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POLYCYCLIC AROMATIC HYDROCARBON IDENTIFICATION IN COALS by GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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ABSTRACT

The coal mining process will increase the distribution of teratogenic, carcinogenic, and mutagenic polycyclic aromatic hydrocarbons (PAHs). Due to the reported potential environmental and health hazards of PAHs, the content of PAHs in Sajau lignite has been investigated. The extraction method and GC-MS were applied to identify the polycyclic aromatic hydrocarbons. The GC-MS results showed that 16 PAHs were detected, and as much as 10,854 ± 1,354 µg/g is the total concentration of PAHs, with a predominance of medium molecular weight. The dominant fraction is the tetracyclic aromatic fraction (71.3% by weight). In contrast, bicyclic aromatics, tricyclic aromatics, pentacyclic aromatics, and hexacyclic are close to each other with the composition of 0.8 wt.%, 26.4 wt.%, and 0.9 wt.%, 0.6% respectively, as PAH and PAH derivatives. Knowledge of identified PAH concentrations to monitor and prevent pollution in this area after the mining closure.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), Coals, Lignite, GC-MS, Berau Basin.

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INTRODUCTION

In the 21st century, coal is an essential energy source; although it has various benefits for human life, it can also cause environmental and health problems. During coal mining operations, or when using coal for various purposes, Polycyclic aromatic hydrocarbons (PAHs) in the air, water, and soil.[1] . The coal mining activities using the open pit mining method often generate air and water pollution, which will cause health hazards to the community around the mine site.[2,3] The most important anthropogenic sources of PAHs in coal mining activities have already been determined, such as steel processing plants and smelters[4-6], steam power installation, and residences.[7,8] In the natural environment, PAHs might present as emerging contaminants in water bodies.[9-12] Materials such as garbage, coals, and fossil fuels that do not burn ideally produce polycyclic aromatic hydrocarbons (PAHs).[13] PAHs are nonpolar compounds, relatively insoluble, and tend to bioaccumulate in organisms.[14,15] Several international protection agencies such as USEPA and EU have identified some PAHs as carcinogenic, mutagenic, and teratogenic; hence, they are priority pollutants. In the international academic community, PAHs have become an essential topic of study as substances that harm human health, especially the priority 16 PAHs. The 16 PAHs have been prioritized as hazardous substances by the EPA.[16,17] This study aims to investigate (a) the composition, distribution, and percentage of the amount of each PAH element and (b) evaluate the potential impact of the dominant PAH elements as a pollutant to the environment.

EXPERIMENTAL

Samples, Materials, and Reagents

We were extracting coal from the location of the coal field in the Kasai area, Berau Regency, Indonesia, and purchased chemical materials from Fisher Scientific and Merck. It consists of solvents for extraction, such as hexane, dichloromethane, acetone, acetonitrile, and sodium sulfate. We experimented in this study at the National Research and Innovation Agency (BRIN) Laboratory, Bandung, Indonesia.

Preparation of Samples and Extraction

The EPA 3540C protocol used Soxhlet Extraction Method[18-21] to extract coal samples. In the coal sample extraction process, 1.0 g of coal powder and dichloromethane (20 ml) put into a flask 50 cm3 in volume. Ultrasonic frequency and power used for extraction are 35 kHZ power and 20 W, respectively. An ultrasonic experiment used a temperature of 25–30 °C for 20 min. Dichloromethane (DCM) for PAH extraction due to DCM is the most widely used and provides the best efficiency.[22-24] The extraction filtering process used a white ribbon filter with a 2.0–2.5 cm thickness and a sodium sulfate drying agent (Na_2SO_4). Purification of the extraction results used a chromatographic column containing aluminum oxide (Al_2O_3); the extraction was washed and cleaned using DCM. For HPLC investigations, the sample evaporated, and the solvent was replaced with acetonitrile, while for GC-MS measurement, hexane solvent until it reaches a final volume of 1 cm^3. Three replicate extraction experiments are required to obtain consistent, accurate, and reliable data during PA measurements to ensure the reproducibility of results.

GC-MS Analysis

Table-1 shows the standard operating conditions for measuring PAHs with GC-MS with a Shimadzu GCMS-QP2010 with Shimadzu GC-2010 instrument. The presence of PAHs in the sample was determined based on RT and quantification/confirmation ion abundance in the PAHs standard.

RESULTS AND DISCUSSION

Method Validation

Linearity, LOD, and LOQ validations are required to obtain consistent, accurate, and reliable data during PA measurements.[25,26] The measurement results of all validation parameters in the studies are shown in Table-1.

Table-1: Concentration and Weight % of PAH in Lignite Coal

PAHs Compound	Abbreviation	Linear Equation	Linearity (R^2)	LOD (ng/g)	LOQ (ng/g)
Naphthhalene	Nap	y=26.12x + 54.21	0.995	0.11	0.42
Acenaphthylene	Acy	y=32.58x + 87.23	0.993	0.53	1.79
Acenaphthene	Ace	y=10.65x + 32.15	0.992	0.30	1.02
Fluorene	Fle	y=25.21x + 57.15	0.994	0.12	0.41
Phenanthrene	Phe	y=32.15x + 66.12	0.993	0.04	0.14
Anthracene	Anth	y=61.12x + 71.21	0.990	0.02	0.12
Fluoranthene	Fla	y=14.12x + 28.65	0.995	0.01	0.04
Pyrene	Pyr	y=6.27x + 13.92	0.996	0.05	0.12
Benzo[a]anthracene	BaA	y=15.46x + 27.86	0.996	0.03	0.11
Chrysene	Chr	y=22.67x + 54.21	0.995	0.02	0.08
Benzo[b]fluoranthene	BbF	y=35.10x + 54.21	0.996	0.03	0.06
Benzo[k]fluoranthene	BkF	y=10.62x + 21.61	0.996	0.04	0.15
Benzo[a]pyrene	BaP	y=11.82x + 22.80	0.994	0.02	0.06
Indeno[1,2,3-cd]pyrene	Ind	y=14.61x+ 28.50	0.996	0.04	0.14
Dibenzo[a,h]anthracene	DaA	y=12.21x + 14.51	0.996	0.07	0.17
Benzo[g,h]perylene	BgP	y= 6.12x + 14.21	0.995	0.03	0.08

The linearity coefficient (R2) of the 16 PAHs ranged from 0.990-0.996, where the range of values is within the permissible limits.[27] The LOD values were in the 0.01-0.05 ng/g range, and LOQ values ranged between 0.06-1.79 ng/g. These values were less than the acceptable limit of requirement value.[28]

Determination of PAHs by GC-MS Analysis

Using GC-MS, the 16 PAH content in lignite coal identified and corresponding GC/MS chromatograms are given in Fig.-1.

Table-2 presents the GC-MS analysis's concentration values and weight percentages (wt.%) of the PAH compounds in lignite coals. Xue *et al.*[23] have divided the 16-PAHs in Sajau coal into three homologous groups based on their molecular weight:(1) LMW-PAHs: *Nap, Acy, Ace, Fle, Phe,* and *Anth*); (2) MMW-PAHs: *Fla, Pyr, BaA, and Chr*), and (3) HMW-PAHs: *BbF, BkF, BaP, Ind, DaA*, and *BgP*). The chromatograms show that Sajau coal contains all 16 PAH compounds, which are dominated remarkably by HMW-PAH distributions.

The results of PAH measurements in the coal of the Sajau Formation indicate a high pyrene concentration. Such conditions will lead to potential health problems for humans or the environment. For humans, high pyrene can damage cell DNA and affect endocrine activity.[29] Additionally, one of the more significant concerns is the accumulation of pyrene in lake and river sediments, disrupting the ecosystem of organisms that live in the aquatic area. Therefore, in the Sajau Formation coal mining, it is necessary to consider good mining practices to minimize potential hazards to human health or environmental damage. The discovery of several PAHs that are harmful to human health; shows that PAH identification research with GC-MS makes a vital contribution to mitigation and environmental monitoring around coal mining areas after mining closure.

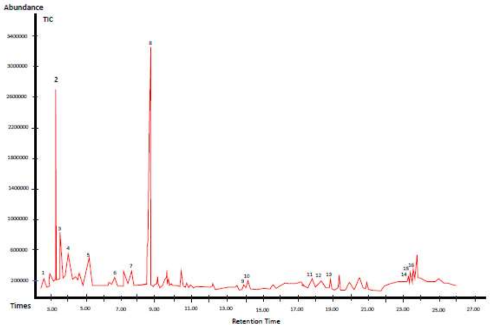

Fig.-1: Total Ion Chromatogram (TIC) of GC-MS from Lignite Coal

Table-2: Concentration and Weight % of PAH in Lignite Coal

Peak No.	PAHs Compound	Retention Time	No. of Rings	Relative amount (wt. %)	Molecular Weight
1	Naphthalene	2.44	2	0.8	LMW
2	Acenaphthylene	3.11	3	21.1	
3	Acenaphthene	3.81	3	2.1	
4	Fluorene	4.01	3	1.2	
5	Phenanthrene	5.16	3	1.1	
6	Anthracene	6.72	3	0.9	
7	Fluoranthene	7.48	4	0.7	MMW
8	Pyrene	8.76	4	69.9	
9	Benzo[a]anthracene	13.52	4	0.3	
10	Chrysene	14.06	4	0.4	
11	Benzo[b]fluoranthene	17.93	5	0.3	MMW
12	Benzo[k]fluoranthene	18.26	5	0.4	
13	Benzo[a]pyrene	19.14	5	0.2	
14	Indeno[1,2,3-cd] pyrene	23.08	6	0.1	
15	Dibenzo [a, h] anthracene	23.14	6	0.2	
16	Benzo [g, h] perylene	23.86	6	0.3	
	Total PAHs			100	

Note: LMW: Low molecular weight; MMW: Medium molecular weight; HMW: High molecular weight

CONCLUSION

The analysis showed that the detection limit criteria (LOD) were still within limits specified by European Commission Regulation 836/2011, which stated that the LOD value must be below 0.30. Each concentration of 16 PAHs varied from 0.018 to 4.237 μg/g, with a total concentration of 10.854 μg/g. Pyrene is one of the highest PAHs (69.9%) identified in the Sajau Formation, followed by acenaphthylene, with a concentration of 21.1%.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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