SHIMADZU

Speciation Analysis of Mercury in Seafood by LC-ICP-MS

Kosuke Naka[1], Yujing Jiang[1], Natsuki Iwata[1], Dominika Gruszecka[2]
(1) Shimadzu Corporation, Japan; (2) Shimadzu Scientific Instruments, USA

1. Introduction

Mercury contamination in seafood poses significant health risks to consumers. Mercury screening using ICPMS alone can provide a total concentration, however some species of mercury are more toxic to humans than others, and a total concentration may not provide adequate information and result in incomplete risk assessments. Generally, methyl mercury is more toxic than inorganic mercury and other organic mercury. Evaluating the toxicity in food requires not only analysis as total mercury but also by the form of mercury.

To address this, we propose the use of Liquid Chromatography coupled with Inductively Coupled Plasma Mass Spectrometry (LC-ICP-MS) for detailed speciation analysis of mercury by connecting an ICPMS-2040/2050 with Nexera XS inert. Furthermore, we also evaluated the automatic dilution function of the Nexera series autosampler for the speciation analysis of mercury.

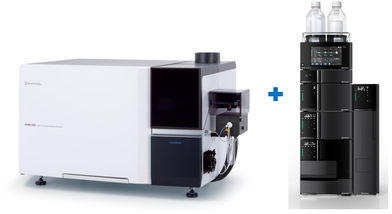

Fig. 1 LC-ICP-MS System

2. Standards and Sample Preparation

Commercially available tuna seafood was pretreated according to the U.S. Food and Drug Administration (FDA) Elemental Analysis Manual (EAM) 4.81).

Briefly, the sample was homogenized, (the mercury standard was added to the sample for spike recovery test at this time) then 25 mL extraction solution (aqueous 1 % (w/v) L-cysteine-HCl-H2O) was added before mixing. Vials were heated for 120 min at 60 °C with shaking by hand at the halfway point. Vials were cooled to room temperature. A portion of the extract was filtered through a 0.45 µm filter directly into the HPLC autosampler vial.

3. Results

Samples were analyzed with the LC-ICP-MS system, which consisted of the ICPMS-2040/2050 connected to a Nexera XS inert (Fig. 1). LabSolutions ICPMS TRM software can control the ICPMS-2040/2050 system and Shimadzu LC units, enabling everything from sample injection to chromatogram analysis to be performed via a single software program. The analytical conditions used for analysis were those included in the LC-ICP-MS Method Package for Mercury Speciation Analysis. Table 1 shows the analytical conditions for HPLC, and Table 2 shows the analytical conditions for ICP-MS.

Table 1 Analysis Conditions of HPLC

System	:	Nexera XS inert
Column*1	:	Shim-pack Scepter™ C18-120 [Metal free column] (150 mm × 4.6 mm I.D., 5 µm)
Eluent	:	0.01 mol/L Ammonium acetate (pH 7.5) : Methanol = 92 : 8
Flowrate	:	1 mL/min
Temp. of Column Oven	:	40 °C
Injection Volume	:	50 µL
Rinse Solution	:	Water
Vial*2	:	Shimadzu Vial, LC, 1.5 mL, Polypropylene

Table 2 Analysis Conditions of ICP-MS

Instrument	:	ICPMS-2040/2050
Nebulizer	:	Nebulizer DC04
Torch	:	Mini-torch
Chamber	:	Cyclone Chamber (electronically cooled)
Sampling Cone	:	Nickel
Skimmer Cone	:	Nickel
RF Power	:	1.20 kW
Sampling Depth	:	7.0 mm
Flowrate of Plasma Gas	:	9.0 L/min
Flowrate of Auxiliary Gas	:	1.10 L/min
Flowrate of Carrier Gas	:	0.85 L/min
Flowrate of Dilution Gas	:	0 L/min
Collision Gas	:	He
Flowrate of Cell Gas	:	6.0 mL/min
Cell Voltage	:	-25 V
Energy Filter	:	7 V

Fig. 2 shows the successful separation and detection of inorganic mercury, methyl mercury and ethyl mercury, each at a concentration of 0.5 µg/L.

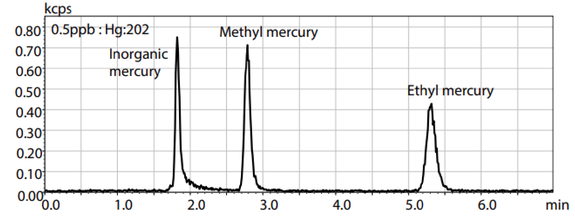

Fig. 2 Chromatogram of 0.5 µg/L Mercury

The calibration curves are shown in Fig. 3. Good linearity with a correlation coefficient of over 0.999 was obtained. The 0.2 µg/L calibration standard was analyzed 10 times to calculate the low limit of detection (LOD). The LOD of each component is shown in Table 3.

Table 3 Correlation Coefficient and LOD of Mercury

Component	Correlation coefficient	LOD (µg/L)
Inorganic mercury	0.99994	0.02
Methyl mercury	0.99996	0.01
Ethyl mercury	0.99988	0.03

4. Speciation Analysis of Mercury in Seafood

Fig. 4. shows a chromatogram of the seafood (tuna) extraction. Speciation analysis of methyl mercury and total mercury in the seafood was performed following FDA EAM 4.8. The results of the seafood analysis and spike recovery tests are shown in Table 4. Good recoveries were obtained for each component (Methylmercury 102 %, total mercury 105 %).

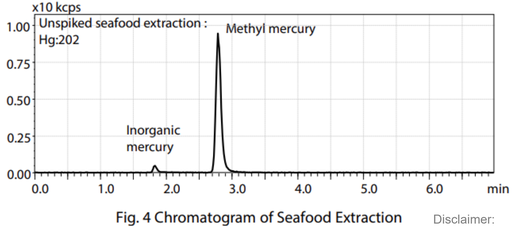

Fig. 4 Chromatogram of Seafood Extraction

Table 4 Analytical Results of Seafood

Species	Methyl mercury	Total mercury
Results in the solution (µg/L)		
Seafood (tuna)	6.16	6.48
Spike conc.	10	20
Recovery	102 %	105 %
Results in the tuna seafood (mg/kg)		
Seafood (tuna)	0.614	0.646
CODEX Standard[2)]	1.0	

Calibration curves were created using the automatic dilution function. For precision confirmation, a 1 µg/L calibration standard containing inorganic mercury, methyl mercury and ethyl mercury (prepared manually) were quantified using the calibration curve created by the automatic dilution function. Furthermore, the automatic dilution function was used to prepare a 1 µg/L standard 6 times to confirm accuracy. The correlation coefficients of the calibration curve and the accuracy and repeatability results are shown in Table 5.

Table 5Evaluation of Automatic Dilution Function

Species	Correlation coefficient	Accuracy % (Result of 1 µg/L standard)	Repeatability % RSD
Inorganic mercury	0.99976	1.02	4.0%
Methyl mercury	0.99997	1.05	1.6%
Ethyl mercury	0.99997	1.05	2.8%

4. Conclusion

Speciation analysis of methyl mercury and total mercury in seafood was performed using an LC-ICP-MS system that connected an ICPMS-2040/2050 to a Nexera XS inert according to the conditions in the “LC-ICP-MS Method Package for Mercury Speciation Analysis.” Analysis of methyl mercury and total mercury in seafood showed good spike recoveries demonstrating system suitability.