

## Analysis of Iron and Manganese in Tap Water by Flameless Atomic Absorption Method

### Introduction

Based on Japan's Water Supply Act, water quality standards for tap water have been established for 51 items<sup>(1)</sup>, among which 14 are metals. In the water quality inspection methods that provide inspection methods<sup>(2)</sup> for those items, the flameless atomic absorption method (flameless atomic absorption spectrophotometry) introduced in this article can be used in determinations of 11 elements.

In cases where the number of measured elements or samples is small, the flameless atomic absorption method enables measurement of 1/10 of the standard values of many target elements without concentration, and running costs are low, as the argon gas flow rate is about 1/10 that in ICP.

Here, iron (Fe) and manganese (Mn) in tap water were measured by the tap water quality inspection method using the flameless atomic absorption method. Fe and Mn mainly cause discoloration, foul odor, and water scale, and in many cases, a certain amount of these elements is also found in ground water, which is used as a source of tap water and in beverage-type drinking water products. This article introduces the results of a validity evaluation of an analysis of these elements based on Validity Evaluation Guidelines for Tap Water Quality Inspection Procedures<sup>(3)</sup>.

T. Kawakami

### Sample Preparation

First, 10 mL of nitric acid was added to 100 mL of tap water, after which the solution was heated. After the solution was reduced to 90 mL or less, it was allowed to cool and then diluted in the flask to 100 mL for use as the measurement sample. For the evaluation of validity with spiked samples, samples spiked with the standard solution of Fe and Mn were also prepared.

### Instrument Configuration and Measurement Conditions

The instruments used here were a Shimadzu AA-7000 atomic absorption spectrophotometer and GFA-7000 graphite furnace atomizer.

Table 1 shows the main measurement conditions. Measurements of Mn were conducted using a high sensitivity condition (calibration curve concentration range: 1 to 5 ppb) and a low sensitivity condition (5 to 50 ppb). Sensitivity was adjusted by flowing argon gas during atomization. Fig. 1 shows the results of an investigation of the relationship between the argon gas flow rate and sensitivity during atomization of Mn. The highest sensitivity was achieved by completely stopping the argon gas flow and using the high sensitivity mode (H). In comparison with those conditions, sensitivity could be reduced to approximately 1/3 to 1/20 by flowing argon gas. The GFA-7000 enables fine sensitivity adjustment, as the argon gas flow rate can be set in units of 0.01 L/min.

Table 1 Measurement Conditions

	Fe	Mn (high sensitivity)	Mn (low sensitivity)
Analytical wavelength	248.3 nm	279.5 nm	
Slit width	0.2 nm		
Measurement mode	BGC-D2		
Tube type	Platform tube		
Standard solution concentration	10, 20, 30, 40 ppb	1, 2, 3, 5 ppb	5, 10, 20, 30, 40, 50 ppb
Injection volume	10 $\mu$ L	10 $\mu$ L	10 or 2 $\mu$ L
Temp. program	Aashing: 900 °C Atomization: 2400 °C		Aashing: 800 °C Atomization: 2300 °C
Gas flow rate during atomization (sensitivity)	0.00 L/min	0.00 L/min(H)	0.04 L/min
Number of repetition	Standard: 3, real samples: 5		
Signal processing	Height	Area	

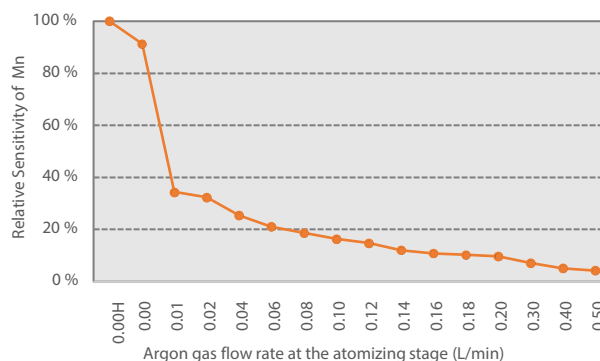


Fig. 1 Change of Sensitivity by Argon Gas Flow Rate during Atomization of Mn

### Results of Validity Evaluation of Calibration Curves and Spiked Samples

A validity evaluation of the calibration curves and real samples was carried out in accordance with the Validity Evaluation Guidelines for Tap Water Quality Inspection Procedures. Table 2 and Table 3 show the results for the calibration curves and the spiked samples, respectively. Because approximately 0.8 ppb of Mn was detected in the unspiked tap water in the measurement with high sensitivity for Mn, this value was subtracted in the evaluation of the recovery rate of the real sample. As an example of analysis of a high concentration sample, a Mn-spiked sample was prepared by spiking the tap water with 200 ppb of Mn, which is 4 times the upper limit concentration of the calibration curve, and the analysis was conducted using the automatic dilution and re-analysis function of the AA-7000. In case the 1<sup>st</sup> measurement exceeds the set upper limit concentration, this automatic dilution and re-analysis function automatically decreases the sampled amount and then conducts a re-analysis. Because the 1<sup>st</sup> measurement in this experiment exceeded the upper limit, the sampled amount was automatically decreased from 10  $\mu$ L to 2  $\mu$ L, and the measurement was conducted 5 times.

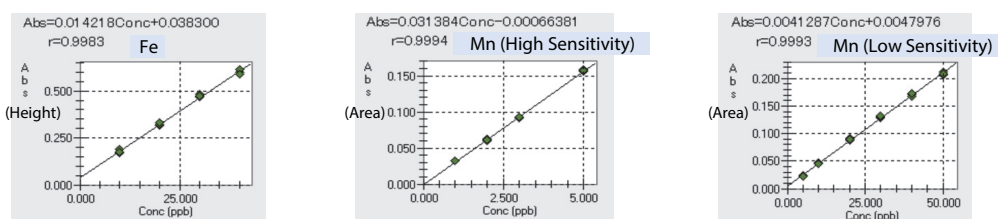
Fig. 2 shows the calibration curve and Fig. 3 shows the peak profiles obtained in the analysis.

**Table 2 Results of Validity Evaluation of Calibration Curves of Fe and Mn**

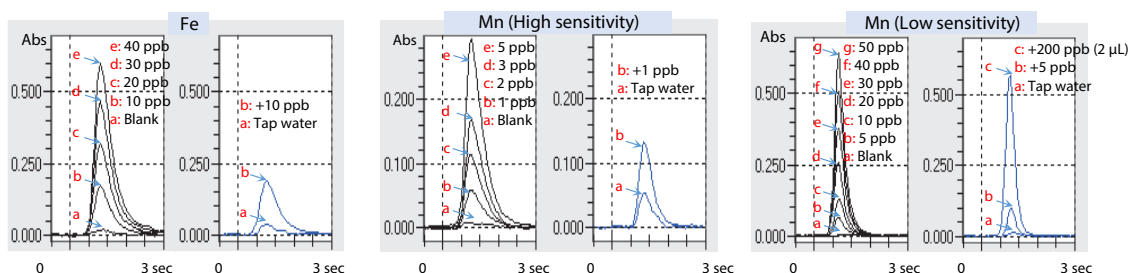
Measured element	Calibration curve concentration (µg/L)	Water quality standard (µg/L) (Control target)	Carryover		Accuracy of concentrations		Repeatability of concentrations (n = 3)	
			Target: Lowest concentration of calibration curve or below		Target: 80 % - 120 %		Target: 10 % or less	
			Judgment	Result	Judgment	Result	Judgment	Result
Fe	10, 20, 30, 40	300	Pass	<5	Pass	98 - 102	Pass	1.7 - 6.9
Mn (high sensitivity)	1, 2, 3, 5	50	Pass	<0.2	Pass	98 - 105	Pass	0.6 - 2.9
Mn (low sensitivity)	5, 10, 20, 30, 40, 50	(10)	Pass	<2	Pass	87 - 104	Pass	1.1 - 3.7

**Table 3 Results of Validity Confirmation of Measured Values of Fe and Mn in Spiked Samples**

Measured element	Spike concentration (µg/L)	Water quality standard (µg/L) (Control target)	Accuracy (recovery rate)		Repeatability (%RSD) of spiked samples (n = 5)	
			Target: 70 % - 130 %		Target: 20 % or less	
			Judgment	Result	Judgment	Result
Fe	10	300	Pass	107 %	Pass	2.0 %
Mn (high sensitivity)	1	50 (10)	Pass	111 %	Pass	0.9 %
Mn (low sensitivity)	5		Pass	108 %	Pass	4.8 %
	200		Pass	98 %	Pass	1.3 %



**Fig. 2 Calibration Curves**



**Fig. 3 Peak Profiles of (Left) Standard Solution and (Right) Measurement Samples (Spiked and Unspiked)**

### Conclusion

Fe and Mn in tap water were measured by the flameless atomic absorption method using a Shimadzu AA-7000 atomic absorption spectrophotometer and GFA-7000 graphite furnace atomizer. The results confirmed that both the calibration curves and the spiked samples satisfied the targets of the Validity Evaluation Guidelines.

Because the atomic absorption method has a narrow linear region, the concentration range in which a one set of conditions can be applied is small, being limited to approximately one order of magnitude. However, as demonstrated in this experiment, measurements corresponding to the applicable concentration range are possible by sensitivity adjustment using an appropriate argon gas flow rate during atomization. It is also possible to measure samples with concentrations several times higher than the upper limit concentration of the calibration curve by using the automatic dilution and re-analysis function of the AA-7000 flameless method.

In cases where the number of measured elements or samples is small, the flameless atomic absorption method enables

measurement of 1/10 of the standard value of many target elements without sample concentration, and running costs are also low, as the argon gas flow rate is about 1/10 of that with ICP. The flameless method also supports measurements of a wide concentration range by utilizing the functions of sensitivity adjustment by the argon gas flow rate during atomization and automatic dilution and re-analysis.

### <References>

- (1) Ministerial Ordinance Concerning Water Quality Standards (Ministry of Health, Labour and Welfare (MHLW) Ordinance No. 101, May 30, 2003; revised in 2020, MHLW Ordinance No. 38)
- (2) Method established by the Japanese Minister of Health, Labour and Welfare Based on Regulations of the Ministerial Ordinance Concerning Water Quality Standards (MHLW Notification No. 261, July 22, 2003; revised in 2020, MHLW Notification No. 95)
- (3) Validity Evaluation Guidelines for Tap Water Quality Inspection Procedures (*Kensui* 0906, Annex No. 1 issued by MHLW, dated Sept. 6, 2008; final revision, *Yakuseisui* 1018, No. 1 issued by MHLW)

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