Microwave-assisted extraction of polycyclic aromatic compounds from coal

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Abstract Microwave-assisted extraction (MAE) of polycyclic aromatic compounds (PACs) from coal is shown to give the same pattern of compounds as Soxhlet extraction. MAE requires only 10 mL solvent and 10 min extraction time whereas Soxhlet uses 200 mL and takes 24 h. Although the yields were lower, dichloromethane (DCM) was preferred to pyridine, N-methyl-2-pyrrolidone (NMP), and NMP with CS₂ because the pattern of the PACs is shown to be independent of solvent and DCM is a much more convenient solvent to work with.

Introduction

Toxic polycyclic aromatic compounds (PACs) are found in emissions from coal combustion. A study of the possibility of reducing such emissions from domestic ovens included the question of the extent to which PACs are produced in the combustion step (pyrolytic source) or are present in the coal (petrogenic source) and are volatilized by the heat of combustion. The pattern of PACs from the two sources is known to be different [1]. In coal PACs can be present both in the chemically free form and covalently bonded to other organic moieties to form macromolecules. Extraction of the coal should be capable of yielding information on the pattern of the free PACs. Although Soxhlet extractions are traditionally used, several alternative techniques have emerged in recent years; these combine the advantages of using smaller amounts of organic solvent, are faster, and often result in more reproducible yields [2]. This paper presents results obtained from microwave-assisted extraction (MAE) of PACs from coal with several solvents that are routinely used for the extraction of PACs from solid matrices, especially coal.

Experimental

Sample treatment. The coal was from Recklinghausen (northern Ruhr area, Germany) and was ground to a particle size of ca 10 μm in a planetary micro mill. Fluorinated PACs were used as internal standards [3]. MAE at 500 W power was performed in a closed Teflon vessel in a household microwave oven (Samsung Compact RE 2000). Ground coal (1 g) was weighed into the vessel. Solvent (dichloromethane (DCM), toluene (TOL), pyridine (PY), N-methyl-2-pyrrolidone (NMP), or 1:1 NMP–CS₂; 10 mL), with or without 10% water, was added. After extraction for 10 min the samples were filtered through filter paper. Extracts obtained with water present were filtered through sodium sulfate (2 g).

Soxhlet extractions of ground coal (2 g) were performed for 24 h with 200 mL solvent (DCM or toluene-ethanol (1:1) (TOL-EtOH)). The filtered extracts in pyridine (PY), N-methyl-2-pyrrolidone (NMP) and 1:1 NMP–CS₂ were mixed with toluene (10 mL) and shaken twice with hydrochloric acid (12 mol L⁻¹, 10 mL), to remove the polar organic solvent, and the aqueous phase was extracted with toluene (2×10 mL). The combined toluene extracts were then treated in the same way as the normal extracts.

Exhaustive extraction was performed by extracting coal (1.05 g), 6-fluoro-2-methylnaphthalene (13.44 μg), 3-fluorobenzenanthrene (8.75 μg), and 1,4-difluorochrysene (8.41 μg) with DCM (10 mL) for 10 min. After filtration the coal was extracted again for 10 min with fresh DCM (10 mL).

Repeatability was assessed by extraction of the coal in triplicate with the same internal standards as above.

Clean-up procedure for all extracts. The volume was reduced to 5 mL by rotary evaporation and then to 1 mL by evaporation with a jet of nitrogen at 40 °C. The extract (50 μL) was mixed with alumina (250 mg), evaporated to dryness with a jet of nitrogen at 40 °C, and added to an open column filled with 5 g alumina (dried at 155 °C, column bed 8 mm×90 mm alumina) in cyclohexane. The column was eluted with cyclohexane (20 mL) then toluene (30 mL). The volume of the toluene fraction was reduced to 1 mL and 3-fluorobenzenanthrene (8.75 μg) was added. For quantification of the PACs extracted with NMP and NMP–CS₂ (1:1), 2-fluoronaphthalene (5.94 μg), 1-fluorobenzo[g]chrysene (7.94 μg) were added before extraction.

Chromatography. PACs were quantified by GC–FID; peak purity was verified by GC–MS. GC–FID was performed with a HP 5890 II chromatograph with splitless/split injector (260 °C). Compounds were separated on a 26 m×0.25 mm i.d.×0.25 μm film DB 17 ms column with hydrogen as carrier gas at 55 cm s⁻¹. The oven temperature was maintained at 80 °C for 2 min after injection then programmed at 10 °C min⁻¹ to 300 °C, which was maintained for 5 min. GC–MS was performed with a Finnigan MAT/GCQ system, with splitless/split injector (275 °C), operated in total-ion mode. Compounds were separated on a 28 m×0.25 mm i.d.×0.25 μm film DB 5 ms column with helium as carrier gas at 40 cm s⁻¹. The oven temperature was maintained at 80 °C for 2 min after injection then programmed at 10 °C min⁻¹ to 300 °C, which was maintained for 15 min.

Results and discussion

Figure 1a illustrates the extraction pattern of PACs obtained using different extraction methods and solvents. All the solvents investigated led to very similar extraction patterns. The extraction yields, based on Soxhlet extraction with DCM, were scattered around a mean value with a standard deviation of 20% when all different extraction methods and solvents are taken into account. This is a low value considering how different the conditions are. The yields are clearly different, but the intention
here is to compare patterns of PACs; then it is important to achieve a representative extraction pattern, not a quantitative extraction yield.

MAE has clear advantages over Soxhlet extraction. It is less time-consuming – 10 min extraction compared with 24 h for Soxhlet extraction – and requires only 10 mL organic solvent for 1 g of extracted material, compared with 200 mL for Soxhlet extraction.

Extraction of coal with pyridine has traditionally been performed using Soxhlet or ultrasonic methods. It is known to lead to high yields but, as Fig. 1a shows, under microwave conditions toluene and DCM give the same extraction pattern and yield for PACs. Extraction with pyridine is, furthermore, more time-consuming than with toluene or DCM; it is an irritant, harmful, and requires an additional clean-up step. The subsequent optimizations were conducted with toluene and DCM.

DCM is generally more efficient than toluene. The average yield from toluene extraction of the ten PACs was 67% of the yield for DCM extraction. Addition of 5–10% water to the matrix often increases the extraction yield in MAE [4], but 10% water added to the coal before the extraction with either toluene or DCM (Fig. 1b) did not produce a clear-cut result. For the more volatile two-ring PACs 25% higher yields were obtained but for the larger ring systems it was lower by approximately 24%. Addition of water was not, therefore, considered necessary for the matrix coal. This also facilitates work-up, because additional drying of the extract was not needed.

N-methyl-2-pyrrolidone (NMP) and the recently investigated mixture of NMP with CS₂ are known to give high extraction yields during ultrasonic extractions of coal [5]. Figure 2 shows the results obtained with these solvents in MAE; it is apparent that both solvents result in improved extraction yields. On average NMP leads to 76% improvement compared with DCM; for NMP–CS₂ it is 16%. Obviously NMP is a very efficient solvent for extraction of PAC from coal under MAE conditions. DCM was, nevertheless, selected as solvent for further investigations because of its experimental simplicity and the nature of the PAC pattern. Figure 3 shows the complexity of the gas chromatogram of the aromatic fraction, including the fluorinated PACs used as internal standards (IS) [3].

Repeatability

The repeatability of the MAE results was investigated by replicate extraction of the coal (n=3) with DCM (Table 1). Results