

## **Report on the QUASIMEME Workshop on the Analysis of PAHs and Alkylated PAHs, Marine Laboratory, Aberdeen, 10-11 December 2009**

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The QUASIMEME workshop on the analysis of polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs addressed the difficulties and new developments in the analysis of these contaminants in environmental matrices. The programme and the slides of the various presentations can be found on the QUASIMEME website ([www.quasimeme.org](http://www.quasimeme.org) – sharepoint).

### **Summary of oral presentations**

An extensive overview of monitoring results was given by Dr. Jacek Tronczynski (IFREMER, Nantes, France). This overview emphasized the importance of analyzing specific alkylated PAHs when identifying sources of PAHs. Examples of multivariate analyses of datasets from the English Channel and the Mediterranean were shown. A specific example was shown from a site in Lebanon. PAHs were analysed after the bombardment of a power plant. In addition to alkylated chrysenes, naphthalenes, pyrenes and phenantrenes also heterocyclic PAHs were found. Levels of alkylated PAHs in fish and shellfish were much higher than those of the parent PAHs. Sediment profiles from France indicated a possible relationship between the use of coal in energy production and PAH concentrations in the marine environment: an increase is seen since the 1800s, followed by a decrease after ca. 1970, when nuclear power for energy production was introduced in France.

Dr. Donata Lerda gave an overview of the Community Reference Laboratory (CRL, IRMM, Geel, Belgium) for PAHs. In particular, she addresses the activities of IRMM for PAHs in foods. This type of analysis is required in several European regulations. Tasks of the CRL include the validation of methods and the provision of certified reference materials required for methods described in the EU legislation. A proficiency test on 16 PAHs in food is organized on an annual basis, as well as an annual workshop. Recent results showed a difference of a factor 100 between the LODs of participants. Data should be reported after correction for recovery. Results can be biased (high) when water is extracted from the food sample.

Dr. George McLeod of Bruker Daltonics Ltd. presented an LC-APLI-ToF-MS technique for the analysis of PAHs. Improved sensitivity and selectivity were reported for this method, which makes use of a laser. In particular a better selectivity and sensitivity was reported for non-polar

PAHs as well as for other aromatic compounds. The method is very robust: ca. 15 million injections can be made before the laser is exhausted. Examples for HPLC and UPLC were given. Dirty matrices did not cause specific problems. The method is not suitable for aliphatic compounds. Coupling to GC is also possible.

Mr. Johan Kuipers of Varian, Middelburg, The Netherlands, presented a new, VF-17MS stationary phase for a better separation of PAHs. Critical separations such as phenanthrene/anthracene were discussed and improvements were shown.

Mrs. Marie Russell, Marine Laboratory, Aberdeen, presented a method for the quantification of alkylated PAHs as is used in the Marine Laboratory. The method and related extraction, clean up and instrumentation were shown in the laboratory. A quadrupole GC-EI-MS was used. It was indicated that the use of metal-free silica was important in order not to lose the dibenzothiophenes. Difficulties were met in the separation of chrysene and triphenylene. A cluster approach was used for the integration of several alkylated PAH peaks. Calibration was carried out per group of alkylated PAHs, based on the degree of alkylation. Matrices analysed included mussels, nephthys, sediments, dredge spoil and fish. Cyclopenta[c,d]pyrene, naphtho[2,1a]pyrene and dibenzopyrene were found in seafood samples.

A presentation of Ewa Skoczynska (IMARES, IJmuiden, The Netherlands) (given by her supervisor Prof. de Boer (IVM, VU University, Amsterdam) as Ewa was ill) showed the advantages of comprehensive multi-dimensional GC (GCxGC) for the analysis of PAHs and alkylated PAHs. It is important that the two stationary phases used are orthogonal, i.e. they should each show a different separation pattern. The recently introduced ionic liquid stationary phases may be an interesting development. The same is true for liquid crystalline phases, but they are often limited in use due to a relatively low maximum allowable temperature. A large number of alkylated PAHs could be identified in a river sediment sample that was not cleaned after extraction.

Mr. Ton van de Zande (QUASIMEME) presented results of a recent QUASIMEME interlaboratory study, as well as a historic overview of PAH interlaboratory study results since the start of the QUASIMEME programme. Both for sediments and biota on average 40 participants join these exercises every year. Three phenylanthracenes, one methylanthracene, 10 methylated chrysenes and 12 methylated benz[a]anthracenes were recently added to the set of PAH compounds for these exercises. No assigned values could be given for most of these in the last exercise due to a low participation degree for these compounds. Difficulties met by participants included chromatographic separation, adsorption and discrimination due to splitless injection.

Finally, Prof. Cofino (QUASIMEME) gave an overview of the developments in the statistical methods used for the evaluation of interlaboratory studies. It was clearly shown that different methods lead to different results. There is an extensive knowledge on statistical programmes within QUASIMEME. The evaluation methods currently used by QUASIMEME seem to be very reliable and insensitive for specific conditions (skew distribution, outliers, etc.) in comparison with other methods.

In addition to these oral presentations, six posters were shown (see website QUASIMEME).

### **Discussion**

During the discussion a number of analytical issues were addressed. There is a need for more alkylated PAHs as standards. Now, there are only ca. 30 of these commercially available. One problem with Chemstation software (Agilent) was discussed. When diluting samples, internal standards are obviously also diluted. Because the software uses ratios, the ratio target peak/internal standard remains the same, which may lead to erratic results. This could lead to incorrect interpretation of calibration curves. The MS is normally very linear, so, in case deviating calibration curves are found, it is most likely a signal of an error. The integration of alkylated PAH peaks was discussed. Some analysts use the entire area under a peak which represents more compounds; others use a “triangle-integration”. The cluster method presented by Marie Russell was suggested as a standard method for the time being. Obviously, a better separation is required. As in many other occasions the analysis of unknown solutions during interlaboratory studies often leads to disappointing results, most likely because analysts are not used to handle unknown solutions. The analysis of hydroxyl-PAHs was briefly discussed. These are only analysed by a few laboratories, e.g. in fish bile.

### **Recommendations**

- It was suggested was to add alkylated naphthalenes to the QUASIMEME programme.
- It is recommended to choose some methylated PAHs as markers to distinguish oil and combustion sources of PAHs. QUASIMEME should seek advice from the ICES (International Council for Exploration of the Sea) Marine Working Group on this matter.
- There is a need for more CRMs, e.g. for PAHs in mussels. Also, it is desirable to have a CRM for total hydrocarbon.
- It would be beneficial for a number of laboratories if QUASIMEME could offer a method and interlaboratory study for total hydrocarbon.