis to the test report. It does not intend to provide precise analytical protocol.

2. SCOPE OF APPLICATION

Any PET or rPET food contact material, preform or article, with or without addition of colour or additives.

3. ABBREVIATION

AA: Acetaldehyde
BPA: Bis Phenol A
FID: Flame Ionisation Detector
GC: Gas Chromatography
GCMS: Gas Chromatography with Mass Spectrometry Detector
HRGCMS: High Resolution Gas Chromatography Mass Spectrometry
HRLCMS: High Resolution Liquid Chromatography Mass Spectrometry
LC: Liquid Chromatography
LCMS: Liquid Chromatography with Mass Spectrometry Detector
LOD: Limit of Detection
LOQ: Limit of Quantification
MW: Molecular Weight
NIAS: Non intentionally Added Substances
PET: Polyethylene terephthalate
rPET: Recycled Polyethylene Terephthalate
SML: Specific Migration Limit
VOC: Volatile Organic Compounds

4. DEFINITIONS

4.1 NIAS

Non-Intentionally Added Substance is an impurity in the substances used, a reaction intermediate formed during the reaction process, a decomposition or reaction product.
NIAS up to a molecular weight (MW) of 1000 Daltons (Da) should to be considered.
A typical NIAS of PET is Acetaldehyde which is a degradation product of PET.

NIAS can be classified into 3 categories:

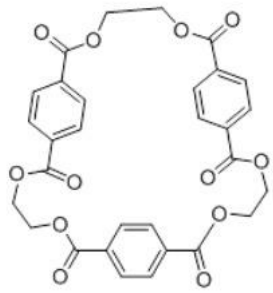
Volatile Substances	Semi-volatile Substances	Non-Volatile Substances
Substances evaporated from solid PET particles without the risk of regeneration, at appropriate combination of temperature/ pressure / time	Substances evaporated from the extraction solution of solid PET particles	Extractable substances which are not evaporated

4.2 OLIGOMERS

Oligomers with three or more monomer units are an intrinsic part of any polymer[1] In condensation polymers such as PET oligomers are components at the lower end of the natural molecular weight distribution of the polymer chains and as such are part of the polymer itself. The natural amount of oligomers depends on the average molecular weight of the polymer. Unless excessive oligomer amounts are present, they are not decomposition products.
Excessive amounts of oligomers should be considered as a possible risk for consumers and as such a risk assessment should be performed.
A low percentage (around 1% w/w) of cyclic oligomers can be found in all commercial bottle grade PET.

The main oligomers of PET are the cyclic oligomers (dimer to nonamer) which are present besides the linear species. Because of ring tension, the first series cyclic trimer is predominant (60–80% of the total amount of cyclic oligomers). It has been shown that the cyclic trimer represents 98% of all surface oligomers[2].

Cyclic trimer Mwt 576
Cyclic tetramer Mwt 768
Cyclic pentamer Mwt 960.4
Cyclic hexamer Mwt 1153



Cyclic PET trimer

[1] REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006, Article 3.5);
2 J.M. Besnoin, K.Y. Choi, Rev. Macromol. Chem. Phys. C29 (1989) 55.

Percentage distribution of Cyclic Oligomers in PET.[3]

C2 (MEG)	2.1
C3 (MEG)	72.0
C3 (DEG)	2.6
C4 (MEG)	13
C4 (DEG)	1.1
C5 (MEG)	4.0
C6 (MEG)	2.7
C7 (MEG)	2.1
C8 (MEG)	0.5
C9 (MEG)	0.2

5. SAMPLING AND SHIPMENT

5.1 SAMPLING

The required sample size for analysis is 200g, half of it to be sent to the laboratory and the other half to be retained in case of double checking.
The sample must be representative. Therefore, for recycled materials, it is recommended to have a mix of at least 3 different production dates.

To avoid contamination of the sample, the person responsible for the sample handling must wear single use clean gloves.

5.2 CONTAINER

The sample must be packed in a clean and dry glass or Pyrex bottle (DURAN-SCHOTT flask with screw cap as illustrated Figure 1). Alternatively, glass stopper on Erlenmeyer type flask could also be used. Do not use any solvent to clean the container.

5.3 PACKAGING CONDITIONS

To avoid contamination of the sample, this step needs to be carried out in a clean room, away from potential contamination and especially solvents.

[3] Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 38, 416–422 (2000) © 2000 John Wiley & Sons, Inc.; Study of the Thermal Evolution of the Cyclic-Oligomer Formation in a Cyclic-Oligomer-Free PET V. VERMYLEN,1 P. LODEFIER,1 J. DEVAUX,1 R. LEGRAS,1 W. A. MAC DONALD,2 R. ROZENBERG,3 E. DE HOFFMANN3

As described in the illustration below, after pouring the resin in the appropriate bottle, it should be closed with new aluminium foil (to prevent cross-contamination of volatile compounds through the cap) and then capped.

1. Use of clean gloves and appropriate tool for sampling

2. Transfer the resin into the clean bottle

3. Don't use only the cap to close the bottle, please add clean Aluminium foil in between

5.4 LABELLING

The sample should be **labelled** with the sample reference, as mentioned in the laboratory request form (see 5.6) to make sure that sample traceability is guaranteed.
Avoid any marker pen or any other element that could potentially bring solvents or other pollutants.

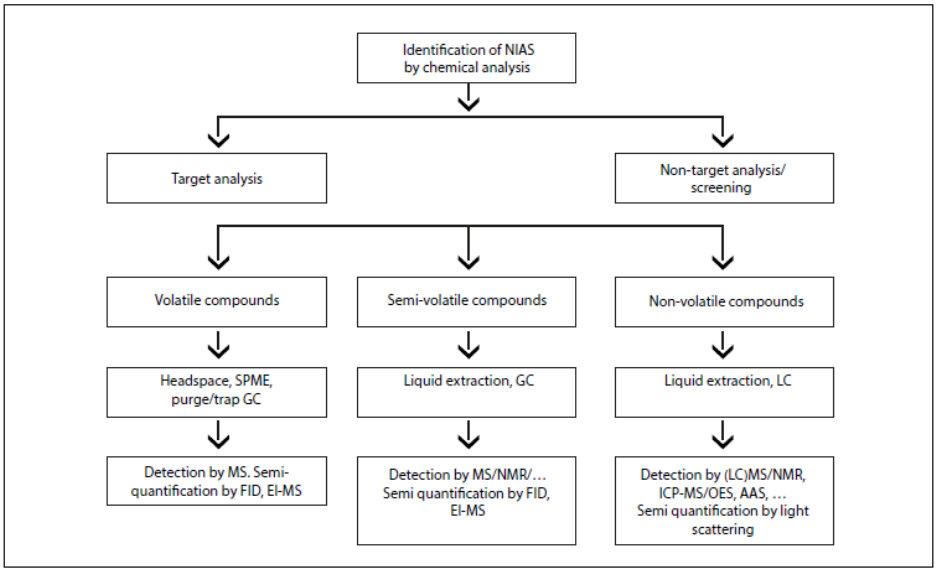
5.5 LABORATORY REQUEST FORM

See attached document – Reference: *Labarotry_NIAS_analysis_request*
This document should be completed and sent to the laboratory together with the sample in order to ensure the right methods will be used to carry out the analysis.

6. CHEMICAL ANALYSIS OF NIAS

6.1 GENERAL INFORMATION

As reported by ILSI Europe (2015), both predicted and unpredicted NIAS need to be analysed, two main types of analytical methods may be considered (see below):



Targeted analytical methods, for the analysis of suspected NIAS.
Suspected NIAS are substances which are known to occur regularly in comparable PET samples. This methodology may also be applied such that unpredicted NIAS are analysed simultaneously. A targeted approach may consist of both screening and targeted analytical methods.

2. Non-targeted analytical methods or screening methods to analyse substances with a wide range of physical/chemical properties. This is used mainly for the detection of unsuspected NIAS, and if present, suspected NIAS and IAS from previous production stages may also be detected.

It should be noted that not all analytical techniques will need to be applied when evaluating a food contact material and article. As a result of previous experience, the choice of analytical techniques to be applied for PET resins and derivatives are described below.

6.2 VOLATILE ANALYSIS

VOC

⇩

Thermal Desorption/Head Space

⇩

Targeted and Non targeted NIAS

GCMS(FID)/HRGCMS

Sample preparation

The sample must be cryogenically ground to a particle size below 750µm in order to be homogenised and to facilitate thermal desorption from small particles; it is very important to avoid both product degradation, losses of volatile substances (placing, weighing and sealing the sample in the HS vial as quick as possible is recommended) and cross contamination between samples when grinding them. The non-grinding method can be applied for specific cases but only when data show that there is no significant difference between grinding and non-grinding.

Thermal desorption

The thermal desorption conditions must be adapted to PET which means temperatures high enough to desorb volatile substances like acetaldehyde and less volatile substances such as limonene; the thermal desorption conditions should be such that they do not generate degradation of the PET sample. The desorption temperature that is recommended is 200°C, other temperatures could be used if data shows the relevance, (ie. acetaldehyde regeneration). The time at 200°C is typically set at 1h.

Quantification of Targeted NIAS:

The main targeted substances listed in the following table:

Name	EC-Number	CAS-Number
Acetaldehyde	200-836-8	75-07-0
1,3-Dioxolane, 2-methyl-	207-841-4	497-26-7
Benzene	200-753-7	71-43-2
Limonene	205-341-0	138-86-3

Volatile substances will be analysed using Headspace HR-GC–MS. Quantification will be done by adding an internal standard. To have a more accurate quantification GC-FID is preferred, with a method sensitivity limit of 10 to 30µg/kg for targeted NIAS. A triplicate analysis is required.

Qualification and Quantification of Non-Targeted NIAS

Regarding HR-GC-MS, the use of The National Institute of Standards and Technology (NIST) library as a well-known and validated data base is preferred. However, other libraries can be used as long as their robustness can be demonstrated. All substances found will be listed and a semi-quantification will be carried out with a Limit of Quantification of 30 µg/kg.

6.3 SEMI-VOLATILE ANALYSIS

Semi–Volatile Organic Compounds

⇩

Solvent Extraction

⇩

Targeted and Non targeted NIAS

HRGCMS

Sample preparation
The sample must be cryogenically ground to a particle size below 750µm in order to be homogenised and to facilitate thermal desorption from small particles; it is very important to avoid both product degradation, losses of volatile substances and cross contamination between samples when grinding them. The non-grinding method can be applied for specific cases but only when data show that there is no significant difference between grinding and non-grinding.

Solvent extraction
The solvent and the extraction conditions must be adapted to PET; the choice of solvent, justification and the extraction method will be reported.

Quantification of Targeted NIAS
Main targeted substance are Bis-Phenol A and some ortho-phthalates GC can be used with appropriate detector. The analytical method including operating settings and calibration method will be reported. It is aimed at having a method sensitivity limit at 0.1mg/kg PET for Bis-Phenol A and at 0.1 to 0.3 mg/kg PET for o-phtalates A triplicate analysis is preferred

Qualification and Quantification of Non-Targeted NIAS
Semi – volatiles substances can be analysed using GC-High Resolution MS The choice of MS library will be reported together with a robustness validation description. All substances found will be listed and a semi-quantification will be carried out with a Limit of Quantification of 0.1 mg/kg.

Some semi-volatile substances can also be detected with a non-volatile analysis method (see 6.4).

6.4 NON-VOLATILE AND OLIGOMERS ANALYSIS

Non - Volatile

⇩

Solvent Extraction

⇩

Targeted and Non targeted NIAS

HRLCMS/other detector

Sample preparation:
The sample must be cryogenically ground to a particle size below 750µm in order to be homogenised and to facilitate thermal desorption from small particles; it is very important to avoid both product degradation, losses of volatile substances and cross contamination between samples when grinding them. The non-grinding method can be applied for specific cases but only when data show that there is no significant difference between grinding and non-grinding.

Solvent extraction:
The solvent and the extraction conditions must be adapted to PET; the choice of solvent, justification and the extraction method will be reported.

Quantification of Targeted NIAS:
The main targeted substances are Bis-Phenol A, oligomers and some ortho- phthalates (if not already considered as a semi-volatile substance). LC will be used with appropriate detector. The analytical method including operating settings and calibration method will be reported. It is aimed at having a method sensitivity limit at 0.1mg/kg PET for Bis-Phenol A and at 0.1 to 0.3 mg/kg PET for ortho-phthalates.

Quantification of Oligomers
Oligomers should be identified and excluded from the non-targeted NIAS evaluation. An overall oligomer amount in mg/kg will be provided.

Qualification and Quantification of Non-Targeted NIAS:
Non- volatile substances can be analysed using LC-HR-MS. The choice of MS library will be reported together with a robustness validation description. All substances found will be listed and a semi-quantification will be carried out with a Limit of Quantification of 0.1 to 0.3 mg/kg.

Some non-volatile substances can also be detected with a semi-volatile analysis method (see 6.3).

6.5 SUBSTANCES IDENTITY CONFIRMATION

Due to the fact that methods of analysis somehow overlap and many substances can fall into the common region of ''heavier'' volatiles and ''lighter'' semi-volatiles, and the same applies with the ''heavier'' semi-volatiles and the ''lighter'' non-volatiles, it is highly recommended to use semi-volatiles analysis method as identification confirmation tool for ''heavier'' volatiles and ''lighter'' non-volatiles and vice versa.

6.6 REMAINING TEST MATERIAL

The laboratory will keep the remaining sample for 6 months, in suitable conditions to avoid any contamination.

7. ANALYTICAL RESULT REPORTING

The analytical report will include the following points:

7.1 GENERAL INFORMATION

All reports will mention:

- Coordinates of laboratory including name of accountable person.
- Date and conditions of sample at reception.
- Reference of the sample as mentioned on the label
- Date of analysis

7.2 METHODS

All methods used to deliver the results will be reported and at least all the elements which are listed in 6-2, 6-3 and 6-4 paragraphs. If no accredited method is used, it must be shown to what level the procedures secure the repeatability of the level of detection. The level of interpretation by a laboratory employee should be limited by clear Standard Operating Procedures (SOP) which guide the tolerance allowed for a triplicate measurement of a sample.

For each method used, the following will be reported:

- Sample preparation conditions
- Thermal desorption conditions and/or solvent extraction conditions
- Gas or Liquid chromatography equipment and analysis conditions including detectors used.
- Calibration method
- Mass Spectroscopy conditions with library reference.

7.3 RESULTS

All substances, targeted and non-targeted will be reported in a table and classified in the 3 categories, volatile – Semi-Volatile and Non-Volatile.

Targeted substances
The result will be expressed in µg/kg or mg/kg as mentioned in paragraph 6
For each substance, both LOD and LOQ will be reported.
If triplicate, the 3 results will be mentioned.

Non–Targeted substances
For each identified substance, the following information will be reported:

- Identification, molecular weight, elemental composition (level of confidence)
- CAS number
- Semi-quantified level for all identified substances, it has to be mentioned even if below LOQ.
- If the substance is listed CMR, has a harmonised classification as a Carcinogen, Mutagen, or Reprotoxic Substance class 1a, 1b, or 2 according to the CLP regulation (1272/2008). The classification should be mentioned in the list..

Migration assessment
The estimation of migration of NIAS can be done using a mathematical model. As for the usual high-volume polymers such as PET, such a pragmatic migration model has been established which is today scientifically recognised and widely used for food law compliance evaluation purposes and to substantiate technical dossiers for petitioning of new polymer additives to authorities such as the EFSA or the US FDA.
The migration model which can be used are available from several companies/institutes such as: INRA Safe Food Packaging Portal version 315, MIGRATEST software16 and AKTS-SML Software, but not limited to.
The laboratory will provide a migration assessment for each identified NIAS, the concentration will be calculated for a PET container with a surface-volume ratio of 6 dm^2 per 1 kg food, storage conditions depending on the application of the final article.