

UNCERTAINTY OF DIOXINS ANALYSIS BY JIS(JAPANESE INDUSTRIAL STANDARD) METHOD

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Introduction

The evaluation of uncertainty in measurement is needed in many fields.¹ It is one of the required conditions specified in ISO/IEC17025. To establish uncertainty evaluation procedures is required for laboratories to issue legal certificates in Japan. We evaluated the uncertainty in dioxin analysis which was performed according to the JIS method²(similar to EPA method 1613³) It turned out that the process of GC/MS measurement has a major contribution to the uncertainty.

Methods and Materials

We examined the uncertainty associated with dioxin analysis after the extraction process. This means that sampling errors were not considered in the present study. The JIS² method is essentially similar to EPA method 1613³. The analysis process consists of extraction, extract cleanup, and HRGC/HRMS analysis by isotope dilution. Fly ashes were used for experiments. Factors of uncertainty were examined based on the following equation. Blank corrections were not considered in the present study.

$$C = \frac{A_s}{A_i} \times \frac{A_{ist}}{A_{st}} \times \frac{C_{st}}{C_{ist}} \times \frac{Q}{M}, \quad (1)$$

where

C = the concentration of PCDD/PCDF (ng/g)

A_s = the area of the sample peak in HRGC/HRMS measurement

A_i = the area of the internal standard peak (labeled standard in the sample) in HRGC/HRMS measurement

Q = weight of internal standard (cleanup standard) added to the sample (ng)

M = weight of the sample (g)

$\frac{A_{ist}}{A_{st}} \times \frac{C_{st}}{C_{ist}}$

= relative response factor^{2,3}; the relative response (labeled to native) vs. concentration in standard solutions.

Substituting a and a_0 defined by

$$a = \frac{A_s}{A_i} \quad \text{and,} \quad a_0 = \frac{A_{st}}{A_{ist}}, \quad (2)$$

we obtain

QUALITY IN POPs ANALYSIS

We evaluated the components of uncertainty based on equation (2). They were evaluated as follows¹.

a : The same sample was measured 4 times per day, and for three days. The standard uncertainty of a , denoted by $u(a)$, was determined from the analysis of variance of these data.

a_o : Mixtures(standards and internal standards) was measured repeatedly five times. The standard uncertainty of a_o , denoted by $u(a_o)$, was calculated as the experimental standard deviation of these values.

C_{st} : The maximum possible error in the concentration of the standard substance is $\pm 2\%$ according to the manufacturer specification. The standard uncertainty of C_{st} , denoted by $u(C_{st})$, was calculated by assuming the rectangular distribution having the half width of $\pm 2\%$.

C_{ist} : The maximum possible error in the concentration of the internal standard is $\pm 2\%$ according to the manufacture specification. The standard uncertainty of C_{ist} , denoted by $u(C_{ist})$, was calculated similarly as $u(C_{st})$.

Q : 30 μL of n-nonane was taken with a micro syringe, and its mass was measured with an electronic digital counting balance. It was repeated 10 times by each of three persons. The standard uncertainty of Q , denoted by $u(Q)$, was determined from the analysis of variance of these data.

M : Error of electronic digital counting balance from vendor and error of calibration, As standard uncertainty of M , It expresses with $u(M)$. They were analyzed statistically. The combined standard uncertainty, $u_c(C)$, is given by the following equation,

$$u_c(C) = C \times \sqrt{\frac{u^2(a)}{a^2} + \frac{u^2(a_o)}{a_o^2} + \frac{u^2(Q)}{Q^2} + \frac{u^2(M)}{M^2} + \frac{u^2(C_{st})}{C_{st}^2} + \frac{u^2(C_{ist})}{C_{ist}^2}} \quad , \quad (3)$$

Native and $^{13}\text{C}_{12}$ -labeled standards of PCDD/PCDF were from Wellington Laboratories Inc.

Results and Discussion

It is expected that the variation in a depends on the signal-to-noise ratio (S/N) of peak. We obtained an empirical relationship between the variation in a and the S/N ratio by the least square fitting procedure. Fig.1 shows the coefficients of variation in a and the empirical equation. Below $a = 0.5$, the coefficient of variation increases. Table 1 summarizes the results of the standard uncertainty in the measurement of TeCDDs(m/z: 321.8936). Table 2 shows the uncertainty of TeCDDs(m/z: 321.8936) measurement. The concentration of 1,3,6,8- T eCDD which had the highest peak among the isomers of TeCDDs was 0.1267 ng/g and the expanded uncertainty was calculated to be ± 0.0097 ng/g. The relative expanded uncertainty was 7.6%. The concentration of 1,2,7,9- TeCDD which had the lowest peak was 0.004601 ng/g and its expanded uncertainty was ± 0.0007 ng/g. The relative expanded uncertainty was 14.3%. It was found that the process of HRGC/HRMS analysis had more than 90% contribution to the combined standard uncertainty.

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References

1. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML The Guide to Expression of Uncertainty in

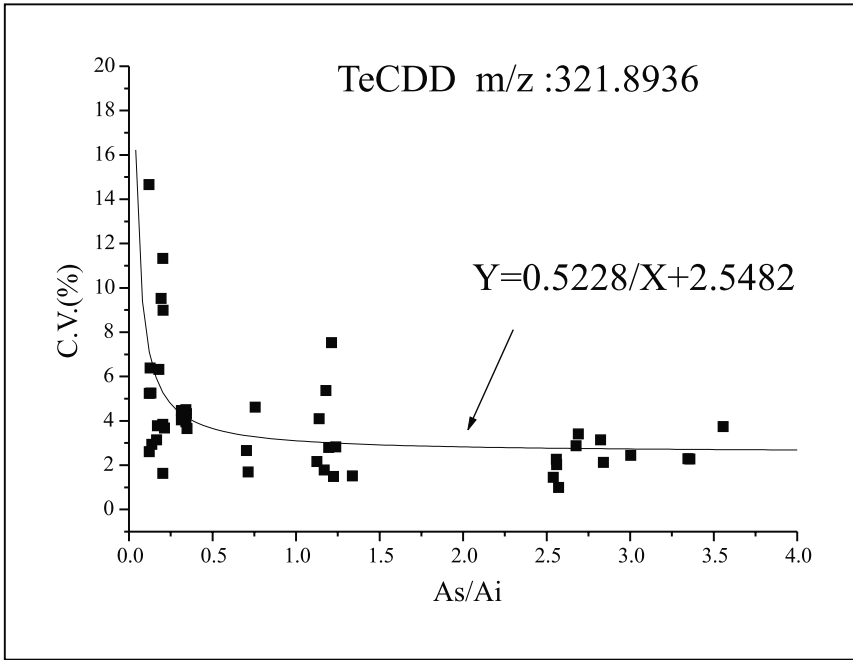


Figure 1. Changes in the coefficient variation at a

Table 1. The summary of standard uncertainty T eCDDs: m/z: 321.8936

Factor	T type of uncertainty	$u_i(y)$
		0.00477
a	A	$\frac{a}{a} + 0.03499$
a_0	A	0.05793
Q	A, B	0.01607 μ l
M	B	0.000005g
Cst	B	0.00005 μ g/ml

Table 2. The result of TeCDDs(m/z: 321.8936)

Isomer	Concentration(ng/g)	u(C)	U(C)*
1368	0.126778	0.004848	0.0097
1379	0.092208	0.003562	0.0071
1378	0.047616	0.001905	0.0038
1369/1247/1248	0.094737	0.003656	0.0073

QUALITY IN POPs ANALYSIS

1268	0.027296	0.001152	0.0023
1478	0.004384	0.000321	0.0006
2378	0.007394	0.000425	0.0009
1237	0.041079	0.001662	0.0033
1234/1246/1249/ 1238	0.105834	0.004069	0.0081
1236/1279	0.042213	0.001704	0.0034
1469/1278	0.011527	0.000573	0.0011
1239	0.011949	0.000588	0.0012
1269	0.006556	0.000396	0.0008
1267	0.007167	0.000417	0.0008
1289	0.004601	0.000328	0.0007

$U(C)^*$: *The expanded uncertainty* $U(C) = u(C) k$ ($k = 2$: *The coverage factor*)

- Measurement ,Kouzou Iizuka (1996) Japanese translated version Japanese Standards Association 4-1-24 Akasaka Minato-ku, Tokyo 107-8440 Japan
2. Japanese Standards Association (1999) JIS K 0311 Method for determination of tetra- through octa-chlorodibenzo-p-dioxins, tetra- through octa-chlorodibenzofurans and coplanar polychlorobiphenyls in stationary source emissions 4-1-24 Akasaka Minato-ku, Tokyo 107-8440 Japan
 3. U.S. Environmental Protection Agency (1994) Method 1613 Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS Office of Water Engineering and Analysis Division (4303) 401 M Street S.W. Washington, D.C. 20460