

Impacts of Extraction Methods and Solvent Systems in the Assessment of Toxic Organic Compounds in a Solid Matrix

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are among the listed persistent organic compounds (POP) which are pollutants of environmental concern due to their toxicity. This study evaluated soxhlet and ultrasonic extraction methods using a three-solvent system (acetone+dichloromethane+n-hexane) in order to compare the ability of the techniques to extract selected PAHs in raw coals collected from a coal mine in Okobo-Enjema, Nigeria. Then, binary solvent mixtures consisting of acetone+dichloromethane; dichloromethane+n-hexane; and acetone+n-hexane, were compared with the ternary solvent system for their ability to extract the target PAHs by soxhlet extraction method. The extracts were quantitatively analysed for sixteen PAHs using Gas Chromatography-Mass Spectrometer (GC-MS). Sonication extraction method extracted higher number of PAHs, required fewer amount of solvents, shorter time of extraction and less energy consumption compared to soxhlet extraction, which extracted higher amount of the target PAHs. The total amount of PAHs determined ranged from 0.02 mg/kg to 0.20 mg/kg in the various solvents' mixtures. The ternary mixture extracted larger quantities of the target toxic PAHs. This report will assist in the choice of analytical methods and solvent systems for environmental studies.

Keywords: Coal, Extraction, PAHs, Solvent Systems, Sonication, Soxhlet

1. Introduction

PAHs are a class of organic compounds whose molecular structure contains two or more fused aromatic rings. They are among the listed persistent organic compounds (POP) which are pollutants of serious environmental and human health concerns due to their widespread occurrence, strong persistence, long-range transportation potential, carcinogenic, mutagenic and teratogenic properties as well as their high environmental concentration^{1,2}. About 75%-90% cancers of human being are said to be mainly caused by PAHs³. The U. S. Environmental Protection Agency (EPA) listed sixteen PAHs that must be controlled due to their potential harm to people's health⁴. PAHs occur naturally in some materials and are also formed from anthropogenic activities⁵.

Coal is a heterogeneous material, consisting of organic and inorganic compounds⁶. It is a primary fuel

that is utilized in many countries to generate electricity, in domestic and industrial heating, production of some chemicals and in making of steel⁷.

Studies of coals have revealed that coal naturally has high PAH concentrations which occurred from the biological materials and processes in the transformation of organic matter to coal⁸⁻¹². Apart from the natural occurrence, PAHs are also formed by incomplete combustion and pyrolysis of coal as well other fossil fuels and vegetation fires^{13,14}.

Extraction of PAH compounds in raw coal using suitable solvents is a crucial step in the stages for the detection and determination of PAHs. PAHs cause pollution and may be released from coal during combustion, coking, pyrolysis, runoff and other coal preparation processes¹⁵.

Various studies of solvent extraction in PAH determination applying different extraction procedures

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and using different solvents such as dichloromethane, acetone, toluene, diethyl ether, cyclohexane, or mixtures thereof have been reported¹⁶⁻²⁰. The common result has shown that the nature of solvents, mixture of solvents, extraction methods, properties of the coal and the nature of PAHs are factors that influence the quality of extraction of PAHs in coals.

To the best of our knowledge, there is no literature on the extraction of PAHs, which are toxic compounds, using a ternary solvent system (three solvents). No information is available on the expected results when soxhlet and sonication methods are used for extraction of PAHs in a ternary solvent system. Also, to the best of our knowledge, a comparison of the use of binary and ternary solvent systems was not found in any literature.

Therefore, the objectives of this work are: 1. To compare soxhlet extraction with ultrasonic agitation using a three-solvent system to extract PAHs, 2. To compare extraction effectiveness of using a binary solvent mixtures with a ternary solvent system for the extraction of PAH compounds, 3. To determine the concentrations of the target PAHs in the extracts of Okobo-Enjema coal samples from the different extraction methods and solvent systems.

This study may contribute to the pollution research of this coal mining area given that coal particles will contaminate the environmental components (air, plants, sediments, soil and water) and may be helpful for putting necessary measures to mitigate adverse environmental effects associated with PAH releases from coals.

2. Materials and Methods

The extracting solvents, acetone, Dichloromethane (DCM) and n-hexane, were analytical grade reagents supplied by Sigma Chemical Limited, Germany. The standard PAH mixture of sixteen PAHs was purchased from AccuStandard, USA.

2.1 Coal Sample Collection and Preparation

The coals used in this investigation were collected from Okobo-Enjema mine. Okobo-Enjema is an agrarian rural community, near Ankpa in North central Nigeria, lying between longitude 7°15'N and 7°30'N and latitude 7°30'E and 7°46'E. The As Received (AR) dry coal samples were homogenized by grinding with mortar and pestle and screening through a 250 µm sieve. The

undersize samples were collected, mixed thoroughly and packaged in plastic bags, labeled accordingly, and kept in a dark cool cupboard to reduce or prevent volatilization and degradation.

2.2 Extraction of PAHs in Coals with Ternary Solvent System using Soxhlet Extraction Method

A ternary solvent system was used for the extraction of the target PAHs in coals by soxhlet extraction method. The PAHs in the pulverized coal samples were extracted with the solvent mixture using EPA 3540 modified method²¹. EPA method 3540 describes the soxhlet procedure for extraction of PAHs from solid matrices. The soxhlet extractor consisted of an electrothermal heater (Serial No.: 0444251, J.P. Selecta S.A., Spain), flask, condenser and water tubing. The 150 mL ternary mixture of acetone, dichloromethane and n-hexane (1:1:1) was placed in a 250 mL soxhlet round-bottomed flask which was connected to the condenser bearing a water tubing. Exactly 7 g of the coal sample, wrapped in a tissue paper, was placed in the thimble in an inner tube and refluxed with solvent in the flask, which was placed on the electrothermal heater. The extractor was operated at between 35 and 40 °C as the solvent slowly extracted the coal and siphons the extracts into the flask, repeatedly, until the extraction was completed in 10 h.

2.3 Extraction of PAHs in Coals with Ternary Solvent System using Ultrasonic Extraction Method

The same amount of weighed sample (7 g) as in soxhlet extraction was introduced in a beaker and mixed with 60 mL of mixed solvent (DCM/acetone/n-hexane (1:1:1)). Following the standard method of the United States Environmental protection Agency, EPA method 3550²², the extraction was carried out by ultrasonic extraction method. EPA method 3550, described under SW-848, outlines the detailed procedure of using ultrasonic energy for extraction of semivolatile organic compounds from solid matrices. The beaker containing the solution was placed in an ultrasonic bath of a sonicator (Model: SALD-BS2, Shimadzu Corporation). The stirrer and the ultrasonic pulse were activated and the extraction was allowed to proceed for 25 min.

The extracts were decanted and further separated

from the sample in a Uniscop laboratory centrifuge (Model: 80-2B, Surgifriend Medicals, England), which was in operation for 30 min at 3500 rpm.

2.4 Evaluation of binary and ternary solvent systems using soxhlet extraction method in the extraction of the target PAHs in coals.

Binary and ternary solvent systems were evaluated using soxhlet extraction method for the extraction of the target PAHs in coals. The coal samples were extracted with solvents using EPA 3540 modified method as described in Section 2.2 above. Four different solvent mixtures in 250 mL Soxhlet round-bottomed flasks (A-D) were tested for the extraction of 7 g of the coal sample wrapped in a tissue paper and placed in the thimble in the four soxhlet extraction units with the following compositions:

- Flask A: 150 mL binary mixture of acetone and DCM (1:1).
- Flask B: 150 mL binary mixture of n-hexane and DCM (1:1).
- Flask C: 150 mL binary mixture of acetone and n-hexane (1:1).
- Flask D: 150 mL ternary mixture of acetone, dichloromethane and n-hexane (1:1:1).

2.5 Concentration of Extracts

Each of the extracts from the soxhlet and sonication extractions was concentrated with a rotary evaporator (Model: RE52 – 2, SearchTech Instruments, England) at the bath temperature of 30 °C.

The extracts from both extraction methods were analysed for selected PAHs by GC-MS.

2.6 GC-MS Analysis of PAHs in Okobo-Enjema Coal Samples

This analysis was carried using a GC-MS instrument, comprising of a gas chromatograph (Model: 7890 A, Agilent technologies, USA) coupled to a Mass Selective Detector (MSD) (Model: 5975, Agilent technologies, USA) in Selected Ion Monitoring (SIM) mode. Samples were introduced through the capillary column (30 m length, 0.25 mm diameter, 0.25 µm film thickness) which separated the analytes via a split/splitless inlet, using an auto-sampler. Helium was used as the carrier gas at a flow

rate of 1.0493 mL/min, pressure of 9.0855 psi and average velocity of 37.604 cm/sec. The column temperature was held at 65°C for 1 min, then increased to 140°C at 25°C/min (Ramp 1); and then, increased to 290°C at 10°C/min for 11 min (Ramp 2). The electron ionization energy was set at 70 eV. The mass spectrometer quadropole analyzer and source temperatures were set at 150°C and 230°C respectively. The PAH standard was analyzed in scan mode first in order to see the fragmentation pattern of each PAH. All the ions were scanned at the scanning range between 50 and 550 amu. After scanning the standard, target and qualifier ions were determined for each PAH compound. Calibrations were prepared using pure standard PAH mixture (AccuStandard, U.S.A) dissolved to desired concentrations with analytical grade acetone²³. The PAHs were identified by comparing the retention time of the samples to the retention time of the external standard used to calibrate the equipment and also by matching the mass spectra of the monitored ions ratios of the compound in the sample with the National Institute of Standards and Technology library database spectra. External standard method was used for quantitation of the PAHs in the extracts by comparing the sample standards with the analytes.

For Quality Control/Quality Assurance (QC/QA), blank samples (solvent) were analyzed for PAH background correction. The limit of detection and limit of quantification of the GCMS were evaluated using a mixture of the target 16 PAHs standards. This sample analysis was done in triplicate and the average results were calculated.

This study was carried out between December, 2015 and May, 2016, at the Fossil energy Laboratory, National Center for Energy Research and Development, in the University of Nigeria, Nsukka, and the GC-MS analysis was carried out at IESL Laboratory, Port Harcourt, Nigeria.

3. Results

Many PAHs are included in the “priority pollutants” listing of the US Environmental Protecting Agency (US EPA) due to the extensive amount of data suggesting the hazards of these compounds. The list of the 16 EPA priority PAHs which are the target for this study are naphthalene (nap), acenaphthylene (ace),

acenaphthene (acen), fluorene (flu), anthracene (anth), phenanthrene (phen), fluoranthene (fluo), pyrene (pyr), benzo[a]anthracene (b[a]anth), chrysene (chry), benzo[b]fluoranthene (b[b]fluo), benzo[k]fluoranthene (b[k]fluo), benzo[a]pyrene (b[a]pyr), benzo[ghi]perylene (b[ghi]pery), indeno[1,2,3-cd]pyrene (indeno[1,2,3-cd]pyr), and dibenzo[a,b]anthracene (dib[a,b]anthr).

Table 1. Comparison of PAHs rings extracted in the most efficient binary solvent system and the ternary solvent system

| PAHs Rings | Binary Solvent System (mg/kg) | Ternary Solvent System (mg/kg) |
|--------------|-------------------------------|--------------------------------|
| 2 | 0.01 | 0.03 |
| 3 | 0.01 | 0.01 |
| 4 | 0.07 | 0.11 |
| 5 | 0.05 | 0.05 |
| Total | 0.14 | 0.19 |

4. Discussion

On QC/QA, the calibration analysis gave results which were in approximation with the concentrations of the standard samples. No PAH compound was detected in the blank samples.

Figure 1 is the result of PAH concentrations extracted from Okobo-Enjema coal by soxhlet extraction and sonication extraction methods. With sonication method, 8 out of the 16 target PAH compounds were extracted as against 7 by the soxhlet method. Sonication extraction method extracted higher number of PAHs, required fewer amount of solvents (60 mL), shorter time of extraction (25 min) and less energy consumption compared to soxhlet extraction. Soxhlet extraction extracted higher amount of the target PAHs when the total amount of PAH compounds extracted with both methods is compared.

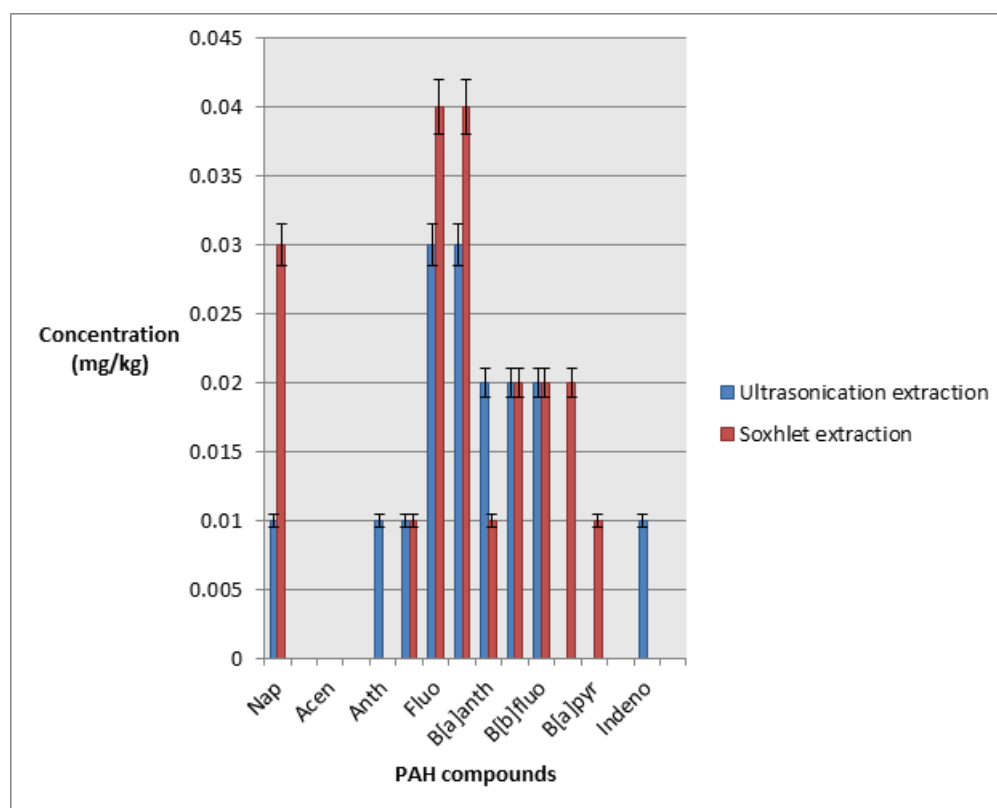


Figure 1. Comparison of mean PAHs extracted using soxhlet and sonication extraction methods (PAHs with no bars were not detected) (5 % error bars).

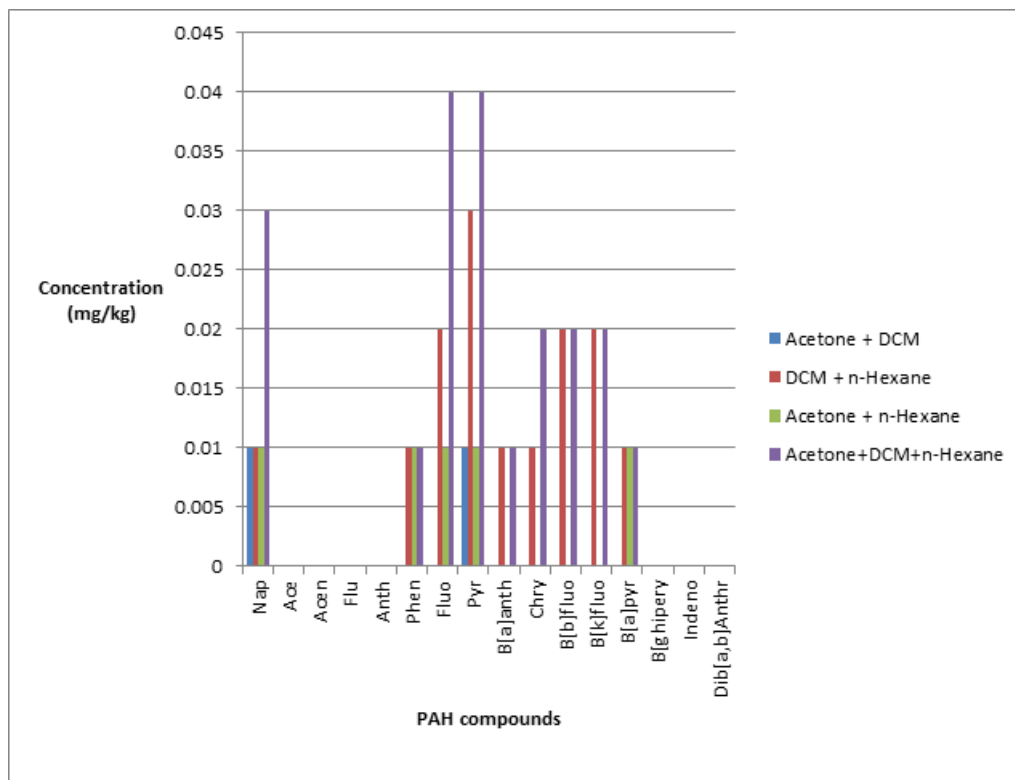


Figure 2. Graphic presentation of mean PAH concentrations in using the different solvent systems (PAHs with no bars were not detected).

Soxhlet extraction method required longer time (10 h) and larger amount of organic solvents (150 mL), involving higher cost and more environmental problems in disposal.

Figure 2 shows the mean PAH concentrations (mg/kg) in Okobo-Enjema coal after GCMS analysis of extracts with different solvent systems by soxhlet extraction method. None of the solvent mixtures extracted ace, acen, flu, anth, b[ghi]pery, indeno and dib[a,h]anthr. The total amount of target PAHs extracted by A was 0.02 mg/kg; 0.14 mg/kg was extracted by B; C extracted 0.05 mg/kg; while 0.20 mg/kg was extracted by D. It was deduced that the ternary solvent system extracted higher amount and higher number of target PAH compounds than the binary solvent mixtures. The ternary system extracted 9 out of the 16 target PAHs while solvents A, B and C extracted 2, 9 and 5 target PAHs respectively. In decreasing order, the total amount of PAHs extracted by the solvent mixtures was D>B>C>A, meaning that the total concentrations of the PAHs in the ternary solvent system was higher than in the binary solvent systems, in the order, acetone:dichloromethane<acetone

and n-hexane < dichloromethane:n-hexane < acetone:dichloromethane:n-hexane. Acetone is a polar solvent which may have better penetration power into the matrix, thereby making way for the less polar DCM and non-polar n-hexane to make contact with the PAH compounds in the samples and dissolving some of them. Acetone and DCM mixture, extracted just nap and pyr among the target PAHs while DCM and n-hexane which were of mixed polarity extracted more target PAHs. Lower polarity solvent (DCM) seemed to extract better than higher polarity solvent (acetone). This investigation revealed that using ternary solvent systems of mixed polarity is more effective than binary solvents (mixed or same polarity) in the extraction of some PAHs in the coal. However, other factors such as the extraction conditions, the type of coal²⁴ and the nature of the PAH compounds may have affected the efficiency of the various extraction procedures to extract the target PAH compounds¹⁹⁻²⁰.

In Table 1, the binary solvent mixture, DCM and n-Hexane, being the most efficient binary solvent system in this study, was compared with the ternary solvent system. The ternary system extracted more 2 and 4-ring

PAHs than the binary solvent system. The two systems extracted the same amount of 3 and 5-ring PAHs.

These extractable PAHs in coal are more likely to be released from coals into the environment. The determination of the PAHs in occurring in raw coals therefore, has implications for environmental studies of air, soils, sediments and water potentially contaminated by coal and the solvent system for the PAH extraction will influence the outcome of the investigation.

5. Conclusion

Sonication extraction method had advantages over soxhlet extraction method when the number of PAHs, amount of solvents required, length of extraction and amount of energy consumed are compared. But soxhlet extraction extracted higher amount of the target PAHs. This report also showed that a ternary solvent system was more efficient compared to binary solvent systems in the extraction of the PAHs in the studied coal. The mixture of two polar solvents had weaker extraction ability than a mixture with mixed polarity. The nature of PAHs extracted however differed. The three-solvent mixture extracted more of 4-ring PAHs than 2, 3 and 5-ring PAHs.

6. References

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