Measurement uncertainty for the determination of uranium in urine by ICP-MS

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1. Introduction

There is growing concern about measurement of radioactive material because of radiation accidents such as Fukushima NPP accidents. Generally radioactive material cause external and internal radiation exposure. KEPCO NF is interested in internal dosimetry and intensely focuses on establishment of urine analysis which is one of indirect method to estimate internal dosimetry. Urine samples are analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Measurement uncertainty for the determination of uranium in urine is generally composed of pre-treatment part and instrument analysis part.

In this study, we have focused on evaluating uncertainty for the determination of uranium in urine by ICP-MS. To achieve it, three main uncertainty factors are considered.

2. Methods and Materials

2.1 Materials and reagents

Natural uranium standard solutions were obtained from PerkinElmer (1 μg L^{-1} Setup Solution, natural uranium, Matrix: 1% HNO_3). For dilution, ultra high pure grade 2% nitric acids were used. Measuring of weight was performed by electric balance (Sartorius Quintix, capacity: 220g).

2.2 Instrumentation

Measurements were performed using a NexION 350X quadruple ICP-MS (PerkinElmer). The instrument parameters are summarized in Table 1. The ICP-MS was operated in standard mode for the analysis of the uranium.

Table 1. Instrument parameters for NexION 350X

RF power	1600 W
Auxiliary gas	1.2 L/min
Nebulizing gas	1.02 L/min
238U dwell time	75 ms
Replicates	3
Sweeps/reading	30
Readings/replicate	1
Detector mode	Dual (pulse+analog)

2.3 Model

In our analysis, three major factors of uncertainty were considered. That is instrument part, initial volume and final volume part. The relation of each factors is described as follows.

$$\mathrm{C} = C_0 \times \frac{V_F}{V_I} \quad (1)$$

C : Uranium concentration of urine spot sample
C_0: Measured concentration of urine sample
V_F: Final Volume
V_I : Initial Volume

Measured concentration of urine sample (C_0) represents instrument analysis process. Pre-treatment process consists of 1 mL initial volume (V_I) and 10 mL final volume (V_F).

In pre-treatment process, pipette and balance uncertainty are included. In instrument part, there are three detail factors which are repeatability, calibration curve, and standard solution dilution. To summarize uncertainty factors, Cause and effect diagram is descried in Fig. 1.

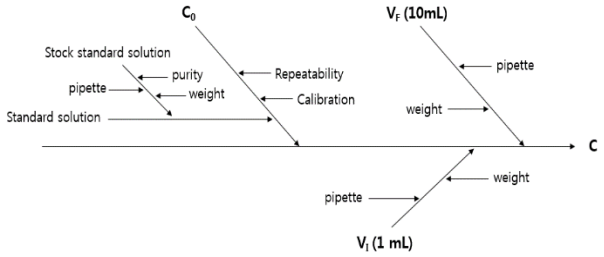

Fig. 1. Cause and effect diagram

2.4 Pre-treatment process

Spot urine sample of worker was pipetted 1 mL and the sample (1 mL urine) was diluted with 2% HNO_3 9 mL.

2.5 Instrument analysis process

ICP-MS calibration standards were prepared by dilution of PerkinElmer Setup solutions into a diluent solution 2% in nitric acids. The five standards solutions were prepared to 20, 40, 60, 80, 100 ng L^{-1} ^{238}U levels. Calibration blank was 2% nitric acids.

For repeatability test, natural uranium standard of 80 ng L^{-1} were measured 10 times repeatedly.

3. Results and Discussion

3.1 Initial volume uncertainty

Pipette uncertainty can be measured by pipette resolution. Expanded uncertainty of 1 mL pipette was 0.003 (k=2). Standard uncertainty and relative standard uncertainty by pipette was calculated as follow.

$$\mathrm{u}(P_{r,I}) = \frac{0.0015}{\sqrt{3}} = 0.00087\ mL$$
$$u_r(P_{r,I}) = \frac{u(P_{r,I})}{P_0} = 0.00087\ (P_0 = 1\ mL)$$
$$\nu = \infty$$

$\mathrm{u}(P_{r,I})$: standard uncertainty of pipette of initial volume
$u_r(P_{r,I})$: relative standard uncertainty of pipette of initial volume
ν : degree of freedom

Electric balance uncertainty was consisted of balance resolution and repeatability. Expanded uncertainty of balance was 0.0003 g (k=2). Standard uncertainty ($\mathrm{u}(W_{r,I})$) and relative standard uncertainty($u_r(W_{r,I})$) caused by balance resolution was calculated as follow.

$$\mathrm{u}(W_{r,I}) = \frac{0.00015}{\sqrt{3}} = 8.7 \times 10^{-5}\ g$$
$$u_r(W_{r,I}) = \frac{u(W_{r,I})}{W_0} = 8.7 \times 10^{-5}\ (W_0 = 1\ g)$$
$$\nu = \infty$$

Initial volume was weighted 10 times and standard deviation was 0.0053 g. Standard uncertainty ($\mathrm{u}(W_{n,I})$) and relative standard uncertainty($u_r(W_{n,I})$) caused by balance repeatability was calculated as follow.

$$\mathrm{u}(W_{n,I}) = 0.0053\ g$$
$$u_r(W_{n,I}) = \frac{u(W_{n,I})}{W_0} = 0.0053(W_0 = 1\ g)$$
$$\nu = 9$$

To estimate relative standard uncertainty of initial volume, following equation was used.

$$u_r(V_I) = \sqrt{u_r(P_{r,I})^2 + u_r(W_{r,I})^2 + u_r(W_{n,I})^2} \quad (2)$$

Relative standard uncertainty of initial volume process ($u_r(V_I)$) was 0.0054, and effective degree of freedom was 9.48 which can be estimated by Welch-Satterthwaite equation.

$$\nu_{eff} = \frac{{u_c}^4}{\sum \frac{{u_i}^4}{\nu_i}} = 9.48 \quad (3)$$

3.2 Final volume uncertainty

Final volume uncertainty evaluation process is the same as initial volume process. The only difference is pipette capacity.

Expanded uncertainty of 10 mL pipette was 0.03 (k=2). Standard uncertainty($\mathrm{u}(P_{r,F})$) and relative standard uncertainty($u_r(P_{r,F})$) by pipette was calculated as follow.

$$\mathrm{u}(P_{r,F}) = \frac{0.015}{\sqrt{3}} = 0.0087\ mL$$
$$u_r(P_{r,F}) = \frac{u(P_{r.F})}{P_0} = 9.6 \times 10^{-4}\ (P_0 = 9\ mL)$$
$$\nu = \infty$$

Relative standard uncertainty of balance of final volume caused by resolution ($u_r(W_{r,F})$) was 8.7×10^{-6} g which can be obtained as same process of initial volume.

To calculate balance repeatability uncertainty of final volume, final volume (10 mL) was weighted 10 times and standard deviation was 0.034 g.

$$\mathrm{u}(W_{n,F}) = 0.034\ g$$
$$u_r(W_{n,F}) = \frac{u(W_{n,F})}{W_0} = 0.0034\ (W_0 = 10\ g)$$
$$\nu = 9$$

Relative standard uncertainty of final volume make-up process ($u_r(V_F)$) was 0.0035 and degree of freedom was 10.49.

$$u_r(V_F) = \sqrt{u_r(P_{r,F})^2 + u_r(W_{r,F})^2 + u_r(W_{n,F})^2} \quad (4)$$

3.3 Instrument uncertainty

While uranium concentration was measured by ICP-MS with external standard, many factors can lead to uncertainties in the determination of result of a measurement. In this study, we established instrument analysis uncertainty as three parts which consist of calibration curve, calibration solution uncertainty and repeatability.

The calibration curve can be described as follow,

$$y_i = (m \times x_i) + b \quad (5)$$

where y is the signal intensity and x is the concentration of the calibration solution.

Uranium calibration curve was made from calibration solutions of five concentrations which are 20, 40, 60, 80, 100 ng L^{-1}. The coefficient of determination of curve (R^2), slope (m) and y-intercept (b) are 0.998, 3, -13, respectively. Using this calibration curve, the urine sample collected worker of KEPCO NF was analyzed and the result of a measurement (C_x) was 89.70 ng L^{-1}.

Standard uncertainty of calibration curve using least square method can be described as below. The degree of freedom was 3.

$$\mathrm{u}(C_{cur}) = \frac{S}{m} \times \sqrt{1 + \frac{1}{n} + \frac{(x - \bar{x})^2}{S_{xx}}} = 1.994\ ng\ L^{-1}$$
$$\mathrm{S} = \sqrt{\frac{\sum_i^n {e_i}^2}{n-2}},\ S_{xx} = \sum_i^n (x_i - \bar{x})^2,\ \bar{x} = \frac{\sum_i^n x_i}{n},$$
$$e_i = y_i - (m \times x_i) - b$$

n : the number of measurements for the calibration
x : result of measurement of urine

$\bar{x}$: average concentration of calibration solution

$$u_r(C_{cur}) = \frac{u(C_{cur})}{C_x} = 0.022 \ (C_x = 89.70 \text{ ng } L^{-1})$$

$u_r(C_{cur})$: relative standard uncertainty of calibration curve

Uncertainty of calibration solution was made up of uncertainty of certified reference material (CRM). Natural uranium concentration of CRM was 1.00 μg L^{-1} and uncertainty was 0.05 μg L^{-1} which was expanded uncertainty where k=2 was the coverage factor at the 95% confidence level. Then the uncertainties of calibration solutions can be estimated as follow.

$$\mathrm{u(CRM)} = \frac{U}{k} = \frac{50}{2} = 25\ ng\ L^{-1}$$
$$\mathrm{u}(C_{20}) = \mathrm{u(CRM)} \times \frac{20}{1000} = 0.5\ ng\ L^{-1}$$
$$\mathrm{u}(C_{40}) = \mathrm{u(CRM)} \times \frac{40}{1000} = 1\ ng\ L^{-1}$$
$$\mathrm{u}(C_{60}) = \mathrm{u(CRM)} \times \frac{60}{1000} = 1.5\ ng\ L^{-1}$$
$$\mathrm{u}(C_{80}) = \mathrm{u(CRM)} \times \frac{80}{1000} = 2\ ng\ L^{-1}$$
$$\mathrm{u}(C_{100}) = \mathrm{u(CRM)} \times \frac{100}{1000} = 2.5\ ng\ L^{-1}$$
$$u_r(C_n) = \frac{u(C_n)}{C_n} \ (C_n = 20, 40, 60, 80, 100\ ng\ L^{-1})$$

$\mathrm{u(CRM)}$: standard uncertainty of CRM
$\mathrm{u}(C_n)$: standard uncertainty of calibration solution

$u_r(C_n)$: relative standard uncertainty of calibration solution

By uncertainty propagation, the uncertainty of calibration solution was calculated as follow.

$$u_r(C_{cal}) = \sqrt{u_r(C_{20})^2 + u_r(C_{40})^2 + u_r(C_{60})^2 + u_r(C_{80})^2 + u_r(C_{100})^2} = 0.025$$

Repeatability can also cause instrument analysis uncertainty. In this study, uranium check solution of 80 ng L^{-1} was analyzed 10 times in short interval. The mean value was 81.61 ng L^{-1} and the standard deviation was 2.08 ng L^{-1}. Therefore, standard uncertainty of repeatability was 2.08 ng L^{-1} and relative standard uncertainty was 0.026. Degree of freedom is 9.

$$\mathrm{u}(C_r) = 2.08\ ng\ L^{-1}$$

$$u_r(C_r) = \frac{u(C_r)}{R_0} = 0.026 \ (R_0 = 80\ ng\ L^{-1})$$

Relative standard uncertainty of instrument analysis ($u_r(I)$) was 0.042 which was estimated by combining three uncertainties as follow and effective degree of freedom was 24.39.

$$u_r(I) = \sqrt{u_r(C_{cur})^2 + u_r(C_{cal})^2 + u_r(C_r)^2} \quad (6)$$

Table 2. Analysis and evaluation of uncertainty

factor		Relative standard uncertainty	Degree of freedom	Contribution (%)
Initial volume	Pipette resolution	0.00087	∞	1
	Balance resolution	8.7×10^{-5}	∞	0
	Balance repeatability	0.0053	9	6
	Relative standard uncertainty($u_r(V_I)$)	0.0054	9.48	-
Final volume	Pipette resolution	9.6×10^{-4}	∞	1
	Balance resolution	8.7×10^{-6}	∞	0
	Balance repeatability	0.0034	9	4
	Relative standard uncertainty($u_r(V_F)$)	0.0035	10.49	-
Instrument	Calibration curve	0.022	3	27
	Calibration solution	0.025	∞	31
	Repeatability	0.026	9	30
	Relative standard uncertainty($u_r(I)$)	0.042	24.39	-
Combined standard uncertainty ($u_c(C)$)		38.43 ng L^{-1}		
Effective degree of freedom (ν_{eff})		25		
Coverage factor (k)		2		
Expanded uncertainty (U(C))		76.85 ng L^{-1}		
Relative expanded uncertainty (%)		9		

3.4 Expanded uncertainty

Table 2 presents the uncertainty factors and value to estimate expanded uncertainty for urine analysis. The combined standard uncertainty of uranium concentration analyzed by ICP-MS was 38.43 ng L^{-1} as follow.

$$\begin{aligned} &\mathrm{u(C)} \\ &= C \times \sqrt{u_r(V_I)^2 + u_r(V_F)^2 + u_r(C_0)^2} \\ &= 38.43\ ng\ L^{-1} \end{aligned}$$

$$\mathrm{C} = C_0 \times \frac{V_F}{V_I} = 897\ ng\ L^{-1}\ (V_F = 10\ mL, V_I = 1\ mL)$$

The effective degree of freedom was 25. Then expanded uncertainty was estimated as follow.

$$\mathrm{U}(C) = \mathrm{u(C)} \times \mathrm{k} = 76.85\ \mathrm{ng}\ L^{-1}$$

Therefore, uranium concentration in urine of worker was (897±77) ng L^{-1} (k=2 at the 95% level of confidence), and relative expanded uncertainty was 9%.

4. Conclusions

In the present work, we estimated uncertainty for the determination of uranium in urine by ICP-MS. We considered the uncertainty factors as three parts which were initial volume uncertainty, final volume uncertainty and instrument analysis uncertainty. Then the relative expanded uncertainty of uranium concentration in urine of worker was 9%.

From an uncertainty contribution point of view, uncertainties caused by calibration curve and ICP-MS repeatability contribute the most to expanded uncertainty.

Therefore, it is essential to maintain ICP-MS clean and use certified standard solution which has low uncertainty when making calibration curve.

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