Explanatory notes for the Horizontal PAH- and PCB-standards

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Introduction

This note shall be read in combination with the following Horizontal standards, available for the phase II consultation.

- Soils, sludges and treated bio-waste – Organic constituents – Polychlorinated biphenyls (PCB) by GC-MS and GC-ECD

- Soils, sludges and treated bio-waste – Organic constituents - Polycyclic aromatic hydrocarbons(PAH) by gas chromatography(GC) and high performance liquid chromatography(HPLC).

The two standards are available on the HORIZONTAL website (www.ecn.nl/horizontal). In this note it is explained how the versions for the phase II consultation have been developed.

The way to second consultation

In 2004 a first draft for a PCB-standard and PAH-standard has been developed in co-operation with experts from CEN 308, CEN 292 and ISO/TC 190. These drafts were further developed into drafts now available for the second consultation within the project HORIZONTAL. Several meetings have been used for further improvement of the draft. Together with the Soil Science and Conservation Research Institute (Slovakia) a program for further validation has been developed. During the whole period, also comments of experts by Email have been used. We both have appreciated this involvement very much. In order to involve non-EU members of ISO/TC190, the standards have been presented on the meetings OF ISO/TC190 in Paris (September 2004) and Tokyo (October 2005).

The standards use procedures already used in other standards (ISO and CEN) and also prescribed in national standards (for references see both standards). Due to the diversity of matrices, sludge soil and waste it was not possible to come up with one single procedure in both standards. Different modules were necessary in order to have the broad horizontal scope. As described by Harmsen and Frintrop (2003) accessibility of the contaminant by the solvent and dissolving in this solvent are both important factors. Which one is most important depends on the sample. Accessibility is important in clay-samples and dissolving becomes important in presence of tar-like

particles. For these different samples different extraction methods can be necessary. For instance, use of acetone and petroleum ether in a shaking procedure for clay and a Soxhlet-extraction if tar-like particles are present. Both methods are described. Clean-up is necessary if interfering compounds are present. Different matrices contain different interfering compounds and the standard should therefore give different possibilities for removal of interfering compounds.

Because PCBs and PAHs have a comparable polarity and behave similar in solid environmental samples, most laboratories prefer to use as much as possible the same procedure. This 'Horizontal' aspect is taken into account. Due to close cooperation of the working package leaders Tin Win and Joop Harmsen, the standard for PCB and the standard for PAH are as far as possible identical, which broadens the Horizontal character of both standards.

The standards make it possible to make different choices (different extraction and clean-up procedures, use of both GC-detectors MS or ECD for PCB and GC-MS or HPLC-Fluorescence for PAH). This may have a negative effect on the comparability. This subject was the most important factor for discussion. Is it possible to compare results if laboratories are using different modules described in the standards? By using internal standards in combination with injection standards, it has become possible to control the performance of the method with each individual sample. The recoveries of internal standards have to be above a described value, which improves the comparability. We tried to introduce the metrological approach (traceability of measurement results to the International standard SI unit-amount of substance) in the standardisation procedure by using the calibration standards of certified concentration accompanied by stated uncertainty. We also take part or organise the international Intercomparison (Key and Pilot Comparisons of CCQM**-** Consultative Committee for Amount of Substance – Metrology in Chemistry) at the highest measurement level of National Metrological Institutes(NMI), where the uncertainty assessment of the final results as well as of the different steps in the measurement procedure are to be made. In CCQM Key Comparison 25- Determination of PCB in sediments (at10-40ppb level), the comparability of the results of the participating laboratories are very good(e.g. 4-5 % of the relative reproducibility standard deviation, while all the laboratories using higher order calibration standards with certified values with stated uncertainties and the corresponding $^{13}C_{12}$ PCB congeners as internal standards. Report on K 25 is available at http://www.bipm.org/en/committees/cc/ccqm/working_groups.html. BAM participate in K 25 applying the combinations of modules prescribed in the draft horizontal standard. The benefit of the use of isotopic internal standard for the check of performance criteria is clearly seen in the Ad hoc group, but it is now under discussion due to the high cost of isotopic materials whether they have to be added to the sample prior to extraction and whether all the target analytes require corresponding internal standards.
For the PAH, it can be concluded clearly from the ruggedness test that the HPLC-method can only be used for screening and for higher contaminated soil samples. GC-MS method using corresponding isotopic or deuterated standards is proven to be more precise and reliable than the HPLC method, also because of the possibility of the performance check of the internal standards. The cost of the internal standards is also one of the future discussion point. When dealing with complicated matrices as sewage sludge, the clean up step become very important, contributing a high portion to the uncertainty budget of the whole procedure. While PCB are very stable and hence can be subjected to vigorous clean up procedures to achieve the final solution which can be analysed gas chromatographically without serious disturbances PAH are less stable and hence can only be subjected to GPC, liquid-liquid partition and column chromatography for clean up leading often to interferences of PAH analysis.

As mentioned, the Horizontal PAH- and PCB-standard has been discussed within ISO/TC190, CEN 308 and CEN 292. Consultation of the existing standardization groups was found to be essential for an international accepted standard, but this process needed some time. Some mistakes in communication have been in the complex communication with different groups. However, despite these mistakes, the consultation has lead to support of the content of the standard by the experts involved and also by Non-EU members active within ISO/TC190. Due to existing rules within CEN, CEN 292 has, unfortunately, being forced to make their own standards. Discussion is going on to incorporate this standard again in the Horizontal one.

Following steps

In the following period two parallel lines will be followed: (1) incorporating of the comments resulting from the phase II consultation, (2) Experimental work to support the following validation

Validation of all combination of modules described in the standards will be impossible. The approach used in the Horizontal standards for PCB and PAH will ask for a new more levelled approach of validation. This has been communicated with CEN 345 (meeting of April 5, 2005 in Brussels) and this committee is further discussing the subject of validation (Terytze et al., 2005).

The first level for these standards is the use of existing modules which have been validated in the past. Experts, giving comment on the standards, are invited to forward validation results for different modules described from their country, group or laboratory. We also welcome information on non-validity of modules for specific matrices. This kind of information is necessary to guide the user to make the proper choices.

BAM has organised in cooperation with Mexican Metrological State laboratory CENAM in 2005 the measurement of PAH in soil for CCQM-P 69 for the international state metrological institutes and BAM has also provided measurement results for the certified reference values for PCB and PAH for IMEP 21 (International Measurement Evaluation Programme) which will be conducted in the beginning of 2006 by Institute for Reference Materials and Measurements (IRMM)– Joint Research Centre, European Commission (http://www.irmm.jrc.be/html/interlaboratory_comparisons/imep).
In both cases the methods prescribed in the respective horizontal standards are used for the measurements.

For the following level an experimental program has been made to test the PCB-standard and PAH-standard, in order to optimise the following validation. Laboratories of BAM (Germany), Alterra Wageningen-UR (The Netherlands) and the Soil Science and Conservation Research Institute (Slovakia) will be involved. In this following part of the study the following aspects will be tested:

For the experiments the following samples supplied by JRC will be used:

- CW 1 Composted garbage
- CW 5 Compost
- SL 4 R Sludge of domestic origin

- SO9 Sludge-amended soil

- The following aspects will be investigated
  - Applicability (no interferences in the chromatogram) of all suggested internal and injection standards
  - Check of the performance criteria. Is it necessary to use them all or is reduction of the number possible, what are the most critical internal standards
  - Evaluation of different clean-up procedures using extracts of the 4 materials

After the phase 2 consultation, the standards will be ready for validation within different European laboratories. In this validation it will be possible to use a limited number of samples and limited combination of modules. Therefore it will be important to use this validation to check if it is possible to control the performance of the method with each individual sample.

References

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