DEDUCTION OF EQUATIONS

1. Basic formulae

To deduce the equations in our present paper, we used the following basic formulae of statistics. Here, E and V represent expectation and variance, respectively. X and Y are independent probability variables, and a is a constant.

Basic properties of expectation.

$$E(a \cdot X) = a \cdot E(X) \tag{A1}$$

$$E(X+Y) = E(X) + E(Y) \tag{A2}$$

$$E(X \cdot Y) = E(X) \cdot E(Y) \tag{A3}$$

Basic properties of variance.

$$V(a \cdot X) = a^2 \cdot V(X) \tag{A4}$$

$$V(X \pm Y) = V(X) + V(Y) \tag{A5}$$

Definition of expectation and variance for an infinite population.

$$E(X) = \frac{1}{n} \cdot \sum_{i=1}^{n} X_i = \mu_{\inf} \tag{A6}$$

$$V(X) = \frac{1}{n-1} \cdot \sum_{i=1}^{n} (X_i - \mu_{\inf})^2 = \sigma_{\inf}^2 \tag{A7}$$

Expectation and variance of the sum of n probability variables sampled from the above infinite population.

$$E\left(\sum_{i=1}^{n} X_i\right) = n \cdot \mu_{\inf} \tag{A8}$$

$$V\left(\sum_{i=1}^{n} X_i\right) = n \cdot \sigma_{\inf}^2 \tag{A9}$$

Definition of expectation and variance for a finite population whose size is N.

$$E(X) = \frac{1}{N} \cdot \sum_{i=1}^{N} X_i = \mu_{fin} \tag{A10}$$

$$V(X) = \frac{1}{N} \cdot \sum_{i=1}^{N} (X_i - \mu_{fin})^2 = \sigma_{fin}^2 \tag{A11}$$

When n samples are sampled form the finite population, "finite population correction" works, and the variance of their sum becomes:

$$V\left(\sum_{i=1}^{n} X_i\right) = n \cdot \frac{N-n}{N-1} \cdot \sigma_{fin}^2 . \tag{A12}$$

Properties of Poisson distribution $Po(\lambda)$, where λ is the arithmetic mean of data.

$$E(Po(\lambda)) = \lambda \quad \text{(A13)}$$

$$V(Po(\lambda)) = \lambda \quad \text{(A14)}$$

$$Po(\lambda_1) + Po(\lambda_2) = Po(\lambda_1 + \lambda_2) \quad \text{(A15)}$$

If a probability variable X is dependent of a parameter Y, where Y is a probability variable, the overall variance $V(X)$ is described as follows [1].

$$V(X) = E_Y(V_X(X \mid Y)) + V_Y(E_{X|Y}(X)) \quad \text{(A16)}$$

Here, $X|Y$ means the conditional probability of X when Y is given.

2. Premises and definitions

The expectation of fluorescent X-ray intensity, w, can be basically expressed by this equation:

$$w = k \cdot g \cdot d \cdot t, \quad \text{(A17)}$$

where k is a constant, g is a glancing-angle-dependent term (or the change of the fluorescent X-ray intensity per unit shift of glancing angle), d is areal density (or concentration) of the analyte element, and t is integration time. Because fluorescence emission is a Poisson process, the actual fluorescence, f, includes "counting statistics." Then f is described as:

$$f = Po(w), \quad \text{(A18)}$$

where Po symbolizes a Poisson distribution whose parameter is w.

We assume an analyte wafer, and divide the surface into N regions, as illustrated in Fig. A1. Each point has concentration d_i, and is measured at a certain glancing angle where the glancing-angle-dependent term is g_i. We define the following terms that describe statistical properties of d_i and g_i.

Expectation of g_i:

$$E(g_i) = \gamma \quad \text{(A19)}$$

Variance of g_i:

$$V(g_i) = V_g \quad \text{(A20)}$$

Expectation of d_i:

$$E(d_i) = \frac{1}{N} \cdot \sum_{i=1}^{N} d_i = \delta \quad \text{(A21)}$$

Variance of d_i:

$$V(d_i)=\frac{1}{N}\cdot\sum_{i=1}^{N}(d_i-\delta)^2=\sigma_d^2 \qquad \text{(A22)}$$

Expectation of d_i^2

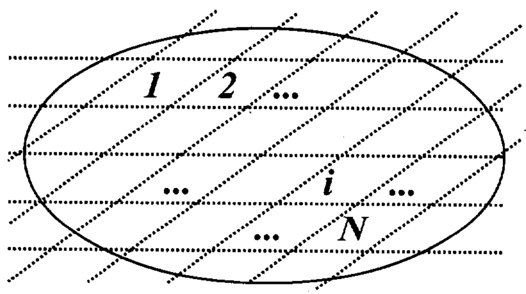
$$E(d_i^2)=\frac{1}{N}\cdot\sum_{i=1}^{N}d_i^2=\Delta=\delta^2+\sigma_d^2 \qquad \text{(A23)}$$

Relative standard deviation (RSD) of g_i:

$$\sqrt{\frac{V_g}{\gamma^2}}=\rho_g \qquad \text{(A24)}$$

Relative standard deviation (RSD) of d_i:

$$\sqrt{\frac{\sigma_d^2}{\delta^2}}=\rho_d \qquad \text{(A25)}$$



Glancing angle for point i :	g_i
RSD of Glancing angle:	ρ_g
Concentration of point i:	d_i
RSD of Concentration:	ρ_d
Integration time:	t
Sampling number:	n
Total points:	N

Fig.A1 Schematic illustration of the concept of our theoretical treatment.

3. Expectation of the accumulated intensity

For $\sum_{i=1}^{n} f_i$ (the sum of n measured fluorescent X-ray intensities, sampled from a finite population whose size is N), its expectation is:

$$E\left(\sum_{i=1}^{n} f_i\right)=E\left(\sum_{i=1}^{n} Po(w_i)\right)$$

$$=E\left(Po\left(\sum_{i=1}^{n} w_i\right)\right)=E\left(\sum_{i=1}^{n} w_i\right)=E\left(\sum_{i=1}^{n} k\cdot g_i\cdot d_i\cdot t\right)=n\cdot k\cdot\gamma\cdot\delta\cdot t. \qquad \text{(A26)}$$

4. Variance of the accumulated intensity

For the fluorescent X-ray intensity of point i, f_i, its variance is as follows by applying Eq. (A16).

$$V(f_i) = E_{w_i}\left(V_{f_i}(f_i \mid w_i)\right) + V_{w_i}\left(E_{f_i|w_i}(f_i)\right)$$
$$= E(w_i) + V(w_i)$$
$$= E(k \cdot g_i \cdot d_i \cdot t) + V(k \cdot g_i \cdot d_i \cdot t)$$
$$= k \cdot t \cdot E(g_i \cdot d_i) + k^2 \cdot t^2 \cdot V(g_i \cdot d_i)$$
$$= k \cdot \gamma \cdot \delta \cdot t + k^2 \cdot t^2 \cdot V(g_i \cdot d_i) \tag{A27}$$

For $\sum_{i=1}^{n} f_i$ (the sum of n measured fluorescent X-ray intensities, sampled from a finite population whose size is N), its variance is:

$$V\left(\sum_{i=1}^{n} f_i\right) = \sum_{i=1}^{n} V(f_i) = \sum_{i=1}^{n}\left(k \cdot \gamma \cdot \delta \cdot t_A + k^2 \cdot t^2 \cdot V(g_i \cdot d_i)\right)$$
$$= n \cdot k \cdot \gamma \cdot \delta \cdot t + k^2 \cdot t^2 \cdot \sum_{i=1}^{n}\left(V(g_i \cdot d_i)\right)$$
$$= n \cdot k \cdot \gamma \cdot \delta \cdot t + k^2 \cdot t^2 \cdot V\left(\sum_{i=1}^{n} g_i \cdot d_i\right). \tag{A28}$$

Because $\sum_{i=1}^{n} g_i \cdot d_i$ is defined for n d_is sampled from a finite population whose size is N, $\sum_{i=1}^{n} g_i \cdot d_i$ is a probability variable. We define $\sum_{i=1}^{n} g_i \cdot d_i = Y$, and applying Eq. (A16) yields:

$$V(Y) = E_{d_i}\left(V_Y(Y \mid d_i)\right) + V_{d_i}\left(E_{Y|d_i}(Y)\right). \tag{A29}$$

The variance included in the first term of the right side of Eq. (A29) becomes:

$$V_Y(Y \mid d_i) = V_Y(g_1 \cdot d_1 + g_2 \cdot d_2 + \ldots + g_n \cdot d_n \mid d_i)$$
$$= d_1^2 \cdot V(g_1) + d_2^2 \cdot V(g_2) + \ldots + d_n^2 \cdot V(g_n)$$
$$= \left(d_1^2 + d_2^2 + \ldots + d_n^2\right) \cdot V_g. \tag{A30}$$

Hence the first term of the right side of Eq. (A29) is:

$$E_{d_i}\left(V_Y(Y \mid d_i)\right) = E_{d_i}\left(\left(d_1^2 + d_2^2 + \ldots + d_n^2\right) \cdot V_g\right)$$
$$= V_g \cdot E_{d_i}\left(d_1^2 + d_2^2 + \ldots + d_n^2\right)$$

$$= V_g \cdot \left(E_{d_i}\left(d_1^2\right) + E_{d_i}\left(d_2^2\right) + \ldots + E_{d_i}\left(d_n^2\right)\right)$$

$$= n \cdot \Delta \cdot V_g . \tag{A31}$$

Next, the expectation included in the second term of the fright side of Eq. (A29) becomes:

$$E_{Y|d_i}(Y) = E_{Y|d_i}(g_1 \cdot d_1 + g_2 \cdot d_2 + \ldots + g_n \cdot d_n)$$

$$= d_1 \cdot E(g_1) + d_2 \cdot E(g_2) + \ldots + d_n \cdot E(g_n)$$

$$= (d_1 + d_2 + \ldots + d_n) \cdot \gamma . \tag{A32}$$

Therefore, the second term of the right side of Eq. (A29) is:

$$V_{d_i}\left(E_{Y|d_i}(Y)\right) = V_{d_i}\left((d_1 + d_2 + \ldots + d_n) \cdot \gamma\right)$$

$$= \gamma^2 \cdot \left(V(d_1) + V(d_2) + \ldots + V(d_n)\right). \tag{A33}$$

Because each d_i is sampled from a finite population, "finite population correction" must be applied to Eq. (A33), yielding:

$$V_{d_i}\left(E_{Y|d_i}(Y)\right) = n \cdot \frac{N-n}{N-1} \cdot \gamma^2 \cdot \sigma_d^2 . \tag{A34}$$

From Eqs. (A31) and (A34), Eq. (A29) becomes:

$$\sum_{i=1}^{n}\left(V(g_i \cdot d_i)\right) = n \cdot V_g \cdot \Delta + n \cdot \frac{N-n}{N-1} \cdot \gamma^2 \cdot \sigma_d^2 . \tag{A35}$$

By applying Eq. (A35) to Eq. (A28), we obtain:

$$V(X) = n \cdot k \cdot \gamma \cdot \delta \cdot t + n \cdot k^2 \cdot V_g \cdot \Delta \cdot t^2 + n \cdot \frac{N-n}{N-1} \cdot k^2 \cdot \gamma^2 \cdot \sigma_d^2 \cdot t^2 . \tag{A36}$$

5. Relative standard deviation (RSD) of the accumulated intensity

By using Eqs. (A26) and (A36), the square of the RSD of the accumulated intensity, ρ^2, becomes:

$$\rho^2 = \frac{V(X)}{(E(X))^2}$$

$$= \frac{n \cdot k \cdot \gamma \cdot \delta \cdot t + n \cdot k^2 \cdot V_g \cdot \Delta \cdot t^2 + n \cdot \frac{N-n}{N-1} \cdot k^2 \cdot \gamma^2 \cdot \sigma_d^2 \cdot t^2}{n^2 \cdot k^2 \cdot \gamma^2 \cdot \delta^2 \cdot t^2}$$

$$= \frac{1}{n \cdot k \cdot \gamma \cdot \delta \cdot t} + \frac{1}{n} \cdot \left(\rho_g^2 \cdot \frac{\Delta}{\delta^2} + n \cdot \frac{N-n}{N-1} \cdot \rho_d^2\right). \tag{A37}$$

6

Since Δ is equal to $\delta^2+\sigma_d^2$ as defined in Eq. (A23), we can rewrite:

$$\frac{\Delta}{\delta^2}=1+\frac{\sigma_d^2}{\delta^2}=1+\rho_d^2. \quad \text{(A38)}$$

Applying Eq. (A38) to Eq. (A37) yields:

$$\rho^2=\frac{1}{n\cdot k\cdot\gamma\cdot\delta\cdot t}+\frac{1}{n}\cdot\left\{\rho_g^2\cdot\left(1+\rho_d^2\right)+n\cdot\frac{N-n}{N-1}\cdot\rho_d^2\right\}. \quad \text{(A39)}$$

Consequently, the RSD of the fluorescent X-ray intensity, ρ, is described as follows.

$$\rho=\sqrt{\frac{1}{n\cdot k\cdot\gamma\cdot\delta\cdot t}+\frac{1}{n}\cdot\left\{\rho_g^2\cdot\left(1+\rho_d^2\right)+n\cdot\frac{N-n}{N-1}\cdot\rho_d^2\right\}} \quad \text{(A40)}$$

6. Range of $1+\rho_d^2$

Using the definitions of Δ and δ shown in Eqs. (A21) and (A23), we can transform $1+\rho_d^2$ in Eq. (A38) into:

$$1+\rho_d^2=\frac{\Delta}{\delta^2}=\frac{\frac{1}{N}\cdot\sum_{i=1}^{N}d_i^2}{\left(\frac{1}{N}\cdot\sum_{i=1}^{N}d_i\right)^2}=N\cdot\frac{d_1^2+d_2^2+...+d_N^2}{\left(d_1+d_2+...+d_N\right)^2}. \quad \text{(A41)}$$

Eq. (A41) represents the nonuniformity of analyte distribution, because the value becomes larger as the uniformity of d_i worsens.

Here, the following inequality is generally valid for N positive variables $x_1, x_2, ..., x_N$.

$$\frac{1}{N}\le\frac{x_1^2+x_2^2+...+x_N^2}{\left(x_1+x_2+...+x_N\right)^2}\le 1. \quad \text{(A42)}$$

By applying this inequality to Eq. (A41), we can determine the range of $1+\rho_d^2$ as follows.

$$1\le 1+\rho_d^2\le N. \quad \text{(A43)}$$

NOMENCLATURE

f	fluorescence intensity
w	expectation of fluorescence intensity
k	proportionality coefficient
g	glancing angle
γ	average glancing angle
d	areal density (concentration) of analyte element

δ	average areal density (concentration) of analyte element
N	number of total measuring points (size of population)
n	number of sampling points (sample size)
t	integration time of each point
ρ	relative standard deviation

REFERENCE

[1] Miyazawa, K. *"Joho-Kettei Riron Josetsu"* (in Japanese); Iwanami Shoten, Publishers: Tokyo, Japan, 1971.