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Application News

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Inductively Coupled Plasma Atomic Emission Spectrometry

Analysis of Heavy Metals in Sewage Sludge and Sewage by ICPE-9820

Introduction

Domestic wastewater or drainage from a particular business plant can only be discharged in public waters or reused as industrial water after being cleaned up in a sewage treatment facility. If such processed water is discharged into public waters, it is required to meet effluent standards.
The increase of sewage sludge generated in the sewage treatment process, however, has become a problem. Thus, for the purposes of waste reduction and recycling, following incineration, sewage sludge is being re-used as cement material, civil engineering material, and fertilizer, etc. However, the reuse of sewage sludge, from the standpoints of environmental protection and potential health hazards, requires that its toxic heavy metal content is carefully examined.
If sewage sludge is to be discarded in a landfill, etc., it is considered to be industrial waste and is therefore subject to regulation under the Japanese Waste Disposal and Public Cleansing Law (Waste Management Law). However, if it is to be reused, it is considered to be a valuable resource, and is subject to regulation under the Japanese Fertilizer Control Act and the Soil Contamination Countermeasures Law.
To ensure that treated sewage water meets effluent standards, sewage sludge ash must be analyzed with high sensitivity to accurately quantify such elements as Pb and Cd, which may be present at trace levels up to high concentrations.
Here, using the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer, we conducted analysis of processed water from a sewage treatment plant, in addition to sewage sludge ash. The ICPE-9820, with its original plasma emission unit, permits high-throughput analysis of elements at trace- to high-concentration levels, with high sensitivity and high accuracy.

Samples

- Treated wastewater (effluent)
- Sewage sludge ash

Sample Preparation

Treated wastewater:
After adding nitric acid and perchloric acid to 50 mL of sample, heat-digestion over a hot plate was conducted until white smoke was generated. After cooling, Y (yttrium) was added as an internal standard element, and hydrochloric acid (1 mol/L) was added to adjust the volume to 10 mL. This solution served as the analytical sample.
Sewage sludge ash:
Nitric acid was added to 10 g of sample, and heat-digestion was conducted over a hot plate. After cooling, Y (yttrium) was added as an internal standard element, and hydrochloric acid (1 mol/L) was added to adjust the volume to 100 mL. This solution served as the analytical sample.

Instrument and Analytical Conditions

For measurement, the Shimadzu ICPE-9820 multi-type ICP atomic emission spectrometer was used. The measurement conditions are shown in Table 1. The ICPE-9820 can conduct measurement while automatically switching between high sensitivity axial viewing (AX) and radial viewing (RD), suitable for high-concentration analysis. This permits simultaneous analysis of elements over a wide concentration range, from trace- to high-concentration levels, such as that found in sewage sludge ash. Further, the plasma torch is oriented vertically to reduce the memory effect. Elements that easily remain in memory, such as boron, can be analyzed efficiently using a short rinse time between analysis of sewage treated water and sewage sludge ash, for example, even if the same element is present at greatly different concentrations.

Table 1 Analytical Conditions

Instrument	: ICPE-9820
Radio frequency power	: 1.2 kW
Plasma gas Flowrate	: 10 L/min
Auxiliary gas Flowrate	: 0.6 L/min
Carrier gas Flowrate	: 0.7 L/min
Sample introduction	: Nebulizer 10
Misting chamber	: Cyclone chamber
Plasma torch	: Mini Torch
Observation	: Axial (AX) / Radial (RD)

Analysis

We conducted quantitative analysis of sewage sludge ash digestion solution and treated wastewater using the internal standard method – calibration curve method. (Regarding the treated wastewater, the same quantitation was conducted by ICP-MS (Shimadzu ICPM-8500) to compare the trace values obtained in analysis.)

[References]
1) Official Specifications Related to Typical Fertilizer Based on the Fertilizer Control Act (Ministry of Agriculture, Forestry and Fisheries Notification No. 284, February 22, 1986, Revised on August 8, 2012 by the Ministry of Agriculture, Forestry and Fisheries Notification No. 1985, Enforced from September 7, 2012)
2) Enforcement Regulations Regarding the Soil Contamination Countermeasures Law (Ministry of the Environment Ordinance No. 29, December 26, 2002)
3) Ordinance on Test Method for Water Quality of Sewage (Ministry of Health and Welfare/Ministry of Construction Ordinance No. 1, December 17, 1962, Revised on May 23, 2012 by the Ministry of Land, Infrastructure, Transport and Tourism/Ministry of the Environment Ordinance No. 2)
4) Ordinance for Determination of Effluent Standards (Prime Minister's Office Ordinance No. 35, June 21, 1971, Revised on September 4, 2013 by the Ministry of the Environment Ordinance No. 20)
5) JIS K0102-2013 (Industrial Wastewater Test Method)

Analytical Results

Table 2 shows the values (memory-related) obtained from measurement of a blank sample directly after measurement of high-concentration sample. As the blank values were reduced to low levels less than 1/1000 of the effluent standards, there was no problem in the analysis of treated trace level sewage water even after introduction of a high-concentration sewage sludge sample.
Table 3 shows the analytical results. The detection limit was less than 1/10 that of the standard values for both sewage sludge ash and treated sewage water. Even with a quantitation value of treated water at less than 1/100 of the effluent standards, the results were almost identical to those obtained by ICP-MS.

Fig. 1 shows the calibration curves for Zn. Using the combination of axial/radial observation makes it possible to increase the quantitation concentration range. Also, as the software automatically determines which calibration curve is to be applied, the time required for data evaluation following analysis can be shortened.

Conclusion

Both trace elements and high-concentration elements in sewage sludge ash and treated wastewater can be accurately measured with high sensitivity using the ICPE-9820.

Table 2 Blank Levels Obtained Directly After Measurement of High-Concentration Sample (Unit: mg/L)

	Cu	B	Zn	Fe
High-concentration sample solution	100 (1000)	10 (100)	100 (1000)	2500 (25000)
Blank value just after injection of high-concentration sample	< 0.0005 (0.005)	< 0.0005 (0.005)	0.0006 (0.006)	0.01 (0.1)

Values in parentheses are solid conversion values (mg/kg)

Table 3 Analytical Results for Sewage Sludge Ash and Treated Sewage

	Sewage Sludge Ash (mg/kg)					Treated Sewage (mg/L)				
	Soil Concentration Standard	Official Standard of Ordinary Fertilizer	Detection Limit	Quantitation Value	Observation Direction	Effluent Standards	Detection Limit	Quantitation Value	Quantitation Value (ICP-MS)	Observation Direction
Cd	150	5	0.002	2.3	AX	0.1	0.00004	0.00007	0.00005	AX
Cr		500	0.004	129	AX	2	0.0001	0.0014	0.0015	AX
Cr^{+6}	250					0.5				
Pb	150	100	0.02	59	AX	0.1	0.0004	0.001	0.0011	AX
B	4000		0.003	18	AX	10	0.0001	0.082	0.084	AX
Cu			0.006	621	RD	3	0.0001	0.01	0.011	AX
Zn			0.003	972	RD	2	0.00006	0.051	0.05	AX
Ni		300	0.004	78	AX		0.0001	0.019	0.017	AX
Mn			0.0004	637	RD	10	0.00001	0.029	0.028	AX
Fe			0.002	22400	RD	10	0.00004	0.098	0.101	AX

Sewage sludge ash concentration = Measurement value × Dilution factor (100 mL/10 g),
Treated sewage concentration = Measurement value × Dilution factor (10 mL/50 mL)
AX: Axial view, RD: Radial view

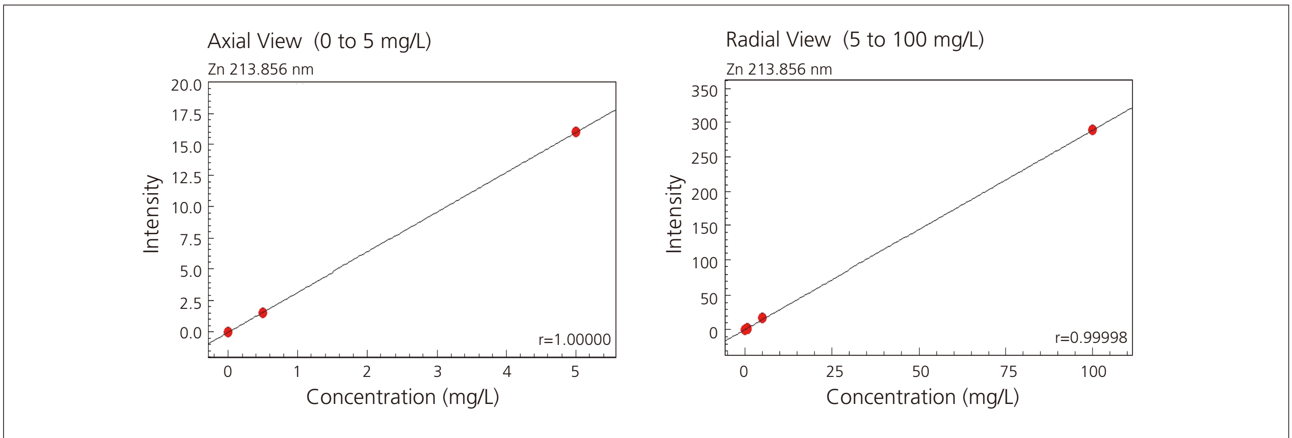

Fig. 1 Calibration Curves of Zn by Axial View and Radial View

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