Dioxin Analysis Method by Indicator Isomers Using Rapid Cleanup and Gas Chromatography - High Resolution Mass Spectrometry.

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–Abstract –

The Rapid analysis method with the indicator isomers that used Gas Chromatography High Resolution Mass Spectrometry was examined. Accurately estimating TEQ became possible in a different sample group depending on this method. It was possible to measure flue gas (3 isomers), ash (2 isomers), and water (4 isomers) with one measurement for low-chlorine PCDD/Fs, and it was possible to measure soil (6 isomers) with one measurement for high-chlorine PCDD/Fs and non ortho-PCB. As for these measurement conditions, it is the same as the one of an official method, and the measurement of the rapid analysis method is also possible do not obstruct the analysis of an official method. These isomers were able to be detected also with the low concentration sample, and the rapid analysis became possible in high sensitivity and high accuracy.

– Introduction –

Dioxin (PCDD/Fs and co-PCB) analysis has some problems, such as measurement using Gas Chromatography - High Resolution Mass Spectrometry (HRGC-HRMS) which is expensive and complex extraction, cleanup, etc. Therefore, excessive time is required until results are obtained and the cost of analysis is high.

In such as this background, rapid analysis methods of PCDD/Fs which enable quicker, lower cost analysis have been developed, and their utility is continuing to be confirmed in recent years.[1-6] In this research, the authors studied a method of estimating total TEQ by measuring several isomers which serve as indicators, using the HRGC-HRMS used in measurements by the conventional official method. Reports on methods of estimating total TEQ using several indicator isomers have been published previously.[7-8] However, these methods also have problems, as many indicate only one isomer, it can not detect in low concentration sample, and the estimated values may be erroneous with samples that show anomalous compositions, like those caused by a high content of an isomer other than the indicator isomer in the total TEQ. Therefore, at facilities or locations which are being analyzed for the first time, it is necessary to perform analyses by both the official method and the rapid method and introduce a conversion factor in each such case.

The authors studied a rapid analysis method using indicator isomers which makes it possible to estimate total TEQ with high accuracy with different sample groups in each medium (flue gas, dust and ash, water, soil). Because quantitative/qualitative analysis is possible with this method based on one measurement of 2-6 isomers, measurement and analysis time are greatly reduced in comparison with the official method. A cleanup method was also examined, and it was possible to shorten the treatment time without losing the purification effect. As a result, higher accuracy was achieved, and it was possible to reduce the time and cost of analysis.

– Materials and Methods –

Test ①: Selection of indicator isomers

Analyses were performed by the official method using 51 samples of flue gas, 58 samples of ash, 34 samples of water, and 37 samples of soil taken from different facilities. After performing extraction–cleanup, the samples were measured by HRGC-HRMS. The measurement columns used were CP-Sil88 for dioxin for Te~HxPCDD/Fs, DB-17 for Hx~OcPCDD/Fs+ non ortho-PCBs and HT-8PCB for mono+di ortho-PCB. The relationship between total TEQ and isomers having TEF was investigated for each medium, and isomers which satisfied the following three conditions were selected as the indicator isomers: 1) Has high correlation with total TEQ, 2) isomer with good separation in the GC and comparatively easy detection, and 3) measurement is possible with one injection using one type of capillary column.

Test ②: Calculation of estimated TEQ by rapid cleanup – indicator isomer measurement method

21 samples of flue gas were purified using a double column formed by coupling a sulfuric acid-silica gel 2-layer column and an alumina column, and measurement and quantification were performed using only the indicator isomers selected in test ①. The correlation between the total TEQ by the official method and the total value of the isomer TEQ, which was obtained by multiplying the raw concentrations of each isomer by TEF was investigated. Estimated TEQ was then obtained by multiplying the total value of TEQ for the indicator isomers by this correlation coefficient, and the result was compared with the total TEQ obtained by the official method.

– ***Results –***

Test ①: Selection of indicator isomers

The correlation between the raw concentration of each isomer and total TEQ was investigated. The results are shown in Table 1. From Table 1, isomers which $R^2 > 0.92$ were selected as indicator isomers. From among these, isomers which satisfied the three conditions of good separation in the GC, easy delectability at low concentrations, and measurement with one type of capillary column were selected as indicator isomers. It may be noted that PCB #126, which was selected as an indicator isomer for soil, did not show a high correlation with total TEQ ($R^2 = 0.5615$); however, this isomer was included in the indicator isomers considering evaluation of PCB contaminated soil.

Table 1 Correlation coefficient （R^2） of raw concentrations of isomers and total TEQ

	Flue gas	Incineration ash/ dust/fly ash	Environmental water/ waste water	Soil
n	51	58	34	37
2378-TeCDD	0.6322	0.8276	0.0816	0.5799
12378-PeCDD	0.9281	0.9180	0.7918	0.9790
123478-HxCDD	***0.9844***	0.8227	0.8036	***0.9993***
123678-HxCDD	***0.9766***	0.8659	***0.9425***	***0.9988***
123789-HxCDD	0.8892	0.8976	***0.9252***	***0.9992***
1234678-HpCDD	0.8311	0.7201	0.9433	***0.9942***
OCDD	0.6480	0.5666	0.1268	0.9806
2378-TeCDF	0.7649	0.8854	0.2519	0.4896
12378-PeCDF	0.9928	0.9452	0.8272	0.9662
23478-PeCDF	***0.9712***	***0.9677***	***0.9587***	0.9987
123478-HxCDF	0.9129	0.9603	0.9036	0.9986
123678-HxCDF	0.9048	***0.9545***	0.8708	0.9980
123789-HxCDF	0.6239	0.9351	0.8766	0.9936
234678-HxCDF	0.9357	0.9184	***0.9269***	0.9846
1234678-HpCDF	0.7782	0.8540	0.6939	***0.9939***
1234789-HpCDF	0.6051	0.7437	0.3078	0.9729
OCDF	0.5227	0.2164	0.0489	0.8949
#126	0.6893	0.8614	0.0086	***0.5615***

Table 2 shows the correlation between the total value of the TEQs of the indicator isomers obtained by multiplying these raw concentrations by TEF and total TEQ obtained by the official method.

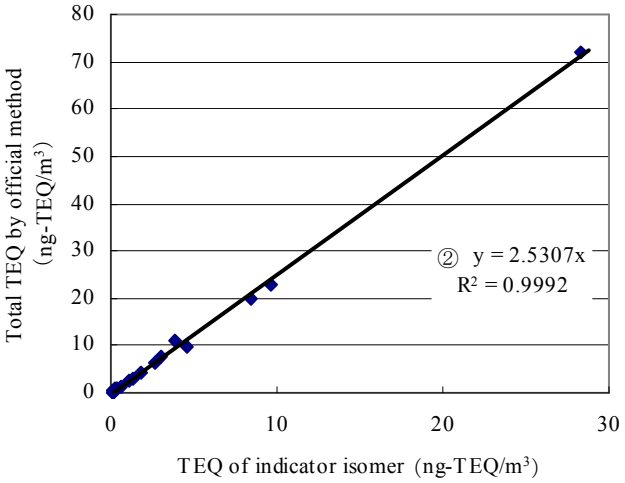
It was possible to measure flue gas (3 isomers), ash (2 isomers), and water (4 isomers) with one measurement by CP-Sil88 for dioxin column for low-chlorine PCDD/Fs, and it was possible to measure soil (6 isomers) with one measurement by DB-17 for high-chlorine PCDD/Fs and non ortho-PCB. The results for all media showed a high correlation with TEQ obtained by the official method (Table 2).

Table 2 Correlation between indicator isomers and total TEQ in each medium and measurement condition

Medium	Isomer	Measurement Condition	Correlation equation
Flue gas	123478-HxCDD 123678-HxCDD 23478-PeCDF	CP-Sil88 for dioxin (60m×0.25mm×0.1 μm) Injection times : 1 (approx. 40min)	Y =2.8413x (R^2= 0.9807) … Eq. ①
Incineration ash/ dust/ fly ash	23478-PeCDF 123678-HxCDF		y=2.6416x (R^2= 0.9823)
Environmental water/ waste water	123678-HxCDD 123789-HxCDD 23478-PeCDF 234678-HxCDF		y=2.4708x (R^2=0.9439)
Soil	123478-HxCDD 123678-HxCDD 123789-HxCDD 1234678-HpCDD 1234678-HpCDF PCB#126	DB-17 (60m×0.25mm×0.25 μm) Injection times : 1 (approx. 60min)	y=4.8799x (R^2=0.9870)

Test ②: Calculation of estimated TEQ by rapid cleanup – indicator isomer measurement method

Figure 1 Correlation between Total TEQ by official method and TEQ of indicator isomer.



Using the rapid cleanup method, 21 samples of flue gas extractant were purified, and the three isomers selected as indicator isomers for flue gas in test ① were measured and quantified. The results showed that the purification effect of the rapid cleanup method is substantially the same as that with the official method, demonstrating that the results with the proposed method are not influenced by interfering substances or other factors.

When the total value of TEQ of the indicator isomers obtained by multiplying the respective indicator isomers by TEF was compared with the total TEQ obtained by the official method, a high correlation was obtained (y = 2.5307x . . . ②, R^2 = 0.9992; Fig. 1). This value showed good agreement with the results when using the cleanup method by official method in test ① (Table 2, Eq. ①; y = 2.8413x (R^2 = 0.9807)). Furthermore, the estimated TEQ by the rapid analysis method obtained by substituting the total value of TEQ of the 3 indicator isomers for X in this Eq. ② showed good agreement with the total TEQ obtained by the official method (Table 3), and a high correlation coefficient was obtained (y = 0.9966x -0.1607, R^2 = 0.9983; Fig. 2).

– Conclusion –

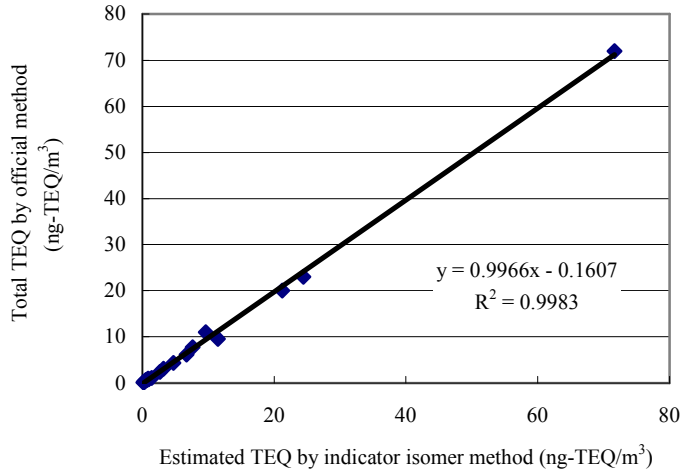
As the indicator isomers selected by the authors showed a high correlation with total TEQ and are easily detected regardless of the concentration level, it was found that this method can adequately respond to analytical requirements, even with low concentration. Selection of several isomers solved problems which had existed with the conventional methods, such the impossibility of detecting isomers in low concentration and erroneous estimated values shown by anomalous compositions, such as those caused by high levels of isomers other than

the indicator isomer in total TEQ. Using this method, application is expected at sites where quick analysis is necessary, for example, in emergency investigations after accidents, monitoring for routine maintenance control, investigations during the demolition of waste incinerators, and others.

Table 3 Estimated total TEQ by indicator isomers and total TEQ by official method (unit: ng-TEQ/m)[)]

No	Total TEQ (official method)	Estimated total TEQ (indicator isomer method)	No	Total TEQ (official method)	Estimated total TEQ (indicator isomer method)
1	4.4	4.7	12	0.57	0.45
2	0.20	0.25	13	0.37	0.38
3	0.76	0.73	14	3.1	3.2
4	0.69	0.60	15	1.1	1.4
5	2.4	2.6	16	0.81	1.0
6	0.78	0.79	17	20	21
7	0.16	0.17	18	6.2	6.7
8	0.28	0.26	19	11	9.6
9	72	72	20	23	24
10	1.0	0.88	21	7.8	7.6
11	9.6	12			

Figure 2 Correlation between Total TEQ by official method and estimated Total TEQ by indicator isomer method.



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