

Analysis of Wastewater for Cd, Mn, Pb and Zn using the MH-5000 Ultra Compact Elemental Analyzer

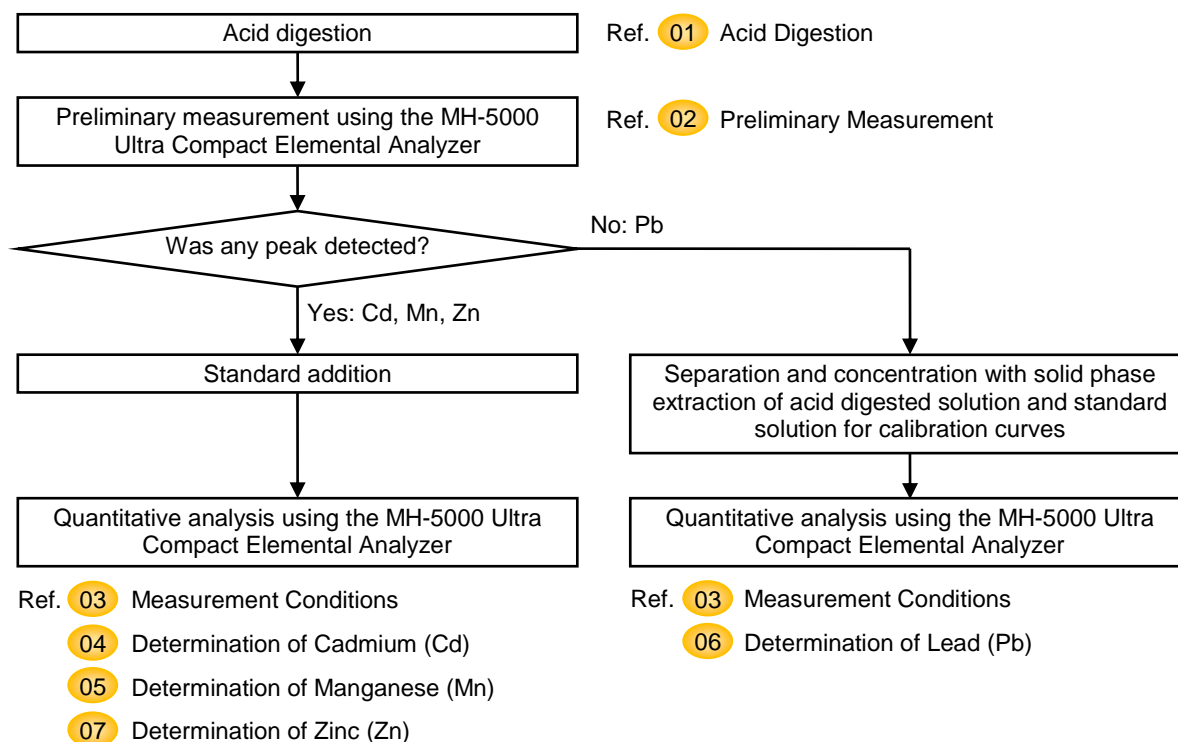
Introduction

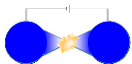
This application note describes an analytical method of the determination for Cd, Mn, Pb and Zn in certified reference material of wastewater specified by Water Pollution Control Law using the MH-5000 Ultra Compact Elemental Analyzer.

Procedure

A wastewater certified reference material (EU-H-3, 'Water, Waste, High Level, Concentrate' *EnviroMAT*TM Certified Reference Materials, SCP SCIENCE) was used to evaluate the accuracy of the method. This CRM was diluted 50-fold with water.

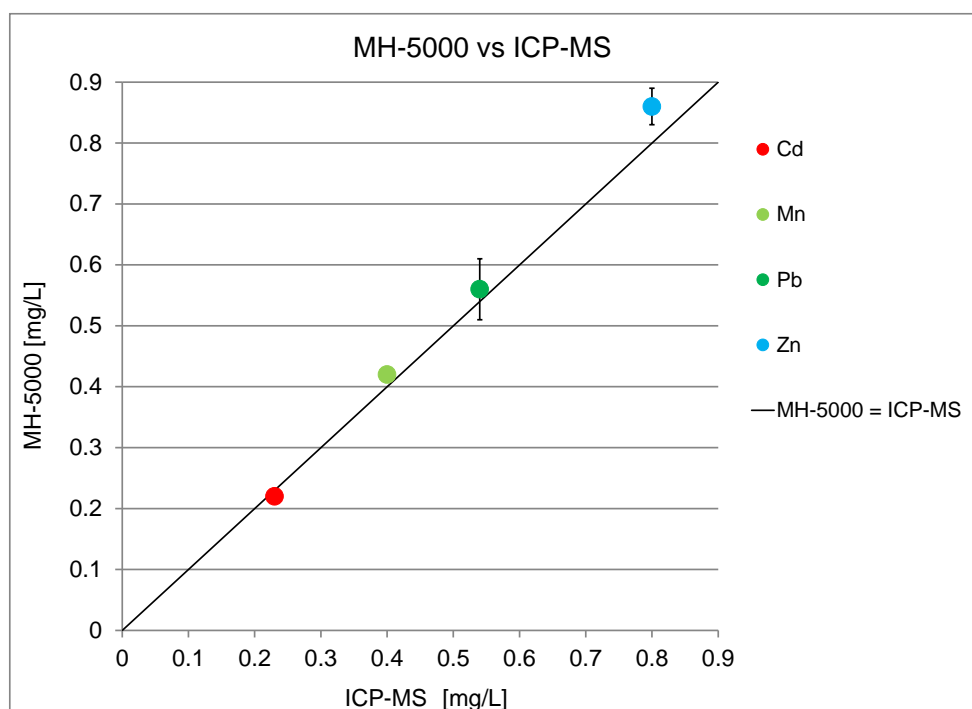
Following figure shows the procedure of analysis:






Results

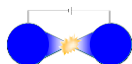
The measurement results were compared with that of ICP-MS certified by the accredited measurement laboratory to guarantee accuracy of the MH-5000.



	(mg/L)	
	ICP-MS	MH-5000
Cd	0.23	0.22 ± 0.01
Mn	0.40	0.42 ± 0.01
Pb	0.54	0.56 ± 0.05
Zn	0.80	0.86 ± 0.03

Refer to the following sections for further information.

- 04 Determination of Cadmium (Cd)
- 05 Determination of Manganese (Mn)
- 06 Determination of Lead (Pb)
- 07 Determination of Zinc (Zn) 



01

Acid Digestion

Acid digestion was performed in accordance with Section 5.2, Decomposition by hydrochloric acid or nitric acid, Chapter 5 of the Testing methods for industrial wastewater, K 0102:2013, the Japanese Industrial Standards.

Reagents: Following acids were used depending on the compatibility with target elements.

Product Name	Grade	Specification	Manufacturer
Nitric acid 1.38	For atomic absorption spectrometry	60 - 61% (T)	KANTO CHEMICAL CO., INC.
Hydrochloric acid	For atomic absorption spectrometry	35.0 - 37.0% (T)	KANTO CHEMICAL CO., INC.

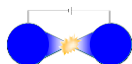
Instrument: Heating block (*Digi* PREP CUBE)

Apparatus: Disposable digestion tube (*Digi* TUBEs 65 mL), disposable watch glass, 20 mL measuring flask, beaker and piston pipette

Procedure:

- 1) 20 mL of 50-fold diluted solution was poured into a digestion tube.
- 2) 1 mL of either acid was added to the solution.
- 3) The digestion tube was inserted into the heating block and disposable watch glass was placed on it.
- 4) The solution was heated at a preset temperature of 95°C for 4 hours.
- 5) The digestion tube was allowed to cool to room temperature and then the solution was diluted to 20 mL with water.

Note: A sufficient amount of acid digested solution depending on the concentration rate is required for solid phase extraction. ●



02

Preliminary Measurement

The acid digested solution was preliminary measured.

Sample: Acid digested solution diluted to 20 mL

Acid digested water as a blank

Cuvettes: LepiCuve-C, quartz cuvette

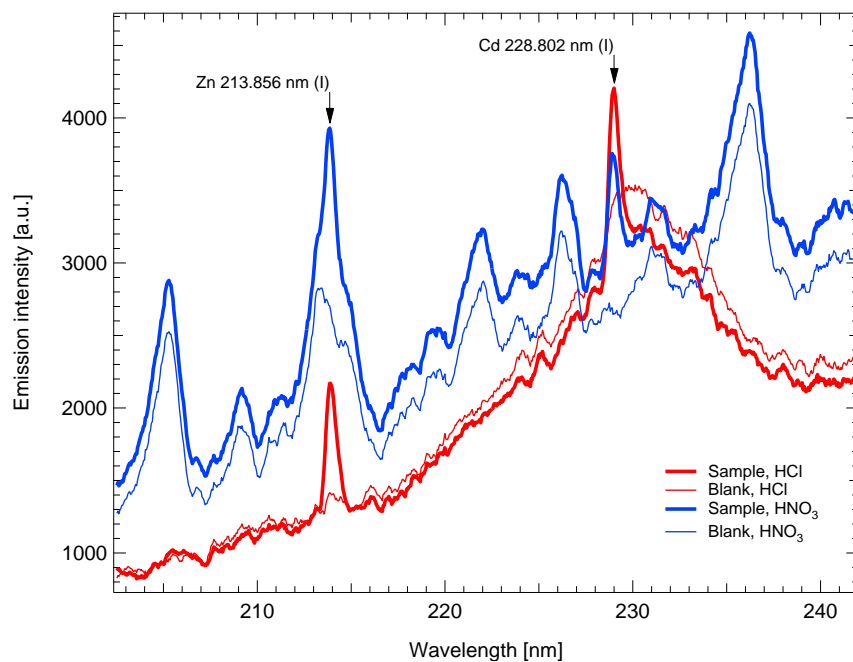
Instrument model and parameters were determined from wavelengths of emission lines.

Preliminary measurement of Cd, Zn and Mn

Instrument model: MH-5000 s2035

Instrument parameters: 750 V, (ON: 2 ms / OFF: 50 ms) × 70 pulses

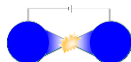
Spectra around emission lines of Cd and Zn



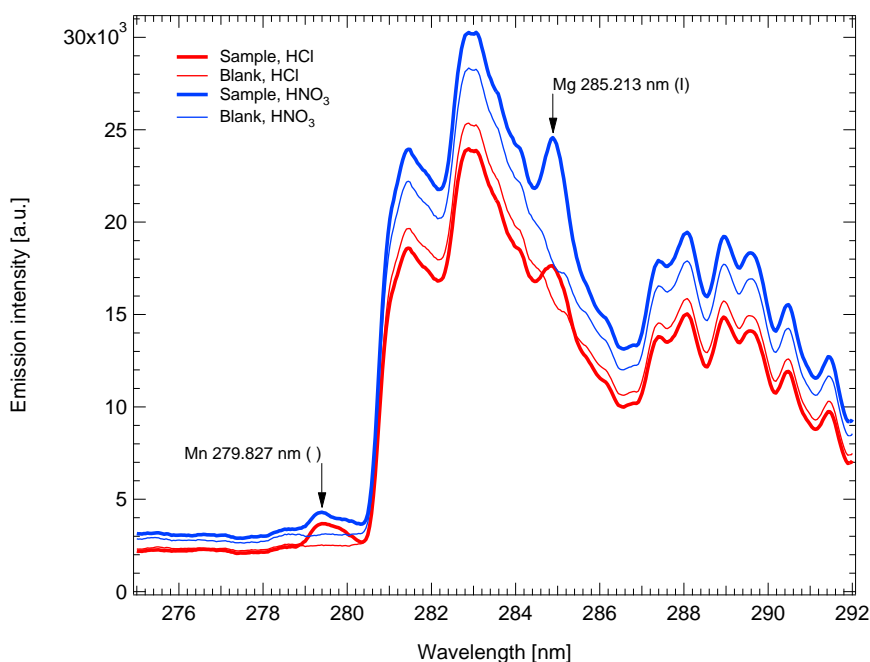
Acid selection

Cd: The 228.802 nm cadmium line was detected between other solvent peaks in the nitric acid digested solution. It was overlapped by peaks in the hydrochloric acid digested solution, thereby using the nitric acid digested solution for determination of cadmium.

Zn: The 213.856 nm zinc line was overlapped with solvent peaks in the nitric acid digested solution. It was distinctly detected in the hydrochloric acid digested solution, thereby using the hydrochloric acid digested solution for determination of zinc.



Spectra around emission lines of Mn

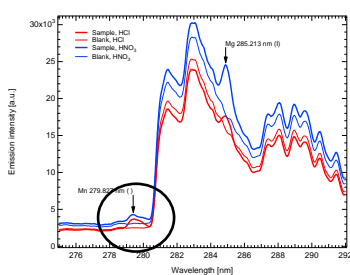


Acid selection

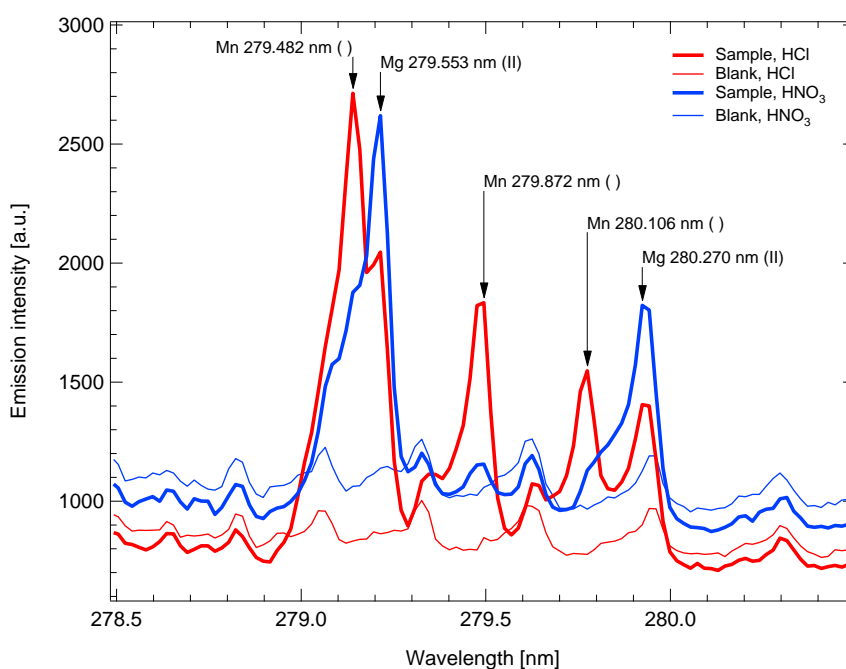
The emission lines of manganese and magnesium contained within the solution were both located near 280 nm. It was detected higher manganese peaks and lower magnesium peaks in the nitric acid digested solution. In contrast, it was detected lower manganese peaks and higher magnesium peaks in the hydrochloric acid digested solution, thereby using hydrochloric acid digested solution for the determination of manganese.

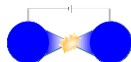
Reference information

The spectra were made a clear distinction between hydrochloric acid and nitric acid digested solution from the measurement around 280 nm with high-performance spectrometer.



Measurement around 280 nm with high-performance spectrometer



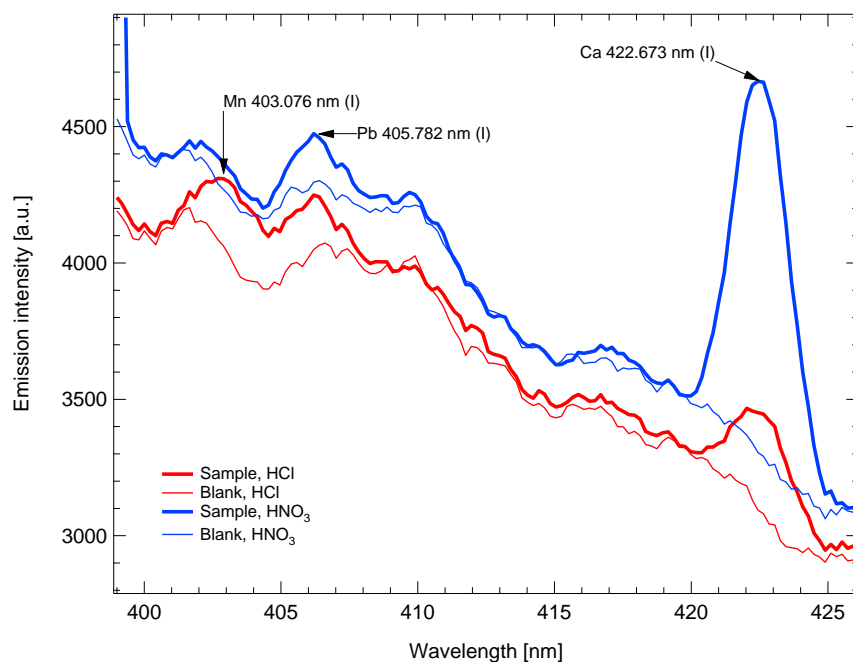


Preliminary measurement of Pb

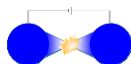
Instrument model: MH-5000 s2086

Instrument parameters: 700 V, (ON: 2 ms / OFF: 50 ms) × 40 pulses

Spectra around emission lines of Pb



A slight 405.782 nm lead line was detected in each hydrochloric and nitric acid digested solution. The 403.076 nm manganese line was located near the line. Separation and concentration with solid phase extraction were needed for the determination of lead. ●



03

Measurement Conditions

Instrument models and parameters

The following table describes measurement conditions suitable for each element. The instrument model was selected from the wavelength of emission lines. Instrument parameters were determined from wavelength of emission lines and solvent.

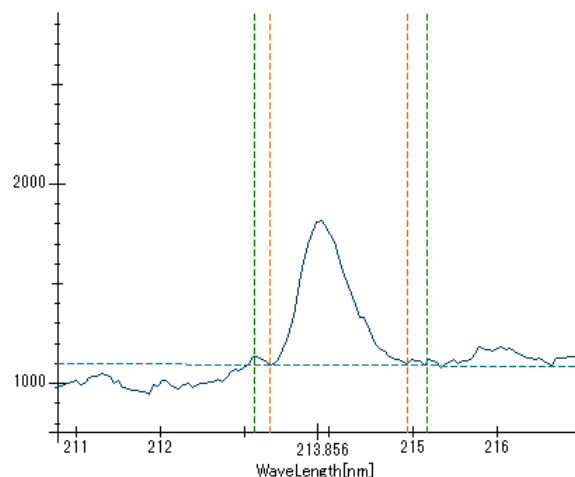
	Wavelength (nm)	Model	Solvent	Instrument parameters
Cd	228.802	s2035	Nitric acid digested solution 0.65 mol/L HNO ₃	750 V, (ON: 2 ms / OFF: 50 ms) x 70 pulses
Mn	279.827	s2035	Hydrochloric acid digested solution 0.56 mol/L HCl	750 V, (ON: 2 ms / OFF: 50 ms) x 70 pulses
Pb	368.347	s2086	The eluate of solid phase extraction 0.03 mol/L EDTA - THAM with the addition of the same amount of 0.03 mol/L EDTA - NH ₄	1000 V, (ON: 3 ms / OFF: 50 ms) x 15 pulses
Zn	213.856	s2035	Hydrochloric acid digested solution 0.56 mol/L HCl	750 V, (ON: 2 ms / OFF: 50 ms) x 70 pulses

Following sections describe two important functions on the LepiSuite LEP_Analyzer particularly for quantitative analysis.

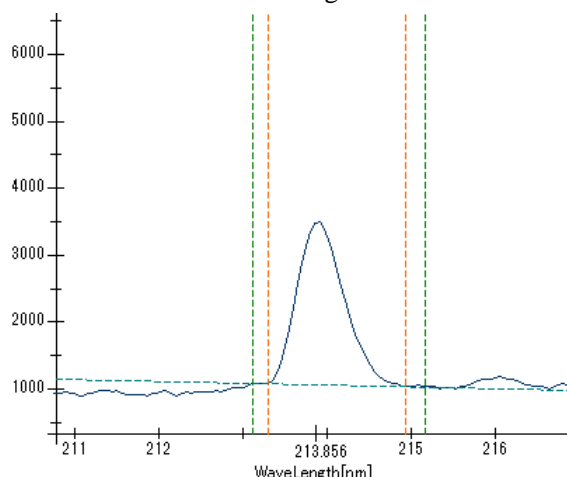
Baseline correction

Baseline correction is required for calculation of the emission intensity. The emission intensity is verified at several concentrations after measurement to allow the baseline to be adjusted as needed.

E.g. Without addition of Zn



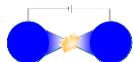
With the addition of 16 mg/L Zn

*Postprocessing*

Following picture shows the settings of postprocessing on the LepiSuite Analyzer. When the Group Count was set to 5, five raw data was treated as one group, thereby performing 15 iterative measurements as three groups.



Concentration of the target element was calculated from the calibration curves obtained by the average and the standard deviation of three groups (n = 3). ●



04

Determination of Cadmium (Cd)

Acid digested solution was directly used for quantitative analysis. The standard addition method was used to prevent effects of coexistence elements. The use of zinc for internal standard substance provided more accuracy of determination.

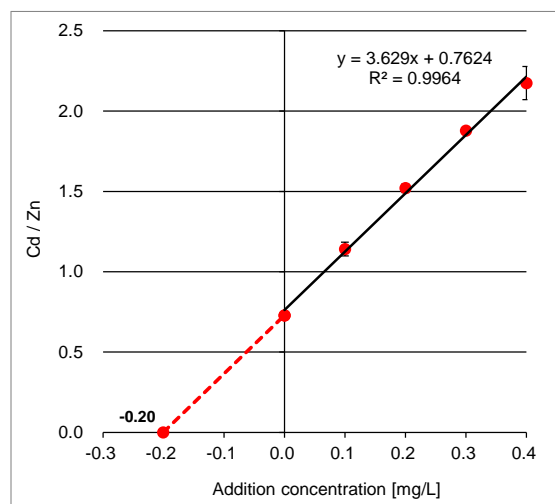
Pretreatment

Acid digestion Ref. **01** Acid Digestion

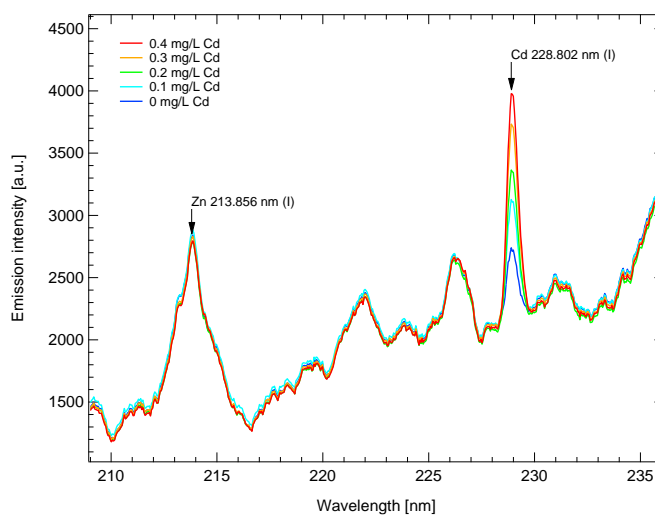
Measurement conditions and results

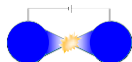
Sample: 90 v/v% acid digested solution, 0 - 0.4 mg/L Cd as the standard
Instrument model: MH-5000 s2035
Cuvette: LepiCuve-C, quartz cuvette
Instrument parameters: 750 V, (ON: 2 ms / OFF: 50 ms) × 70 pulses
Emission line of target element: Cd 228.802 nm (I)
Emission line of internal standard substance: Zn 213.856 nm (I)
Calculated concentration: 0.22 ± 0.01 mg/L Cd (97% of ICP-MS)

Calibration curves



Spectra





05

Determination of Manganese (Mn)

Acid digested solution was directly used for quantitative analysis. The standard addition method was used to prevent effects of coexistence elements.

Pretreatment

Acid digestion Ref. 01 Acid Digestion

Measurement conditions and results

Sample: 90 v/v% acid digested solution, 0 - 0.8 mg/L Mn as the standard

Instrument model: MH-5000 s2035

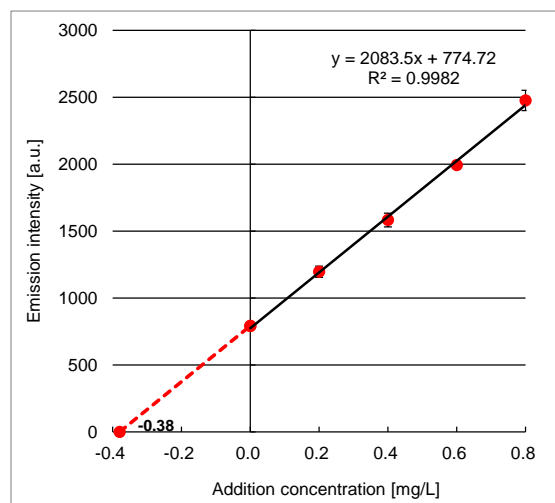
Cuvette: LepiCuve-C, Quartz cuvette

Instrument parameters: 750 V, (ON: 2 ms / OFF: 50 ms) × 70 pulses

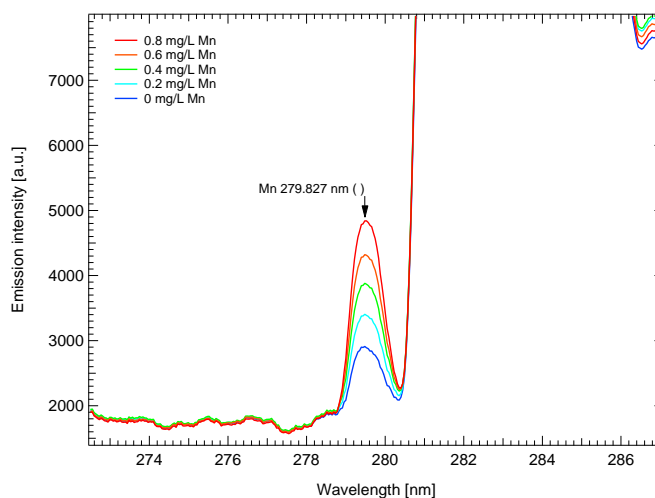
Emission line of target element: Mn 279.827 nm ()

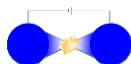
Calculated concentration: 0.42 ± 0.01 mg/L Mn (106% of ICP-MS)

Calibration curves



Spectra





06

Determination of Lead (Pb)

Acid digested solution was used by separating and concentrating for quantitative analysis. The use of solid-phase extraction cartridge of Msep Pb(A)-Pin enables selective trapping of lead out of multiple metals, thereby using the absolute calibration curve method, which was less affected by coexistence elements.

Pretreatment

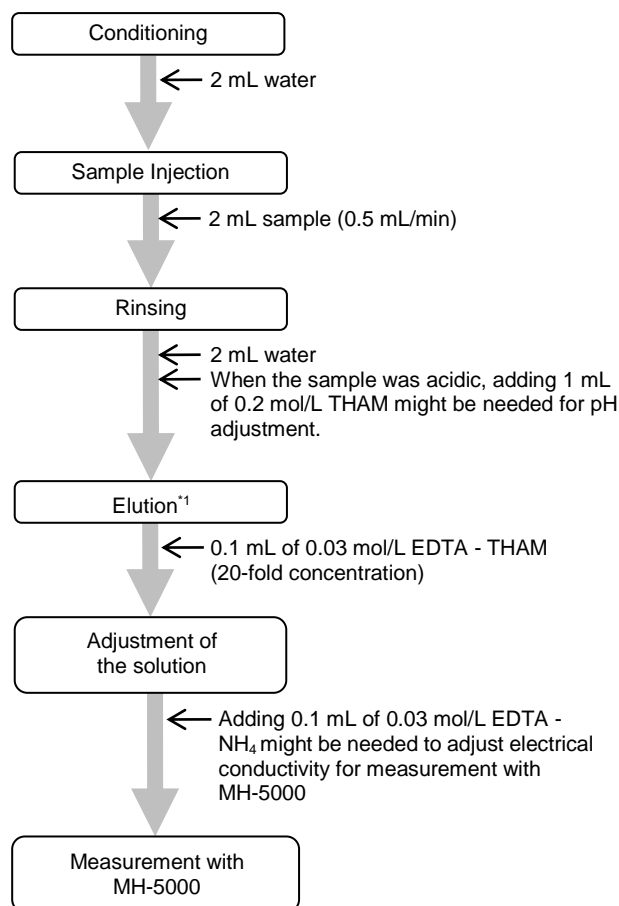
Acid digestion Ref. **01** Acid Digestion

Solid phase extraction

Resin: Msep Pb(A)-Pin

Sample: (1) Acid digested solution
(2) Pb standard solution

Procedure:



Composition of solution used for rinsing, elution, and adjusting electrical conductivity

0.2 mol/L THAM

2.42 grams of tris (hydroxymethyl) aminomethane, THAM, MW: 121.14 was dissolved in water to make exactly 100 mL of solution.

0.03 mol/L EDTA - THAM

0.88 grams of ethylenediaminetetraacetic acid, EDTA, MW: 292.24 and 1 mol/L THAM* 40 mL were dissolved in water to make exactly 100 mL of solution

* 1 mol/L THAM

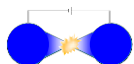
12.1 grams of tris (hydroxymethyl) aminomethane, THAM, MW: 121.14 was dissolved in water to make exactly 100 mL of solution.

0.03 mol/L EDTA - NH₄

0.88 grams of ethylenediaminetetraacetic acid, EDTA, MW: 292.24 and 6 mL of ammonia buffer solution (pH10)** were dissolved in water to make exactly 100 mL of solution

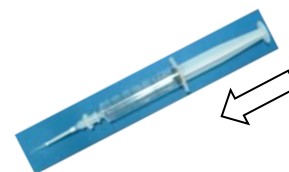
** ammonia buffer solution (pH10)

67.7 grams of ammonium chloride was dissolved in 572 mL of ammonia water 25%



*1 Treat carefully for steady elution of the target element trapped by resin.

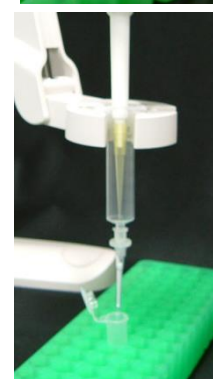
- 1) Remove as much of the residual water as possible by drawing a vacuum from the solid-phase extraction cartridge.



- 2) Insert the tip of solid-phase extraction cartridge to the reservoir.



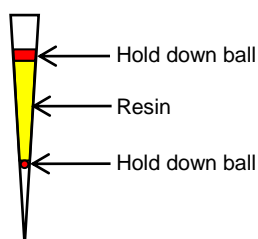
- 3) Drop the 0.1 mL of 0.03 mol/L EDTA - THAM into the cartridge.



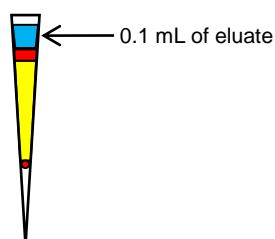
- 4) Insert a tip of piston to a syringe slowly.



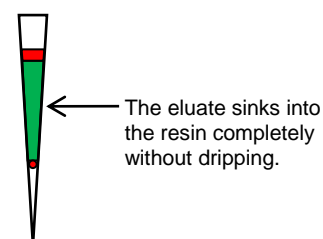
- 5) Withdraw the piston and allow it to soak for a minute, after the eluate sinks into the resin.



This figure was colored for the purpose of illustration. The color of hold down balls and resins are actually white.



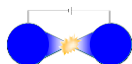
Immediately after injection of eluate



Withdraw the piston and allow it to soak for a minute, after the eluate sinks into the resin.

Note: In case the tip was injected suddenly or was left inside the cartridge, the eluate might drip out immediately without eluting target elements.

- 6) Reinsert the tip of piston to a syringe slowly.



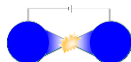
- 7) Adjust the piston to give one drop every 5 to 10 seconds.
- 8) Force the air several times to remove remaining eluate off the cartridge after dripping.

Note: Pay attention to the potassium content of the sample, because the Msep Pb(A)-Pin of solid phase extraction also undesirably traps potassium except for lead.

This is a typical procedure, which the concentration of potassium is 100-fold higher than that of lead. When the concentration of potassium is less than that of lead, adjustment of the solution may be skipped by using other eluates.

Concentration of potassium (K) compared to that of lead (Pb)	1 - 1000 fold	Less than 1
Eluate	0.03 mol/L EDTA - THAM 0.1 mL	0.03 mol/L EDTA - NH ₄ 0.1 mL
Eluting elements	Pb	Pb, K
Adjustment of the solution	The addition of the same amount of 0.03 mol/L EDTA - NH ₄ may be required to increase the electrical conductivity of the eluate.	Unnecessary
Note	The solution was diluted two-fold by the adjustment. When the electrical conductivity remains at a low level after this adjustment, change of measurement condition may be required.	

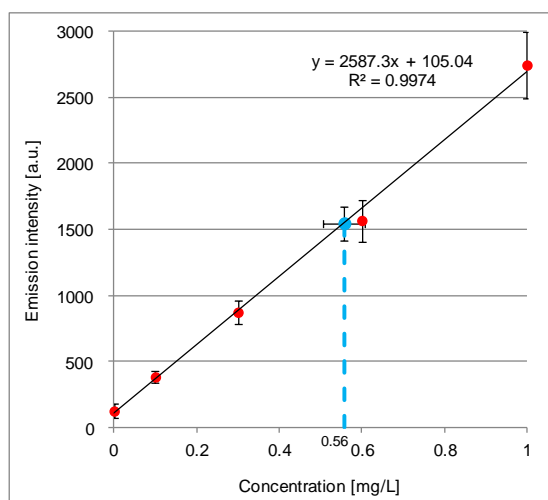
When the concentration of potassium is 1000-fold higher than that of lead, the solid phase extraction is not recommended. The trapping efficiency of lead may decrease for potassium in excess of the resin capacity.



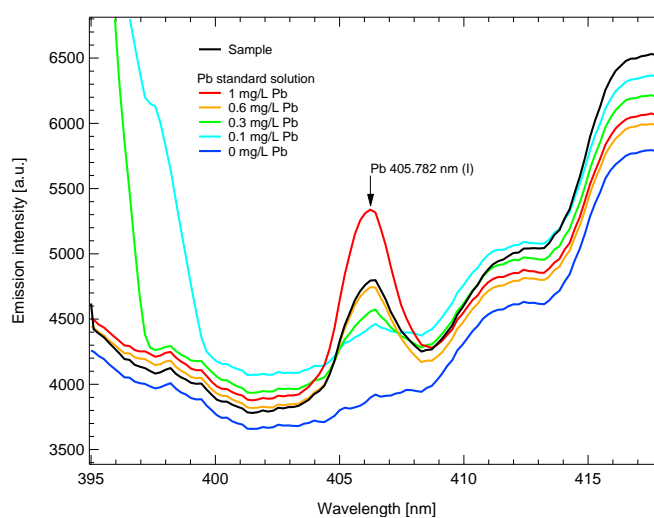
Measurement conditions and results

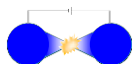
Sample:	The eluate by solid phase extraction
Instrument model:	MH-5000 s2086
Cuvette:	LepiCuve-C, Quartz cuvette
Instrument parameters:	1000 V, (ON: 3 ms / OFF: 50 ms) × 15 pulses
Emission line of target element:	Pb 405.782 nm (I)
Calculated concentration:	0.56 ± 0.05 mg/L Pb (103% of ICP-MS)

Calibration curves



Spectra





07

Determination of Zinc (Zn)

Acid digested solution was directly used for quantitative analysis. The standard addition method was used to prevent effects of coexistence elements. The use of cadmium for internal standard substance provided more accuracy of determination.

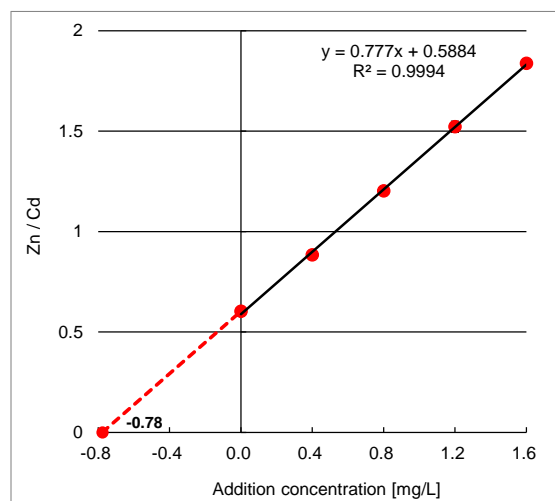
Pretreatment

Acid digestion Ref. **01** Acid Digestion

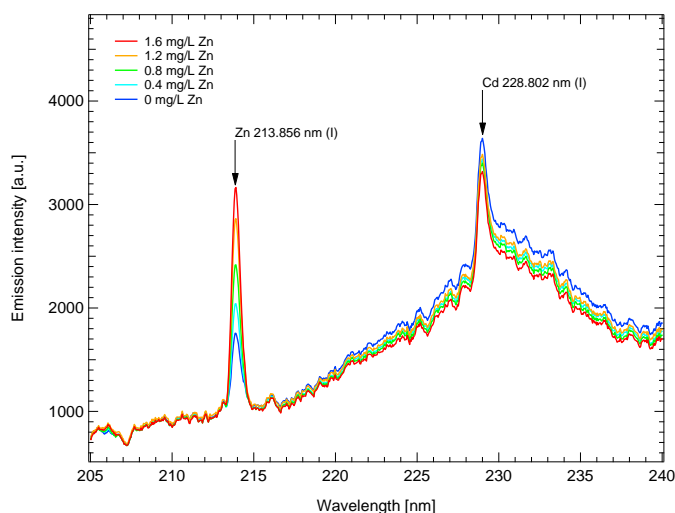
Measurement conditions and results

Sample: 90 v/v% acid digested solution, 0 - 1.6 mg/L Zn as the standard
Instrument model: MH-5000 s2035
Cuvette: LepiCuve-C, quartz cuvette
Instrument parameters: 750 V, (ON: 2 ms / OFF: 50 ms) × 70 pulses
Emission line of target element: Zn 213.856 nm (I)
Emission line of internal standard substance: Cd 228.802 nm (I)
Calculated solution: 0.86 ± 0.03 mg/L Zn (108% of ICP-MS)

Calibration curves



Spectra

**MICRO EMISSION**

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