

Uncertainties of Concentration and Peak Energy

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The standard deviation of n -times repeatedly measured data is $s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n}}$. The GUM (Guide to the Expression of Uncertainty in Measurement, 1993, 1995, 2008) in ISO Standard defines the uncertainty as $u = \frac{s}{\sqrt{n}}$. This is so-called the SDOM (standard deviation of the mean). The standard deviation of the population can be expressed as $\sigma \cong \sqrt{\frac{n}{n-1}}s = \sigma_{n-1}$. Therefore the GUM expression $\frac{s}{\sqrt{n}}$ is better by $\frac{1}{\sqrt{n}}$ than $\sigma \cong \sigma_{n-1}$.

When we estimate the concentration of a sample by measuring n specimens made from one sample, the concentration of an element in the sample should be expressed as $\bar{x} \pm \sigma_{n-1}$ with the n explicitly shown. The σ_{n-1} is a good estimate of the error including the sample inhomogeneity, operator's skill, instrument steadiness, and so on.

On the other hand, if we want to measure the true energy of Cu $K\alpha_1$ peak position as a physically true value using a double-crystal XRF spectrometer, we must use the expression $\bar{x} \pm \frac{s}{\sqrt{n}}$. We know experimentally $\Delta E \cong 2$ eV for the natural width of Cu $K\alpha_1$. This is originated from Heisenberg uncertainty principle $\Delta t \Delta E \cong \hbar$, because the $1s$ and $2p$ core holes have exponentially decaying lifetimes due to the vacuum fluctuation. The natural width of $K\alpha_1$ is the sum of the natural widths of the initial and final core hole states. Though $\frac{s}{\sqrt{n}}$ may be much smaller than the natural width determined by the uncertainty principle, this is physically allowed because $\pm \frac{s}{\sqrt{n}}$ limits the peak position of the $K\alpha_1$.

In conclusion, we must use $\bar{x} \pm \sigma_{n-1}$ for most of the measured values; the expression $\bar{x} \pm \frac{s}{\sqrt{n}}$ is not needed mostly, except for the cases for the physically true values such as $K\alpha_1$ peak position. The latter measurement is not required in practical elemental analysis.