Development of Rapid Urine Analysis Method for Uranium

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1. INTRODUCTION

In nuclear facilities where uranium compounds are treated, bioassay is useful for individual internal exposure monitoring of uranium. The inductively coupled plasma mass spectrometer (ICP-MS) has very high performance for the trace element analysis. Recently, this machine began to be used for bioassay of uranium (1, 2). The ICP-MS can detect uranium in urine with two or three orders of magnitude higher sensitivity than the ordinary method, such as a conventional fluorescence analysis (3, 4). However the bioassay using ICP-MS requires longer time than the ordinary fluorescence analysis. This is because the bioassay of uranium using ICP-MS needs some chemical separation processes due to the limit of permissible total salt concentration in sample solution. To solve this problem, a new rapid method for uranium analysis by the ICP-MS joined with flow-injection system was developed (5). The flow-injection system minimizes the amount of sample injection into ICP-MS and a matrix effect caused by dissolved substance without chemical separation processes.

Usually fresh urine sample does not contain suspended or precipitated substances, which disturb stable measurement by ICP-MS. But the urine is easy to generate suspended or precipitated substance at cool state. Only one night keeping in refrigerator, these substances are often generated in urine sample. Occasionally, these precipitated or suspended matters can not be re-dissolved sufficiently by acidification. In order to avoid the problem of suspended or precipitated substances, a digestion procedure using microwave oven was incorporated with the rapid uranium bioassay method using ICP-MS. In this paper, a sample preparation procedure, a flow-injection mechanism, a detection limit, etc. are described.

2. EXPERIMENTAL

A commercial ICP-MS (Agilent Technologies, HP-4500), flow-injection system (Agilent Technologies, G3138A), auto sampler (CETAC, ASX500) and microwave oven (OI Analytical, Model 7195) were used in the experiment. In the sample preparation procedure, a digestion step using microwave oven is the only necessary chemical treatment. In this procedure, urine samples were digested in closed vessels. Therefore, a correction of chemical yield is not necessary, so that a use of chemical yield tracer is not required.

2.1 Digestion

The purpose of the digestion process is to decompose organic matter and dissolve inorganic precipitates contained in a urine sample. The microwave oven used in this experiment has a maximum power of 950 W and can digest 10 samples at once. One of the digestion vessels can be joined with temperature and pressure sensors. Operation of the microwave oven is fully controlled by a personal computer.

Before the microwave process, nitric acid of 5 ml is added to the same amount of urine. The digestion completes by keeping temperature at 180 ºC for 20 minutes. Including cooling time, the microwave digestion procedure requires about an hour. The volumes of digested sample solutions are adjusted to 10ml by adding nitric acid prior to the measurement.

Fig. 1 Sample preparation procedure.
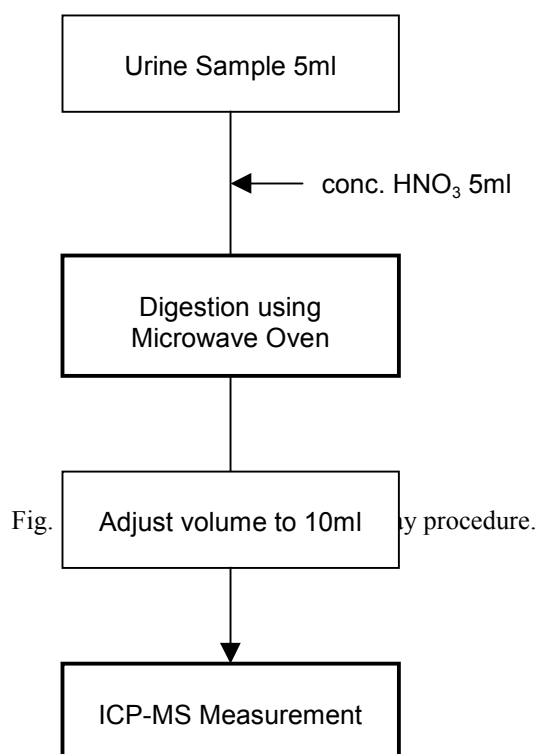
2.2   Measurement

The ICP-MS is joined to a flow-injection system and auto sampler. These instruments are fully controlled by the computer. The flow-injection system can inject a small amount of sample solution (100 μl) into ICP-MS.   Figure 2 shows the outline of flow-injection mechanism.   The sample load and injection stages are alternately changed by rotation of six-port valve. At the sample load stage, the sample solution is filled in the sample loop.   When the valve is changed to the sample injection stage, a small amount of sample solution filled in the sample loop is joined to the carrier stream.   Simultaneously with the change of the valve to sample injection stage, the ICP-MS star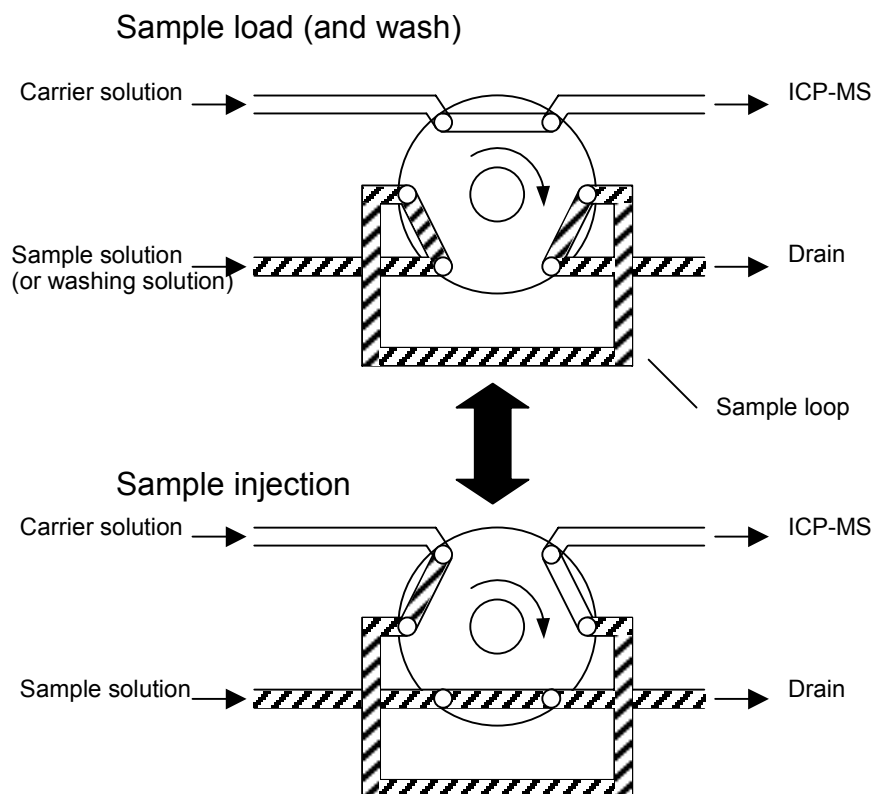ts the measurement.   The ICP-MS is operated under the condition shown in Table 1.   By a time resolved analysis, a time trend of count rate of mass 238, instead of mass spectrum, is recorded on the computer as shown in Fig. 3.   A signal of U-238 in the injected solution began to rise about 10 sec after the measurement started, reached maximum 20-25 sec after and then decreased exponentially. After the sample solution was injected to ICP-MS, the flow-injection system switches to the sample load stage.   Then the auto sampler changes the solution from the sample solution to the washing one.   After the washing of the sample loop was completed, the auto sampler starts the loading of next sample solution.   A series of measurement is automatically continued by repeating the load, inject and wash steps.

Fig. 2   Outline of flow-injection mechanism.

As an example, Fig. 4 shows the response of ICP-MS for a urine sample processed as above.   For this sample, the uranium concentration was found to be 38 ng/l.   For all measurement, including standard solutions, integrated counts for the period from 15 to 45 sec were used for calculation of uranium concentration.   The total time required for the analysis of 10 urine samples was within 4 hours. For more than 10 samples, about 1.5 hours per 10 samples may be additionally required.

Table 1   Instrument and acquisition parameters for uranium measurement with the HP4500 ICP-MS.

Instrument parameters	
RF power	1200 W
Plasma gas flow rate	15 l/min
Auxiliary gas flow rate	1.0 l/min
Carrier gas flow rate	1.2 l/min
Nebulizer type	Babington
Spray chamber temperature	2 °C
Acquisition parameters	
Acquisition mode	Time resolved analysis
Integration time	0.1 sec
Acquisition time	60 sec
Target mass number	238

3.   RESULTS AND DISCUSSION

3.1 Detection limit

A uranium detection limit defined by 3 standard deviation of the blank measurements was obtained as shown in Table 2. The detection limit of this method is sufficiently low to detect uranium in almost all the

ordinary urine sample. A calibration curve obtained from measurement of standard solutions is shown in Fig. 5. The curve has good linearity over the range from 0 to 100 ng/l.

3.2 Problem of matrix effect

Actual urine sample contains much matrix substance, which disturbs stable measurement occurring matrix effect. Therefore the urine measurement using ICP-MS without chemical separation procedure necessarily involves some matrix effect. In addition, the degree of matrix effect may vary among each sample. Generally in the ICP-MS measurement, an internal standard method is adopted to correct the matrix effect. To confirm applicability of thallium and bismuth, which is often used for high mass measurement, as an internal standard, two solutions were prepared and measured. One is the solution of nitric acid added thallium, bismuth and uranium. The other is the solution of digested urine sample added the same elements. The uranium concentration of both solutions was 300 ng/l. A uranium concentration existing originally in urine sample used for this measurement was 7.5 ng/l. The difference of uranium concentration between urine and nitric acid solution was under 3 %. The result of measurements is shown in Table 3. By the matrix effect, the U-238 counts of urine sample decreased to 75% of that of nitric acid. Unfortunately, thallium and bismuth did not monitor the matrix effect of uranium sufficiently. To correct the matrix effect exactly, the standard addition technique is known to be useful. But the technique has to prepare at least two
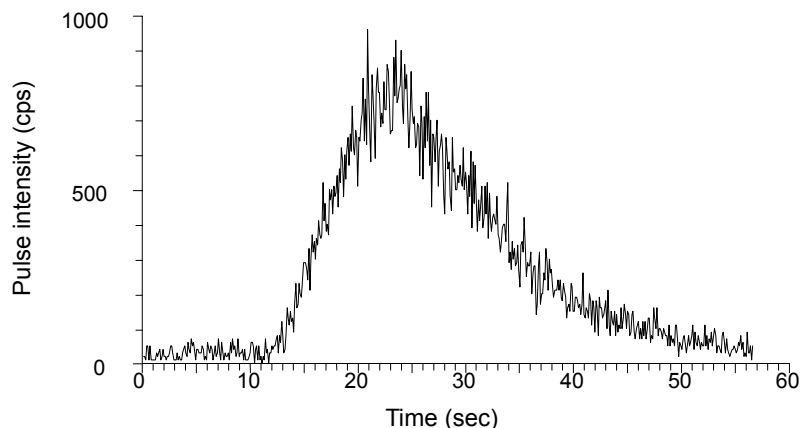

Fig.3 Response of the flow-injection system to the standard 100 ppt uranium solution.
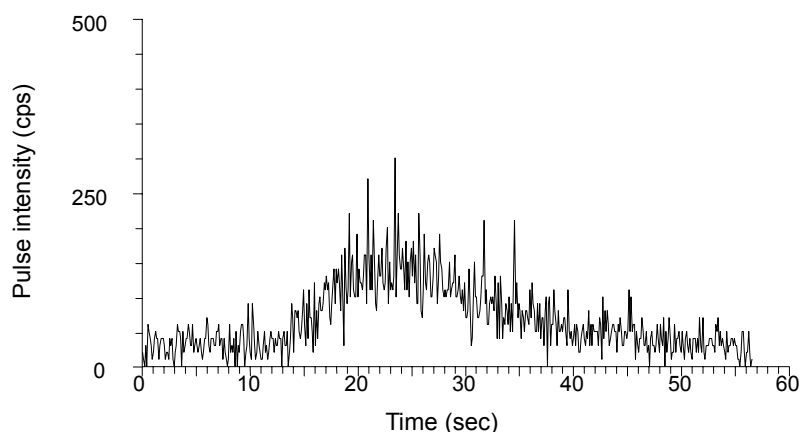

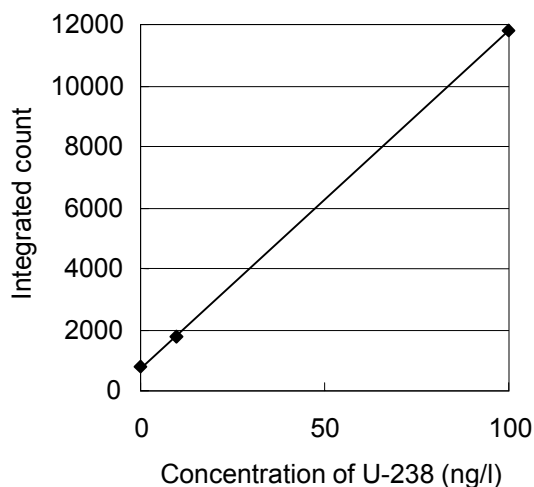Fig.4 Response of the flow-injection system to the urine sample.

Fig. 5 Calibration curve for uranium measurement by ICP-MS.

Table 2 Detection limit based on 3σ value of blank measurements (n=3).

Average integrated count	Standard deviation	Detection limit (ng-U/l-urine)
811	43.5	1.2

Table 3 Comparison of integrated count of U, Tl and Bi spiked urine and nitric acid solution.

Solution	U-238 (count)	Tl-205 (count)	Bi-209 (count)
Nitric acid (1st measurement)	16265	9145	15353
Nitric acid (2nd measurement)	15139	8823	14929
Urine sample (1st measurement)	12653	8419	27125
Urine sample (2nd measurement)	12948	8534	25737
Ratio: Urine sample/Nitric acid (average)	75%	94%	57%

solutions (normal sample solution and uranium spiked solution) for one sample.   A further study is planned about appropriate elements for the internal standard in uranium measurement.

4. CONCLUSION

The uranium bioassay method using ICP-MS and microwave oven was developed.   By the adoption of microwave digestion method, a time loss in the analysis is minimized and urine samples can be sufficiently mineralized.   This method can be applied to almost all the usual urine sample with a sensitivity of 1.2 ng/l. The flow-injection system enables simple measurement of uranium in urine without chemical separation procedures.   The incorporation of the microwave digestion step allowed the measurement of urine sample containing suspended or precipitated substances.   For 10-sample measurement, total required time of the analysis was within 4 hours.   Thallium and bismuth were not appropriate elements for the internal standard on uranium measurement.   If increasing of number of sample solutions is allowable, the standard addition technique may enable more exact measurement.

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