

DETERMINATION OF 2,3,7,8-CHLORINATED DIBENZO-*p*-DIOXINS AND -FURANS BASED ON PRE-COLUMN SEPARATION TECHNIQUE

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Introduction

Many methods using high resolution gas chromatograph-high resolution mass spectrometer (HRGC/HRMS) had been proposed including an official method and JIS method on the analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and analytical cost and analytical time were needed.^{1,2} Therefore, development of a summary measuring method of PCDD/DFs with the aim of speedup and cost reduction of the analysis became urgency. The speedup was examined even in a process of pretreatment operation and data processing, and it has been evaluated on the validity.³ There are some methods for estimation on the calculation of total-TEQ values from TEQ values of specific toxicity congeners. In the cost reduction, analysis procedures using used equipments have also been introduced.⁴ In this study, in considering that it can apply existing conditions for examining by the conventional method and possibility of a quick analysis in a sampling field, the system with a portable mass spectrometer having a double-focus was constructed. The characteristics are to selectively detect only purpose fractions by separation of injected sample at the pre-column in gas chromatograph. Drastic increase in *S/N* ratio by combining with LVI is expected, because only optional congeners can be introduced into the analytical column. Measurement of 2,3,7,8-chlorinated congeners of 4 chlorination or 5 chlorination of which especially, toxicity was strong even in the inside of PCDD/DFs from the viewpoint of simplification was tried. In addition, the result of applying this system to soil samples is also reported.

Materials and Methods

Chemicals

Acetone, toluene, hexane and dichloromethane for dioxins analysis were purchased from Wako Pure Chemical Industries, Ltd. A standard reference material CRM No. 21 Soil (National Institute for Environmental Studies, Japan) was used as an example of soil samples. All the other chemicals were of highest grade available and used without further purification.

Apparatus

Instrumental analysis was carried out with GC/MS. The system consists of a portable mass spectrometer JMS-GCmate (JEOL Ltd., Japan) having a double focus and a HP6890 series gas chromatograph (Hewlett Packard Company, USA) coupled to a Pre-column Inlet Separation System (APEX Technologies Inc., USA). An auto injector Combi PAL (CTC Analytics AG, Switzerland) was used for injections.

Sample preparation

Eight grams of a soil sample was weighed into a pre-cleaned quartz thimble and extracted for 16 hours with toluene using a Soxhlet extractor. After the extraction, the extract was spiked with a $^{13}\text{C}_{12}$ -labeled solution (PCDD/DFs: 1 ppb, OCDD/DF: 2 ppb) and concentrated prior to a sulfate treatment. The concentrated sample in toluene and a sulfuric acid were placed in a separatory funnel. The mixture was then shaken. After the phases were allowed to separate, the sulfuric acid phase was discarded. Fifty milliliters of a 1:100 hexane-water mixture was added; the mixture was shaken vigorously. The sample was further purified using a 300 mm*10 mm i.d. chromatographic column containing from top to bottom: 10 mm of sodium sulfate, 3 g of silica gel (Silica Gel 60, Merck, USA), 5 mm of sodium sulfate and a quartz wool plug. After the column was pre-rinsed with hexane, and the sample loaded, the column was eluted with 120 ml of hexane. The collected eluate was then evaporated to 1 ml using a rotary evaporator and applied to a 300 mm*10 mm i.d. chromatographic column containing from top to bottom: 2 mm of sodium sulfate, 1 g of active charcoal-silica (Wako Pure Chemical Industries, Ltd., Japan), 2 mm of sodium sulfate and a quartz wool plug. The column is then eluted first with 150 ml of a 75:25 hexane-dichloromethane mixture; the eluate was discarded. Fractions containing PCDD/DFs was then collected by eluting the column with 200ml of toluene.

Results and Discussion

Performance of LVI

LVI was examined using standard solutions of PCDD/DFs. As the result, in examined injection volume, calibration curves showed good linear relationship regardless of different boiling points of congeners. No significant changes in peak-band widths or peak shapes could be recognized, even if either solvent of decane, toluene, hexane was used in LVI.

GC Split

It was proven that peak area ratio of each substitution isomer depended on duration in the split. Especially, this tendency was strong as 2,3,7,8-chlorinated congeners having a low boiling point, and those were lost by the vaporization. Nevertheless, there was no large changes for peak area ratios of each 2,3,7,8-chlorinated congener in the duration for 1.60-2.50 min. Switching time to a splitless from a split was decided after 1.75 min of a sample injection.

ProSep Split

In the ProSep split, peak area ratios per unit time showed large fluctuation. Especially, a split effectively affected it for PCDD/DFs of 6 and of 7 chlorination. Starting time for Prosep split was defined as after 3.80 min from a sample injection. The reason is due to judge that the most part of detected peak is 2,3,7,8-chlorinated congeners of 4 chlorination or of 5 chlorination.

Programming Rate of Pre-column

The peak areas of low chlorinated PCDD/DFs rapidly increased with increase in programming rate. Nevertheless, large change showed the almost fixed peak area without observing at the gradient of the plotting in programming rate over 50 °C/min. It was judged that 55 °C/min was appropriate with fears of local heating of the pre-column and of extension of band widths for the programming rate of the pre-column.

Pre-column Temperature

A gradient of plotting of 4-chlorinated PCDD/DFs or of plotting of 5-chlorinated PCDD/DFs rapidly increased with a rise in temperature. And, splitless pre-column temperature was decided at 200 °C, because the gradient of the plotting of PCDD/DFs was decreasing 210 °C in the boundary. GC conditions for determining the 4-chlorinated PCDD/DFs and for determining the 5-chlorinated PCDD/DFs quantitatively were shown in the following.

Table I Separating conditions for 4-chlorinated and for 5-chlorinated toxic congeners

Analytical column	CP-Sil88 (Chrompack; 60 m*0.25 mm i.d. 0.10 um)
Oven temp.	60 °C (5.00 min)-30 °C/min-180 °C (0 min)-5 °C/min-270 °C (18.00 min)
Pre-column	HT-5 (APEX Technologies; 0.24 m*1 mm i.d. 25 um)
Injection mode	GC Split (0 min)-Splitless (1.75 min)-ProSep Split (3.80 min)
Injection temp.	60 °C (0.20 min)-55 °C/min-280 °C (40.80 min)

Conclusions

Following conclusions were obtained from the above examination. 1) By exactly setting conditions of the pre-column, decrease of baseline noise and selective detection of a purpose fraction became possible. 2) *S/N* ratio was also improved without accepting extension of peak band width in LVI. 3) Simplification of pretreatment and of operation is expected.

Acknowledgments

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References

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