

## Development and evaluation of uncertainty of precise quantitative analysis by XAS for a primary standard

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### Introduction

All data of measurement and analytical technique should be evaluated with internationally approved reference and traceable to the SI.

X-ray absorption by an absorption edge follows Lambert-Beer law so can be primary standard if the coefficient is exactly determined. The technical problem is determination of the edge jump without affection of state of absorbing atom. We have developed the method to determine the edge jump automatically by modifying a method for EXAFS analysis.

### Experimental

XAFS spectra of Zr K-edge (18 keV), Mo K-edge (20 keV), and Sn K-edge (29 keV) of standard solution in transmission mode were measured at BL-10B using precise quartz cells with 1, 2, 4, 5 cm thickness which are calibrated by the three-dimensional measurement system (Carl Zeiss UMM550) traceable to national standard of Iodine-stabilized He-Ne laser (NMIJ). The error was below 3  $\mu\text{m}$  in 4 points on optical windows at 293 K.

### Results and Discussion

Though the shape of the absorption edge just above the threshold depend on element, oxidation state and coordination structure, we have developed analysis algorithm to remove structure of XANES and EXAFS automatically without arbitrariness. An absorption edge jump of excitation cross section of a specific core electron of an isolation atom that removed structure by this method is in proportion to the number of atom on optical path, and an absorption edge jump per optical path length 1 m of the density of element 1 mol/m<sup>3</sup> is defined as mol absorption edge jump coefficient,  $C_{\Delta\mu}$  (m<sup>2</sup>/mol), relation of  $\Delta\mu = C_{\Delta\mu} C L$ , where  $\Delta\mu$  is absorption edge jump,  $C$  is mol density (mol/m<sup>3</sup>),  $L$  is optical path length (m).

Figure 1 shows effect of collection time on standard deviation( $\sigma$ ) for edge jump ( $\Delta\mu$ ) of Mo in solutions of various concentration by 4 cm-cell. Each scan was taken by 10 min. Each numbers of sample data was 12, 38, 45, for 990, 99, 9.9 ppm, respectively. Each average of  $\Delta\mu$  was 0.291, 0.0286, 0.0023 for 990, 99, 9.9 ppm, respectively. These results suggest that it is possible even for lower concentration than 10 ppm by long collection time. A dispersion of data every scan (standard deviation) decreases by increasing collection time.

Figure 2 shows coefficient parameter of absorption edge jump ( $C_{\Delta\mu}$ ) vs. atomic number obtained by measurements of some standard solutions using 2 cm cell.

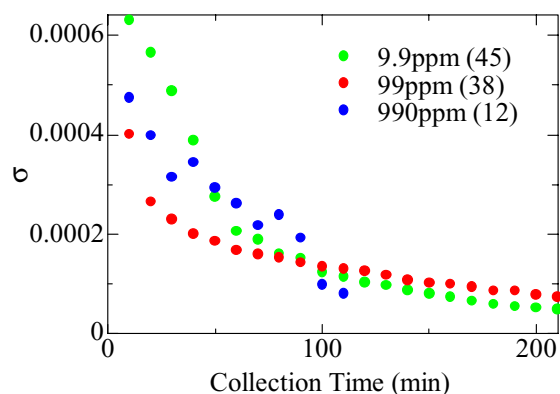


Fig.1 Effect of collection time on standard deviation( $\sigma$ ) for Mo solution of various concentration.

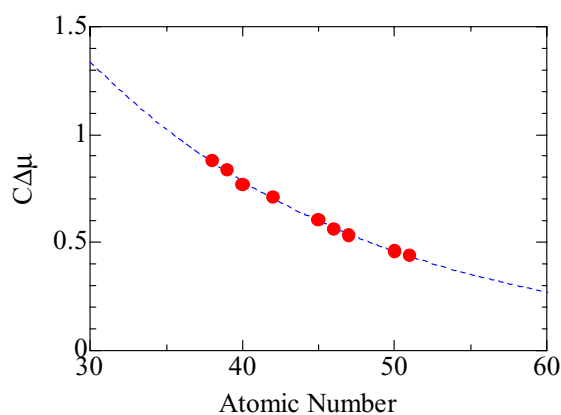


Fig.2 Coefficient parameter of absorption edge jump vs atomic number.

The results indicate that the coefficient parameter ( $C_{\Delta\mu}$ ) can be expressed first order exponential function of atomic number ( $Z$ ). The result of a least square fitting was

$$C_{\Delta\mu} = \exp(1.894 - 0.05345 \times Z)$$

This indicates that we can estimate a value by interpolation and extrapolation on the element that a standard sample is not provided.

We will extend the measurements to determine the  $C_{\Delta\mu}$  of other period elements and L absorption edges.

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