SHIMADZU
Excellence in Science

Application News

No. A564

Atomic Absorption

# Direct Measurement of Lithium (Li) in Seawater Using the Flame Micro Sampling Method

Flame atomic absorption spectrophotometers feature easy maintainability and can also measure samples with a complex matrix. However, when conducting multi-sample measurement of samples with complex matrices, the burner slot may get blocked due to deposits of solid material. In such a case, burner slot blockage can be reduced by using the flame micro sampling method in which only a small amount of sample is injected.

This article demonstrates the effectiveness of the flame micro sampling method by introducing example measurements of lithium (Li) in seawater, which has a complex matrix, using the conventional continuous injection method and the flame micro sampling method.

Lithium, which is well-known as a battery material, exists in seawater at trace amounts of about 0.1 to 0.2 mg/L (10 to 20 µg/100 mL) and technologies for recovering that lithium as a resource are being researched.

T. Kawakami

## Flame Micro Sampling Method and Its Advantages

The conventional flame continuous injection method (referred to as the continuous method hereafter) determines absorbance by first injecting the sample, and upon stabilization, integrating the absorbance for a certain time and taking the average value as the absorbance. In this case, the sample injection time is (stabilization time) + (pre-spray time) + (integration time) × (repetition times). For example, if the pre-spray time is 5 s, integration time is 3 s, and repetition is three times, the sample injection time is about 20 s in total including the stabilization time. On the other hand, the flame micro sampling method (referred to as the micro sampling method hereafter) determines absorbance by injecting the sample for about 2 to 3 s and taking the height of the resulting trapezoidal signal as the absorbance. Even if this process is repeated three times, the total sample injection time is under 10 s. This process also means that measurement is possible with small sample volumes. Furthermore, when samples have a complex matrix, burner slot blockage can be reduced to allow stable measurement of samples in more numbers.

## Measurement Samples and Method

The sample for measurement was prepared by sampling and filtering seawater.

Measurement was done by the calibration curve method. The standard solution was prepared by adding 2.5 wt/v% sodium chloride.

Also, to evaluate the validity of the measurement method, a solution comprising the sample and the standard solution added at constant volumes was measured to determine the recovery rate.

Sixty samples of the same seawater were measured consecutively to compare the stability over a long period.

## Instrument Configuration and Measurement Conditions

The atomic absorption spectrophotometer AA-7000 was used. Table 1 lists the main measurement conditions.

**Table 1 Measurement Conditions**

| | | |
|---|---|---|
| Measurement Element | : | Li |
| Analytical Wavelength | : | 670.8 nm |
| Ignition Mode | : | NON-BGC |
| Slit Width | : | 0.7 nm |
| Burner Height | : | 7 mm |
| Peak Processing | : | Cont. method: Time average<br>Micro sampling method: Peak height |
| Signal Processing Time and Repetition Times | : | Cont. method: Integration 3 s × three times<br>Micro sampling method: Sampling 10 s × three times |
| Standard Solution Concentration (µg/100 mL) | : | 0 (Blank), 5, 10, 20, 30 |

* Of the 10 seconds, sample injection is 2 to 3 seconds.

## Measurement Results and Conclusions

Table 2 lists the measurement results of the standard solution using the continuous and micro sampling methods respectively. Fig. 1 shows the obtained calibration curves. These results show that the obtained absorbance is nearly the same. The relative standard deviation (%RSD) regarding the simple repetition was more favorable with the continuous method which incorporates a certain integration time.

Table 3 shows the measurement results of the seawater. The obtained values are nearly the same and the recovery rates are both favorable at above 90 %. The sample volume per each measurement by the micro sampling method was approx. 0.3 mL.

Fig. 2 shows examples of profiles obtained via micro sampling method measurement.

Fig. 3 shows the result of consecutively measuring 60 samples of the same seawater. Whereas the flame started to split after about 20 measurements and values dropped when using the continuous method, there were no conspicuous splits in the flame using the micro sampling method and values were more stable with the drop in values being more moderate compared to the continuous method. Fig. 4 shows the appearance of the flame after measurement of 60 samples respectively.

This shows that by using the micro sampling method for direct measurement of lithium in seawater, which has a complex matrix, blocking of the burner slot was reduced and measurement was stable with the %RSD for 60 samples being 1.0 %.

Since the micro sampling method requires only small sample volumes, it is also effective in the measurement of samples for which only a small volume can be obtained. Measurement using the micro sampling method introduced in this article is possible on the AA-7000 by the standard system configuration.

**Table 2 Measurement Results of the Standard Solution**

| | Continuous Method | | Micro Sampling Method | |
|---|---|---|---|---|
| Set Concentration | Absorbance | %RSD (n=3) | Absorbance | %RSD (n=3) |
| 0 | -0.0001 | 100 | 0.0008 | 30 |
| 5 | 0.0109 | 1.40 | 0.0119 | 5.74 |
| 10 | 0.0221 | 0.90 | 0.0214 | 1.17 |
| 20 | 0.0432 | 0.48 | 0.0425 | 1.08 |
| 30 | 0.0642 | 0.31 | 0.0631 | 1.11 |

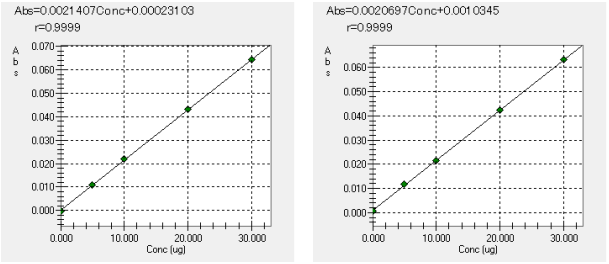


**Fig. 1 Calibration Curves of the Continuous Method (Left) and the Micro Sampling Method (Right)**

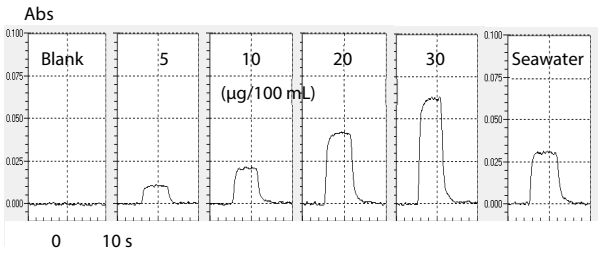


**Fig. 2 Profile from Measurement Using the Micro Sampling Method**

**Table 3 Measurement Results of Lithium in Seawater**

| | Continuous Method | Micro Sampling Method |
|---|---|---|
| Absorbance | 0.0313 | 0.0312 |
| Measurement Concentration (µg/100 mL) | 14.5 | 14.6 |
| Recovery Rate | 94 % | 93 % |

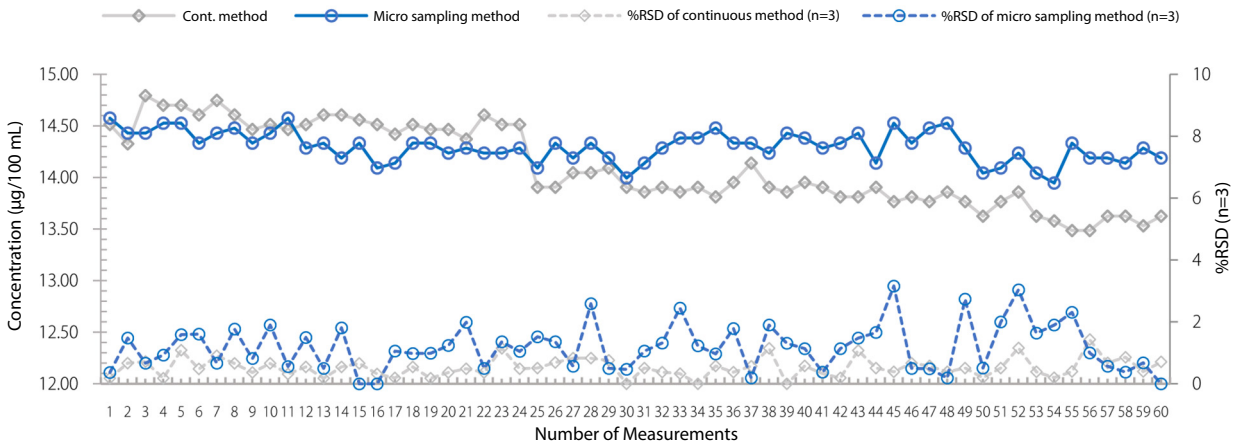


**Fig. 3 Change in Values over Consecutive Measurement of 60 Samples**

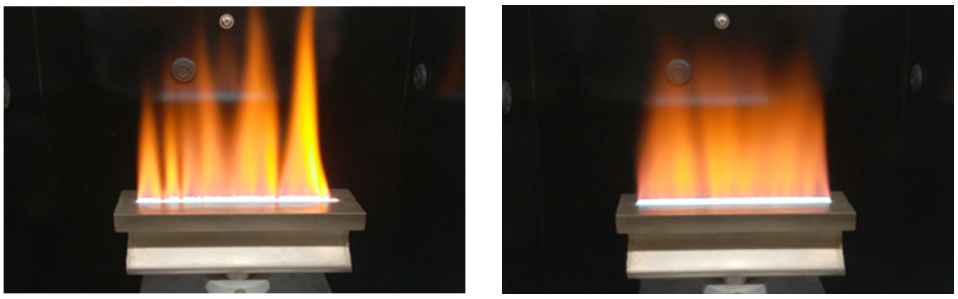

**Fig. 4 Flame Status After Consecutive Measurement of 60 Samples (Left: Continuous Method, Right: Micro Sampling Method)**

First Edition: Jul. 2018

Shimadzu Corporation
www.shimadzu.com/an/