AN AUTOMATED DIRECT DIOXIN MONITOR Using APCI-ITMS COUPLED with ASE

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Introduction

One way to reduce the level of dioxins emitted from incinerators is to control the combustion. For this method to be effective, however, the dioxin level must be monitored immediately. Legally defined dioxin analysis, which is performed using HRGC/HRMS, takes more than one week due to the complicated sample preparation process. Therefore, this analysis cannot be used for the feedback control. There are two approaches that enable high-speed monitoring of the dioxin level. One is analyzing the precursors of dioxin. Because it does not require sample preparation, real-time monitoring has already been realized for some compounds (e.g., chlorophenol). The real-time monitor can output the chlorophenol concentration within one minute[1]. The other approach is analyzing some of the dioxin isomers. We have focused on the second one. We selected some isomers of polychlorinated dibenzo-*p*-dioxins (PCDDs) as target compounds for monitoring because a good correlation between the total dioxin concentration and the dioxin TEQ concentration has been reported[2]. We have developed system for high-speed (within 1 hour) monitoring dioxin in flue gas. As shown in Fig.1, it consists of an atmospheric-pressure chemical-ionization (APCI), ion-trap mass spectrometer (ITMS), and an accelerated solvent extraction (ASE). It enables to automatically analyze sub-ng dioxin levels in one hour.

Experiment

We tested our monitoring system by using the set-up illustrated in Fig.1. Incinerator flue gas was pumped through sampling sorbent at 5 l/min for 60 min. In the extraction chamber, firstly the sampled sorbent was set in the sample holder. Extraction solvent was introduced into the holder and accelerated solvent extraction (ASE) was done under high pressure (3 atm) and high temperature (150 ℃) condition for about 15 minutes×2 times. Table 1 shows the recovery rates for three solvents. Toluene was the most efficient. The extracted solution (25 ml×2) was introduced into the concentration chamber condensed to 1 ml by use of low-pressure distillation. This took about 20 minutes. The condensed solution (500 μl) was injected into the ionization

source to be ionized, then transported to ion source in the analysis chamber. The temperature in the ion source was about 200℃. The liquid sample was converted to a gas state by heating and declustering here. Atmospheric-pressure chemical ionization (APCI) was used because PCDDs are ionized with high selectivity by APCI. The APCI was performed using a high-voltage needle electrode. Compounds other than PCDDs also have high ionization efficiencies by APCI and thus reduce the ionization efficiencies of the PCDDs. The ionization efficiency of PCDDs thus depends on the incineration conditions; that is, the sensitivity for the quantification of PCDDs is also changed. To calibrate this change in sensitivity, PCDDs labeled with ^{13}C at a constant amount was added to the sampled sorbent. The ionization efficiencies of the ^{13}C-labeled PCDDs change the same as those of the PCDDs; therefore, the ionization efficiencies of PCDDs can be determined by observing the sensitivity of the added ^{13}C-labeled PCDDs. The concentration of the added ^{13}C-labeled PCDDs was 0.1-1 μg. Ions generated by APCI were sent to ITMS. The ions were trapped in the space surrounded by the ring electrode and the end-cap electrodes, then they were analyzed. The principles of ITMS are elsewhere [3),4)].

Results and Discussion

Figure 2 shows the mass chromatogram of the 1,2,3,4,6,7,9-HpCDD at an intensity of *m/z* 405. Sample solution was injected at the times shown by the arrows. It took less than 1 minute to analyze one sample. It is thus possible to have multiple injections within ten minutes to ensure the accurate analysis values. Figure 3 shows the calibration curve for the HpCDD. The signal intensity was linear for the sample amounts of 500-5000 pg. Table 2 shows the detection limits for the detector obtained by each calibration curve. Most of the detection limits were sub-ng range. They are enough high sensitivities to monitor the most of municipal incinerators. Therefore, the monitoring system is useful for real-time feedback control.

Acknowledgements

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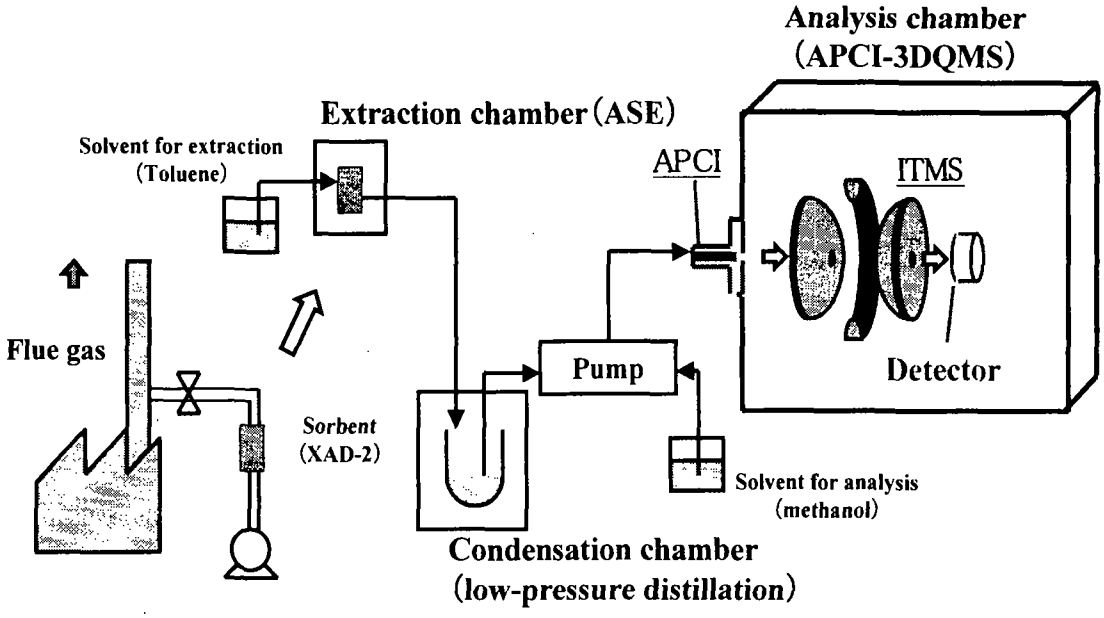

Figure 1 Schematic diagram of monitoring system and set-up for experiment

Table 1 Recovery rates (sorbent: XAD-2, 150℃,150 kg/ cm^2, 15 minutes)

Extraction Solvent	Recovery rates (%)	
	TCDD	HpCDD
toluene	80	63
acetone	63	40
dichloromethane	69	37

Table 2 Detection limits

Compound	Detection Limit(ng)
1,2,3,4-TCDD	1.5
1,2,3,4,6,7,9-HpCDD	0.075
OCDD	0.15
1,2,3,4-TCDF	0.24
OCDF	0.040

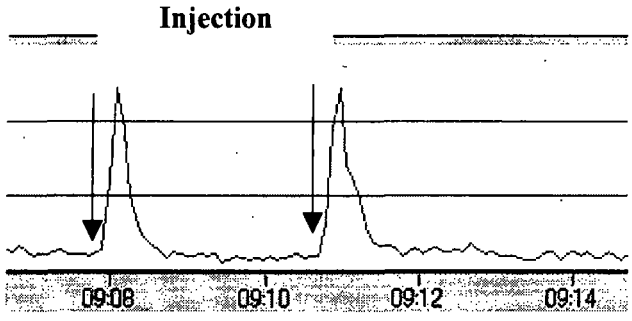

Figure 2 Ms chromstogrsm
(HpCDD 1 ng/10 μl methanol)

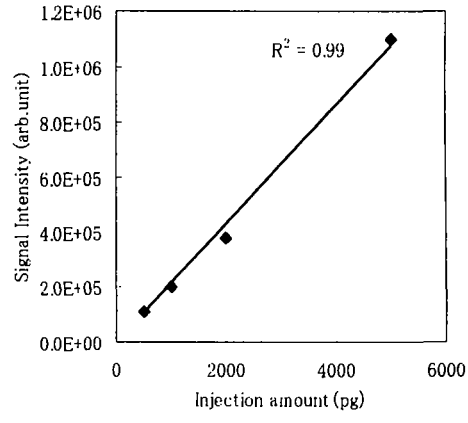

Figure 3 Cslibrstion curve
(HpCDD)

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