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## Study On Techniques For Estimation Of Benzo(a)pyrene In Coal Tar Pitch

### Corresponding Author

Rakesh K.Khandal  
Shriram Institute for Industrial Research,  
19 University Road, P.B.No.2122,  
Delhi 110007 (INDIA)  
Tel.:+91-11-27667267; Fax:+91-11-27667676  
E-mail: rkhandal@shriraminstitute.org

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### Co-Authors

Sapana Kaushik<sup>1</sup>, Rajesh K.Raina<sup>1</sup>, Manjeet Aggarwal<sup>1</sup>,  
Gurucharan L.Verma<sup>2</sup>, Gopal Bhatia<sup>3</sup>  
<sup>1</sup>Shriram Institute for Industrial Research, 19 University Road,  
P.B.No.2122, Delhi-110007 (INDIA)  
<sup>2</sup>Delhi college of Engineering, Delhi (INDIA)  
<sup>3</sup>National Physical laboratory, Delhi (INDIA)

### ABSTRACT

Coal tar pitch is mainly a mixture of high molecular weight polycyclic aromatic hydrocarbons (PAHs), their alkyl derivatives and their heterocyclic analogs. Out of the numerous PAHs found in coal tar pitch, benzo[a]pyrene (B(a)P) is one of the most prominently reported carcinogens for humans. B(a)P is released into the atmosphere during processing of coal tar pitch for manufacturing various carbon products. In order to ensure their safe levels in the environment, maximum residual limits (MRLs) for various PAHs including B(a)P have been specified by regulatory authorities. To meet the prescribed requirements, it becomes necessary to characterize the coal tar pitch, especially with reference to B(a)P to ensure its application in an environmentally safe manner. In the present paper, the coal tar pitch from two different sources has been evaluated for B(a)P content using a sensitive, accurate, well developed and a validated method. Since coal tar pitch involves a complex matrix, certain components in the matrix are expected to cause interference during the analysis of B(a)P. To avoid interferences from the matrix it is necessary to selectively extract and isolate B(a)P using a suitable extraction technique before quantification. For this purpose, different extraction techniques were tried and the results were compared for the maximum recoveries of B(a)P from the coal tar pitch. The estimation of the extracted B(a)P was done using high performance liquid chromatography (HPLC). It was found that extraction in toluene using controlled soxhlet technique gave the best recoveries ranging between 87% and 95% with percent relative standard deviation(RSD) of 2.77%. Based on these studies, it is observed that the method developed can be used as a standard method for estimating B(a)P in coal tar pitch before approving the latter for application for various purposes.

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### KEYWORDS

Coal tar pitch;  
Benzo(a)pyrene;  
Soxhlet extraction;  
HPLC;  
Method validation

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## INTRODUCTION

Coal tar pitch is defined as the residue of coal tar distillation. It is generally dark or black thermoplastic material with broad spectrum of molecular mass<sup>[1]</sup>. Coal tar pitch obtained from coke ovens is a mixture of condensed aromatic hydrocarbons and heterocyclic compounds<sup>[2]</sup>. Its major constituents are polycyclic aromatic hydrocarbons (PAHs). It is known to have complicated chemical composition with different physico-chemical characteristics based on which the quality and grade are generally checked by the user industries. Of all, certain PAHs are known to be carcinogenic e.g. B(a)P. Nevertheless, the specified requirement for B(a)P content in the coal tar pitch for quality control purposes is rarely included in the specifications for the coal tar pitch. PAHs comprise the dominant class of compounds in coal tar pitch<sup>[3]</sup>. Alkylated PAHs may be present as minor fractions. Coal tar pitch is mainly used as a binder for aluminium smelting electrodes, as roofing materials, in surface coatings, black varnishes, pipe coating enamels etc<sup>[4]</sup>. The Environmental Protection Agency (EPA) of USA has identified sixteen PAHs present in the coal tar pitch to be highly toxic<sup>[5]</sup>.

While the inhalation of or exposure to, coal tar pitch vapours, volatiles or dust are known to be harmful to human beings and other living organisms, some of the PAHs present in the coal tar pitch have been found to be carcinogenic or mutagenic<sup>[6-15]</sup>. These carcinogenic or mutagenic PAHs are typically those consisting of 4-6 condensed rings.

Out of these sixteen PAHs, B(a)P has been proved to be one of strongest carcinogens<sup>[16-17]</sup>. OSHA regulates exposure limits to B(a)P indirectly as 'Coal tar pitch volatiles'<sup>[18]</sup>. The removal of B(a)P from crude as well as processed coal tar pitch has been reported to be difficult as the physical properties of this particular compound does not differ significantly from other PAHs contained in the pitch. Thus, because of the complexities of the matrix as also due to the fact that the physical properties of B(a)P are similar with other PAHs, estimation of B(a)P in coal tar pitch has always been a challenge.

## EXPERIMENTAL

### Materials and reagents

Binder grade coal tar pitch procured from the local sources have been used in the study. Redistilled laboratory grade solvents were used for extraction. Water and acetonitrile were of HPLC grade from Ranbaxy Fine Chemicals, India. Reference standard of B(a)P (97% purity) was purchased from Supelco, U.S.A. Silica gel 60 (particle size 0.063-0.200 mm) and sodium sulfate (AR grade) were purchased from Merck.

### Procedure

The experimentation involved the following steps: a) Sample preparation b) Extraction c) Cleanup and d) Quantification of analyte using the validated method, as detailed below:

**a) Sample preparation:** Two different samples of binder grade coal tar pitch named as BG1 and BG2 were procured from two different local sources and their physical properties were determined (TABLE 1).

From the results of the physical-chemical characteristics, both samples meet the minimum requirements for binder grade as specified<sup>[19]</sup>. The material in the form of lumps was thoroughly crushed and sieved so as to get a uniform particle size of 300 $\mu$ m. This powder was immediately used for extraction and

**TABLE 1: Characteristics of coal tar pitch**

Characteristics	BG1	BG2	Specified
			limits for binder Grade pitch
Softening point ( $^{\circ}$ C)	112.7	108.5	>90
Quinoline insolubles (%)	13.6	6.0	>3.0
Toluene insolubles (%)	43.2	26.5	>24
Coking values (%)	54.3	53.4	>50
Specific gravity (%)	1.28	1.32	>1.28

quantification of B(a)P.

### b) Extraction

The extraction procedure was carried out in dark room to avoid any photodecomposition of PAHs<sup>[20]</sup>. Several solvents were studied, not only for maximiz-

ing the extraction but also for minimizing the interferences. The extraction of B(a)P from coal tar pitch therefore, was carried out by using toluene, acetonitrile, chloroform, cyclohexane, hexane and acetone. The other most important factor for maximizing extraction is the method of extraction and hence, four different methods as detailed below were tried<sup>[21]</sup>.

### Ultrasonic extraction

3 g portions of dried, finely ground and sieved sample of coal tar pitch were taken in 5 different conical flasks and 50 mL of solvent was poured into each one of them. The samples were then ultrasonicated at ambient temperature for 1, 2, 3, 4 and 5 h, respectively to optimize the time required for maximum extraction. The extracts were then filtered through Whatmann filter paper no. 42. The same procedure was repeated with all the solvents. The filtered extracts were kept for further clean up and determination of the B(a)P content.

### Refluxing

3 g portions of dried, finely crushed and sieved sample were refluxed with 200 mL of all the six solvents in round bottom flasks containing anti bumping granules for different time periods i.e. 4, 5, 6, 7, 8 and 10 h, respectively, so as to optimize the time period to extract the maximum B(a)P content. The extracts were filtered through Whatmann filter paper no. 42 and used for further processing.

### Soxhlet extraction

3 g portions of dried, finely crushed and sieved sample was loaded into a porous cellulose sample thimble and placed into the thimble holder. 250 mL of solvent along with few anti bumping granules was added to the flask attached to thimble holder. The flask was then gently heated on a heating mantle giving several cycles of extraction<sup>[22]</sup>. In order to maximize the extraction of B(a)P the extraction process was repeated with different sample portions for varying periods of time, ranging from 5h to 24h and with different solvents. The obtained extracts were filtered and used for further cleanup.

### Automated soxhlet extraction

3 g portions of dried, finely crushed and sieved sample was taken in the sample thimble and immersed in the boiling solvent. The sample thimble was then lifted above the boiling solvent and the sample in the thimble was extracted giving several cycles of extraction. The process was carried out for 1, 2, 3, 4 and 5h, respectively with different portions of the sample. The same was repeated with different solvents.

### c) Column cleanup

The respective extracts so obtained were rotary evaporated to dryness. The dried residues were dissolved in 2mL of hexane. This solution was then used for further column cleanup.

A glass column (20 x 300 mm) with a fritted glass disc was filled with 30 g of activated silica gel and covered with 0.25 cm layer of anhydrous sodium.

The prepared column was conditioned with three portions of 30 ml of iso-octane. The hexane extract was poured on to the column and eluted with 75 mL of hexane four times.

### d) Concentration of B(a)P

The combined eluate obtained from the column cleanup was then concentrated by evaporating using vacuum rotary evaporator. During the procedure few millilitres of iso-octane were added and the solution again evaporated to eliminate any traces of hexane. The residue containing B(a)P was dissolved in acetonitrile and made to volume for further estimation using HPLC.

### e) Quantification

The quantitative estimation of B(a)P in the two samples i.e. BG1 and BG2 was carried out using a modular HPLC system from Waters, U.S.A.

Chromatographic conditions:

Column	: Phenomenex C18 (250x4.60 mm; 10 $\mu$ s.s)
Mobile Phase	: Acetonitrile:Water(80:20)
Flow rate	: 0.5 mL/min
Detector	: Fluorescence(excitation 254nm; emission 400nm)
Temperature	: 30°C,
Injection Volume	: 10 ml

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The percent of B(a)P in the samples was calculated with reference to the peak response of reference standard of B(a)P.

### RESULTS AND DISCUSSIONS

The chromatograms for reference standard of B(a)P and one of the samples of the coal tar pitch are shown in figure 1 and 2, respectively. The chro-

matogram of the sample indicates a well resolved peak of B(a)P from the other components in the matrix. The results for the B(a)P content in the coal tar pitch extracted by different methods using different solvents for both the samples using optimized time duration were calculated (TABLE 2).

The results indicate that soxhlet extraction gave better results than both ultrasonic extraction and refluxing. Automated soxhlet extraction proved to be

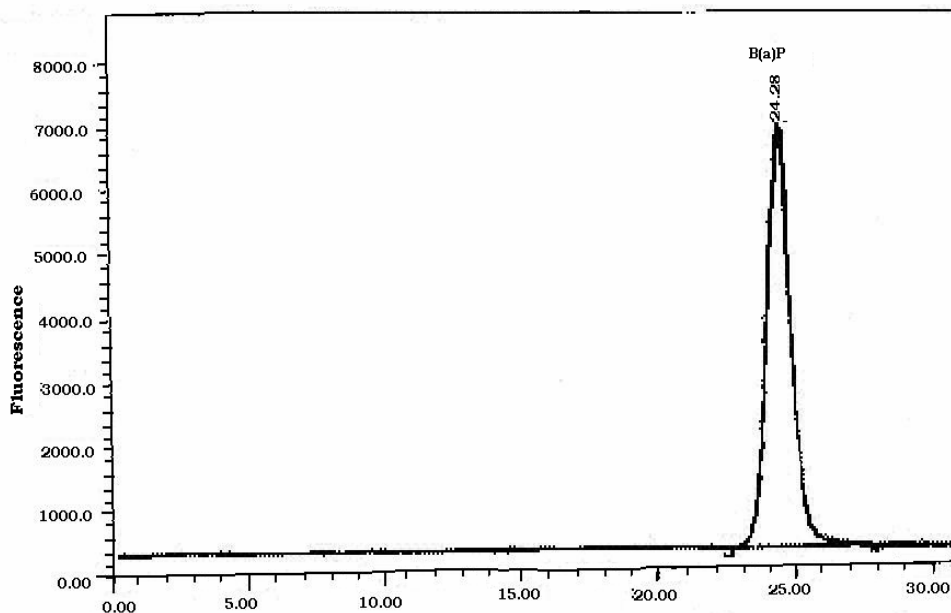


Figure 1: Chromatogram showing peak of B(a)P standard

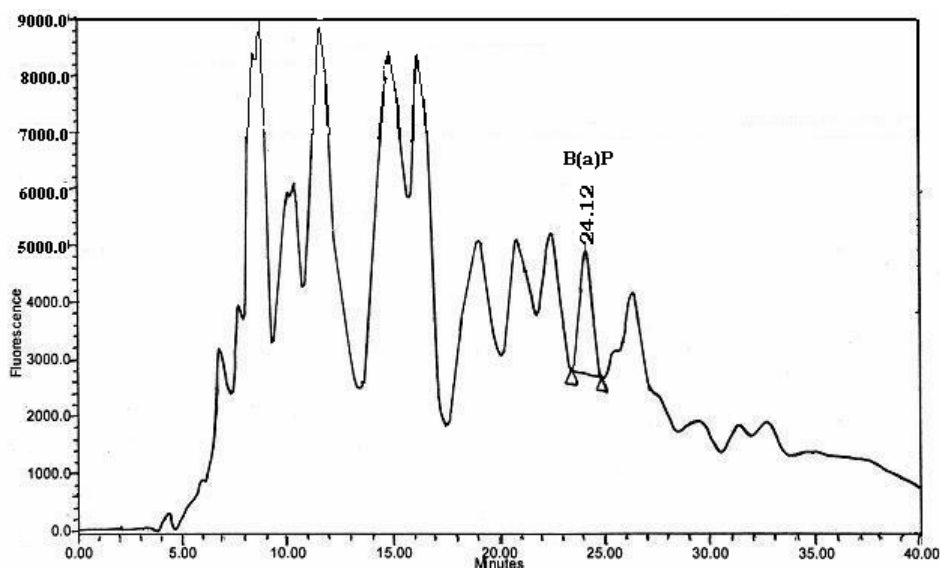


Figure 2: Chromatogram showing separation of PAHs in coal tar pitch

**TABLE 2: B(a)P content in BG1 and BG2 coal tar pitch (%/mass B(a)P content  $\pm$  %RSD)<sup>a</sup> using different extraction techniques and with various solvents**

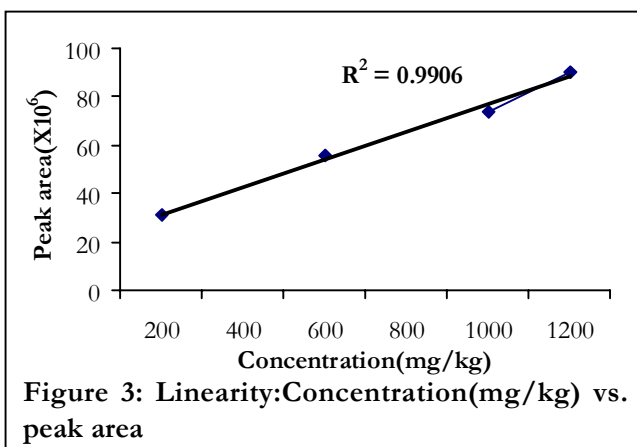
Extraction techniques solvents	Ultrasonic	Refluxing	Soxhlet	Automated soxhlet
Toluene	BG1 0.60 $\pm$ 1.36	0.72 $\pm$ 2.00	1.20 $\pm$ 2.79	1.22 $\pm$ 2.08
	BG2 0.57 $\pm$ 2.86	0.63 $\pm$ 1.29	1.10 $\pm$ 2.26	1.13 $\pm$ 2.16
Acetonitrile	BG1 0.59 $\pm$ 1.38	0.68 $\pm$ 1.20	1.19 $\pm$ 1.43	1.20 $\pm$ 2.45
	BG2 0.49 $\pm$ 2.33	0.58 $\pm$ 1.40	1.07 $\pm$ 2.41	1.10 $\pm$ 2.70
Acetone	BG1 0.43 $\pm$ 2.05	0.60 $\pm$ 1.92	0.99 $\pm$ 1.3	1.01 $\pm$ 2.0
	BG2 0.41 $\pm$ 1.01	0.51 $\pm$ 1.60	0.96 $\pm$ 0.85	0.97 $\pm$ 2.06
Chloroform	BG1 0.40 $\pm$ 2.30	0.57 $\pm$ 2.81	0.91 $\pm$ 1.70	0.95 $\pm$ 2.76
	BG2 0.38 $\pm$ 2.80	0.49 $\pm$ 2.33	0.66 $\pm$ 1.23	0.83 $\pm$ 2.65
Cyclohexane	BG1 0.33 $\pm$ 2.5	0.46 $\pm$ 2.50	0.77 $\pm$ 2.48	0.79 $\pm$ 2.23
	BG2 0.30 $\pm$ 2.72	0.34 $\pm$ 2.30	0.54 $\pm$ 3.30	0.74 $\pm$ 2.72
Hexane	BG1 0.32 $\pm$ 1.03	0.49 $\pm$ 2.35	0.75 $\pm$ 2.21	1) 0.80 $\pm$ 1.90
	BG2 0.29 $\pm$ 2.4	0.32 $\pm$ 2.55	0.55 $\pm$ 2.67	2) 0.73 $\pm$ 1.60

<sup>a</sup> Above results are the mean of 4 replicates**TABLE 3: Results of recovery samples**

B(a)P content (initial)(ngmL <sup>-1</sup> )	B(a)P content (spiked)(ngmL <sup>-1</sup> )	B(a)P content (detected) <sup>a</sup> (ngmL <sup>-1</sup> )	Recovery (n=5)%	Mean Recovery%	RSD%
200	400	533	85.4,86.7,88.1,91.6,92.2	88.8	3.37
200	800	957	93.2,91.6,95.1,94.6,94.0	93.7	1.46
200	1200	1266	87.5,88.1,92.6,90.7,93.1	90.4	2.81
200	1400	1557	89.1,93.2,97.1,96.1,96.0	94.3	3.44

<sup>a</sup>The results are mean of 5 replicates**TABLE 4: Precision of the method**

Sample	B(a)P content (% by Wt.) n=5	Mean B(a)P content(% by Wt.)	Standard deviation	RSD %
BG1	1.25,1.24,1.22,1.19,1.20,1.18,1.20,1.24,1.24,1.24	1.22	0.02538	2.08
BG2	1.15,1.17,1.16,1.10,1.12,1.11,1.10,1.13,1.14,1.12	1.13	0.02449	2.16



the best technique for extraction of B(a)P from the complex coal tar matrix. It was also observed that although the maximum solubility of pitch was observed in chloroform, the maximum extraction of B(a)P was obtained within toluene. Acetonitrile also gave results comparable to those of toluene. Extract-

ing the samples for different periods of time indicated maximum extraction within 2 h using ultrasonication, within 8h using refluxing, within 16 h using soxhlet extraction and 1 h using automated soxhlet extraction. It was observed that by increasing the extraction time, no further increase in the B(a)P content was obtained.

The B(a)P content in BG1 and BG2 was found to be 1.22 and 1.13% by weight respectively using automated soxhlet extraction and toluene as the extraction solvent.

### Recoveries of B(a)P from coal tar pitch

In order to study the efficiency of the extraction technique the samples of coal tar pitch were spiked with varying known concentrations of B(a)P standard and extracted using automated soxhlet extraction with toluene as extraction solvent. Percent re-

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coveries from the different spiked sample were calculated and were between 87 and 95 (n=5) for the different spiked samples (TABLE 3). A graph was plotted between the different concentrations of the spiked sample vs. the detector response (Figure 3). This gave a linear curve with correlation coefficient of 0.9906. The method is capable of detecting B(a)P content as low as 1ng mL<sup>-1</sup> in the samples of coal tar pitch.

### Reproducibility and precision

Repeated analysis of the two samples of B(a)P was performed to check the reproducibility and precision of the analytical technique. The results indicate a good precision with % RSD as 2.08 and 2.16 for the two samples of coal tar pitch (TABLE 4).

### CONCLUSION

A simple, accurate and a reproducible method has been developed for determination of B(a)P content in coal tar pitch. The method involves extraction of the B(a)P using simple automated soxhlet extraction and toluene as solvent. Further clean up of the extract using silica gel selectively isolates B(a)P from the rest of the matrix, thus eliminating any possible interferences during the final estimation using HPLC.

Since B(a)P is one of the most carcinogenic polycyclic aromatic hydrocarbon and may be released into the environment during any of applications of coal tar pitch, its estimation in the pitch can form the basis for deciding the quality parameters for the particular grade of the coal tar pitch.

### REFERENCES

- [1] 'Ullmann's Encyclopaedia of Industrial Chemistry', **A26**, 91 (1995).
- [2] G.P.Blumer, R.Thomas, Zander, M.Erdol, Kohle Erdgas; Petrochem., **31**, 197 (1978).
- [3] M.Zander; Fuel, **66**, 1536 (1987).
- [4] IARC; 'Industrial Exposure in Aluminium Production, Iron & Steel Founding', Lyon, France, IARC, **34**, 219 (1984).
- [5] J.R.Smith, D.V.Nakles, D.F.Sherman, E.F.Neuhauser, R.C.Loehr; Third International Conference on New Frontiers for Hazardous Waste Management, U.S., 397-405 (1989).
- [6] IARC; Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Polynuclear Aromatic Compounds, Part 4, 'Bitumens, Coal Tars and Derived products, Shale Oils and Soots, Lyon', France, IARC, **35**, 271 (1985).
- [7] IARC; Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, 'Overall Evaluations of Carcinogenicity', Lyon, France, IARC, Supplement, **7**, 440 (1987).
- [8] W.Boenigk, J.W.Stadelhofer; Proc. 5<sup>th</sup> Int.Conf. Carbon (Carbon'92), Essen, 30-33 (1992).
- [9] R.Roussel, A.Gaboury, C.Larriviere; Light Metals, 503-507 (1991).
- [10] A.A.Mirtchi, A.L.Proulx, L.Castonguay; Light Metals, 601-607 (1995).
- [11] G.W.Gibbs, I.Horowitz; J.Occup.Med., **21(5)**, 347-353 (1979).
- [12] A.A.Mirtchi, L.Noel; **94**, 749-795 (1994).
- [13] M.Eie, M.Sorlie, A.H.Oye; Light Metals, 469-475 (1996).
- [14] M.Eie, M.Sorlie; Extended Abstracts-Carbon, **94**, 824-825 (1994).
- [15] J.Zelinski, B.Osowiecka, B.Liszynska, W.Giesinska, J.Polaczek, K.Kubika; Fuel, **75**, 1543-1548 (1996).
- [16] IARC Monographs on the Evaluation of Carcinogenic Risk to Human, **32**, 95-452 (1983).
- [17] J.Santodonatro, P.Howard, D.Basu; J. Environ. Pathol. Toxicol., **54** (1981).
- [18] NIOSH pocket guide to chemical hazards, Cincinnati, Ohio, National Institute for Occupational Safety and Health, DHHS(NIOSH), 97-140 (1997).
- [19] 'Ullmann's Encyclopaedia of Industrial Chemistry', **A(5)**, 106.
- [20] M.Kuratsune, T.Hirohata; Nat.Cancer Inst. Monograph, 117-125 (1962).
- [21] S.Mitra Ed.; 'Sample Preparation Techniques in Analytical Chemistry', John Wiley & Sons Inc., 140-147, (2003). (Chemical Analysis: A Series of Monographs on Analytical Chemistry and its application, **162**, Winefordner, JD Series Ed.)
- [22] EPA Method 3540.