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

by Paul H. Roberts, Kerry L. Baker and Carole Kelly

CEFAS
The Centre for Environment, Fisheries & Aquaculture Science

Introduction

The current methodology for the extraction of PAH from marine sediments and biota samples, utilised at CEFAS since the mid 1970's, is alkaline saponification followed by liquid-liquid extraction. Other studies have investigated the use of Microwave Assisted Solvent Extraction (MASE) for the extraction of a variety of organic pollutants from environmental samples, and these have led to publication of EPA Method 3546. Currently there has not been any data published on the use of MAAS as a technique for extracting PAH from environmental samples.

Current Method

The method, although well proven and robust, has both advantages and disadvantages. In addition to the extraction of PAH from environmental samples, the extraction process achieves a large proportion of the clean-up necessary prior to analysis by gas chromatography/mass spectrometry (GC/MS).

Advantages of saponification include the quantitative breakdown of elemental sulphur and mercaptans that are often present in high concentrations in anoxic sediment samples, which interfere chromatographically. Lipids are also destroyed during the saponification process and thus only minimal column clean up is required before GC/MS analysis.

Disadvantages of the method are that large amounts of solvents and glassware are used. Only four samples per analytical batch can be extracted and it is time consuming as an extraction takes two hours.

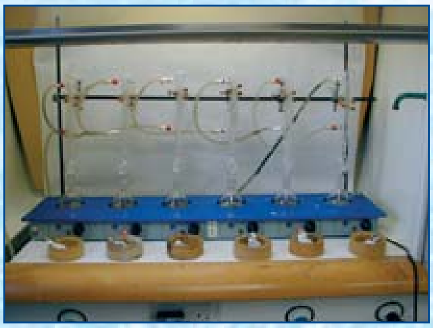

Figure 1: Showing Traditional Extraction Apparatus.

Microwave method

MAAS was evaluated using a Milestone Analytical UK Limited ETHOS SEL microwave system (Figure 2). Experiments were carried out to establish whether limits of detection (LOD) similar to the existing technique could be achieved using a certified reference material (CRM) and marine sediment samples spanning the range of environmental PAH concentrations encountered. These were extracted in parallel with the traditional method (Figure 1).

Figure 2: Microwave extraction system.

Marine sediment samples were extracted using the following method; 5g of material was weighed into an extraction vessel (Figure 3) containing a Teflon stirrer bar, followed by addition of 2g potassium hydroxide, 25ml methanol and surrogate standards. Only a gram of the CRM was used during extraction and 2ml of water was added to this vessel to optimise the extraction of the dried material.

The samples were heated to a temperature of 140°C over a period of 10 minutes with 550 watts of microwave power. This temperature was maintained for 12 minutes, then the system was vented for 5 minutes, and the samples removed and allowed to cool. The samples were stirred during the entire extraction process. Once cool, the samples were extracted using a scaled down version of the normal liquid-liquid extraction process.

Figure 3: Extraction Vessel.

Key to PAH compounds

N, Naphthalene; **Athy**, Acenaphthylene; **Alene**, Acenaphthene; **DBThio**, Dibenzothiophene; **P**, Phenanthrene; **A**, Anthracene; **Fl**, Fluoranthene; **P**, Pyrene; **BaA**, 1,2-Benzanthracene; **Chry**, Chrysene; **BNThio**, Benzo[*b*]naphtha[2,1-*d*]thiothene; **BbF**, Benzo[*b*]fluoranthene; **BkF**, Benzo[*k*]fluoranthene; **BeP**, Benzo[e]pyrene; **BaP**, Benzo[*a*]pyrene; **I123-cdP**, Indeno[1,2,3-cd]pyrene; **BghiP**, Benzo[*ghi*]perylene; **DahA**, Dibenz[*a,h*]anthracene.

C1-C3, denotes the degree of alkylation in substituted PAH.

Results/Validation

Extracts were analysed using GC/MS. The results for the CRM when using alkaline saponification were in good agreement to within ±9% of the results generated using MAAS. The values for the CRM still fall within the accepted concentration ranges when using MAAS. Figure 4 gives the percentage difference between the certified values and the two techniques.

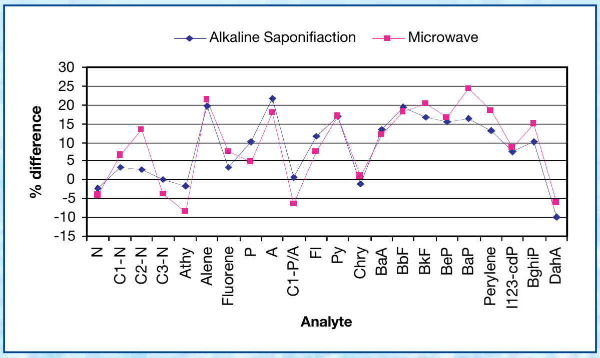

Figure 4: Illustrating the percentage difference between the certified values and the two techniques.

The results of the MAAS extracted marine sediment were compared to the values obtained using traditional alkaline saponification. The results generated using MAAS compared well with the existing technique, with variations across the range of analyte concentrations of -15% and +13% from the traditional saponification (Figure 5). There is some indication that the MAAS method may be more effective for naphthalene and the C1- and C2-naphthalenes. The marine sediment represented in Figure 5 is an anoxic mud sample from the northeast of England containing both oil-derived and combustion-derived PAHs.

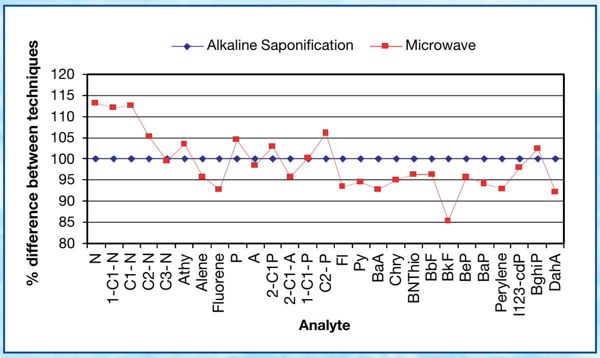

Figure 5: Gives the results of a marine sediment extracted using both techniques.

Validation of the method was accomplished by repeat analysis of a single sediment over a period of time to determine the reproducibility of the method. A mud sample from the southwest of England with a combustion dominated PAH composition was selected. The sample was extracted 23 times, over a period of one week, enabling mean values and RSD values to be calculated (Figure 6).

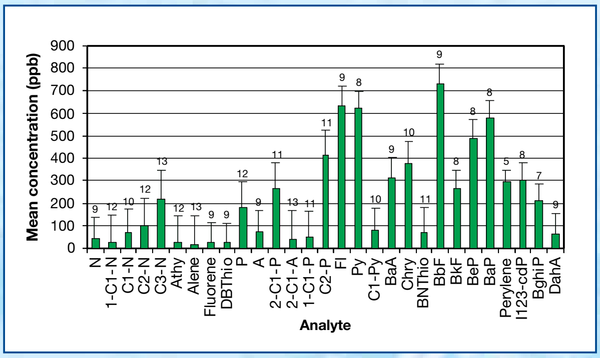

Figure 6: Showing the average PAH concentration and the mean RSD n % of the validation sediment. (RSD n % shown at top of bar.)

Conclusion

The MAAS method described here provides clear advantages over the traditional saponification method. Ten samples can be extracted in each analytical batch (plus a blank and a reference material) and the extraction time is greatly reduced from two hours to 20 minutes.
In addition, the extraction process uses less glassware and approximately a third less solvent. The RSD values of between 3-13% prove that MAAS is a viable alternative to the traditional method, and one that CEFAS is implementing for routine analyses.

Further Work

Completion of validation experiments to establish the feasibility of using this method to extract PAH from biota samples.

Investigations into the application of MAAS to extract Nitro-PAH from sediments.

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The Centre for Environment, Fisheries and Aquaculture Science (CEFAS), Burnham Laboratory, Remembrance Avenue, Burnham on Crouch, Essex CM0 8HA, UK. http://www.cefas.co.uk