

Quantitative Auger and X-Ray Photoelectron Analysis of Au-Cu Alloys with Three Kinds of Relative Sensitivity Factors

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We have carried out the evaluation of the RSF method for XPS and AES quantitative analysis using three kinds of Au-Cu alloys. Recently, the average matrix relative sensitivity factors were proposed by Seah. Further more, International Standards Organization (ISO)/Technical Committee (TC) 201 has proposed "Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials", which includes three types of RSFs (elemental RSF (ERSF), atomic RSF (ARSF), and average matrix RSF (AMRSF)). The AMRSFs are considered most accurate among them because they take account of the almost complete matrix correction. However, no practical evaluation of AMRSFs has been made on AES and XPS analysis. We have, then, applied the RSF to the analysis of three kinds of Au-Cu alloys by XPS and AES, and evaluated the effectiveness of three kinds of RSFs on practical quantitative surface analysis. In conclusion, the AMRSF method gave sufficient results; the relative errors were within 6% in all alloys and the measured lines. The Q correction parameters were negligible small (less than 3%) in this study. The IMFP correction factors showed large contribution (up to 30%), which could be corrected sufficiently with TPP-2M formula. Then, AMRSF method could be applied to the practical quantitative surface analysis by XPS and AES.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are widely used for surface analysis of various materials. As for the quantitative surface analysis by AES and XPS, the matrix factor correction must be applied. The matrix factor is complicated and usually consists of the corrections of atomic density, electron escape depth or inelastic mean free path, electron elastic scattering, and electron backscattering (for AES only).

Sekine et al. proposed a matrix correction method for AES based on ZAF method in electron probe microanalysis (EPMA) and applied to the analysis several alloys[1]. Tanuma-Sekine-Yoshiahara evaluated matrix correction schemes for AES in 1990 using round robin measurements results for three kinds of Au-Cu alloys[2]. The most reliable correction equation combination (atomic density, Ichimura-Shimizu backscattering correction[3] and TPP equation[4] for inelastic mean free paths) gave excellent results; the rms error was about 5%[2].

The matrix correction method is useful, but it is rather complicated or tedious work to do the matrix correction described above for daily analysis work in industrial applications. Then, the relative sensitivity factors (RSFs) are commonly used for the surface analysis by AES and XPS. Recently, ISO/TC 201 SC5 proposed "Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials"[5]. This international standard includes three types of RSFs, which are elemental RSF (ERSF), atomic RSF (ARSF), and average matrix RSF (AMRSF). Although the ERSFs, which do not include any matrix correction factor, are widely used and easiest to apply the analysis, they may give a large error due to the matrix effect. The matrix correction factors for AES can vary with between 0.1 and 8[6], while for XPS they can vary between 0.3 to 3[7]. On the other hand, the AMRSFs, which were proposed by Seah[6], are considered most accurate among them because they take account of the almost complete matrix

Table 1 Average Auger peak intensity ratios (I^{mk}/I^{std}) for Au-Cu alloys of different compositions measured by eighteen institute. The used standards for Au and Cu are pure Au and Cu metal, respectively.

peak	specimen	average intensity ratios	σ
Au 239eV	Au75-Cu25	0.774	0.061
	Au50-Cu50	0.591	0.053
	Au25-Cu75	0.344	0.044
Au2024eV	Au75-Cu25	0.801	0.084
	Au50-Cu50	0.619	0.070
	Au25-Cu75	0.362	0.067
Cu920eV	Au25-Cu75	0.675	0.086
	Au50-Cu50	0.440	0.062
	Au75-Cu25	0.229	0.029

Table 2. Average photoelectron peak intensity ratios (I^{mk}/I^{std}) for Au-Cu alloys of different compositions measured by eighteen institute. The used standards for Au and Cu are pure Au and Cu metal, respectively.

peak	specimen	average intensity ratios	σ
Au 4f	Au75-Cu25	0.830	0.048
	Au50-Cu50	0.627	0.041
	Au25-Cu75	0.383	0.028
Cu2p3/2	Au25-Cu75	0.668	0.054
	Au50-Cu50	0.418	0.036
	Au75-Cu25	0.224	0.020

correction effects. However, no practical evolution of AMRSFs has been made on AES and XPS analysis. We have, then, applied the RSF to the analysis of three kinds of Au-Cu alloys by XPS and AES, and evaluated the effectiveness of three kinds of RSFs on practical quantitative surface analysis.

EXPERIMENTAL

The average measurement data of three kinds of alloys (Au75-Cu25: Au 73.2 at.%-Cu 26.8 at.%, Au50-Cu50: Au 50.2 at.%-Cu 49.8 at.%, Au25-Cu75: Au 24.7 at.%-Cu 75.3 at.%) by AES and XPS are listed in Tables 1(AES) and 2 (XPS)[2,8]. They were measured by 18 institutes as a VAMAS activity long ago.

Measurement conditions required the quantitative calculations were as follows; for AES, primary beam energy

was 5 keV, beam current was about 1 μ A, spectrum mode was dN/dE, modulations were 5eVp-p for Au 239 eV and Cu 920 eV and 10 eVp-p for Au2024 eV. For XPS, X-ray source was Al K α , analyzer resolution was 0.5 eV, and the used peaks were Au4f (kinetic energy: 1400eV) and Cu 2p_{3/2} (553 eV). The details were already reported[2,8,9]. Before measurements, the surface was cleaned with Ar ions, the energy of which was 1keV for AES and 2keV for XPS.

Relative sensitivity factors

There are tree type of RSF, I_i^{RSF} , defined below; elemental RSFs, atomic RSFs, and average matrix RSFs that are designated I_i^E , I_i^{At} , and I_i^{Av} , respectively[5].

The elemental RSF can be obtained from measurements of I_i^{ref} for standard material and a measurement of the peak intensity for the selected key material, I_{key} .

$$I_i^E = \frac{I_i^{ref}}{I_{key}} \tag{1}$$

The atomic RSF, I_i^{At} , can be described as

$$I_i^{At} = \left(\frac{N^{key}}{N_i} \right) I_i^E \tag{2}$$

where, N^{key} and N_i are the atomic densities for the key element and for the element i , respectively.

The average matrix RSF, I_i^{Av} , can be defined as[5]

$$I_i^{Av} = \left(\frac{N_{av} Q_{av} (1 + r_{av}) \lambda_{av}}{N_i Q_i (1 + r_i) \lambda_i} \right) I_i^E \tag{3}$$

where the terms N_{av} , Q_{av} , r_{av} , and λ_{av} are the atomic density, the elastic-scattering correction, the backscattering factor, and the inelastic mean free path for a hypothetical average matrix, respectively. The corresponding terms in the denominator of equation (3) are for the element i in elemental solid in this work.

The parameters in equation (3) can be obtained as follows.

1) Atomic density N

When A_i is the atomic weight of the element i , N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), and ρ_i is the density of the elemental solid (g cm^{-3}), the atomic density N_i of Au and Cu standard can be calculated from

$$N_i = \rho_i N_A / A_i \tag{4}$$

For average matrix [5],

$$N_{av} = 5.20 \times 10^{22} \text{ atoms cm}^{-3} \tag{5}$$

2) Elastic scattering correction Q

The parameter Q was calculated from the following equation[10].

For , $\omega_i \geq 0.245$

$$Q_i = (1 - \omega_i)^{0.5} \left[0.091 + 0.0923 \left(\frac{1 + 1.908}{1 + 1.908(1 - \omega_i)^{0.5}} \right) \right] \quad (6-a)$$

For , $\omega_i < 0.245$

$$Q_i = (1 - \omega_i)^{0.5} (1 + 0.412 \omega_i) \quad (6-b)$$

where ω_i is single scattering albedo and can be calculated from[11]

$$\omega_i = \frac{1}{1 + \zeta_i} \quad (7)$$

where ζ_i is the ratio of the transport mean free path

$$\zeta_i = \exp[\Gamma_{i,3} \ln^3 E_i + \Gamma_{i,2} \ln^2 E_i + \Gamma_{i,1} \ln E_i + \Gamma_{i,0}] \quad (8)$$

to the inelastic mean free path for element i , and the values of $\Gamma_{i,3}$, $\Gamma_{i,2}$, $\Gamma_{i,1}$ and $\Gamma_{i,0}$ for element i can be obtained from the reference[11].

The Q_{av} for average matrix can be calculated from[1]

$$Q_{av} = 0.951 - \left(\frac{E_i - 2310}{10300} \right)^2 \quad (9)$$

where E_i is the Auger or photoelectron energy (eV, kinetic energy).

3) backscattering factor $1 + r$

The backscattering factor $1 + r_i$ at $\theta = 30^\circ$ for AES were calculated from[3]

$$r_i = (0.462 - 0.777 Z^{0.20}) U_0^{-0.32} + 1.15 Z^{0.20} - 1.05 \quad (10)$$

where U_0 is the ratio of the incident electron energy E_{pr} to the binding energy $E_{b,i}$ of the core level for element i being ionized by backscattered electrons. θ is the primary beam incident angel from the surface normal.

The backscattering factor $1 + r_{av}$ for AES for average matrix can be estimated from[5]

$$r_{av} = 1.362 - 1.168 U_0^{-0.32} \quad (\theta = 30^\circ) \quad (11)$$

4) Inelastic mean free path λ_i

The inelastic mean free paths, IMFPs, for Au and Cu standard were calculated from[4]

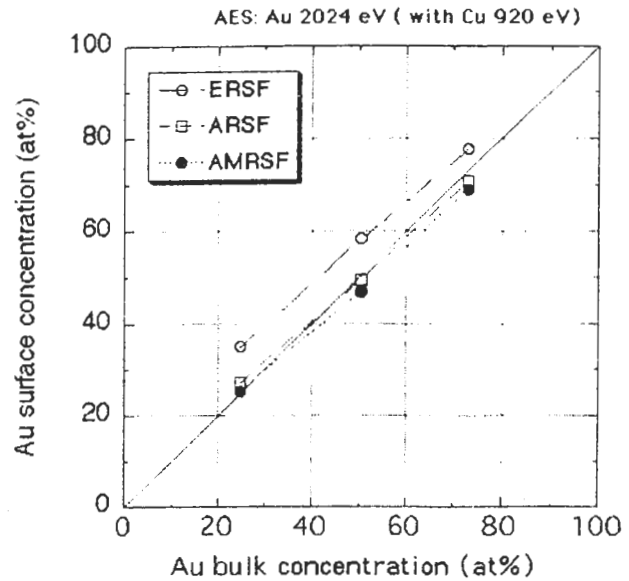


Fig. 1. Resulting surface Au concentration of Au-Cu alloy by AES with three kinds of RSFs as a function of bulk Au concentration. The used Auger peaks were 2024 eV for Au and 920 eV for Cu. ERSF is the elemental relative sensitivity factor defined by equation (1). ARSF is the atomic relative sensitivity factor defined by equation (2). AMRSF is the average matrix relative sensitivity factor defined by equation (3).

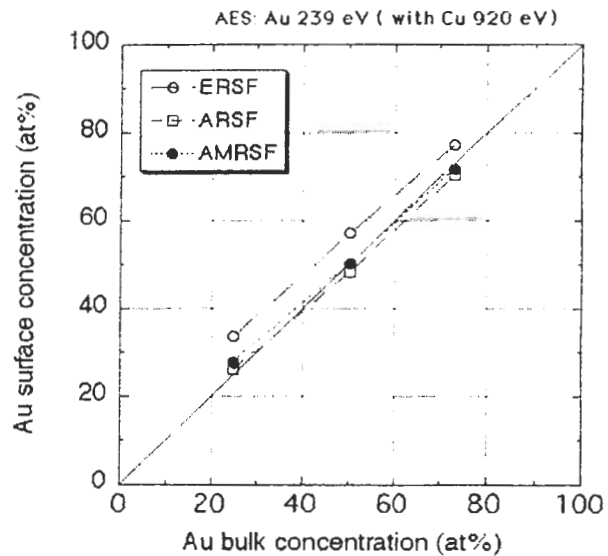


Fig. 2. Resulting surface Au concentration of Au-Cu alloy by AES with three kinds of RSFs as a function of bulk Au concentration. The used Auger peaks were 239 eV for Au and 920 eV for Cu. See the caption in Fig. 1.

$$\lambda_i = \frac{E_i}{E_p^2 [\beta \ln(\gamma E_i) - (C/E_i) + (D/E_i^2)]} \text{ (\AA)} \quad (12)$$

$$\beta = -0.10 + 0.944 (E_p^2 + E_g^2)^{-0.5} + 0.069 \rho^{0.1} \quad (13a)$$

$$\gamma = 0.191 \rho^{-0.5} \quad (13b)$$

$$C = 1.97 - 0.91U \quad (13c)$$

$$D = 53.4 - 20.8U \quad (13d)$$

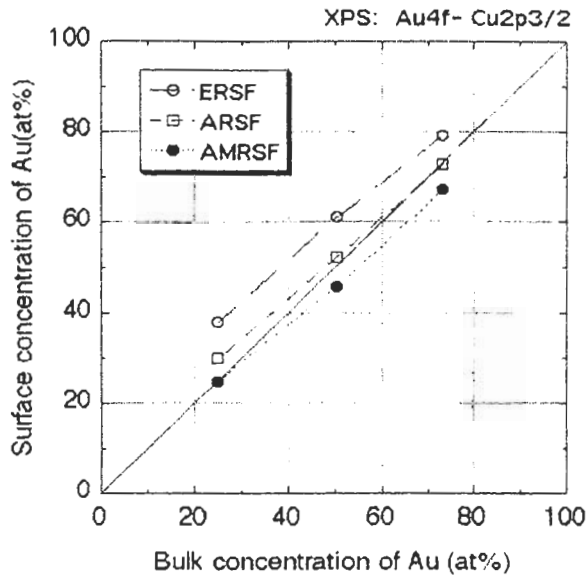


Fig. 3. Resulting surface Au concentration of Au-Cu alloy by XPS with three kinds of RSFs as a function of bulk Au concentration. The used photoelectron peaks were Au4f for Au and Cu2p for Cu. See the caption in figure 1.

$$U = N_v \rho / M_i \quad (13e)$$

$$E_g = 28.8 (N_v \rho / M_i)^{0.5} \quad (\text{eV}) \quad (13f)$$

where E_i is electron energy (eV), ρ is density of the sample (g cm^{-3}), N_v is number of valence electrons per atom or molecule, E_g is band-gap energy (eV) and M_i is atomic weight.

The IMFPs for average matrix was calculated from[5]

$$\lambda_{av} = \frac{0.00523 E_i^3}{48.6 - 1.76 E_i + 0.0518 E_i^2 (-2.61 + \ln E_i)} \quad (\text{\AA}) \quad (14)$$

The above equation was obtained from equation (12)-(13f) using the physical parameters for the hypothetical average matrix ($Z = 40.5$, $Nv = 4.684$, $\rho = 6.767 \text{ gcm}^{-3}$, $M_i = 137.51$, $E_g = 0 \text{ eV}$ [6]).

Quantitative calculation

Using RSFs, I_i^{RSF} , the surface atomic concentration C_{Au} in Au-Cu alloy can be determined from

$$C_{Au} = \frac{I_{Au}^{alloy} / I_{Au}^{RSF}}{I_{Au}^{alloy} / I_{Au}^{RSF} + I_{Cu}^{alloy} / I_{Cu}^{RSF}} \quad (15)$$

where I_{Au}^{alloy} , I_{Cu}^{alloy} means the measured peak intensity of Au and Cu for AES or XPS, respectively.

RESULTS AND DISCUSSION

AES

The resulting surface concentrations of gold in three kinds of alloys determined with RSF method are shown in Figs. 1 and 2. From these figures, the ERSF method gave larger errors for Au surface concentrations in Au-Cu alloys than those with ARSF or AMRSF method. The rms errors with ERSF were 24.5% in Au concentration, and the relative errors were in the 5 - 41% range. On the other hand, the rms errors of surface gold concentration with ARSF were 5.5% in Au, and the error is in the range of -3% to 10%. The errors of Au concentration determined with AMRSF were 6.3%, and the relative error is in the range of -6% to 12%. Then, the ARSF method gave the almost the same accuracies compared to the results with AMRSF method. Since their relative errors were within 10% except one case, these RSFs could be applied to the practical AES analysis.

XPS

The resulting surface concentrations of gold in the Au-Cu alloys with three kinds of RSFs are shown in Fig. 3 as a function of bulk Au-concentration. This figure shows the resulting surface Au concentrations with ERSF were larger than those with ARSF or AMRSF in all Au-Cu alloys. The rms error of Au concentration with ERSF was 34%. The Au surface concentration obtained from ARSF and AMRSF were good agreement with those of bulk concentrations. The rms errors of Au concentration with ARSF and AMRSF were 12.5 and 6.9%, respectively. However, the quantitative results with ARSF seem to be good from Fig.3 compared to those with AMRSF. The reason is why the relative error of Au concentration at Au25-Cu75 specimen is large (21% larger than the bulk concentration). Then, we could recommend to use AMRSF to the quantitative XPS analysis.

Matrix effect

From equations (1) -(3), the RSF can be described as

$$I_i^A = F_i \cdot I_i^E \quad (16)$$

where I_i^A corresponds to ARSF or AMRSF, and F_i is a matrix correction factor. Then, equation (15) could be expressed as

$$C_{Au} = \left[1 + \left(\frac{I_{Cu}^{alloy}}{I_{Cu}^E} \right) \left(\frac{I_{Au}^{alloy}}{I_{Au}^E} \right)^{-1} \left(\frac{F_{Au}}{F_{Cu}} \right) \right]^{-1} \quad (17)$$

Table 3 Values of the correction factors for average matrix relative sensitive factors

	N	Q	1+r	λ
AES(Au2024-Cu920)	1.43	1.02	0.85	1.29
AES(Au239-Cu920)	1.43	0.97	0.83	1.15
XPS	1.43	1.01	----	1.28

The two terms $I_{Cu}^{alloy} / I_{Cu}^i$ and $I_{Au}^{alloy} / I_{Au}^i$ are determined experimentally in this study (from Table 1-3). For ARSF, the matrix factor is described as

$$\frac{F_{Au}}{F_{Cu}} = \frac{N_{Cu}}{N_{Au}} \tag{18}$$

For AMRSF, the matrix factor can be described as

$$\frac{F_{Au}}{F_{Cu}} = \left(\frac{N_{Cu}}{N_{Au}} \right) \left(\frac{Q_{Cu}}{Q_{Au}} \right) \left(\frac{Q_{av}(E_{Cu})}{Q_{av}(E_{Au})} \right)^{-1} \left\{ \left(\frac{Q_{av}(E_{Cu})}{Q_{av}(E_{Au})} \right) \left(\frac{1+r_{av}(E_{Cu})}{1+r_{av}(E_{Au})} \right) \left(\frac{\lambda_{av}(E_{Cu})}{\lambda_{av}(E_{Au})} \right) \right\}^{-1} \tag{19}$$

In equations (18) and (19), the term of atomic density ratio can be calculated from pure elemental solid standard specimen, which equals to 1.43. The second term is the ratios of matrix factors of pure copper to pure gold, and is the same as the full matrix correction. The third one is the matrix factor ratios at electron energies of Cu peaks and those of gold peaks in a hypothetical average matrix, and a function of peak energy only. This point is quite different from the full matrix correction method. In a same specimen, the magnitude of the correction parameters largely depend on Auger or photoelectron energy compared with the factor of elemental composition if the analyzed lines have large different energy values.

To get the correction parameters, equation (19) could be described as

$$\frac{F_{Au}}{F_{Cu}} = \left(\frac{N_{Cu}}{N_{Au}} \right) \left\{ \left(\frac{Q_{Cu}}{Q_{Au}} \right) \left(\frac{1+r_{Cu}}{1+r_{Au}} \right) \left(\frac{\lambda_{Cu}}{\lambda_{Au}} \right) \right\} \cdot \left(\frac{1+r_{Cu}}{1+r_{Au}} \right) \left(\frac{1+r_{av}(E_{Cu})}{1+r_{av}(E_{Au})} \right)^{-1} \left(\frac{\lambda_{Cu}}{\lambda_{Au}} \right) \left(\frac{\lambda_{av}(E_{Cu})}{\lambda_{av}(E_{Au})} \right)^{-1} = NQ(1+r)\lambda \tag{20}$$

The ratios of the parameters in equation (20) are shown in Table 3. For AES, this table shows that the atomic density correction factor is the largest (over 40%). However, this correction parameter can be calculated correctly

because it requires the atomic density of standard specimens only. On the other hand, the factors Q are the smallest in the correction factors in AES and XPS, and are less 3%. They might be ignored in this case. The values of IMFP corrections are larger than those of backscattering corrections in AES, and their magnitude are in the 15% - 30% range.

For example, a Au50-Cu50 specimen, the physical parameters ($Z = 54, Nv = 11, \rho = 12.2 \text{ gcm}^{-3}, M = 130.3$) are quite different from a hypothetical average matrix ($(Z = 40.5, Nv = 4.684, \rho = 6.767 \text{ gcm}^{-3}, M = 137.51[6])$). In spite of differences, the factors in IMFP ratios in the third term in equation (19) calculated from Au-Cu specimen are in good agreement with a hypothetical one at all measured peak energies within 6% relative differences.

SUMMARY

We have carried out the evaluation of the RSF method for XPS and AES quantitative analysis using three kinds of Au-Cu alloys. The AMRSF method gave sufficient results; the relative errors were within 6% in all alloys and the combinations of measured lines. The ARSF gave also excellent results except Au25-Cu75 alloy in XPS analysis.

We also investigated the influence of the correction factors in AMRSFs. The Q parameters correction was negligible small (less than 3%) in this study. Although the largest effect was atomic density correction, it can be corrected easily from the atomic densities of standard materials. The IMFP correction factors showed large contribution (up to 30%), which could be corrected sufficiently with TPP-2M formula. Then, AMRSF method could be applied to the practical quantitative surface analysis by XPS and AES.

References

- [1] T. Sekine, K. Hirata, and A. Mogami, *Surf. Sci.* **125**, 565 (1983).
- [2] S. Tanuma, T. Sekine, K. Yoshihara and et al., *Surf. Interface Anal.* **15**, 466 (1990).
- [3] S. Ichimura, R. Shimizu, and J.P. Langeron, *Surf. Sci.* **124**, L49 (1983).
- [4] S. Tanuma, C.J. Powell, and D.R. Penn, *Surf. Interface Anal.* **21**, 165(1994).
- [5] ISO/DIS 18118
- [6] M.P. Seah and I.S. Gilmore, *J. Electron. Surf. Interface Anal.* **26**, 908 (1998).

- [7] M.P. Seah and I.S. Gilmore, *J. Electron. Spectrosc. Relat. Phenom.* **120**, 93 (2001).
- [8] S. Tanuma, *J. Surf. Anal.* **1**, 24 (1995).
- [9] M. Yoshitake and K. Yoshihara, *Surf. Interface Anal.* **17**, 711 (1991).
- [10] M.P. Seah and I.S. Gilmore, *Surf. Interface Anal.* **31**, 835 (2001).
- [11] A. Jablonski and C.J. Powell, *J. Vac. Sci. Technol.* **A15**, 2095 (1997).