EUROPEAN COMMISSION
DIRECTORATE-GENERAL
ENVIRONMENT
Directorate D - Water, Chemicals and Biotechnology
ENV.D.3 – Chemicals, Biocides and Nanomaterials

Brussels, 29 June 2012
POP-CA9/2012/04

NINTH MEETING OF THE COMPETENT AUTHORITIES FOR THE IMPLEMENTATION OF REGULATION (EC) NR 850/2004 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL ON PERSISTENT ORGANIC POLLUTANTS

Centre de Conférence A. Borschette, room 0 C, rue Froissart 36, Brussels

6 July 2011 (09:00 – 17:30)

Concerns: **PFOS – CEN measurement method**

Agenda Point: **5**

Action Requested: **The POP-CA is invited to:**

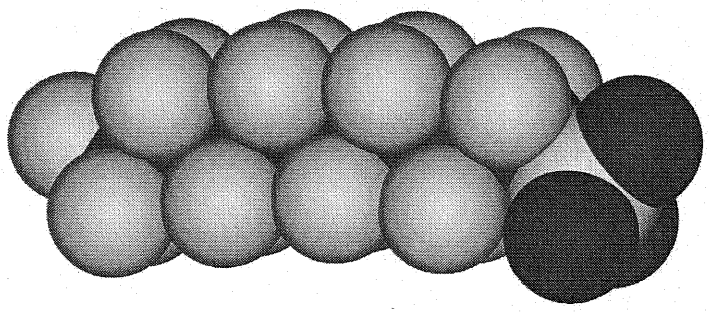
- take note of this document and provide comments and advise on whether to aim for validation of the measurement methods

- Indicate what potential resources can be made available in case validation is called for

NEN

CEN/TS 15968 "Determination of extractable perfluorooctanesulfonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LCMS/ MS or LC-MS"

Further development of the Technical Specification to a full European Standard - Answers to the questions of the European Commission, May 2012



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Content

1. Introduction

In 2010, CEN published the Technical Specification CEN/TS 15968 "Determination of extractable perfluorooctanesulfonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams - Method for sampling, extraction and analysis by LCMS/ MS or LC-MS" [1]. This TS has been developed by CEN/TC 382 'Project Committee PFOS'.

The Technical Specification has been prepared under mandate M/402 given to CEN by the European Commission and the European Free Trade Association [2], and in that time supported essential requirements of Directive 2006/122/EC [3].

In 2009, when the project started, the document intended to support European legislation that was about to enter into force. Due to the short time frame of the project (about 1 year), it was decided to write a Technical Specification first, and to upgrade the document to a European Standard (EN) afterwards [4].

In order to publish the method as given in the Technical Specification CEN/TS 15968 as a full European Standard (EN), the method needs to be validated in a round-robin test to investigate the trueness and the repeatability of the method.

This validation has been widely discussed in CEN/TC 382 and is a difficult subject, as in 2010, no certified reference material and no sampling material for the different matrices were available, except for the firefighting foams.

This note is meant to give a clarification and to answer questions from the European Commission with respect to what has been done already and can be done next, especially regarding:

- The costs of the validation of the method and the question whether it is possible to carry out a validation without reference material;
- In case reference materials are needed, the number of reference materials that would be needed, for mixtures or articles;
- The costs of obtaining the reference materials in terms of purchasing them and also the difficulties to find them on the market.

All this, to be able to make a decision on how the development of the European Standard can be realized.

2 History

2.1 Mandate M/402, regulation - limits

Directive 2006/122/EC [3] states that the substances that are under the Directive are perfluorooctanesulfonates (PFOS), that means substances with the formula $C_8F_{17}SO_2X$ (where X=OH, Metal salt (O-M+), halide, amide and other derivatives including polymers).

Limits that are set, are:

- **0,005% by mass**
  for PFOS placed on the market or used as a substance or constituent of preparations
- **0,1% by mass**
  in semi-finished products or articles or parts thereof calculated with reference to the mass of structually or microstructurally distinct parts that contain PFOS
- **1 µg/m^2**
  of coated material for PFOS in textiles or other coated materials

Materials that fall within the scope of Directive 2006/122/EC are:

- textile
- leather
- carpets
- paints
- paper/carton
- extinguishing foams

The Technical Specification (CEN/TS) that has been published focuses on these materials.

2.2 History of the TS

During the work on the Technical Specification, the validation of the method has been widely discussed. In fact, some of the experts were only willing to work on the TS after they had been guaranteed that a full validation of the method would be done afterwards. Some initial experiments, set up to indicate that the method would be usable, have been carried out during the project.

The following problems were discussed:

(1) the fact that no certified reference material was available at that time;
(2) that samples evidently containing PFOS were not available except for firefighting foam;
(3) a technical discussion about PFOS bound to polymers. In 2010, it was not clear whether this polymer-bound PFOS was loosely bound to the surface or 'strongly' bound in the matrix of the polymer. While trying to detect PFOS within such a polymer it was not clear whether only the surface bound PFOS would be measured, or whether the sample had to be treated in such a way that matrix bound PFOS would be extracted too. Neither was clear whether the PFOS, present in the polymer, would remain the original PFOS.

3 Validation – a required step?

In CEN Guide 13 [5], the environmental Technical Committees within the European Standardization Institute CEN made the following statement on validation:

'The environmental TCs recognize that the environmental test methods published as standards are very often used as reference methods in regulations and/or in contracts between several parties. Therefore, a known quality is considered as vital prior to publishing an environmental test method as a standard. Hence a general need for validation tasks interacts with the elaboration of the draft standards, and so there is also a general need to document the performed validation tasks and their results in the standard.'

Furthermore, the following is emphasized:

'In general, the common view is that a test method can only be published as an EN when fully validated (first and second validation steps have been performed). It may happen that the results are considered by the WG expert as very poor and that they recommend to the TC to publish a TS instead. When no or only partial (e.g. first step) validation results are available at the time of completion of the CEN enquiry, the test method is to be published as a Technical Specification (TS).'

Although there seems to be no directive urging validation before publication of a test method as EN, CEN Guide 13 strongly recommends to do so. From a liability point of few, it can probably also be expected that test results will not be accepted legally if a non-validated method has been used.

The description above leads to the (prudent) conclusion that, in order to be able to publish CEN/TS 15968 as a full European Standard, the method has to be validated.

4 Certified reference materials

In CEN Guide 13, *'reference methods are test methods that have been validated and of which the quality of the test method is, given a specific field of application, accepted by experts and users. It might be the experts that state that the method is a reference method, but in general, the claim that it is a reference method is not made within the standardization process.'*

CEN Guide 13 gives furthermore: 'In order to have knowledge on the quality of the method and accepting that, information on the quality is essential in order to be defined as a reference method. Validation is therefore an essential step in the standardization process from which this method originates.

Reference methods can be used as a legal reference in legislation/regulation and/or in contracts between two or more parties. They need, therefore, to be self supportive. Reference methods are not necessarily of the highest metrological quality, however, experts define a reference method as 'reliable' and a good basis for decisions. In general, reference methods are 'fit for purpose'.

Standardized reference methods are developed for 'common and repeated use'. They are not of the same nature as the utmost metrological quality that is required for Certified Reference Material developed in National Reference Laboratories (BAM, LNE, NPL....etc).'

'In order to secure comparable data, the associated uncertainty of the test methods will often be based on traceability to SI units. However, this is not, per definition, possible in all cases.

Alternatively, the quantification of the uncertainty can also be based on the analysis of certified reference materials. Indeed, in the environmental field certified reference materials are, in most cases, more logical (and applicable) than SI units.

Unfortunately, there is also a clear disadvantage with certified reference materials as these are only available for a limited number of components and matrices and are, in general, so expensive that it is not financially possible to use certified reference materials for validation or routine checks to determine if the analyses are still within the predefined bandwidth. A third option, therefore, is also important in the environmental field using (informal) reference materials that are not certified.

Certainly in the environmental field, more often the uncertainty is to be quantified by means of a relative comparison to (informal) reference materials. Therefore, the standardized method shall specify the minimum requirements to be fulfilled in the analysis by:
• a quantification using a set of measurement traceable to SI units; or
• a quantification using certified reference materials; or
• a quantification using reference material specified in the standard'

As a consequence of the statements given above, it can be concluded that the use of certified reference materials is not strictly necessary.

5 Validation of alternative methods

In addition to the validation of reference methods Guide 13 gives another possibility if the method is what the guide defines as an 'alternative method'.

If the proposed test method is a secondary, simplified or indirect method, it is called 'alternative method'.

Guide 13 states: 'An alternative method will differ from the reference method. Consequently, it might have an enlarged chance of finding biased results and/or results with a larger degree of variability. Thus the uncertainty of the method might be larger than that of the reference method. An alternative method may also be more focused on a narrower field of application than a reference method covering wider applications and, therefore, exhibiting a lower uncertainty.

For the validation of alternative methods, two approaches are available:
• Full validation as applies to reference methods;
• Relative validation in which a comparison is made to the reference method

As validation has to take place prior to the practical application of the method, the method of validation will determine if the alternative method can be used on a stand-alone basis (after full validation), or only in conjunction with the reference method (relative validation).
In the first situation there is, from the perspective of validation, no difference with the reference method.

Therefore, this clause focuses on the concept of relative validation, also known as 'cross comparison testing'.

'For the practical application of alternative methods, it will often prove necessary, in addition to relative validation, to do an in-situ calibration with the reference method. This means checking if the results of the alternative method are indeed representative in comparison with the reference

method when applied to the same samples coming from a specific site. Cross comparison can be made on the resulting paired samples.

After a relative validation, the application of an alternative method may normally be insufficient for legal purposes.'

6 Investigation of trueness and repeatability - validation

6.1 Different matrices en parts of the method that require validation

Validation of the method written down in CEN/TS 15968 as a reference method according to CEN Guide 13 needs to be carried out in a round robin test to investigate the trueness and the repeatability of the methods. This involves the entire process, from the sampling up to the measurement:

Matrix	Sampling	Sample preparation	Measurement
Textile			
Leather			
Carpets			
Paints			
Paper/carton			
Extinguisher foams			

Sampling is probably no major issue so the necessity of this step can therefore be discussed, but the sample preparation and the measurement itself are vital elements of the validation.

6.2 Validation

Guide 13 describes for the validation:
'Validation of standardized reference methods is generally performed in two steps including performance characteristics relevant for the considered method:
- *robustness testing;*
- *interlaboratory testing (repeatability and reproducibility)*

As the first step is based on a first draft of the standard and each of the validation steps will result in a revised draft standard, the implementation of validation in the standardization process normally relates to three different draft standards, the last one of which will be published as an EN-standard. These steps are depicted in Figure 1.
It is to be noted that the actual state of the art may not be sufficient for the efficient further development of the envisaged standard. In such a case, a so-called pre-normative research may be needed prior to any standardization with validation. '

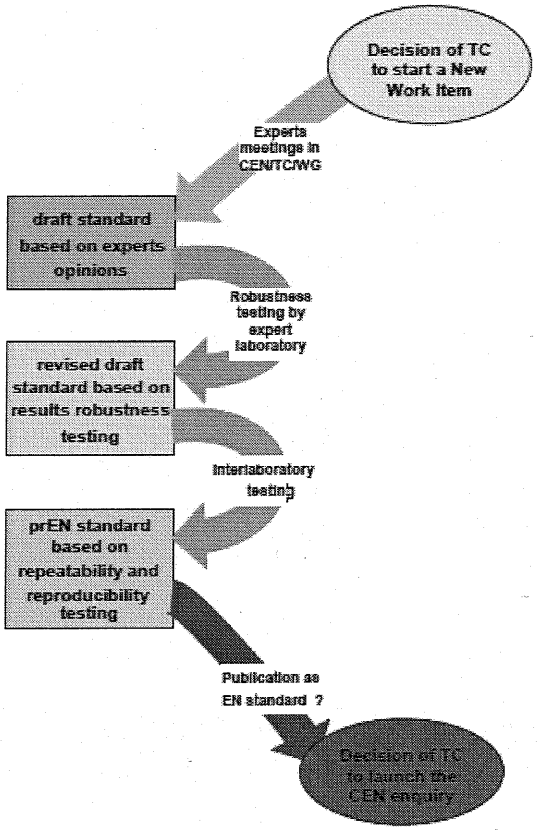

Figure 1: Flow chart of the validation steps in the standardization process

6.3 Deliverables

Within the validation as described above, different deliverables will become available during the process:

D0 Draft standard based on experts' opinions, CEN/TS 15968 [1]
D1 Report on the robustness testing (step 1 of the validation)
D2 Revised draft standard based on results robustness testing
D3 Report on interlaboratory testing (step 2 of the validation)
D4 prEN standard based on repeatability and reproducibility testing (stage 30.99)

6.4 Time schedule of the development of a European Standard

The development of the European Standard starts with the method as laid down in Technical Specification CEN/TS 15968:2010. This Technical Specification will be the basis for the first step of the validation of the method, i.e. the **robustness testing**.

The results of those tests are taken on board in a second draft of the test method which is the basis for the second step of the validation, i.e. **interlaboratory testing (repeatability and reproducibility)**. The results of the second step of the validation are implemented in the third draft of the standard, thus adding detailed information on the validation results to the draft standard.

When the results of the second validation phase are acceptable for the experts, the resulting third draft is a draft prEN, published for public comments. This prEN will be processed within the CEN-system for final publication as an EN-standard.

The CEN timeframe for developing a European Standard is 36 months.

In this timeframe, there is a 12 months period for the process of the validation of the method, resulting in a draft prEN ready to be dispatched to CCMC.

A more detailed time schedule is given in below:

Step (stage-code)	**Deadline**
Registration of the active work item	t_0
Dispatch of Enquiry draft to CMC (30.99)	t_0 + 12 months
Submission to Enquiry (40.20)	t_0 + 14,5 months
Closure of Enquiry (40.60)	t_0 + 19,5 months
Dispatch of Formal Vote draft to CMC (45.99)	t_0 + 27,5 months
Submission to Formal Vote (50.20)	t_0 + 31 months
Closure of Formal Vote (50.60)	t_0 + 33 months
DAV/Definitive text available (60.60)	t_0 + 36 months

6.5 Sampling

During the drafting of the Technical Specification, validation has been widely discussed, since obtaining samples was a major issue at that time. In order to get a first indication whether the method worked, few experiments have been carried out on extinguisher foam that was still available at that time, on textile that we were able to get in small amounts via one of our American partners, and leather that had been spiked by one of our French partners. All the samples we could get in that time were not sufficient for a complete round-robin test, with the exception of the extinguisher foam.

6.6 Sample preparation

The samples used in the validation should be homogeneous and stable for the duration of the validation. A study on the stability and homogeneity of for instance the extinguisher (firefighting) foams should be carried out. That could be done by for instance JRC (Joint Research Center).

6.7 Measurement

If it is possible to find homogeneous and stable samples, the test method can be tested in a round-robin-test, probably managed by for instance JRC.

7 Conclusions and recommendations

It can be concluded that:

a In order to be able to develop the TS to a full EN, it is not necessary to have certified reference materials for the validation of the method;

b It is necessary to carry out validations for the samples preparation, the measurement and, if possible, for the sampling;

c In order to carry out the complete validation, all matrices, textile, leather, carpets, paints, paper/carton and extinguishing foams need to be measured;

d The most difficult issue is to get samples. In an earlier attempt, spiked leather, foam and a small amount of textile have been used;

c Before submitting samples to a round-robin test, their homogeneity and stability should be tested (for instance by JRC).

Recommendations:

In order to be sure that the method described in CEN/TS 15968 works properly, a project plan for the validation of the method and the development of the European Standard should be drafted. The secretariat of CEN/TC 381 is willing to do so, in close cooperation with for instance JRC.

The project plan needs to include an enquiry among the members of CEN/TC 382 regarding the possibilities to deliver samples and the related costs. The enquiry required can be carried out by the secretariat of CEN/TC 382.

After that, a project plan can be written containing:

- the procedure and costs of the collection of the samples;
- the procedure and costs of the measurement of the homogeneity and stability by for instance JRC;
- the procedure and costs of the validation (probably best managed by for instance JRC);
- the procedure and costs of the standardization process;
- a time table for the complete project.

Critical is the collection or possible preparation of the samples. It is not sure yet if this is possible and how much it will cost, so an estimate cannot be given at the moment.

Bibliography

[1] CEN/TS 15968:2010 *Determination of extractable perfluorooctanesulfonate (PFOS) in coated and impregnated solid articles, liquids and fire fighting foams — Method for sampling, extraction and analysis by LC-MS/MS or LC-MS, to be published*

[2] Methods of analysis to detect perfluoro-octaansulfates (PFOS), Mandate M/402, For CEN/BT TF 198, December 2007

[3] 2006/122/EC: Directive 2006/122/EC of the European parliament and of the council of 12 December 2006 amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates)

[4] Project plan CEN/TC 15968 (available in CEN/TC 382)

[5] CEN GUIDE 13 *Validation of environmental test methods*, Version dated 2008-10-29