

Measuring Arsenic in Algae with Bench-Top Micro X-ray Fluorescence Analyzer

1. Introduction

Arsenic accumulates in high densities in marine organisms such as algae. Conventional methods used for quantitative analysis of arsenic include oxide decomposition with nitric acid, atomic absorption of a dissolved solution, ICP atomic emission spectroscopy, and ICP-Mass. But such requirements as sample dissolution are troublesome and time consuming. Here we quantitatively analyze each element in the algae, in solid form, without sample modification, using the energy dispersion type Bench-Top Micro X-ray Fluorescence Analyzer, and compared our findings with the quantitative results of analyzing the dissolved sample by ICP-AES.

2. Measurement Method

2-1 Fluorescent X-ray Analysis method

- Instrument: SEA5120 Bench-Top Micro X-ray Fluorescence Analyzer
- Sample: Dried algae ground to powder with a mortar
- Sample Pre-Treatment: performed the following two pre-treatments
 - (1) Place sample in the tablet forming device shown in Photo 1, add 10 kg/cm² of pressure, form a tablet 2 cm in diameter.
 - (2) Place sample in mylar cup and measure
- Standard Sample: NIES Gulfweed

Form a tablet of the gulfweed (NIES standard sample No. 9). This standard sample is similar to experiments with algae and matrices. Using this as the standard sample allowed us to improve quantitative accuracy by the FP method (FP method using one standard sample) and to confirm a certified value for arsenic of 115 ± 9 ppm.

Table 1 SEA2120 Measurement Conditions

X-ray tube	Rh
Applied voltage	15/50 kV
Tube current	6 μ A
Collimator	10 mm
Filter	Primary
Atmosphere	Vacuum
Measurement time	500 seconds



Photo 1 Tablet Forming Device

2-2 ICP-AES method

- Instrument: SPS1700H type ICP-AES Analyzer
- Sample: 0.2 g dried algae
- Pretreatment: Add 10 ml (1+2) nitric acid to sample, add 1 ml sulfuric acid, then add 2 ml nitric acid. Dissolve then add 20 ml filtered water.

Table 2 SPS1700H Measurement Conditions

Wavelength	189.042 nm
High frequency output	1.30 kW
Flame height	10 mm
Carrier gas	2.0 kg/cm ²
Plasma gas	16.0 l/min
Auxiliary gas	1.5 l/min

3. Fluorescent X-ray Spectrum

Figures 1 and 2 show the fluorescent X-ray spectrum of algae in tablet form. Elements from sodium (Na) to calcium (Ca) were measured at a tube voltage of 15 kV using the primary filter. This is because scattered X-rays of the Rh target and the Cl K alpha line overlap. At a voltage of 50 kV measurement was done for elements Fe to I. The SEA2100 combines three voltages and lets you to select one of 5 kV, 15 kV, or 50 kV.

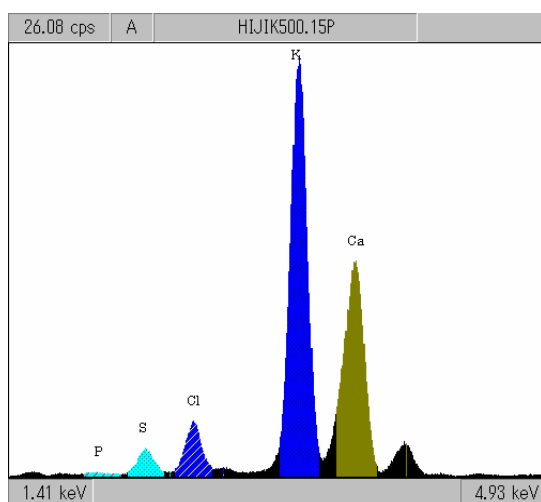


Figure 1 Fluorescent X-ray Spectrum
(Voltage: 15 kV)

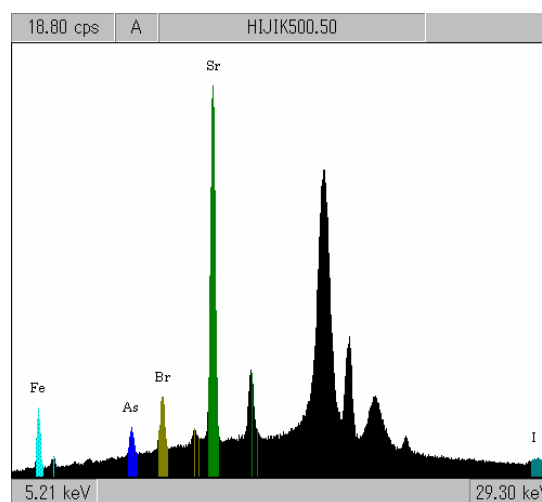


Figure 2 Fluorescent X-ray Spectrum
(Voltage: 50 kV)

4. Measurement Results

Table 1 displays results of the measurement by the FP method. With a sample in the tablet form, the FP method with one standard sample was suitable. With a sample in the powder form, the FP method was suitable without a standard sample.

Since we considered the matrix of this sample to be polysucrose the remaining elements were input as CH₂O.

Table 1 Algae Measurement by FP Method

Element	Tablet method	Mylar method
S	1.06	0.890
Cl	1.37	1.12
K	3.65	2.61
Ca	1.29	0.772
Fe	0.075	0.103
As	0.012	0.011
Br	0.018	0.018
Sr	0.100	0.085
I	0.048	0.018
CH ₂ O	92.1	91.5

Units: wt%

Table 2 Algae Measurement by FP Method

Analysis Method	As	Fe
ICP-AES Analysis	0.010	0.086
Fluorescent X-ray Analysis (tablet)	0.012	0.075
Fluorescent X-ray Analysis (mylar)	0.011	0.103

Units: wt%

5. Summary

Fluorescent X-ray analysis allows quick measurement of solid samples without requiring samples to be dissolved in solution. Comparing results from the tablet method and mylar method for As and Fe with ICP-AES analysis showed that both methods produce comparatively close values.