STUDY TO USE ALKALI-TREATED COAL FLY ASH AS AN ABSORBENT TO CLEAN-UP DIOXIN/FURAN SAMPLE IN FISH, MEAT SAMPLES

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1. Introduction

Dioxin is commonly referred to 75 congeners of polychlorinated dibenzo-p-dioxins (PCDDs) and 135 congeners of polychlorinated dibenzofuzans (PCDFs) [1]. These are compounds of highly toxic, persistence in environment and classified in the list of 22 substances, group of persistent organic pollutants (POP) [2-3]. In order to analyse dioxins/furans, the methods which use gas chromatography/low and high resolution mass spectrometry (GC/MS) have been currently most preferred [4-7]. In addition to the traditional absorbents commonly used in sample clean-up and enrichment to analyse dioxins/furans such as silicagel, florisil, aluminum oxide, actived carbon… the current studies showed that coal fly ash discharged from Pha Lai Thermal Power Plant in Vietnam, after alkali hydrothermal treatment, has produced various zeolite products which are capable of absorbing 17 toxic congeners of dioxins/furans [8-10]. The product which is obtained from alkali hydrothermal treatment of coal fly ash from Pha Lai Thermal Power Plant using NaOH, marked as FAP(M)32-3,5(7-1), composed of zeolite P1, zeolite X and zeolite Upsilon, in substitution for silicagel and actived carbon in sample clean-up procedure to analyse 17 toxic congeners of dioxins/furans in the soil and sediment samples on gas chromatography/low resolution mass spectrometry showed a good result, meeting the criteria of a method to be used for analysing dioxins/furans regulated by US.EPA 8280 [11]. In this article, we present the evaluation of the method using FAP(M)32-3,5(7-1) in substitution for silicagel and active carbon in the procedure of analysing 17 toxic congeners of dioxins/furans in fish and meat samples, using low resolution mass spectrometry.

2. Material and method

2.1. Material

2.1.1. Material as absorbent marked as FAP(M)32-3,5(7-1) prepared from coal fly ash discharged from Pha Lai Thermal Power Plant in Vietnam by alkali hydrothermal treatment [10].

2.1.2. Chemicals: Solvents, chemicals purchased from Merck, Aldrich Sigma, which are at grade for gas chromatography.

2.1.3. Standards: All standards used for dioxins/furans analysis: EDF-2519-B, EDF-2520, ED-2521, ED-2522, EDF-7999-10X, purchased from Cambridge Isotope Laboratories (CIL), USA.

2.2. Method of analysis

2.2.1. Determine the detection limit of the method, accuracy, precision of the analysing results of 17 toxic congeners of dioxins/furans using FAP(M)32-3,5(7-1)

- 7 fish samples did not have PCDD/PCDF, each 95g sample was added with 5g of pork fat, 100 µl of ^{12}C (EDF-7999-10X) containing from 80 pg to 800 pg of 17 toxic congeners of PCDDs/PCDFs and 0,5 mL of internal standards ^{13}C-labeled (EDF-2520) with the concentration of 20-40 ng/mL. Samples are extracted by ultrasonic bath, 3 times and 30 minutes each time using hexane : acetone 1: 1; decanted and filtered the mixture to have the sample.

- Add the cleanup standard ^{37}Cl-2,3,7,8-TCDD; discard acetone from the samples by the rotary evaporator.

+ Determine the accurate quantity of sample obtained; Take 5 % of sample and put into petri dish to determine the percentage of lipid in the sample.

+ Wash the samples with concentrated H_2SO_4, NaCl, KOH until colorless solutions are obtained; Dried the solutions by using Na_2SO_4.

+ Put the samples on the columns containing 200 mg of FAP(M)32-3,5(7-1) and 600 mg of celite which have been mixed well; Clean the column with 10 mL of n-hexane.

+ Elute PCDDs/PCDFs from the column by using 30 mL of toluene.

+ Concentrate the solvent using the rotary evaporator until having the volume of 0,5 mL; add 30 mL of n-hexane.

- Aluminum oxide column: the sample continues to be put on the column containing 4g of neutral aluminum oxide which has been activated for 24 hours at 600^{o}C; Eliminate the unexpected compounds using n-

hexane, mixture of n-hexane:methylene chloride 95:5; Obtain the fraction containing PCDDs/PCDFs by using mixture of n-hexane:methylene chloride 1:1.

- Add 0,5 mL ^{13}C-labeled standards (ED-2521) with concentration of 20-40 ng/mL to the fractions containing PCDDs/PCDFs after the aluminum oxide column, evaporate the samples until having the volume of 20 µL and analyse them on GC/MS.

2.2.2. Analysis for determining concentration of 17 toxic congeners of dioxins/furans

The concentration of 17 toxic congeners of dioxins/furans has been analysed and determined by high gas chromatography/low resolution mass spectrometry GC 7890A/MSD 5975C of Agilent, USA, with the column DB-5MS, 60 m x 0,32 mm x 0,25 µm. Detector MSD is used with the SIM mode for the specified ions of dioxins/furans.

3. Results and discussion

The absorbent marked as FAP(M)32-3,5(7-1) is one of the two products which are the most capable of absorbing 17 toxic congeners of dioxins/furans among 27 products produced by alkali hydrothermal treatment of coal fly ash discharged from Pha Lai Thermal Power Plant, Viet Nam (marked as FAP) at 90 ± 1^{o}C using with NaOH in different conditions [10]. In the composition of FAP(M)32-3,5(7-1), there are zeolite P1, zeolite X and zeolite Upsilon which are the reason of increasing absorption of dioxins/furans [10-11]. The distinction in term of surface properties and state of FAP and FAP(M)32-3,5(7-1) may be seen in Figure 1. Their main composition determined by X-ray is showed in the table 1.

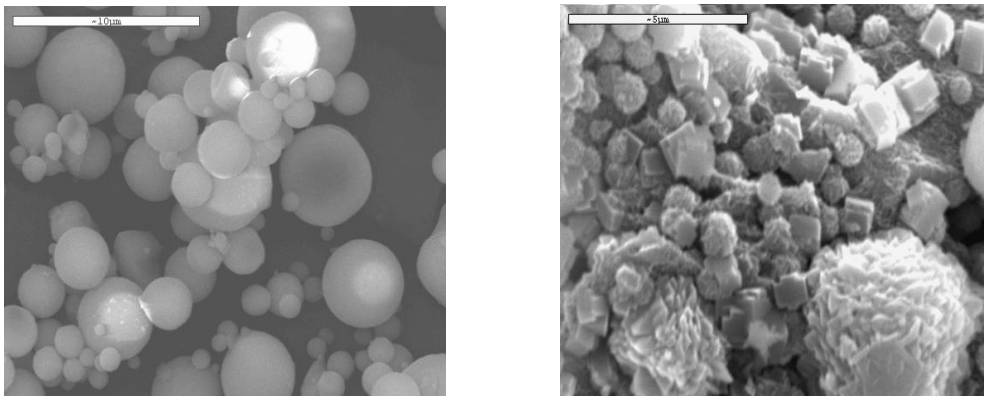

Figure 1: SEM of FAP and FAP(M)32-3,5(7-1)

Table 1. Main chemical composition of FAP and FAP(M)32-3,5(7-1)

No.	Substance	Composition (%)	
		FAP	FAP(M)32-3,5(7-1)
1	Zeolite P1	-	7.12
2	Zeolite X	-	34.65
3	Zeolite Upsilon	-	17.72
4	Quart (SiO_2)	21.98	22.10
5	Mulit ($Al_6Si_2O_{13}$)	15.79	12.82

The preliminary result of the absorption efficiency of 17 toxic congeners of dioxins/furans indicated that FAP(M)32-3,5(7-1) may absorb > 2.89 10^{-8} mol/g [12] and 200 mg of this material is enough to absorb a possible amount of dioxins/furans in an analytic sample containing about 2.05 µg TEQ. The studying results of solvent and the volume necessary to elute dioxins/furans congeners away from the column containing 200 mg of this material indicated that only 30 mL of toluene at normal condition is enough [12].

The use of FAP(M)32-3,5(7-1) in the preparation of fish, meat samples for analysing 17 toxic congeners of dioxins/furans on low resolution mass spectrometry modified from the standard method TCQS 01:2010/NĐVN [5] as detailed in item 2.2 and showed in Figure 2.

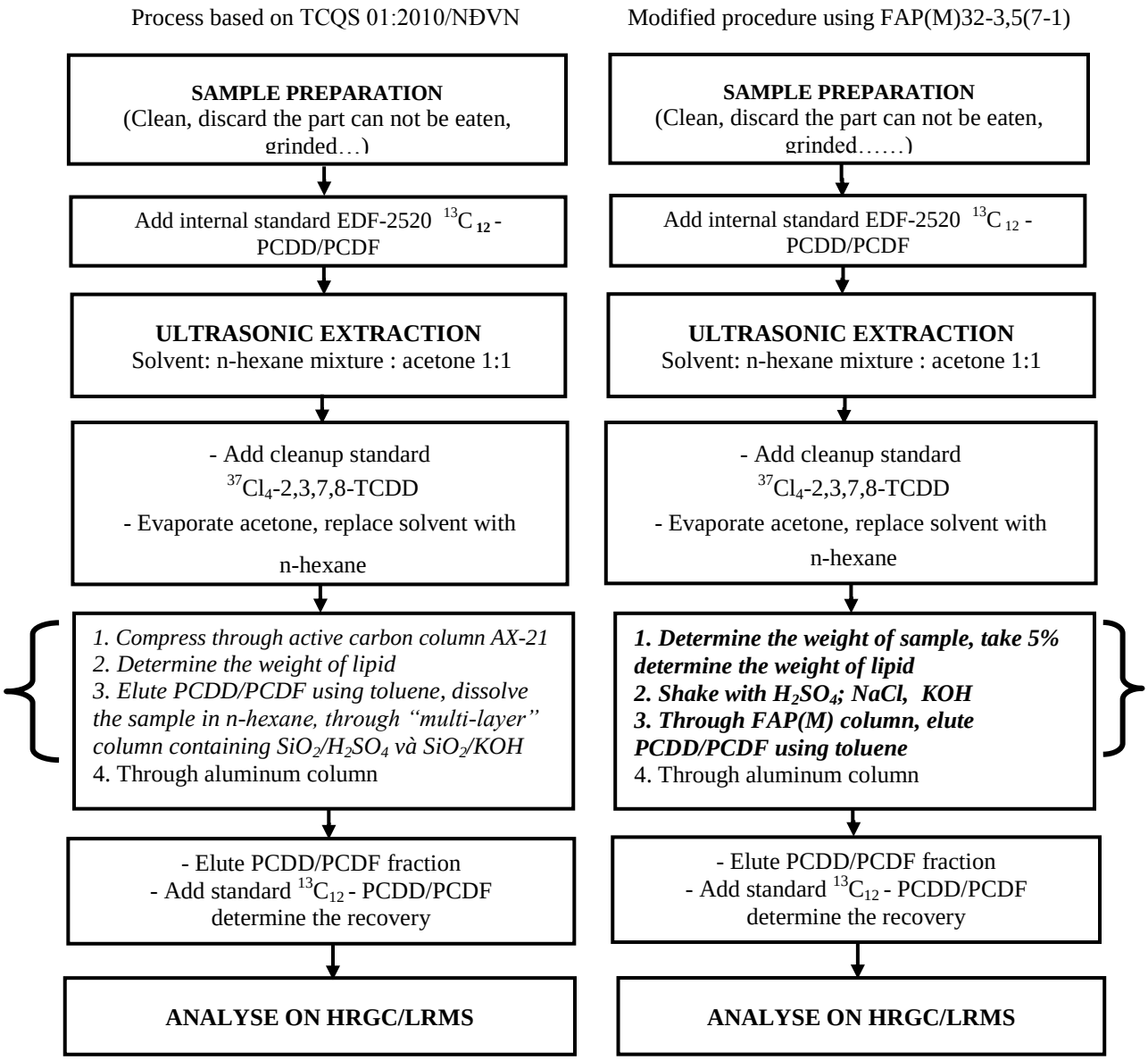

Figure 2. Modified procedure using FAP(M)32-3,5(7-1) for analysing 17 toxic congeners of dioxins/furans in biological samples (fish, meat)

The accuracy, precision of the results, detection limit of the method calculated by US.EPA [13] when analysing 7 replicated samples using FAP(M)32-3,5(7-1), the recovery of internal standards ($^{13}C_{12}$-PCDD/PCDF) in EDF-2520 is showed in table 2.

The accuracy of the results were evaluating based on the recovery of standards ^{12}C in the standard 7999-10-X added to the sample, the result in table 2 showed that this value varied in range from 84.5 to 96.4 %.

The precision of the results were evaluating based on the relative standard deviation of the results, using the methods regulated by US.EPA [4], [6-7], this value is acceptable if ≤ 20%, the results in table 2 showed that the percentage of relative standard deviation of 17 toxic congeners of dioxins/furans varied in range from 2.9 to 6.7 %.

Table 2. Standard deviation, relative standard deviation, detection limit, recovery by the method using FAP(M)32-3,5(7-1) to analyse the fish, meat samples (n=7, t = 3,143)

No.	Analyte	Fortified (pg/g)	Average found value (pg/g)	Recovery (%)	Standard deviation (pg/g)	Relative standard deviation (%)	LOD (pg/g)
1	2,3,7,8-TCDD	0.8	0.77	96.3	0.04	5.19	0.13
2	1,2,3,7,8-PeCDD	4.0	3.52	88.0	0.16	4.55	0.50
3	1,2,3,4,7,8-HxCDD	4.0	3.38	84.5	0.18	5.33	0.57
4	1,2,3,6,7,8-HxCDD	4.0	3.62	90.5	0.24	6.63	0.75
5	1,2,3,7,8,9-HxCDD	4.0	3.50	87.5	0.18	5.14	0.57
6	1,2,3,4,6,7,8-HpCDD	4.0	3.57	89.3	0.24	6.72	0.75
7	OCDD	8.0	7.68	96.0	0.29	3.78	0.91
8	2,3,7,8-TCDF	0.8	0.73	91.3	0.04	5.48	0.13
9	1,2,3,7,8-PeCDF	4.0	3.51	87.8	0.20	5.70	0.63
10	2,3,4,7,8-PeCDF	4.0	3.49	87.3	0.19	5.44	0.60
11	1,2,3,4,7,8-HxCDF	4.0	3.39	84.8	0.20	5.90	0.63
12	1,2,3,6,7,8-HxCDF	4.0	3.45	86.3	0.18	5.22	0.57
13	1,2,3,7,8,9-HxCDD	4.0	3.45	86.3	0.21	6.09	0.66
14	2,3,4,6,7,8-HxCDF	4.0	3.45	86.3	0.14	4.06	0.44
15	1,2,3,4,6,7,8-HpCDF	4.0	3.45	86.3	0.19	5.51	0.60
16	1,2,3,4,7,8,9-HpCDF	4.0	3.54	88.5	0.24	6.78	0.75
17	OCDF	8.0	7.71	96.4	0.23	2.98	0.72
18	$^{13}C_{12}$-2,3,7,8-TCDF			63.1			
19	$^{13}C_{12}$-2,3,7,8-TCDD			64.1			
20	^{37}Cl-2,3,7,8-TCDD			66.7			
21	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD			68.0			
22	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF			68.4			
23	$^{13}C_{12}$-OCDD			76.0			

Recovery of internal standard in EDF-2520 based on the method of US. EPA 8280 is acceptable in range of 25 %-150 %, the results in table 2 indicated that the value varied from 63.1 % to 76.0 %.

Detection limit of 17 toxic congeners of dioxins/furans by this method varied from 0.13 pg/g to 0.91 pg/g as the case may be.

Therefore, based on the comparison, the method using FAP(M)32-3,5(7-1) as an absorbent in substitution for activated carbon and chromatography column containing silicagel impregnated with acid and

alkali during the preparation of fish, meat sample met all criteria for a method used to analyse 17 toxic congeners of dioxins/furans by low resolution mass spectrometry.

4. Conclusion

The method using alkali treatment of coal fly ash discharged from Pha Lai Thermal Power Plant as FAP(M)32-3,5(7-1) to clean-up fish and meat samples met all criteria for a method used to analyse 17 toxic congeners of dioxins/furans by High-resolution gas chromatography/Low resolution mass spectrometry.

5. Acknowledgement

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13. Appendix B to part 136 – Definition and procedure for the determination of the method detection limit – Revision 1.11. U.S Environmental Protection Agency.