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EVALUATION OF UNCERTAINTY FOR THE DIOXIN ANALYSIS OF SERUM

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) are well-known environmental contaminants. Because these contaminants exist as infinitesimal in the environment, it is very complicate to detect the concentration of PCDDs and PCDFs in the sample, correctly. Therefore, what expresses confidence of measurement results is very difficulty and complex, but this issue of uncertainty is considered as a very important part in the field of analytical chemistry. According to the present situation, uncertainty expression of analytical results is required by the accreditation based on ISO 17025[1]. And, when analytical results are expressed necessity to indicate uncertainty with results is getting bigger so that domestic and international comparisons of measurement quality are more qualitatively possible.

In this study, uncertainty estimation of dioxin analysis in blood sample was carried out in accordance with the methods of the Guide to the expression of Uncertainty in Measurement (GUM). GUM was published jointly by seven international organizations such as International Bureau of Weights and Measures (BIPM), International Electrotechnical Commission (IEC), International Federation of Clinical Chemistry (IFCC), International Organisation for Standardization (ISO), International Union of Pure and Applied Chemistry (IUPAC), International Union of Pure and Applied Physics (IUPAP) and The International Laboratory Accreditation Cooperation (OIML). These seven organizations have now set up a Joint Committee for Guides in Metrology (JCGM) in which also ILAC, the International Laboratory Accreditation Cooperation, has become a member[2].

The methods of uncertainty estimation consist of 4 steps such as specification of measurand, identification of uncertainty sources, quantification of uncertainty components and calculation of combined uncertainty[3]. Uncertainty evaluation methods including these steps were applied to the dioxin analysis experiments. Figure 1 shows the simple flow chart of the dioxin analytical procedure and the possible uncertainty sources in each stage.

Methods and Materials

2.1 Specification of measurand

In this step, the measurand indicating relationship between the measurement results and the input quantities is defined. In dioxin analysis, the measurand can be shown as relation expressions as following.

(1) $\mathbf{C_i} = \frac{(Ax1 + Ax2) \times Qis}{(Ais1 + Ais2) \times RRF}$

A_x1, A_x2: peak area of sample

$A_{is}1$, A_{is}: peak area of standards

Q_{is}: quantity of standards

(2) RRF = $\frac{(An1 + An2) \times Cis}{(Ais1 + Ais2) \times Cn}$

A_n1, A_n2: peak area of the first and second selective ions of Calibration Standard (CS)

$A_{is}1$, $A_{is}2$: peak area of the first and second selective ions of internal std. included to CS

C_{is}: concentration of internal std. included to CS

C_n: concentration of CS

(3) $\mathbf{C_T = (K_1 \times C_1 + K_2 \times C_2 \ldots\ldots K_{17} \times C_{17})/W}$

W: weight of sample, C_i: quantity of individual congener (i = 1 to 17)

K_i: TEF value of individual congener (constant value)

Each expression, (1), (2), and (3), indicates the quantity of the individual congener (C_i), RRF (Relative Response Factor) value, and total TEQ concentration of 17 dioxin congeners (C_T).

2.2 Identification of uncertainty sources

This step is a stage that lists the possible sources of uncertainty including sources that contribute to the uncertainty on the parameters in the relationship specified in step 1. Uncertainty sources of dioxin analytical procedure are shown in Figure 1.

2.3 Quantification of uncertainty components

This step is a process that measures or estimates the size of the uncertainty components associated with each potential source of uncertainty identified. In dioxin analysis, the size of the uncertainty components was quantified as following.

[1] Measurement of sample weight or lipid weight: This is a process that estimates the uncertainty for measuring the weight of sample or lipids (W). In this process, experiments measuring uncertainty were composed of two cases. One was what measures the weight of sample or lipid in several times and the other was what searches the reference uncertainty about the balance. Then, these two uncertainties were considered as standard uncertainties about W.

[2] Standard solutions*:* This is a process that evaluates the uncertainty about the purity and volume of standard solution (Q_{is}, $C_{is,}$ C_n). The uncertainty of the purity was measured by searching for the reference uncertainty in the proof book. The uncertainty of the volume was calculated by measuring the volume of standard solution, repeatedly, and searching for the reference uncertainty of syringe in the proof book. These uncertainties were also regarded as standard uncertainties.

[3] Peak assignment*:* The method of measuring uncertainty of peak area (A_x1, A_x2, $A_{is}1$, $A_{is}2$, A_n1, A_n 2) is to search for the maximum peak area and the minimum peak area in the range of satisfying proper peak's conditions. The difference between these two values is divided by 2 and the result is termed 'a', in other words, 'half range'. Standard uncertainties of these variables were calculated by dividing 'a' into the square root of 3 according to the rectangular distribution.

2.4 Calculation of combined and expanded uncertainties

Standard uncertainties obtained above should be combined to calculate the final uncertainty. Combined uncertainty and expanded uncertainty were calculated according to the rule of error propagation[4].

Results and Discussion

This study evaluated the total uncertainty in the dioxin analysis of serum by quantifying uncertainty components and combining standard uncertainties of each stage. At first, in the measurement of weight, because the uncertainty of the repetitive measurement was very smaller than that of the balance, the combined uncertainty of variable W was the same as the uncertainty of the balance. Therefore, the standard uncertainties for measuring the weight of both sample and lipids were 0.0001 g. In the next stage, the reference uncertainties of both standard solution and

syringe were 5%. In the peak assignment procedure, the uncertainty of each peak area was obtained by measuring the maximum and minimum peak areas according to the previous methods. The consideration in this procedure is necessarily, in which peak area should be in the range of satisfying the proper peak's conditions. The assumption of this procedure is that peak areas are distributed according to the rectangular distribution. Standard uncertainties obtained through these measurement procedures can be arranged as in Table 1.

After measuring standard uncertainties, a combined uncertainty was calculated according to the rule of error propagation. And an Expanded uncertainty was calculated by multiplying the combined uncertainty by coverage factor, k. In conclusion, the expanded uncertainty for the confidence at 95% obtained in this study was 0.00312 pg/g weight or 0.86456 pg/g lipid. The final expression of measurement results of dioxin concentration in serum can be indicated as 0.07392±0.00312 pg/g weight or 20.4724±0.86456 pg/g lipid.

The uncertainty cannot be calculated exactly, but only be evaluated. Namely, it is not simple to express the measurement results of dioxin concentration with correct uncertainty, but this is possible. The meaning of this study is in that the uncertainty evaluation was attempted in a trace-level dioxin analysis procedure of serum. The further consideration is to search for more uncertainty sources, to add the uncertainty of trueness test and precision test, to estimate the uncertainty of dioxin concentration in the high concentration sample, and so on.

Acknowledgements
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Figure 1: Flow chart of uncertainty sources in dioxin analysis procedure of serum

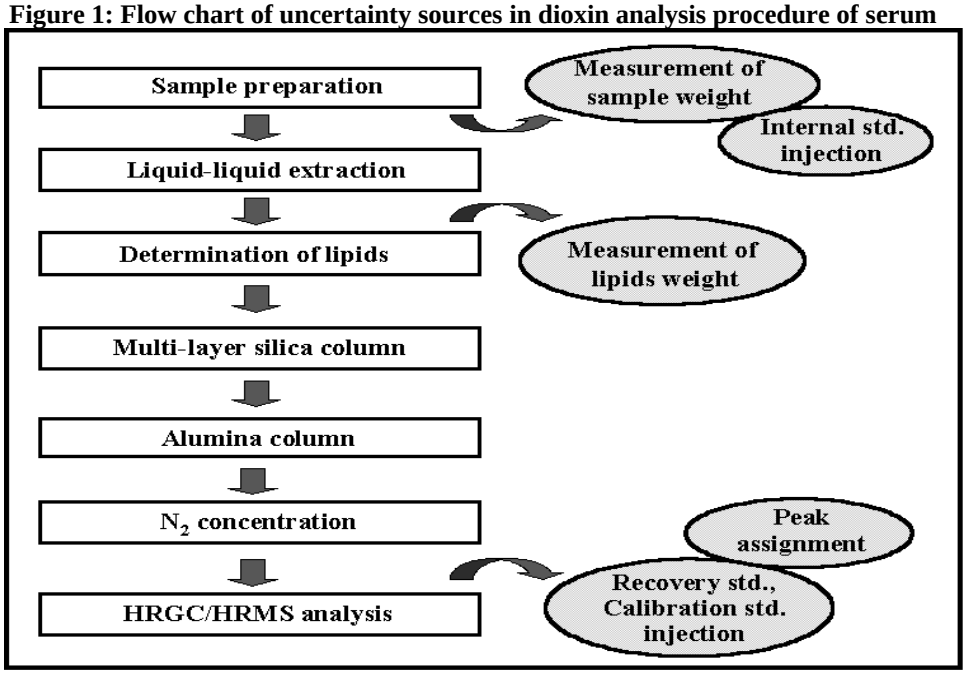

Table 1: The example of standard uncertainties for each variable of a TCDF

variables			value	uncertainty	A or B type
RRF	RRF1	An 1	40.7	0.8660	B
		An 2	58.5	0.6928	B
	RRF2	An 1	82.6	1.1547	B
		An 2	96.7	1.4722	B
	RRF3	An 1	362.3	1.9919	B
		An 2	485.5	5.3982	B
	Cn		0.5/2/10	0.025/0.1/0.5	B
	Cis		100	5	B
C tcdf	Ax 1		4.8	1.2413	B
	Ax 2		12	1.9053	B
	Qis	Cis	100	5	B
		Vis	10	0.5	B
W			38.4977	0.0001	A
Lipids			0.1390	0.0001	A

A type: uncertainty evaluation through repeat measurement
B type: uncertainty evaluation through information of the past