Optimized Ionization Condition for the Trace Analysis of PCDD/PCDF with Ion Trap MS/MS

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Introduction.

Clean-up step is one of the bottlenecks in the conventional dioxin analysis with "single mode-of-the-operation" mass spectrometer. Tandem mass spectrometry (MS/MS) technique is highly selective due to its characteristic PCDD/PCDF fragment ions produced by the secondary ionization, so that the optimized MS/MS condition can be regarded as a part of the clean-up. Consequently, the MS/MS makes it possible to reduce the clean-up procedures. Along with the gas chromatography, it presents highly reliable information which helps identification of the PCDD/PCDF[1-3].

Once the ionized molecules are introduced into the ion trap, PCDD/PCDF and other substances are easily distinguished during the MS/MS process. It means that the qualitative analysis can be done without a hitch. However, the quantitative analysis is a different matter. While the PCDD/PCDF analysis, ^{13}C labeled PCDD/PCDF isomers are added into each sample to be used as internal standards (IS) for the quantification. The analytes (native PCDD/PCDF) and the IS are measured in the individual scan step. For the quantification, the amount of the ions, both the analytes and the IS, should maintain the same ratio. In case there is huge amount of interfering compounds in the sample matrices, this ratio could be changed and may affects the quantification.

The aim of this study is to optimize the ionization condition in order to perform the reproducible PCDD/PCDF quantitative analysis using ion trap MS/MS. The sensitivity and the signal-to-noise ratio (S/N) of three different types of samples; standard, waste water extract (a sample with small amount of interfering compounds) and soil extract (a sample with lots of interfering compounds) were measured and the ionization condition has been optimized.

Materials and Methods.

Sample Preparation. Sample extract was evaporated to approximately 1mL, then transferred onto a sulfuric acid coated silica column. PCDD/PCDF were eluted with 30mL of dichloromethane 1:2 *n*-hexane. The eluate was evaporated again to approximately 500μL, then transferred onto a silica-gel column. PCDD/PCDF were eluted with 12mL of toluene and the eluate was transferred to a vial and concentrated to 200μL under N_2. These samples have been quantified by the conventional PCDD/PCDF analytical method with double-focus mass analyzer. Wellington laboratories' EPA-1623CS1 was used as standard PCDD/PCDF sample.

Ionization Condition. Ion trap MS/MS was performed on a ThermoQuest (Austin, TX) GCQ plus ion trap mass spectrometer. The MS/MS condition is already published[4]. PCDD/PCDF were ionized in the external ionization chamber with the thermal electron emitted from the filament. The voltage, the current and the temperature of the chamber are the parameters for the ionization condition optimization. The electron energy (EI) was set from 30eV to 100eV. The emission current (EC) was set from 150μA to 350μA. The temperature of the ion source was 250 degree Celsius. The optimized condition may vary depending on the isomers. In this study, the ionization condition is optimized for the P5CDD, T4CDF, P5CDFs and H6CDFs since these isomers share the major part in the TEQ contribution.

Results and Discussion

The amount of 12378-P5CDF and 23478-P5CDF are the same in the standard sample. So, these peaks should have the same area counts. No matter what the ionization conditions are, the counts are almost the same for both native and ^{13}C-labeled P5CDF as shown in the figure 1.. It seems that the optimization is not necessary.
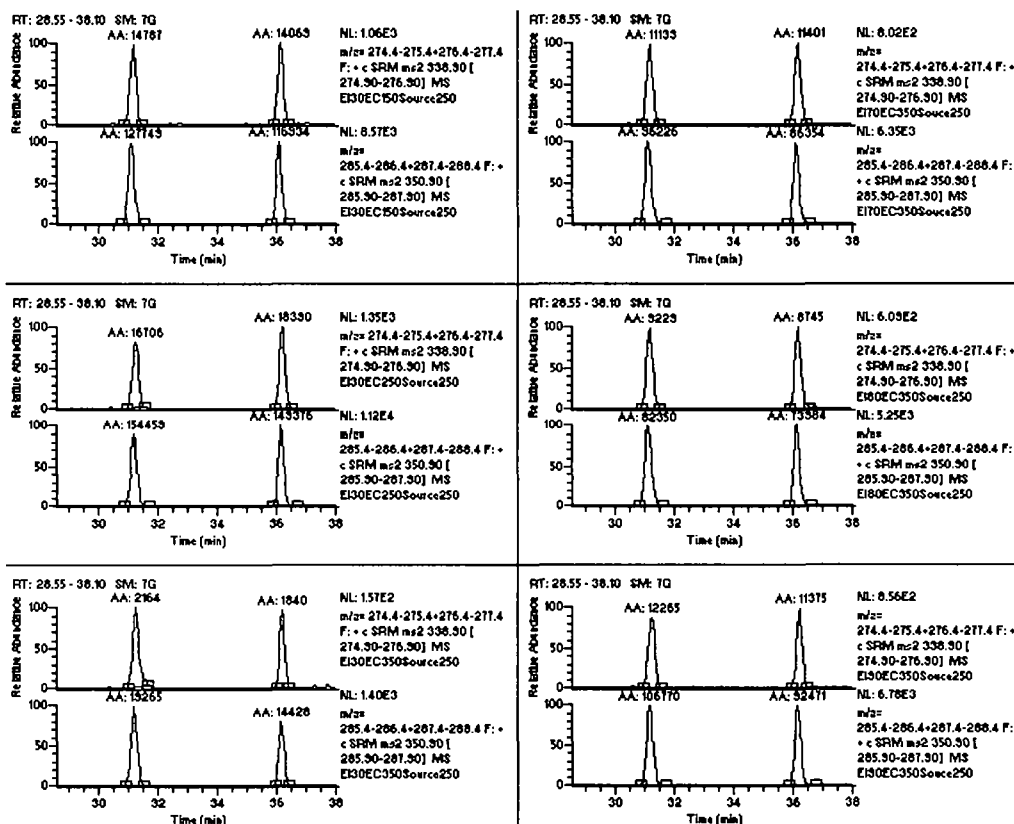
Figure 1.Ionization Condition and Area Count (Standard Sample, P5CDF)

However, the circumstances were different when environmental samples were quantified. As an example, the P5CDF chromatograms of soil extract were shown in figure 2. When the condition was EI=30eV/EC=50μA (lower left), the ratio had not been the same any more. The emission current should be lower when the electron energy is 30eV (middle left=30eV/250μA, upper left=30eV/150μA). Or when the EC=350μA , the electron energy should be higher (upper right=70eV/350μA, middle right=80eV/350μA, lower right=90eV/350μA,)
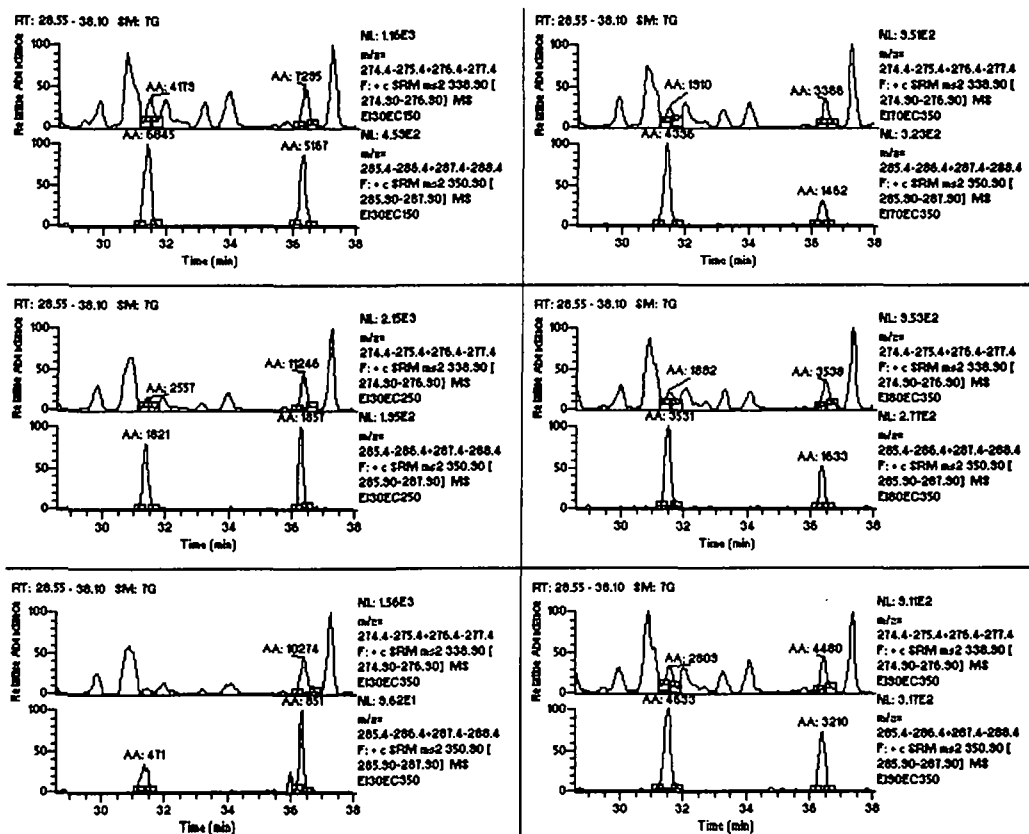

Figure 2.Ionization Condition and Area Count (Soil Extract, P5CDF)

Along with these area count change, the quantified value had also been changed. In order to evaluate the results, the   deviation has been calculated following the equation below.

X = Quantified Value of each of isomers (n=48).

Table 1. Deviation of the Quantified Value

Emission Current	Electron Energy [eV]							
	30	40	50	60	70	80	90	100
150μA	0.9%	0.8%	1.1%	1.4%	5%	1.4%	1.4%	11%
250μA	109%	339%	0.6%	5.1%	1.3%	4.7%	0.4%	1.7%
350μA	533%	7497%	389%	1.7%	12%	7.5%	3.6%	9.3%

As shown in the table 1., the deviation were minimized when the emission current was 150μA or the electron energy was 90eV. It means that the quantification using ion trap MS/MS spectrometer produces stable results with these ionization conditions. These quantification value (6.7pg for EI=30eV/EC=150μA and 6.5pg for EI=90eV/EC=250μA) are equivalent to the results by the conventional analytical method (6.5pg).

Ionization condition is one of the most important parameters for the PCDD/PCDF analysis with ion trap MS/MS technique. Once the conditions are optimized, the reproducible results can be obtained. The results are equivalent to those analyzed by the conventional method.

References
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