IMPROVEMENT OF CLEAN-UP EFFICIENCY FOR DIOXINS ANALYSIS BY HPLC

Dong Gi Kim, Yoon Ki Min, Yo Yong Kim, Jong Chan Kim, Kyu Hong Cho

Kyonggi-do Institute of Health & Environment, 324-1 Pajang-dong, Jangan-gu, Suwon, Kyonggi-do, 440-290, Korea

Introduction

Currently, the development of various pretreatment and analysis instruments has produced more reliable and accurate dioxin analytical results. However, compared with the analysis for other pollutants, dioxins analysis is subject to greater costs and longer pretreatment time, and the safety security of dioxins analyst is a very important issue. The automation method for pretreatment of dioxins analysis has been studied very actively[1,2].

In this study, we used the HPLC clean-up method to improve the efficiency of the existing clean-up in dioxins pretreatment. Clean-up condition was selected by dioxins standards, and the manual method of the Korea Official Method[3] and HPLC method were adopted to compare and evaluate the clean-up efficiency, clean-up time and solvent amount required for emission gas and fly ash from a municipal solid waste incinerator.

Materials and Methods

Chemicals and materials: EPA 1613 standard solutions in nonane (CS-1 to CS-5, IS, RS, LCS, Cambridge Isotope Lab., Andover, MA, USA) were used for instrument calibration, quantification, recovery and quality control. Solvents (dichloromethane, hexane, toluene, ethyl acetate) for organic trace analysis were purchased from J.T Baker (Philipshurg, NJ, USA) and Wako Pure Chemical Industries Inc. (Osaka, Japan). For the manual clean-up process silica (0.063~0.200㎜) and basic alumina(0.063~0.200㎜), both from Merck (Darmstadt, Germany), were employed as adsorbents in glass columns at atmospheric pressure. For the HPLC clean-up process multilayer silica (11(i.d)×177(L)㎜), basic alumina (11(i.d)×177(L)㎜, and carbon adsorbents (11(i.d)× 10(L)㎜) all from Fluid Management Systems Inc. (MA, USA), were prepacked in Teflon columns and sealed.

Clean-up : The clean-up procedure is shown in Figure 1.

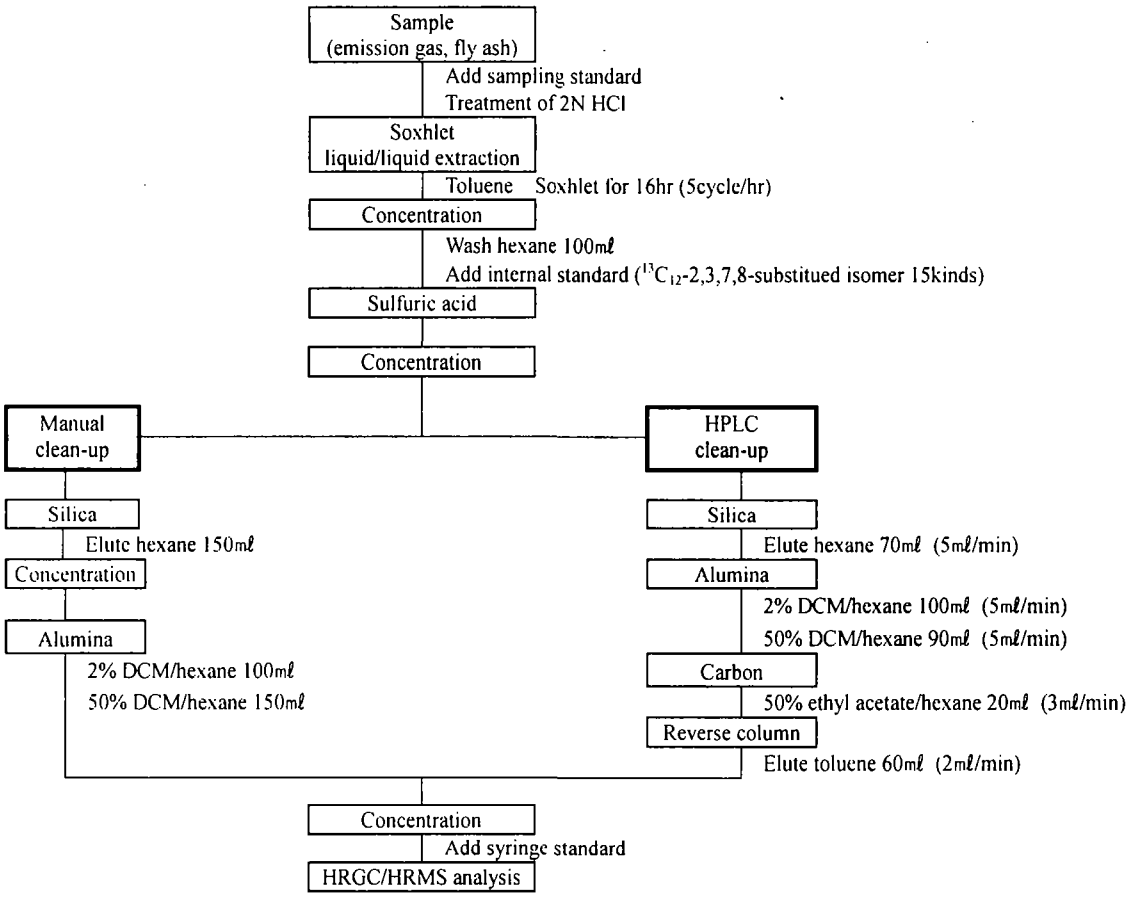


Figure 1. Flowchart of manual and HPLC clean-up

Continuous clean-up of silica, alumina and carbon by HPLC: Silica and alumina column were connected in series followed by a sample injection, and the sample was adsorbed from silica column to alumina column, and then the silica column was removed. Alumina column was eluted with 2% dichloromethane/hexane and was connected to the carbon column. The sample was adsorbed to the carbon column by eluting 50% dichloromethane/hexane and then the alumina column was removed. The hindrance material in carbon column was removed by eluting with 50% ethyl acetate/hexane, and then conducted back-elution by toluene.

HRGC/HRMS analysis: The samples were analyzed by HRGC/HRMS on GC 8000 series (Fisons Instruments, Italy) equipped with a CTC 200S auto sampler and coupled to an Autospec Ultima Mass Spectrometer (Micromass, UK).

RESULTS AND DISCUSSION

Manual column clean-up: The recoveries of manual clean-up by the Korea Official Method are represented in Figure 2, and show 82-102% and 83-101% respectively.

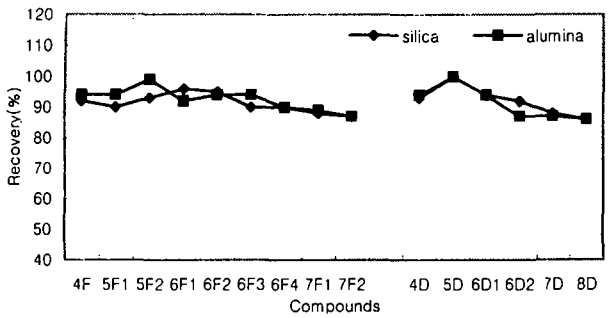
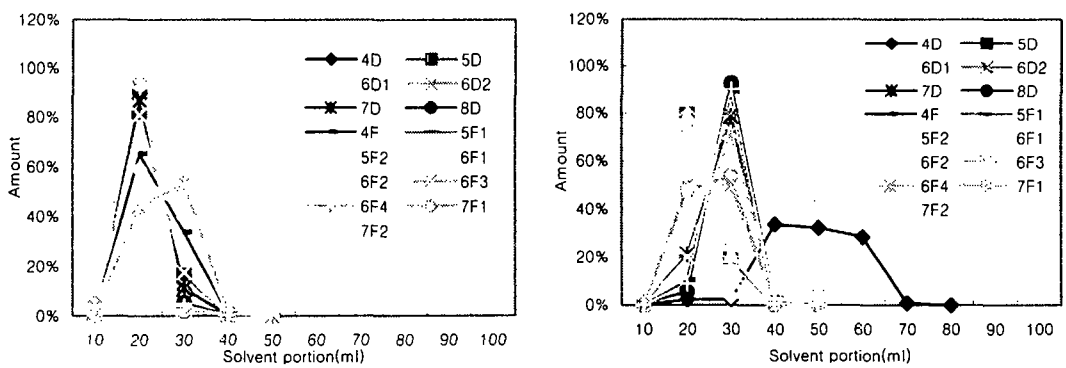


Figure 2. Recoveries of silica and alumina column by manual clean-up

HPLC column clean-up: The results of solvent portion experiment by the HPLC clean-up are shown in Figure 3. The results of the solvent portion experiment were that the recoveries of silica, alumina and carbon column were 72~109%, 75~ 110 % and 74~109%.



(a) silica **(b) alumina**

Figure 3. Results of solvent portion experiment for silica and alumina column by HPLC

Continuous clean-up of silica gel, alumina and activated carbon by HPLC: The recoveries of silica, alumina, and carbon column connected in series were 75-109%. The recoveries of EDF-7999 and EDF-4147 used a sample were 87-123% and 87-98% respectively.

Evaluation of clean-up efficiency : Manual clean-up and HPLC clean up showed that the detected concentrations were 81.01pg-TEQ/Nm^3 and 78.98pg-TEQ/Nm^3, and the recoveries were 65-86% and 67-87% respectively. The recoveries and detection concentrations for fly ash and emission gas showed similar results by the detected concentrations of sample 1 were 2.201ng and 2.151ng, and those of sample 2 were 2.349ng and 2.356ng in manual and HPLC clean up.

The results of time and solvent amount required for three samples in manual and the HPLC clean-up are shown in Table 1 and 2. The HPLC clean up showed half of the time was required and 50% of solvent amount required in manual clean-up. Therefore, in consideration of time and solvent amount required in clean-up, the HPLC clean-up provided better clean-up efficiency than manual clean-up.

Table 1. Comparison of time required for three samples in manual & HPLC clean-up

Task		Manual column clean up		HPLC column clean-up	
		System operating (hr)	Personnel working (hr)	System operating (hr)	Personnel working (hr)
Silica	condition	18.0	0.5	-	-
	packing	-	0.5	-	-
	cleaning	-	1.0	0.5	0.5
	loading	-	0.5	0.5	0.5
	processing	-	2.0	1.0	1.0
concentration		0.5	0.5	-	-
Alumina	condition	30.0	0.5	-	-
	packing	-	0.5	-	-
	cleaning	-	1.0	0.5	0.5
	loading	-	0.5	-	-
	processing	-	3.0	2.0	2.0
concentration		0.5	0.5	-	-
Carbon	packing	-	0.5	-	-
	cleaning	-	0.5	-	-
	loading	-	0.5	-	-
	processing	-	2.0	1.5	1.5
Total		**49.0**	**14.5**	**6.0**	**6.0**

Table 2. Comparison of solvent required for three samples in manual & HPLC clean-up

Task		Manual clean up(mℓ)	HPLC clean-up(mℓ)
Silica column	pack & clean column	600	60
	process samples	450	300
	Total	1,100	360
Alumina column	pack & clean column	600	60
	process samples	800	600
	Total	1,400	660
Carbon column	pack & clean column	600	60
	process samples	200	200
	total	800	260
Total		**3,300**	**1,280**

Reference

1. EPA, Method 3545A. Pressurized fluid extraction(PFE). Washinton DC, 1998
2. E.Abad, J.Saulo, J.Caixach and J.Rivera. Evaluation of a new automated cleanup system for the analysis of PCDD/PCDF in environmental samples. Fluid management system, 2001
3. The Korean Standard Testing Method for Dioxins and Furans, 2000