SHIMADZU
Excellence in Science

Application News

ICP Mass Spectrometer ICPMS-2040/2050 Series

Determination of Arsenic Species in Apple Juice by LC-ICP-MS Analysis

Sachiko Wakasugi and Tadashi Taniguchi

User Benefits

- Arsenic species can be analyzed using an LC-ICP-MS system.
- Enables the safety level of arsenic in food to be evaluated.
- Using a method package for analyzing arsenic species eliminates the need to register analytical conditions, etc.

■ Introduction

The natural environment contains many kinds of substances. These include hazardous substances such as arsenic. However, arsenic exists in a variety of forms, and the toxicity differs depending on the form. Generally, arsenite is more toxic than arsenate, and organic arsenic is less toxic than inorganic arsenic.

It is difficult to completely avoid arsenic in the natural environment since it is also contained in drinking water and agricultural/livestock products. The foods we eat also might contain various types of arsenic. U.S. Food and Drug Administration (FDA) sets action levels when a level of a contaminant is unavoidable, to inform industry on the level of contamination above which the FDA may regard certain foods as adulterated.[1)] For these reasons, various surveys and studies on arsenic in food products are being conducted around the world.

One method for analyzing trace quantities of arsenic with high sensitivity is ICP-MS. However, although ICP-MS can measure the total concentration of arsenic, it cannot discriminate between different forms of the element. While determining the total concentration of arsenic is important, it is also important to determine the concentrations of specific forms.

The arsenic species can be separated using a liquid chromatograph (LC). By connecting the LC unit to an ICP-MS on-line, the arsenic species can be analyzed with high sensitivity. This article describes an example of analyzing the arsenic species contained in apple juice using an LC-ICP-MS.

■ Sample

Commercially available apple juice

■ Sample Pretreatment

A 2 mL sample was measured, 0.1 mL of 100 mmol/L phosphoric acid was added, and the mixture was diluted with 0.15 mol/L nitric acid solution to make 10 mL.

■ Calibration Curve Sample

0.1 mL of 100 mmol/L phosphoric acid was added to accurately measure standard samples of arsenite (As III), arsenate (As V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and arsenocholine (AsC) and the mixtures were diluted with 0.15 mol/L nitric acid solution to make 10 mL.

■ Mobile Phase Preparation

10 g of methanol was measured and placed in a 1 L bottle. Then about 900 mL of purified water, 1 mL of 98 wt% formic acid, and 1 mL of a 25 % tetramethylammonium hydroxide solution were added and diluted with purified water to make 1 L.

■ Column Stabilizer Solution

About 900 mL of purified water was added to a 1-L bottle, and then 0.85 mL of 98 wt% formic acid was added. 0.115 mL of 85 wt% phosphoric acid was added, and the mixture was diluted with purified water to make 1 L.

ICPMS-2040/2050 Series　　Nexera™ Series

Fig. 1 LC-ICP-MS System Components

■ Analytical Conditions

Samples were analyzed with an LC-ICP-MS system, which consisted of an ICPMS-2040/2050 series ICP Mass Spectrometer connected to a Nexera™ series HPLC system (Fig. 1). Using LabSolutions™ ICPMS TRM software, the ICPMS system can control Shimadzu LC units. This enables 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 Arsenic Speciation Analysis Type 2.

For new columns, stable analysis is enabled by introducing a column stabilizer solution through the column for at least 2 hours.

Table 1 shows the analytical conditions for LC, and Table 2 shows the analytical conditions for ICP-MS.

Table 1 LC Analytical Conditions

Instrument:	Nexera Series
Column:	Sigma-Aldrich Discovery HS F5 (250 mm × 4.6 mm I.D., 5 µm)
Guard Column:	Shim-pack™ GIST (G) [Metal free] (10 mm × 3.0 mm I.D., 5 µm)
Mobile Phase:	0.1 % Formic acid (including 1 % methanol and 0.025 % tetramethylammonium hydroxide solutions)
Mobile Phase Flowrate:	0.75 mL/min
Column Oven Temp.:	40 °C
Injection Volume:	10 µL
Analysis Time per Sample:	6 min

Table 2 ICP-MS Analytical Conditions

Instrument:	ICPMS-2040
RF Power:	1.2 kW
Plasma Gas Flowrate:	9 L/min
Auxiliary Gas Flowrate:	1.1 L/min
Carrier Gas Flowrate:	0.85 L/min
Nebulizer:	Nebulizer DC04
Chamber:	Cyclone Chamber (electronically cooled)
Plasma Torch:	Mini-Torch
Collision Gas:	He

■ Analysis

Arsenite (As III), arsenate (As V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and arsenocholine (AsC) were quantitated by the calibration curve method.

A sample for spike-and-recovery testing was prepared to validate analysis values by spiking the measurement solution with a standard solution of each arsenic species that results in 1 µg/L concentrations and then analyzing that solution.

A calibration curve sample solution with a minimum concentration of 0.2 µg/L was measured 10 times to determine the standard deviation. Then the lower limit of detection was calculated as the concentration that gave a signal three times the standard deviation.

■ Results

Chromatograms for each arsenic species measured from the 1 µg/L solution and the actual sample are shown in Fig. 2. Calibration curves for each arsenic species are shown in Fig. 3.

Quantitative analysis results are shown in Table 3. Those results indicate that the minimum concentration detectable (lower limit of detection) in the measurement solution (3σ) is lower than 0.1 µg/L, which confirms that the system offers sufficient sensitivity for detecting trace quantities of arsenic species.

Spike recovery rates for each arsenic species were also good, ranging from 101 to 106 %.

■ Conclusion

This study confirmed that the LC-ICP-MS system can be used to analyze arsenic species in apple juice spiked with arsenic and pretreated simply by dilution.

And this result is below the action level of 10 µg/kg for inorganic arsenic set by The Food and Drug Administration's (FDA) and this apple juice is generally considered safe.[2)]

Reference Documents

1) FDA Issues Final Guidance to Industry on Action Level for Inorganic Arsenic in Apple Juice
https://www.fda.gov/food/cfsan-constituent-updates/fda-issues-final-guidance-industry-action-level-inorganic-arsenic-apple-juice (June 8, 2023.)

2) Guidance for Industry: Action Level for Inorganic Arsenic in Apple Juice
https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-action-level-inorganic-arsenic-apple-juice(June 8, 2023.)

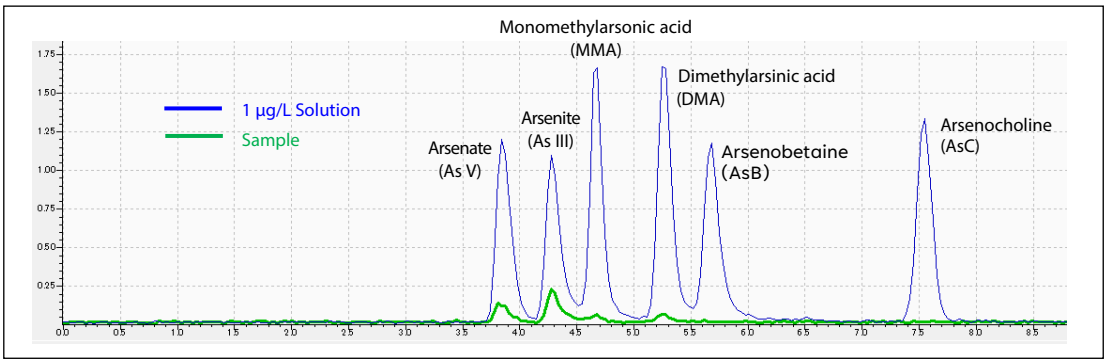


Fig. 2 Chromatograms for Each Arsenic Species Measured from 1 µg/L Solution and Actual Sample

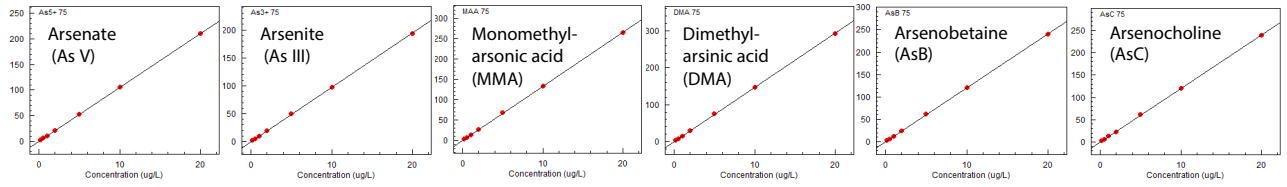


Fig. 3 Calibration Curves

Table 3 Quantitation Results

Arsenic Species	Arsenate (As V)	Arsenite (As III)	Monomethylarsonic acid (MMA)	Dimethylarsinic acid (DMA)	Arsenobetaine (AsB)	Arsenocholine (AsC)
Concentration in Measurement Solution (µg/L)						
Apple Juice	0.08	0.18	0.02	0.02	N.D.	N.D.
Spiked Sample	1.11	1.24	1.05	1.02	1.04	1.02
Spike Recovery Rate (%)	103	106	102	101	104	102
Lower Limit of Detection (3σ)	0.02	0.02	0.02	0.02	0.03	0.04
Concentration in Sample Stock Solution (µg/L)						
Apple Juice	0.4	0.9	0.1	0.1	N.D.	N.D.

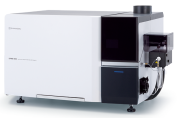
N.D.: Less than the lower limit of detection
Lower Limit of Detection (3σ) = 3 × (Standard Deviation from 10 Measurements of 0.2 µg/L Solution) × Calibration Curve Slope
Spike Recovery Rate (%) = (Quantitation Value of Spiked Sample - Quantitation Value of Unspiked Sample) / Spike Concentration × 100

01-00802-EN First Edition: Sep. 2024

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/

› Please fill out the survey

Related Products Some products may be updated to newer models.



› ICPMS-2040 Series / ICPMS-2050 Series
Inductively Coupled Plasma Mass Spectrometry

› Nexera series
Ultra High Performance Liquid Chromatograph

› LC-ICP-MS

Related Solutions

› Food and Beverages

› Heavy Metals

› Environment

› Water

› Price Inquiry

› Product Inquiry

› Technical Service / Support Inquiry

› Other Inquiry