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Application News

Inductively Coupled Plasma Mass Spectrometer

raBit

Determination of Elemental Impurities in Bioethanol Using ICP-MS

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User Benefits

- Bioethanol samples can be directly injected into ICP-MS for analysis.
- Trace elements can be accurately determined with high sensitivity.

Introduction

To achieve carbon neutrality, bioethanol is expected to be one of the alternative energy sources to fossil fuels. First-generation bioethanol, produced mainly from corn, sugarcane, and similar crops, has been widely used. However, to avoid competition with food supplies, research and development are also advancing on second-generation bioethanol produced from non-food raw materials such as cellulosic materials. For example in Japan, seven companies including Toyota Motor Corporation have formed the raBit (Research Association of Biomass Innovation for Next Generation Automobile Fuels) to advance technologies for next-generation bioethanol. Shimadzu is also participating as a supporting member to promote R&D through technical cooperation for analysis.

Fuels in which bioethanol is blended into gasoline are referred to as E5 (up to 5% bioethanol), E10 (up to 10% bioethanol), etc.; using these fuels in vehicles can reduce environmental impact. At the same time, ethanol blended into gasoline and used as a fuel is required to meet trace element concentration limits (e.g., for copper) specified in standards such as ASTM D4806[1)] and EN 15376[2)]. ICP-OES is commonly used for these analyses, but when ultra-trace impurity levels must be measured, higher-sensitivity ICP-MS is more suitable.

In this Application, trace elements in first-generation and second-generation bioethanol were determined using the ICPMS-2050 (Fig. 1). Spike recoveries were also evaluated to confirm the validity of the analytical results.

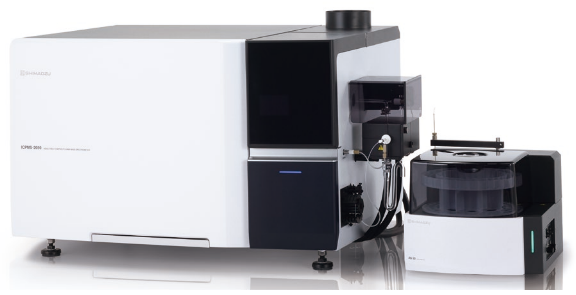

Fig. 1 ICPMS-2050 and AS-20

Samples

A first-generation bioethanol product, and three second-generation bioethanol products, which were produced by raBit, were used as samples.

Preparation of Samples and Standards

- Sample Preparation

As internal standards, commercially available Sc, Ga, and Bi standard solutions were mixed into the samples, and nitric acid was added to reach 0.5 w/w%. The concentrations of Sc and Ga in the samples are 0.2 mg/kg, and Bi is 0.02 mg/kg. For spike-recovery testing, samples spiked with standards were prepared in the same way.

- Calibration Standards

Single-element standard solutions (Na, Si, P, Ca, Mn, Fe, Cu, Zn, Pb) were diluted and mixed in electronic-grade ethanol to prepare the calibration standards. For each calibration standard, the internal standard elements (Sc, Ga, Bi) and nitric acid were added so that their concentrations matched those in the analytical samples. The concentrations of each element in the calibration standards are shown in Table 1.

Configurations and Analytical Conditions

Table 2 shows the configuration of the ICP-MS. The "Organic Solvent Injection System" was used as the introduction system. By utilizing a platinum sampling cone, damage to the cone from prolonged exposure to organic solvents can be minimized.

Table 3 shows the analytical conditions. To prevent the precipitation of carbon from the organic solvent in the interface, a mixed gas of argon (70 %) and oxygen (30 %) was introduced into the quadrupole structure organic solvent torch.

Table 2 ICP-MS System Configuration

Instrument	:	ICPMS-2050
Nebulizer	:	Nebulizer DC04
Chamber	:	Cyclone Chamber
Torch	:	Organic Solvent Torch
Sampling Cone	:	Platinum
Skimmer Cone	:	Nickel
Auto Sampler	:	AS-20 (Rinse station for organic solvents)
Peristaltic Pump Tubing	:	I.D. 0.64 mm for sample*1 (materials: Tygon MH)

I.D.: Internal Diameter
*1 P/N: 018-31558-32

Table 1 Concentrations in Calibration Standards

Elements	Calibration Standards (mg/kg)			
	STD0	STD1	STD2	STD3
Na, Si, P, Ca, Mn, Fe, Cu, Zn, Pb	0	0.1	0.5	1
Sc, Ga	0.2			
Bi	0.02			
HNO3	0.5 w/w%			

Table 3 Analytical Conditions

RF Power	: 1.60 kW	
Sampling Depth	: 8.0 mm	
Plasma Gas Flowrate	: 20.0 L/min	
Auxiliary Gas Flowrate	: 0.50 L/min	
Carrier Gas Flowrate	: 0.55 L/min	
Dilution Gas Flowrate	: 0 L/min	
Ar-O_2 Mixed Gas Flowrate	: 0.35 L/min	
Chamber Temperature	: -5 ˚C	
Pump Rotation Speed	: 28 r.p.m. (Low) / 60 r.p.m. (High)	
Cell Gas	: He	H_2
Cell Gas Flowrate (mL/min)	: 6.0	7.0
Cell Voltage (V)	: -35	-30
Energy Filter (V)	: 7.0	7.0

■ Spike Recoveries and Quantitative Results

Calibration curves (Fig. 2) were made using the standards listed in Table 1. As shown in Table 4, all calibration curves for the analytes showed excellent correlation coefficients of 0.999 or greater.

Spike recoveries were evaluated using one second-generation bioethanol sample to confirm the validity of the analytical results. The results are presented in Table 4. Good recoveries in the range of 100–105% were obtained, demonstrating that bioethanol can be introduced directly into the ICPMS-2050 and analyzed accurately.

The quantitative results for the bioethanol samples are shown in Table 5. All elements were quantified at ultra-trace levels in the ng/kg to µg/kg range, confirming that the bioethanol samples meet quality expectations.

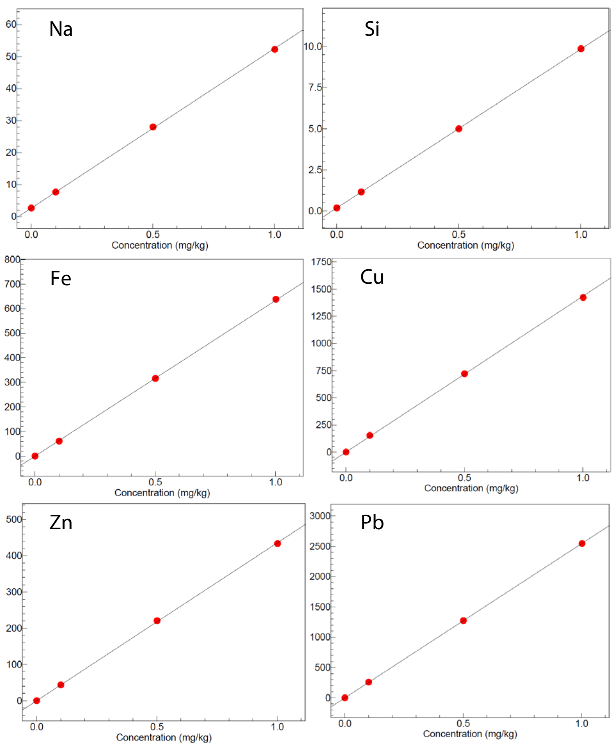

Fig. 2 Calibration Curves of Several Analytes
Vertical Axis: Intensity Ratio, Horizontal Axis: Concentration (mg/kg)

Table 4 Correlation Coefficient, Detection Limit and Spike Recovery

Element	Cell Gas	Internal Standard	Correlation Coefficient	IDL (mg/kg)	Spike Conc. (mg/kg)	Recovery (%)
^{23}Na	H_2	^{45}Sc	0.99994	0.002	0.503	105
^{28}Si	H_2	^{45}Sc	0.99999	0.0009	0.503	104
^{31}P	He	^{45}Sc	0.99997	0.003	0.503	102
^{40}Ca*	H_2	^{45}Sc	0.99996	0.0002	0.503	105
^{44}Ca	H_2	^{45}Sc	0.99992	0.0009	0.503	103
^{55}Mn	H_2	^{45}Sc	0.99994	0.00001	0.503	102
^{56}Fe	H_2	^{45}Sc	0.99993	0.00007	0.503	102
^{63}Cu	He	^{71}Ga	0.99982	0.00004	0.503	100
^{66}Zn	He	^{71}Ga	0.99996	0.00002	0.503	100
^{208}Pb	He	^{209}Bi	0.99999	0.000003	0.503	100

IDL (Instrument Detection Limit) : 3σ (Standard Deviation of STD0) × Slope of Calibration Curve
Recoveries (%) : (Spiked Sample – Unspiked Sample) / Spike Conc. ×100
* : Analysis of Ca with a mass number of 40 is permitted exclusively in LabSolutions ICPMS Ver2.10 and later.

Table 5 Quantitative Results

Element	Quantitative Result of Bioethanol (mg/kg)			
	First-Generation	Second-Generation A	Second-Generation B	Second-Generation C
^{23}Na	0.087	0.014	0.046	0.017
^{28}Si	0.009	0.044	0.022	0.023
^{31}P	N.D.	N.D.	N.D.	N.D.
^{40}Ca*	0.0016	0.0031	0.0028	0.0023
^{44}Ca	0.001	0.003	0.002	0.002
^{55}Mn	N.D.	0.00061	0.00012	0.00009
^{56}Fe	N.D.	0.00050	0.00012	N.D.
^{63}Cu	0.00008	0.00780	0.00633	0.00919
^{66}Zn	N.D.	0.00399	0.00161	0.00139
^{208}Pb	0.000011	0.000009	0.000006	0.000008

* : Analysis of Ca with a mass number of 40 is permitted exclusively in LabSolutions ICPMS Ver2.10 and later.
N.D.: Not Detected

■ Conclusion

In this Application, bioethanol was introduced directly into the ICPMS-2050 using an organic solvent introduction system to determine trace elements. Good spike recoveries were obtained, demonstrating that bioethanol can be analyzed accurately by direct injection.

<Acknowledgements>

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<References>

1) ASTM D4806-21 Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
2) EN 15376 Automotive fuels - Ethanol as a blending component for petrol - Requirements and test methods

<Related Applications>

1. Determination of Elemental Impurities in Petroleum Distillates Using ICP-MS ~ASTM D8110-17~ Application News No. 01-00922A
2. Determination of Organic Impurities in Bioethanol Using JIS K2190 Application News No. 01-01074
3. Analysis of Chloride and Sulfate Ions in Fuel Ethanol Application News No. 01-00265

01-01021-EN First Edition: Apr. 2026

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