THE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) FROM SEDIMENTS AND BIOTA USING MICROWAVE-ASSISTED ALKALINE SAPONIFICATION (MAAS)

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Introduction

The method of alkaline saponification for the extraction of PAH from marine sediment and biota samples was originally developed in the mid-1970s. It has a number of advantages over solvent extraction. As well as extracting PAH from the samples, the digestion process conducts a large part of the clean-up which is necessary before GC/MS analysis. Sediment samples often contain high concentrations of sulphur which interferes at the chromatographic stage, and alkaline saponification is able to quantitatively destroy elemental sulphur and mercaptans. Any lipids present in sediments or biota are also destroyed during the process. Minimal column clean-up using alumina is then adequate to remove residual pigments and other co-extractives.

Figure 1: Sediment reference material from freeze dried habour mud

Current Methodology

The method currently in use at CEFAS for the extraction of PAHs from solid environmental samples is alkyl saponification followed by liquid-liquid extraction. It is, however, time consuming, as extraction takes 2 hours, and it also uses large volumes of solvents. Limitations of the current methodology relate primarily to the small batch size, and to heavy solvent and glassware use. The use of MAAS alleviates these problems, and also reduces the extraction time needed. The method has been evaluated using a sediment certified reference material (Figure 1) and a mussel tissue laboratory reference material (Figure2) prepared in-house.

Figure 2: The biota reference material was made from mussels

Microwave Method

Two microwave systems were evaluated. The first being the MARSX, Microwave Accelerated Reaction System on loan from CEM Microwave Technology Ltd, and the second loaned to us by Milestone Analytical UK Limited. Both systems claimed to decrease extraction time to less than 15 minutes; for a batch of 14 samples for the CEM system and 12 samples for the Milestone; to reduce solvent consumption, and to improve extraction efficiency, and so therefore to increase laboratory productivity.

Microwave assisted extraction labstation

The recommended MASE method is that samples are extracted using solvents and the most generally used solvent system for PAH is 1:1 acetone:hexane. This solvent system was used to extract samples of a freeze-dried sediment certified reference material and an in-house biota laboratory reference material. The Microwave units were programmed to run at 600 watts to a temperature of 140°C, hold this temperature for 20 minutes, vent for 5 minutes, and then the samples were removed and allowed to cool. The procedure was then repeated using alkaline saponification with 20% methanolic potassium hydroxide instead of solvent extraction.

Microwave extraction vessel

Acknowledgement

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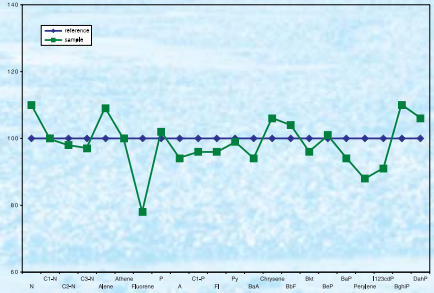
Results

The extracts were analysed by GC/MS and the results compared to the accepted concentrations and ranges for PAH in the reference materials. The coefficient of variation was calculated for each compound and data set and fell within 0. 9 - 10%. The results from acetone:hexane extraction came out consistently low compared to the accepted values and so it was decided not to proceed any further using this solvent extraction technique. The solvent extracted sediments showed a slightly higher level of extraneous/contaminating peaks such as sulphur. This meant a full clean-up would be required for solvent extracted samples.

The results from alkaline saponification compared well with the certified values so it was decided to repeat the experiment, this again produced accurate and precise results.

Chart 1 (right) shows the results from the biota reference material compared to the accepted values.



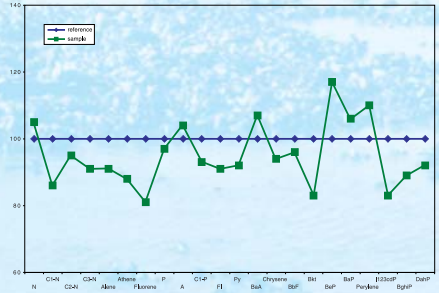


Chart 2 (left) gives the results of the sediment reference material compared to the certified values.

Key to PAH compounds
N, naphthalene; **Alene,** acenaphtylene; **Athene,** acenaphthene; **P,** phenanthrene; **A,** anthracene; **Fl,** fluoranthene; **Py,** pyrene; **BaA,** benz[a]anthracene; **BbF,** benzo[b]fluoranthenes; **Bkf,** benzo[k]fluoranthenes; **BeP,** benzo[e]pyrene; **BaP,** benzo[a]pyrene; **I123cdP,** indeno[1,2,3-*cd*]pyrene; **BghiP,** benzo[*ghi*]perylene; **DahA,** dibenz[a,*h*]anthracene; **C1-C3,** denote degree of alkylation in substituted PAH

Conclusion

Microwave-assisted extraction, demonstrated the capability to produce reliable results, and to process larger sample batches.

Both systems confirmed:

- That more samples could be extracted at one time, twelve or fourteen compared to six.
- The extraction time was reduced from two hours to twenty minutes and also the sample cooling period was much shorter.
- Less glassware could be used and laboratory productivity increased.

The extraction process used approximately a third less solvent, however there was insufficient time to allow evaluation of the claim that the microwaves would improve sample extraction efficiency.

CEFAS have now purchased a laboratory microwave system and the method will be applied routinely in the future.

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