

# **HORIZONTAL STANDARDISATION FOR SLUDGE, WASTE, SOIL AND SEDIMENT**

**Report of the final desk study on the determination of  
PAH's**

**for the European project HORIZONTAL**

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Scheme of communication between Standardisation bodies and Ad hoc Joint Working Group

## SUMMARY

This report describes the desk study to the horizontal standardisation of the determination of Polycyclic aromatic hydrocarbons (PAH's) in sludge, waste soil and sediment . The work is based on a critical evaluation of existing standards and draft standards. A discussion paper is in preparation for the relevant working groups of CEN/ TC 292 (waste), CEN/ TC 308( sludge) and ISO/TC190 (soil). A joint group of CEN 292 and CEN 308 and ISO TC 190 was founded in mid 2003, where this paper was discussed and commented thoroughly.

Important parts in the standard to develop will be the modular approach, because it is not possible to make one single working procedure for the matrices involved (waste, sludge and soil). Especially it will be necessary to have different procedures and steps for extraction and clean-up and measurement. To assure reliable and comparable results it will be necessary to set minimum requirements for different procedures and steps in the method.

After acceptance of the approach described, a framework can be made that can hopefully be filled in with procedures already described in existing methods. Limited new procedures will need description. Critical steps in the procedure can be evaluated by pre-normative as well as in co-normative research followed by in-House-Validation and Inter laboratory comparisons.

## 1. INTRODUCTION

The European project HORIZONTAL is focussed on the standardisation of test procedures in environmental samples. During the preparation of the project, several desk studies have been started to elaborate the possibility of horizontal standardisation on specific subjects. One of the subject was the horizontal standardisation of Polycyclic Aromatic Hydrocarbons (PAH's) as described in this report.

PAH's are subject of international standardisation in ISO TC 147 (water) and ISO TC190 (soil). There exists also a number of national standards in sludge and waste in this field. CEN 292 (waste) and CEN 308 (sludge) has now taken up this matter in their respective work programme. Interaction between these groups has been stimulated already in the last years. Horizontal standardisation should lead to one standard suitable to analyse the matrices waste, sludge and soil.

In the desk study on PAH's, the method of determination in the different existing standards and drafts are compared which leads to a discussion paper. This discussion paper is an intermediate to a framework, which will be resulted in the final standard. This paper was discussed with the relevant working groups of CEN 292 and CEN 308 and on the meeting of ISO TC 190 in Brno in September 2003 and at the meeting of HORIZONTAL Ad hoc Working Group PAH/PCB in Copenhagen in January 2004.

Due to the fact that the active drafting members are the same for PAH's as well as for PCB's it is to be expected that the general line of the frame work for the two horizontal standardisation will be developed and formulated parallel and in the same direction, where ever possible and appropriate.

A horizontal method applicable for all environmental solid matrices of different PAH- contamination levels (soil, waste, sludge and bio waste) with modules for extraction and clean up followed by two alternative detection techniques HPLC-UV/FLD and GC/MS is under preparation in the frame of this HORIZONTAL-Project.

## 2. A FRAMEWORK FOR A HORIZONTAL STANDARD FOR PAH's

### 1.1 General description

PAH's are ubiquitous because of the fact that they are released in appreciable quantities every year into the environment through the combustion of organic matters such as coal, fuel oils, petrol, wood, refuse and plant materials. Since some of these PAH compounds are carcinogenic or mutagenic, their presence in the environment (air, water, soils) are regularly monitored and controlled. PAH's are determined in these matrices in routine practice, following the written procedures and steps for sampling, pre-treatment, extraction, clean up and measurement of specific PAH by appropriate chromatography in combination with appropriate detection technique. At present the two determination methods using HPLC-UV-DAD/FLD as well as GC-MS are applied in most of the routine laboratories.

Several standards and/or draft standards (see annex 1) are available for the determination of PAH's in different environmental matrices. Some prescribe for specific matrix the whole procedure starting from sample pre-treatment, extraction, clean up followed by specific measurement technique and others already the modular approach. Reading these documents it becomes clear that depending on the properties of the matrix different or slightly different steps in the method can be necessary. Not all procedures are applicable for all different matrices. In a standard the choices to be made must be clear and hence, a decision structure has to be described. Later on, all the steps necessary to analyse the different matrices can be described in more detail using the technical content of the existing documents or using additional text.

An ideal method should be “*a method which allows the extraction of an original sample for all solid matrices (without pre-treatment) with a solvent of high and specific solubility and extractability for PAH's and direct analysis without any clean up*”. Just because of the fact that this kind of ideal method is not and will not be available, the development of the horizontal standard can only aim to obtain as much as possible of the ideal method taking into consideration of the differences of the matrices as well as of the specific PAH and its contamination level.

From the horizontal point of view it is of great benefit that the methods applied for the different matrices are comparable and making use of the same principles and instrumentation. But regarding the PAH-Standardisation, there may be two approaches with steps which are slightly or mainly differ from one another resulting from the application of two different methods of measurement, e.g. Liquid-(HPLC) and Gas chromatography(GC).

The analysis of PAH's can be described in the same manner for PCB's with the following steps:

- Pre-treatment of the sample and preparing of the test portion
- Extraction
- Clean-up
- Measurement by GC in combination with mass spectrometric detection(GC-MS) or by HPLC in combination with UV-DAD- or Fluorescence-detection(HPLC-UV-DAD/FLD)
- Requirements for identification and calculations

### 1.1.1 Pre-treatment

Pre-treatment is necessary to deliver a homogeneous sample and a sample suitable for extraction. The procedure depends on the material to be treated. Important is the reduction of the water content to less than 25%. Pretreatment procedures are available for soil and waste and in development for sludge. The horizontal standard for PAH's should refer to these procedures, especially taken into account of the fact that some of the target PAH's are highly volatile.

### 1.1.2 Extraction

Waste, sludge and soil may differ in properties and also within one matrix properties may differ very much. For instance, waste can be soil-like, but may also contain wood residuals. These differences make it impossible to describe one general extraction procedure. Choices in a standard must be clear. The final standard should contain a decision table based on the properties of the sample and the extraction procedure to be described in the standard. Two general lines will be followed, an agitation procedure or use of Soxhlet/ASE.

The choice of extraction solvent is more crucial than the procedure and the extraction devices itself for the extraction of PAH's from the matrices. Since some of the target PAH's are not so good soluble in the usual solvents such as petroleum ether and other hydrocarbons the choice of the solvents has to be made in accordance with the expected contamination level and also to be applicable to the measurement procedures. It is to be underlined that the target contamination level of PAH can lay in the range of about 0.1 mg/kg (sediment) to about 200mg/kg and higher (contaminated soil at coking plant). Depending on the extraction procedure an existing clean up procedure should be followed.

### 1.1.3 Clean-up

Clean up is necessary to remove present disturbing components. When they are not present, clean-up is not necessary. If present, the specific disturbing components have to be removed which asks for different procedures described in the standard. Again it will be necessary to include a decision table. One has to be aware about the fact the PAH's are in contrary to the PCB's not so stable and persistent so that extreme clean up conditions are not applicable .

### 1.1.4 Measurement by High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC)

Although Thin Layer Chromatography (TLC) is described in some of the standards, it will be not considered for the horizontal standardisation, because it is not widely used in the laboratories for PAH-measurement. Therefore only HPLC and GC methods will be included here for the measurement , taken into account of their specific limitations.

HPLC in combination with UV-DAD or Fluorescence Detection:

A sufficient chromatographic separation of the target PAH's with an appropriate column is possible. The detection limits for UV- and Diode Array Detection is rather high, so that it is applicable for higher PAH-contamination levels, where additional identification/confirmation information using the UV-Spectra are available.

Due to the high sensitivity of the fluorescence spectrometry very low level of PAH-contamination can be determined herewith. One of the target PAH's acenaphthylene cannot be detected. Additional Identification/ confirmation information is not available. Interaction of emission signals with the matrix compounds, such as quenching effect is possible, which may lead to errors in PAH-determination.



New available measurement instruments:

It is to be discussed in the relevant working/expert group, whether the new techniques such as HPLC-MS or HPLC-Scanning Fluorescence Spectrometry should be included to reflect upon the coming future development, which will definitely have a pre-normative research character.

GC-MS:

GC in combination with MS is the very often used combination for measurement of PAH's, where proper quantification and identification ( by mass fractions) of specific target compounds are possible. Internal standards (e.g. deuterated C 13-isotopic PAH's) are necessary for quantification . The proper choice of a capillary GC- column is the prerequisite for the gas chromatographic separation of the target PAH's.

#### 1.1.5 Requirements for identification and calculations

The principles described in ISO/DIS 22892 (GC-MS identification) will be used for identification. This standard makes use of identification points as already used in an European document.

### 3. EXISTING STANDARDS OR DRAFT STANDARDS FOR CONSIDERATION

#### **General:**

**ISO/TC 190: ISO/FDIS 14507**, Pre-treatment of soil (organic contaminants)

**ISO/TC 190: ISO/CD 11464** , Pre-treatment of soil (physico-chemical analysis)

**CEN/TC292: WG5 N0296**, Waste: preparation of test portions

**ISO/TC 147: ISO/FDIS 5667**, part 3 and 15, Water Quality, Sampling

**ISO/TC 190: ISO/DIS 22892**, GC-MS Identification

#### **PAH:**

**DIN 38414- S 21**, 6 PAH for sludge and sediment (HPLC/FLD)

**DIN 38414- S 23**, 15 PAH for sludge and sediment (HPLC/FLD)

**ISO/TC 190: ISO 13877**, PAH for soil (HPLC/DAD/FLD)

**ISO/TC 190: ISO DIS 18287**, PAH for soil (GC/MS)

**ÖNORM L 1200**, PAH for soil, sewage sludge and compost (HPLC/DAD/FLD; GC/MS)

**DANISH Standard**, 9 PAH (together with DEHP and NPE) for sludge (GC/MS)

**Belgium Standard**, PAH for sludge, sediment and waste (HPLC/DAD/FLD; GC/MS)

**CEN/ TC 308/1/TG4 French Standard XP X 33-012**, 6 PAH( together with PCB) for sludge  
(HPLC/DAD/FLD; GC/MS)

**DIN 38407-F7**, 6 PAH(screening and quantification) in water, waste water and sludge (HPTLC/F)

**DIN 38407-F8**, 6 PAH for drinking water, (HPLC/F)

**BSI method 061(Environmental Agency)**- 11PAH for potable and waste water, (HPLC/F)

**DIN 38407-F18**, 15 PAH for surface water and ground water, (HPLC/F )

**UNI ? (Italian Standard)** for waste and soil, based on US-EPA SW-846 proced. 16 PAH(GC/MS)

**US EPA 610**, Measurement method for 16 PAH (HPLC/UV/FLD; GC/FID)

**US EPA 8100**, 16 PAH for waste ( GC/FID)

**US EPA 8310**, 16 PAH for ground water and waste ( HPLC/UV/FLD )

**US EPA 8270 B**, 16 PAH for ground water and waste and soil ( GC-MS )

## 4. EVALUATION OF DRAFTING A HORIZONTAL STANDARD

### 4.1 Discussion

As described in previous chapters it is not possible to make a standard with single procedures for each separate step that can be used for every sample to be analysed. A horizontal standard has to contain different possibilities. It has to be prevented that everything is allowed. Multiplying all the different steps will lead to a too large number of possibilities. A solution for this is the introduction of decision tables. Depending on the nature of the sample to be investigated and the goal to achieve ( pre-treatment, extraction, clean-up, measurement etc) the table has to give a limited number of possibilities. This procedure has to be secured with description of effectiveness of the procedure.

In case of PAH- determination there must be decision tables at each step for the following step taken into account of the nature and characteristic of the matrix under investigation (such as water content, contamination level, interfering matrix) and also the availability of the specific measuring instrument.

A second option to limit the number of procedures is pre-normative work. Experimental work in a limited number of laboratories will make it possible to limit the number of procedures for a certain matrix and to evaluate critical steps. This has been discussed with Joop Harmsen and should be possible in conjunction with the working package on PCB's.

A horizontal standard can be developed for the matrices:

- Solid wastes, especially Biowastes(Liquid wastes like oil and water are excluded)
- Sludges
- Soils

Validation of the standard for all matrices on the short term will be difficult (too expensive). This has to be an ongoing process and needs co-ordination, which can be a task of the project HORIZONTAL. Validation may also lead to steps not yet described or excluding a specific step for a specific matrix. This will make adjusting of the decision tables necessary in new versions of the standard.

### 4.2 Steps to be taken

Horizontal standardisation will be successful if all parties involved are in favour of such a procedure. It is the experience that experts become enthusiastic seeing the similarities for different matrices. But it has to be decided in all the relevant working groups of CEN TC/292, CEN TC 308 and ISO TC 190 whether or how to proceed with the existing CD or DIS or prEN and work items, e.g. for PAH ISO DIS 18287 or for PCB's FDIS 10382 and WI 028 CEN/TC 292. Should they be brought to the end status of Standards while at the same time discussing in the same working group on the horizontal standardisation of the same subject? In case of ISO DIS 18287 validation data for soils through interlaboratory comparisons are already available. In this case, the decision for further proceeding on ISO DIS 18287 was made at this year ISO meeting in Brno. The validation of the horizontal standardisation will need much more longer time with at least 2 years later, assuming that the acceptable draft standard is existing in one year.

ISO TC 190 has decided to co-operate and the next step will be preparing a framework of the standard including all the decision tables needed. This has to be discussed in a joined group with experts from both CEN and ISO. If the framework is accepted, the technical details can be filled in using description in existing standards and drafts.

As described above it will be necessary to look to the possibilities of pre-normative research to limit the allowed possibilities in the standard. This can be in co-operation with studies within the Workpackage „Horizontal – Organic micropollutants“.

### **4.3 Communications**

The following communication scheme as discussed and suggested by ISO/TC190 (figure 1) is taken over. To be sure that also the Non-European members, which members are positive on the initiative and are willing to support, will be involved in the process of Horizontal standardisation.

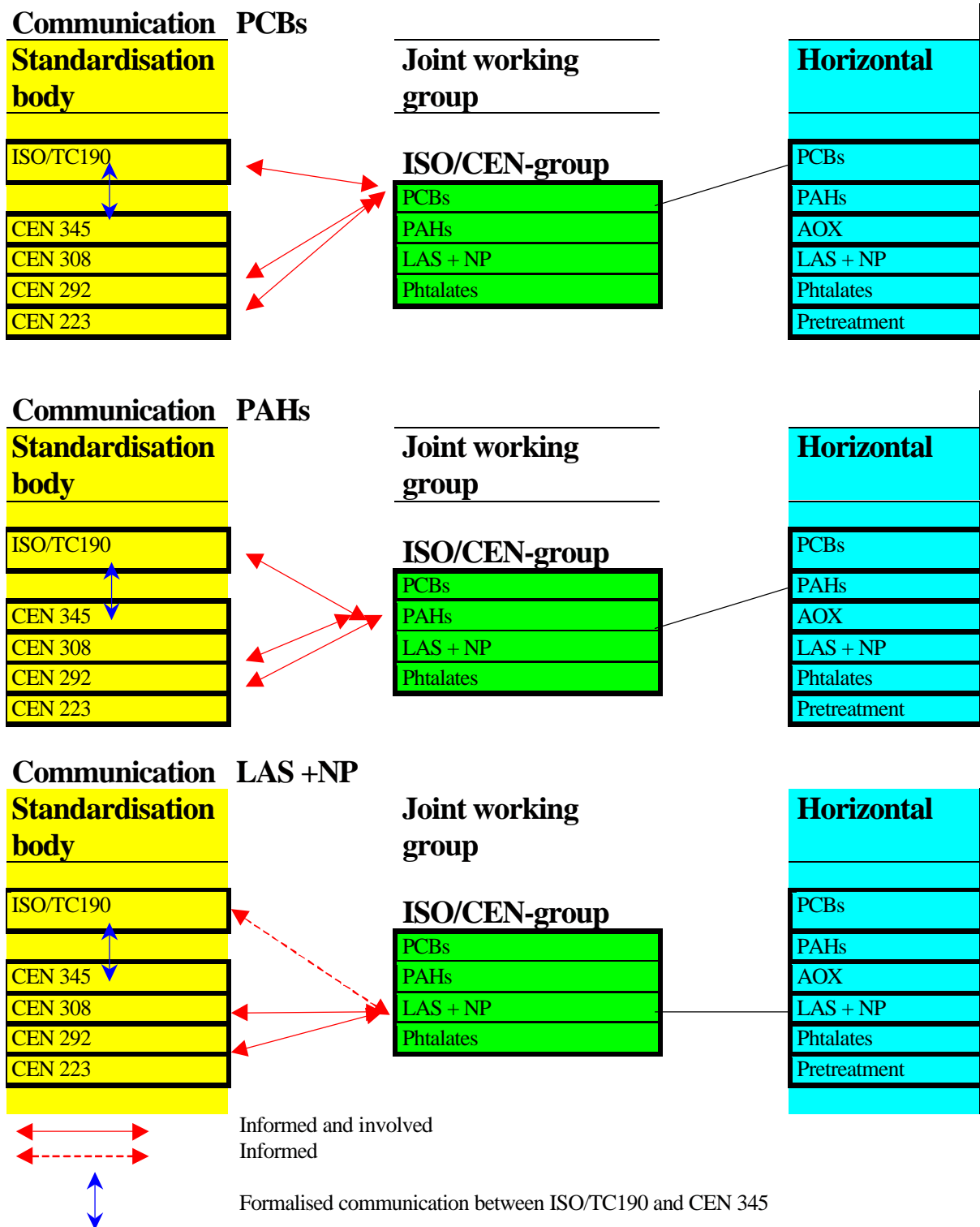
The communication schemes for all the analytes of the European Project “HORIZONTAL org” are described here because co-operation is expected for all the sub work packages dealing with different organic pollutants . But the pathway especially for PAH and PCB will be very similar, since they will be handled in the same Horizontal Ad hoc Working Group of CEN 292,CEN 308 and ISO 190. The way of working will be comparable, as follows from the scheme.

The lower scheme is for LAS and NP. These compounds are not on the working program of TC 190. It is possible that they will be on the program in the near future. In order to stimulate the horizontal approach, TC190 would like to be informed, to be able to give information on the matrix soil, which may lead to incorporation of the matrix soil in the scope.

AOX is not an important item for soil and it is not necessary to inform TC190. Soil should therefore not be included in the scope of the horizontal standard to develop

For all measurements pretreatment is very important. A good communication within the work package pretreatment and the analytical measurements has to be stimulated.

Figure 1:



## 5. CRITICAL POINT AND RECOMMENDATIONS

Standardisation of analytes and methods under discussion for horizontal approach has been carried out in all the respective working groups of the relevant TCs, e.g. CEN /TC292 CEN /TC308 and ISO/ TC 190 and has reached for different parameters different status of draft- or full standards . Some are only in starting position as work item proposal but some are already in the WD, CD, DIS or FDIS or for final voting with all the validation data included but of course for one specific matrix. It has to be decided in the respective working group whether and how to proceed with the existing draft standards. Horizontal standardisation should not hinder the progress of a standard, especially when the draft standard as well as validation data are expected to have in two or more years time.

For the drafting of the horizontal standardisation, decision steps for the matrix specific modular approach has to be discussed and accepted by the members of the joint working groups. Pre-normative work and in House validation are to be done according to the elaborated draft standard on samples which are representative for different matrices. Only after a successful in House validation interlaboratory comparison will be carried out, matrix by matrix. It is expected that a complete validation of the Horizontal standard will be too expensive to do it in one comparison. It will be also necessary but not easy to find sufficient number of European laboratories , who are interested to participate in horizontal validation with different matrices. It may be the task of the Co-ordinator to assure or to take under obligation that the partner laboratories of this horizontal project at least are participating in these horizontal validation.

### **Comments and recommendations to Desk study-PAH submitted by the standardisation bodies and the steering committee**

Some of the comments given up by different bodies are very valuable and constructive, so that they will be taken into consideration for the elaboration of the horizontal standard for PAH, e.g.

**Two different methods for the determination of PAH are mentioned (HPLC and GC-MS). The current decision of the Joint Working Group on this item is to take them both into the standard**

**Both methods will be included in the standard.**

**The GC method covers 16 PAH, the HPLC method 15. The desk study should contain a suggestion how to handle this problem. The limit of determination should match annex 2 of the landfill directive.**

**The numbers of PAHs as well as the limit of determination has to reflect upon the existing national and international directives of the relevant matrices under consideration.**

**Either the original sample or the sample dried by use of sodium sulphate shall be used.**

**Both the original field moist samples as well as the chemically dried samples will be included in the horizontal standardisation**

**It would be helpful to have one extraction procedure for both PAH and PCB – if possible.**

**One extraction procedure is foreseen for both PAH and PCB, where ever possible. But it is only possible for low contaminated soil, sludge and waste. But for high contaminated soil and waste , such as from coking plant with tar particles other more polar extraction solvent is to be used, because of the limited solubility of PAHs( in opposite to PCBs) in unpolar solvent. Therefore the modular approach depending upon the contamination level is planned for this horizontal standard.**

The Hungarian national standard on determination of PAH in waste should be considered. The extraction by shaking is supposed to result in poor recoveries. Data on this item can be provided by Hilda Farkas, Hungarian Ministry of the Environment.

**The data are not yet up to this moment made available. However this point will be checked thoroughly in the ruggedness test.**

General Hazards shall be added as informative part (introduction)

**This point will be included in a harmonised way in accordance with other CEN Standards**

The title of a new European standard on the determination of PAH in soil, waste and sludge should not specify the number of individual PAHs to be measured. A more general wording e.g. “Determination of selected PAHs.....” might be appropriate. This would allow the determination of PAHs according to the needs of the user. At least all PAHs mentioned in European and/or national regulations on waste, soil, sludge shall be included in validation intercomparison studies

**The title will have a generalised wording e.g.” Horizontal standard for the determination of selected PAH in soil ,sediment sludge and waste” and all the stated matrices will be included in the validation studies**

The author of the desk study used the term modular approach to describe that the user can choose from different options depending on the type of sample to be analysed and the question to be answered. This is indeed correct, but it should also be mentioned that horizontal standards are performance-based methods. This denotes that in many cases minimum requirements with regard to a particular parameter e.g. chromatographic resolution, retention time, sensitivity, recovery etc. have to be met without specifying in the standard how to do or only by giving examples.

**Minimum requirements and criteria will be set for performance based methods.**

It should be taken in consideration that the two proposed approaches for detecting PAHs are not compatible with respect to solvents that are in general used for dissolving the final sample extract and injecting it into the analytical system (HPLC requires water miscible, GC-MS non-polar solvents). This has also implications for the choice of the extraction solvent as well as the clean-up and might lead to the conclusion that two separate standard have to be prepared.

**There will be only one standard with two different determination methods**

**- HPLC -DAD/F**

**- GC-MS**

**and different extraction steps according to the contamination level and water content and also different clean up steps according to the disturbing matrices.**

The statement that no additional identification/confirmation is available when using fluorescence detection is not agreed upon: The Agilent 1100 series fluorescence detector provides online fluorescence spectra (both excitation and emission spectra), which can be used for identification of PAHs especially if concentrations are well above limit of determination. This can be assumed to be the case for the majority of waste, soil, and sludge samples. This information should be added in chapter 1.1.4

**This information will be added, but at present very limited number of laboratories possess this kind of scanning fluorimeter. The applicability of this detector for fitness of the purpose has to be checked.**

**The Italian national draft standard on determination of PAH in waste should be considered . A validation study on this draft has been carried out during 2002 and the final report is available Information about the draft Italian standard for PAH determination in waste - to be added to table in annex 1 of desk study document on PAH.**

**The Italian standard is taken into consideration and added to the Annex 1 of the desk study**

Neither of these reports provided any evidence as to why Horizontal standards should be developed. There are no critiques of methods currently in use. There are no comments on what fit for purpose methods should look like in terms of range of determination, precision and accuracy.

**It was shown in the desk study what standards are existing for which matrices and what limitations as well as advantages and disadvantages are existing in each method. To solve out the existing problems shown in the desk study is the goal of the horizontal project.**

## 6. DRAFT STANDARD (CEN TEMPLATE)

A draft standard is under development within the HORIZONTAL Ad hoc Working Group of CEN 292, CEN 308 and ISO 190 for the determination of PAH and PCB in soil, sediment, sludge and waste.



## References

See list of standards involved in chapter 3

EU, 2002. Commission Decision 12 August 2002. Implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Docnr: C(2002) 3044