# Orthogonal Array Design for Optimization of Microwave-Assisted Extration of Polycyclic Aromatic Hydrocarbon on Fly Ash

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## 1.Introdution

Incinerators are used in large cities of Taiwan , R.O.C. to deal with the problem of solid waste like the rest of world. When the trash is burned , the polycyclic aromatic hydrocarbons (PAHs) and other compound are produced and released into the atmosphere. Thousands of tons of fly ash may be isolated by an electrostatic precipitator and required disposal. This posed a threat to our land and water supply.The extration of PAHs from solid sample sush as fly ash are usually performed with liquid solvents.Most recently, microwave-assisted extration (MAE) has been investigated in several laboratories [1-4] and is gaining an important place among sample preparation techniques for solid matrices because it requires much less volume of organic solvent (~30ml) ,reduces extraction time (typical 10 min) and increases sample throughput by the multivessel systems (up to 12 samples) .

In recent years, orthogonal array design has been widely used as a chemometric method for optimization of analytical procedures [5-7] . The chemometric approach is a sophisticated time and cost-saving testing procedures to extract more precise information for the optimization with fewer experimental trials. In this study , the microwave assisted extraction for PAHs from fly ash was optimized by orthogonal array design which allows the several variables for extraction to be studied simultaneously. The resultant procedure requires for fewer experiments to be carried out which are now capable of giving more imformation than the conventional "alter one factor at a time " evaluation. The optimum extraction method thus demonstrated the application to MAE of PAHs in the fly ash from different sources.

2.Experimental

The apparatus used in this study was an MES-1000 microwave solvent extration system (CEM Corp.Mattews,NC,U.S.A.) which consists of a magnetron tube (950w) , a sample oven where 12 extration vessels with Teflon-lined microwave cavity are set up on turntable. The extraction condition are controlled by temperature and pressure using an in-board fiber optic system which allows extraction temperature to be selected from 20 to 200 ℃ in 1 ℃ increments. Safty of the system are intended to prevent ignition of flammable and explosive extration solvents.

High-performance liquid chromatography (HPLC) has been the selected technique for PAH determination. Ultraviolet (UV) absorption (high concentration ) and fluorescence (FLU) spectroscopy (low concentration) provide sensitive and selective detection for PAHs in HPLC. HPLC analysis were carried out with a ALCOTT 7600 pump, a Rheodyne injection valve and 5μl sample loop,Linear UV-vis 200 detector and Linear Fluorescence LC304 detector, Phenomenex Envirosep-PP column(4±1μm $C_{18}$ , 0.32×12.5cm) for 16 PAHs analysis or homemade column (10μm $C_{18}$ ,0.46×25cm) for pyrene analysis and Chem-Lab data processor.

Spiking of the fly ash sample with pyrene was performed as follows. The sample (1g) was weighed into an alminum cup, and 100μg of 0.1μg/μl pyrene solution was added to the sample with a syringe, ensureing the solution did not contact the cup. The spiked fly ash stands for five minutes and were added the solvent after transfering into the Teflon-lined extraction vessel.After ensuring that a new rupture membran was in place the extration vessel was closed. Extraction were performed at designed condition according to orthognal array design at eighty percent power.

The vessels,after extraction, were allowed to cool to room temperature for ~25min before they were opened.The supernatant was filtered on glass fiber filter (Tape A/E) and then combined with ~5ml acetone rinse of exacted sample.The extraction was concentarted to 1ml using nitrogen blowdown evaporation for HPLC/FLU (low concentration) or HPLC/UV (high concentration) analysis.Three variables that may affect the extraction efficiency were examined by using a three-level orthogonal array design: extraction temperature , volume of extraction solvent , extraction time . The selection of the variables and their levels were based on previous knowledge of MAE [1-4] and some scouting trials. The average recovery of pyrene was used as the response. The assignment of the factors and levels is shown in Table 1.

3.Results and Discussion

The recovery data from nine pre-designed experimental trials together with $r_1$,$r_2$ and $r_3$

(average of the recoveries from experimental trials for variables set at three levels) are given in Table 1. Although the microwave extraction using pure acetone was suggested for PAHs in soil[8].The analysis of variance table was constructed for testing the significance of the effects in Table 2 .The importance of each effect was calculated using the relative contribution (RC) which was calculated by using the equation RC $=SS_i/\sum$ SS (SS:sum of sequare) . The ANOVA results indicated the extraction temperature has significant effect on the average recovery (RC=68.4%) .The results of

Table 1. Three-level orthogonal array design using $L_9(4^3)$ matrix along with the recovery results of respone by microwave-assitanted extraction (n=3)

| *Trial* | *Column* | *No.* | | | *Respone* |
|---|---|---|---|---|---|
| *No.* | A(℃)* | B(min) | C(ml) | D | %Recovery(Av.±S.D.) |
| *1* | I(40) | I(10) | I(30) | I | 59.2±2.6 |
| *2* | I(40) | II(20) | II(40) | II | 63.1±1.5 |
| *3* | I(40) | III(30) | III(50) | III | 59.3±2.1 |
| *4* | II(80) | I(10) | II(40) | III | 67.9±4.1 |
| *5* | II(80) | II(20) | III(50) | I | 76.7±2.9 |
| *6* | II(80) | III(30) | I(30) | II | 64.5±1.5 |
| *7* | III(120) | I(10) | III(50) | II | 60.9±2.4 |
| *8* | III(120) | II(20) | I(30) | III | 57.9±2.6 |
| *9* | III(120) | III(30) | II(40) | I | 57.0±1.1 |
| $r_1$ | 60.5 | 62.6 | 60.5 | 64.3 | |
| $r_2$ | 69.5 | 65.9 | 62.6 | 62.8 | |
| $r_3$ | 58.6 | 60.2 | 68.9 | 61.7 | |

*A : Extraction Temperature,B : Extraction Time,
C : Extraction Solvent (Acetone) Volume
1g fly ash (100-140mesh) : 10μg/g Pyrene spiked

Table2. An ANOVA Table for $L_9(4^3)$ experiments

| Source of variance | Sum of Sequare(RC) | Degrees of freedom | Mean Sequare | F -value | Significance * |
|---|---|---|---|---|---|
| Extraction temperature(A) | 211.0(68.4%) | 2 | 105.5 | 20.6 | p<0.05 |
| Extraction time(B) | 48.0 | 2 | 24.0 | 4.7 | |
| Solvent volume(C) | 39.2 | 2 | 19.6 | 3.8 | |
| Error (D) | 10.2 | 2 | 5.1 | | |
| Total | 308.4 | 8 | | | |

* The critical F valve is 19.0 at 95% confidence and 9.00 at 90%

Table 3 Results of microwave-assitanted extraction using mixed solvent and temperature on fly ash (n=3)

| Trial No. | Temperature ℃ | Acetone/Hexane ( v/v ) | %Recovery (Av.±S.D.) |
|---|---|---|---|
| 1 | 90 | 100/0 | 76.4±3.2 |
| 2 | 90 | 90/10 | 85.4±2.1 |
| 3 | 90 | 80/20 | 64.1±5.0 |
| 4 | 80 | 100/0 | 78.1±1.4 |
| 5 | 80 | 90/10 | 82.9±6.4 |
| 6 | 80 | 80/20 | 71.3±1.6 |
| 7 | 70 | 100/0 | 80.6±2.0 |
| 8 | 70 | 90/10 | 89.6±2.0 |
| 9 | 70 | 80/20 | 76.0±1.6 |

* 1g fly ash spiked 10μg/g pyrene.

Table4.The results of PAHs in fly ash* from three different sources (ng/g)

| PAHs | T-sample** | S-sample | L-sample |
|---|---|---|---|
| Naphthalene | N.D.*** | N.D. | N.D. |
| Acenaphthene | N.D. | N.D. | 9.31 |
| Fluorene | N.D. | N.D. | 1.59 |
| Phenanthrene | N.D. | N.D. | N.D. |
| Anthracene | N.D. | 2.97 | 3.61 |
| Fluoranthene | N.D. | N.D. | N.D. |
| Pyrene | 40.57 | 73.28 | 85.51 |
| Benz (a)anthracene | 2.65 | 2.84 | 8.51 |
| Chrysene | 2.84 | N.D. | 12.08 |
| Benzo(b)fluoranthene | N.D. | 4.67 | 8.84 |
| Benzo(k)fluoranthene | 1.44 | 4.61 | 7.76 |
| Benzo(a)pyrene | 4.31 | 7.67 | 9.23 |
| Dibenzo(a,h)anthracene | 4.75 | 7.78 | 8.88 |
| Benzo(ghi)perylene | 3.73 | 7.12 | 7.78 |

* 40ml of 9:1(v/v)acetone-hexane at 70 ℃ for 20min on15g fly ash

** T-sample from municipal solid incinerator.
S- and L-samples from coal power plant.

*** N.D.=not detected, n=2

second set of experiments which the spiked fly ash samples were extracted using microwave extraction with 40ml mixed solvent (Acetone/Hexane) for 20min in Table 3. The three identical microwave extractions were carried out simultaneously in all trials. It is apparent from the results shown in Table 3. that the optimum MAE condition for PAHs in fly ash were chosen as follows : temperature 70 ℃ , extraction solvents, acetone/hexane (90/10 v/v ) and solvent volume : 40ml. These microwave extraction conditions have employed to extract the PAHs on fly ash from three different sources.In general ,the PAHs content of fly ash from coal power plant are higher than those from municipal solid incinerator.

5.References

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