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Quantitative Analysis of Pt Mole Fraction in Pt_xNi_{1-x} Alloy Films

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We performed a pilot study P-248 in the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM) for the quantitative surface analysis of Pt_xNi_{1-x} binary alloy films. The mole fractions of Pt in Pt_xNi_{1-x} alloy thin films were measured using X-ray Photoelectron Spectrometry (XPS), X-ray Fluorescence analysis (XRF), and Scanning Electron Microscopy / Energy Dispersive X-ray Spectrometry (SEM/EDX).

Five Pt_xNi_{1-x} alloy films of different nominal compositions (x=0.2, 0.35, 0.5, 0.65, and 0.8) and one test sample with unknown composition, as well as a pure Pt and a pure Ni sample, were distributed for P248. As certified values, we used the mole fractions of the five reference Pt_xNi_{1-x} alloy thin films measured by Rutherford Backscattering Spectrometry (RBS), which agreed well with those measured by isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS) within a 1.1% difference.

Eight laboratories from seven NMIs and one DI using XPS, XRF, and SEM/EDX participated in this pilot study. The mole fractions of Pt_xNi_{1-x} alloy thin films were determined using pure element relative sensitivity factor (PERSF) in XPS analysis and showed severe matrix effect even after multiple-point calibration. The mole fractions of the test specimen using alloy reference RSF (ARRSF) and multi-alloy reference RSF (MRRSF) showed better agreement among measurement methods. We suggest the quantification analysis of Pt_xNi_{1-x} alloy films as a candidate subject for a new key comparison of CCQM.

1. INTRODUCTION

Several key comparisons (KCs) about surface analysis have been performed by the Surface Analysis Working Group (SAWG) of the Consultative Committee for Amount of Substance (CCQM).[1-5] The first pilot study (P38) in 2004 was about the thickness measurements of ultra-thin SiO_2 thin films on Si(100) and Si(111) substrates.[6] The aim of the PS and KC is to ensure equivalency in the measurement of National Metrology Institutes (NMIs) and Designated Institutes (DIs).

Quantitative surface analysis is one of the most essential applications of surface analysis techniques. Among five KCs performed by SAWG, two KCs are for the quantitative surface analyses of alloy films. K-67 is for the quantitative analysis of binary alloy (Fe_xNi_{1-x}) films [2], and K-129 is for the quantitative analysis of multi-element alloy ($Cu(In_xGa_{1-x})Se_2$) film.[3] Although XPS and AES are generally used for the surface compositional analysis of multi-component alloy systems, accurate surface composition analysis is not trivial due to the matrix effect. The pure element relative sensitivity factors (PERSFs) determined from pure metals are generally applied for the quantification of alloy materials. However, the matrix effect due to atomic density, attenuation lengths of electrons and electron backscattering factor in the matrix materials should be taken into account for the correct and reliable quantitative analysis. [7-10]

A calibration method using alloy reference materials is recommended for the quantitative analysis of binary alloys to compensate for the matrix effect. The best method for the quantification of binary alloys is to use an alloy reference RSF (ARRSF) with a similar composition to the analysis sample as used in K-67 and K-129. The next best one is to use a calibration curve measured using a series of alloy reference materials with different compositions spanning the unknown composition, as reported in P98.

In this study, the results of the CCQM pilot study P248 on the measurement of mole fractions of Pt_xNi_{1-x} alloy films are reported. In the case of XPS analysis, the mole fraction of a test Pt_xNi_{1-x} film was investigated by multiple point calibration method using the PERSFs determined from the pure Pt and Ni films. The mole fraction of a test Pt_xNi_{1-x} film was determined using an ARRSF derived from an alloy reference sample, and a multi-element alloy reference RSF (MRRSF) was compared.

2. PREPARATION OF THE SAMPLES

Fabrication of the Reference and Test Specimens

Pt_xNi_{1-x} films were grown by an ion beam sputtering deposition system at KRISS. Pt and Ni target materials were sputtered by a 1 keV Ar^+ ion beam produced by a Kaufmann-type DC ion gun and deposited on substrates at room temperature. Pt_xNi_{1-x} films were grown on 150 mm diameter Si (100) wafers rotating with a speed of about 30 revolutions per minute to improve the uniformity of composition. Thin films grown on silicon wafers were divided into 10 mm x 10 mm specimens. The specimens taken from near the centre or the edge of the wafer were not used as reference specimens. Alloy films with five different nominal compositions were produced: $Pt_{0.2}Ni_{0.8}$, $Pt_{0.35}Ni_{0.65}$, $Pt_{0.5}Ni_{0.5}$, $Pt_{0.65}Ni_{0.35}$, and $Pt_{0.8}Ni_{0.2}$. The film thicknesses were controlled to be about 100 nm. The test specimen was grown using the same method as reference specimens. The approximate composition was $Pt_{0.5}Ni_{0.5}$.

Quantitative Analysis of Reference Specimens using RBS

Rutherford Backscattering Spectrometry (RBS) was found to be traceable for the quantitative analysis of binary alloy films from the comparative analysis of the mole fractions of the Ag_xCu_{1-x} alloy films. [11] In this study, the mole fractions of the Pt_xNi_{1-x} alloy films with a nominal thickness of 100 nm were analyzed by RBS in Eurofins EAG Materials Science (Sunnyvale, CA 94086, USA). RBS spectra of the Pt_xNi_{1-x} alloy films are acquired at a backscattering angle of 160° and an appropriate grazing angle (with the sample oriented perpendicular to the incident ion beam). The sample is rotated or tilted with a slight angle to present a random geometry to the incident beam. This avoids channeling in both the film and the substrate. Using two detector angles can significantly improve the measurement accuracy for composition when thin surface layers need to be analyzed.

In the RBS analysis of Pt_xNi_{1-x} alloy films, the areal densities of Ni and Pt were obtained by the peak integration method that integrates the areas of corresponding peaks. The areal density ratios measured for thin film analysis directly yield the stoichiometric ratios of elements in the film. Figure 1 shows the RBS spectra of the Pt_xNi_{1-x} alloy films with a nominal thickness of 100 nm. The peaks of Pt and Ni are fully separated, and the RBS spectra were fit by applying a theoretical layer model and iteratively adjusting elemental concentrations and thickness. The relative mole fractions of the alloy films could be well determined by a simulation program with iterative adjusting elemental concentrations and thickness until the root-mean-square error between the theoretical and the experimental spectra is minimized.

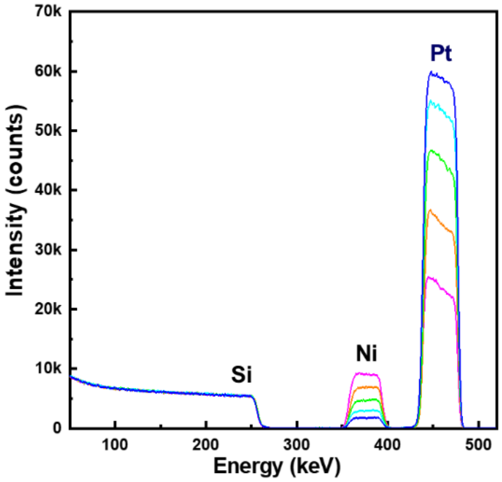

Figure 1. RBS spectra of the Pt_xNi_{1-x} alloy films with the nominal thickness of 100 nm.

The mole fractions and uncertainties of Pt and Ni in the alloy films measured by RBS are given in Table 1. Small amounts of Ar atoms involved during sputtering deposition of the alloy films by 1 keV Ar ion beam were detected in all alloy films with the range of 0.7 ~ 1.5 cmol/mol. The relative mole fractions, excluding the amount of Ar, were determined to compare the relative mole fractions of Pt and Ni measured by RBS to those measured by isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS). The measurement uncertainties by RBS are expressed as expanded uncertainties $U = ku_c$, where k is the coverage factor of 2, giving an approximate level of confidence of 95%, and u_c is the combined standard uncertainty calculated in accordance with the ISO "Guide to the Expression of Uncertainty in Measurement". The expanded measurement uncertainties of Pt and Ni are 0.5 cmol/mol.

Table 1. Mole fractions of Pt and Ni in the Pt_xNi_{1-x} alloy films measured by RBS

Sample	Mole Fraction (cmol/mol)	
	Pt	Ni
$Pt_{0.20}Ni_{0.80}$	25.8 ± 0.5	74.2 ± 0.5
$Pt_{0.35}Ni_{0.65}$	40.6 ± 0.5	59.4 ± 0.5
$Pt_{0.50}Ni_{0.50}$	56.0 ± 0.5	44.0 ± 0.5
$Pt_{0.65}Ni_{0.35}$	71.0 ± 0.5	29.0 ± 0.5
$Pt_{0.80}Ni_{0.20}$	81.8 ± 0.5	18.2 ± 0.5

Quantitative Analysis of Reference Specimens using ID ICP-MS

The relative mole fractions of Pt and Ni in the five Pt_xNi_{1-x} alloy films were also measured by isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS) to confirm the traceability of RBS for the quantitative analysis of binary alloy films. The ICP-MS equipment used was ICP-MS-QQQ, 8800 ICP-MS Triple Quad model, from Agilent Technologies. Quantitative analysis of Pt and Ni in the Pt_xNi_{1-x} alloy films was performed using isotope dilution mass spectrometry (IDMS).

Five alloy films deposited on Si (100) substrates were heated on a hot plate with aqua regia (nitric acid: hydrochloric acid = 1:3) and HF. The measurement conditions of Pt and Ni were optimized to provide maximum sensitivity for each element. The isotope standard solutions of ^{62}Ni and ^{196}Pt were used, and the primary reference materials for each element were produced by LGC Ltd, KRISS, NIST ISOFLEX and AccuStandard. Pt_xNi_{1-x} alloy films without isotope addition were separately pretreated to determine the effect of the medium.

The enriched spike isotopic standards were added quantitatively to an aliquot of the sample solution to yield the isotope ratio (reference isotope/enriched isotope) to be 1. This isotope ratio minimizes the error magnification factor (EMF) and measurement uncertainty. The spiked sample solutions were diluted with deionized water appropriately for ICP-MS measurement.

The mole fractions and corresponding expanded uncertainties of Pt and Ni in Pt_xNi_{1-x} alloy films with different compositions and thicknesses are shown in Table 2. For the quantitative analysis of Pt_xNi_{1-x} films, the measured mole fractions by ID ICP-MS and RBS were plotted in Figure 2, showing the linearity between them. The slope of 1.011 indicates that the mole fractions of the Pt_xNi_{1-x} alloy films measured by RBS are close to those by ID ICP-MS, within a difference of 1.1%. This and the recent result [11] for the comparative results of the quantitative analysis of binary alloy films support the traceability of RBS.

Table 2. Mole fractions of Pt and Ni in the Pt_xNi_{1-x} alloy films measured by ID-ICP/MS

Sample	Mole Fraction (cmol/mol)	
	Pt	Ni
$Pt_{0.20}Ni_{0.80}$	25.8 ± 0.7	74.2 ± 0.7
$Pt_{0.35}Ni_{0.65}$	40.2 ± 0.8	59.8 ± 0.8
$Pt_{0.50}Ni_{0.50}$	55.9 ± 0.7	44.1 ± 0.7
$Pt_{0.65}Ni_{0.35}$	70.4 ± 0.4	29.6 ± 0.4
$Pt_{0.80}Ni_{0.20}$	81.1 ± 0.4	18.9 ± 0.4

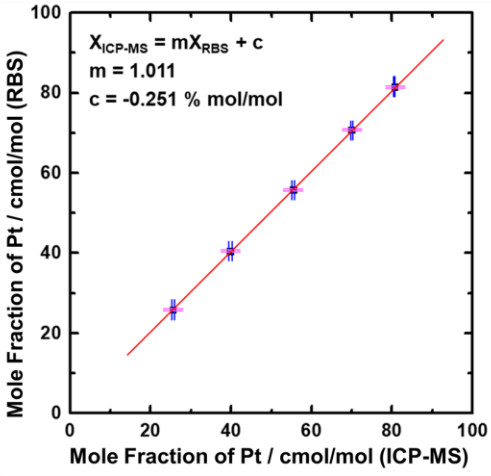

Figure 2. Linear plot for the mole fractions of Pt in the Pt_xNi_{1-x} films by ID ICP-MS and RBS. The blue and pink error bars represent the expanded uncertainties of ID ICP-MS and RBS.

Certification of Reference Specimens

The final certified values of the five Pt_xNi_{1-x} alloy reference materials were obtained by averaging the values of RBS and ID ICP-MS analysis, and the uncertainties were expressed by following equation combining two measurement methods, as recommended by NPL. The results are listed in Table 3.

$$U^2 = \frac{U_{RBS}^2 + U_{ICPMS}^2}{2} + (X_{RBS} - X_{ICPMS})^2 \text{ --- } (1)$$

Table 3. Certified mole fractions of the five Pt_xNi_{1-x} alloy reference specimens.

Sample	Mole fractions (cmol/mol) and expanded uncertainty	
	Pt	Ni
$Pt_{0.20}Ni_{0.80}$	25.8 ± 0.6	74.2 ± 0.6
$Pt_{0.35}Ni_{0.65}$	40.4 ± 0.8	59.6 ± 0.8
$Pt_{0.50}Ni_{0.50}$	55.9 ± 0.6	44.1 ± 0.6
$Pt_{0.65}Ni_{0.35}$	70.6 ± 0.8	29.4 ± 0.8
$Pt_{0.80}Ni_{0.20}$	81.3 ± 0.8	18.7 ± 0.8

3. OUTLINE OF THE PILOT STUDY

3.1. Objective, Timetable and Participation

The objective of the CCQM-P248 pilot study is to determine the mole fractions of Pt_xNi_{1-x} alloy films and to compare the equivalency of NMIs and DIs in the measurement of the composition of alloy films. There was no limitation in choosing an analytical technique for the quantification of alloy films. In April 2023, the quantification of Pt_xNi_{1-x} alloy films was suggested as a new subject for the pilot study in CCQM SAWG, showing the measured mole fractions by XPS with the reference mole fractions certified by Rutherford Backscattering Spectrometry (RBS). After discussion, it was approved as a project for a pilot study in the CCQM meeting in April 2023. The pilot study's original number was P229, but it was renumbered on February 25, 2025, to avoid confusion between P229.a of SAWG and P229.b of GAWG (Gas Analysis Working Group).

The protocol and the test specimens have been delivered to the participants by the end of September 2023. One of our participants, the National Metrology Institute of Japan (NMIJ), could not report their measurement data due to Japan’s export control regulation after the participation of VNIIM in P248. The results of the pilot study determined from the basis of the certified mole fractions by RBS were gathered by March 2024 and reported at the CCQM meeting in April 2024.

In the 2024 CCQM meeting, the RSFs determined from the certified mole fractions of the Pt_xNi_{1-x} alloy films measured by Isotope Dilution Inductively Coupled Plasma-Mass Spectrometry -ICP-MS (ID-ICP/MS) were discussed. By the end of December 2024, additional data from the participants using XPS were gathered. Eight laboratories, seven NMIs and one DI participated in this pilot study, as shown in Table 4.

Table 4. Participants in P248.

Country	Laboratory	Method	NMI or DI
China	National Institute of Metrology (NIM)	XPS	NMI
Denmark	Danish Fundamental Metrology (DFM)	SEM/EDX	NMI
Germany	Bundesanstalt für Materialforschung und – Prüfung (BAM)	XPS	DI
Germany	Physikalisch-Technische Bundesanstalt (PTB)	XRF	NMI
Korea	Korea Research Institute of Standards & Science (KRISS)	XPS	NMI
Russia	A.I. Mendeleev All-Russian Institute for Metrology (VNIIM)	XRF	NMI
UK	National Physical Laboratory (NPL)	XPS	NMI
USA	National Institute of Standards and Technology (NIST)	XPS, XRF	NMI

3.2. Quantification Methods using XPS

Each participant used each measurement method: XPS, XRF, and SEM/EDX as shown in Table 4. The three quantification methods using XPS measurement are described below.

(1) Quantification by Multiple-Point Calibration using PERSF

Quantification by pure element relative sensitivity factors (PERSF) is a general method to measure the composition of alloy films. However, the mole fractions of some alloy films with severe matrix effects can be distorted from the actual values due to the matrix effects. If PERSFs determine the mole fractions of Pt and Ni in Pt_xNi_{1-x} alloy films, they will be changed from the actual values due to the severe matrix effect.

Before XPS analysis, the surface contaminants should be removed by sputtering with an Ar^+ ion beam. To minimize the surface compositional change of the alloy films by preferential sputtering, the sputtering energy of an Ar^+ ion beam lower than 1 keV is recommended. Sputtering to the peak intensities of O *1s* and C *1s* less than 2% of the heights of the most intense metal peak is recommended.

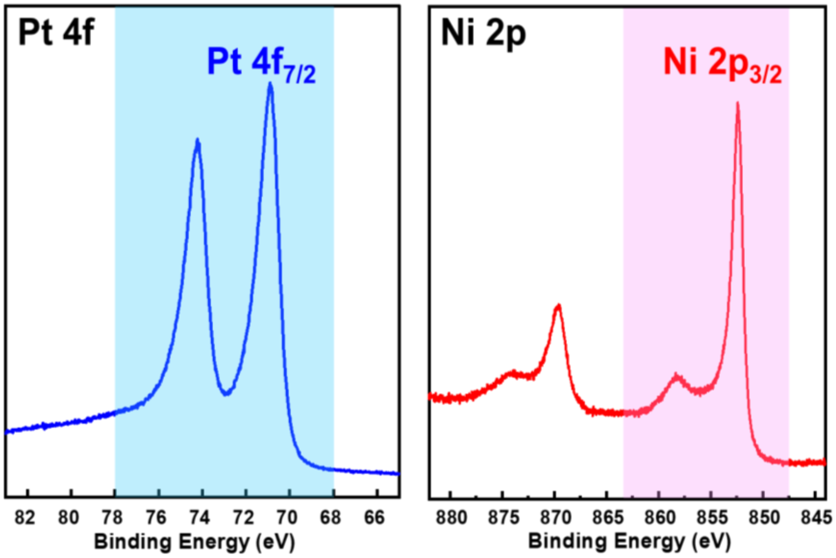

Figure 3. Measurement of peak areas of Pt and Ni in the colored regions in the Pt *4f* and Ni *2p* core level spectra

This study introduced the multiple-point calibration method with PESRFs to correct the changed mole fractions to the original value. First of all, we determine PERSFs of Pt (S_{Pt}) and Ni (S_{Ni}) from the peak areas of pure Pt (A_{Pt}^{∞}) and Ni (A_{Ni}^{∞}) films, respectively. Figure 3 shows the Pt

4f and Ni *2p* core level spectra to determine the peak areas of pure Pt (A_{Pt}^{∞}) and Ni (A_{Ni}^{∞}) films. Peak areas are determined by integrating the two peak intensities after peak smoothing and background subtraction by the Shirley method in the colored regions in Figure 3. The recommended integration range for the area measurement of Pt *4f* peak is from Pt *4f*$_{7/2}$ + 7 eV to Pt *4f*$_{7/2}$ - 3 eV, and those for Ni *2p* peak is from Ni *2p*$_{3/2}$ + 11 eV to Ni *2p*$_{3/2}$ - 5 eV, respectively.

The average peak areas of Pf *4f* and Ni *2p*$_{3/2}$ peaks in the pure Pt and pure Ni films are used as the pure element relative sensitivity factors (PERSFs) of Pt (S_{Pt}) and Ni (S_{Ni}).

$$S_{Pt} = A_{Pt}^{\infty},\ S_{Ni} = A_{Ni}^{\infty} \quad \text{------------------------------------} \quad (2)$$

The mole fraction of Pt (X_{Pt}^{al}) in an alloy film can be derived from the peak areas of Pt (A_{Pt}^{al}) and Ni (A_{Ni}^{al}) by the following equations using S_{Pt} and S_{Ni} without correction of the matrix effect.

$$X_{Pt}^{al} = \frac{(A_{Pt}^{al}/S_{Pt})}{(A_{Pt}^{al}/S_{Pt})+(A_{Ni}^{al}/S_{Ni})} \quad \text{------------------------------------} \quad (3)$$

For reliable analysis, the same analysis conditions should be applied to all specimens, and the measurements should be repeated more than five times to minimize the measurement uncertainty. Table 4 shows an example of the measured mole fractions of Pt and Ni in the five Pt_xNi_{1-x} alloy reference films and the test Pt_xNi_{1-x} alloy film using the PERSFs.

Table 4. Example of the measured mole fraction of Pt in the five Pt_xNi_{1-x} alloy reference films and the test Pt_xNi_{1-x} alloy film.

Sample		Composition (Pt cmol/mol)	
		XPS	Certified
Reference Specimens	$Pt_{0.20}Ni_{0.80}$	42.5	25.8 ± 0.6
	$Pt_{0.35}Ni_{0.65}$	57.9	40.4 ± 0.8
	$Pt_{0.50}Ni_{0.50}$	71.7	55.9 ± 0.6
	$Pt_{0.65}Ni_{0.35}$	83.0	70.6 ± 0.8
	$Pt_{0.80}Ni_{0.20}$	90.0	81.3 ± 0.8
Test Specimen	Pt_xNi_{1-x}	70.0	-

An equation of multiple-point calibration to compensate for the matrix and sputtering effect in the quantitative analysis of the Pt_xNi_{1-x} alloy films is extracted from the measured and certified mole fractions of Pt in the five Pt_xNi_{1-x} alloy reference films. The 2nd-order equation is derived from quadratic polynomial fitting using the measured mole fractions of Pt (X_{Pt}^{al}) by XPS in the five Pt_xNi_{1-x} alloy reference films in x-axis and the certified mole fractions (C_{Pt}^{al}) of Pt in y-axis. For example, a quadratic polynomial fitting can be extracted from the measured and certified mole fractions shown in Table 4.

The mole fraction of Pt in the test film is determined by dividing the peak areas of Pf *4f* and Ni $2p_{3/2}$ by the PERSFs and normalization to 100%. Then, the mole fraction of Pt is corrected by the calibration equation (4). The corrected mole fraction C_{Pt}^{Test} is determined by putting the measured mole fraction (70.0 cmol/mol) as X_{Pt}^{Test} in the calibration equation, as shown in Figure 4.

$$C_{Pt}^{Test} = 0.0073{X_{Pt}^{Test}}^2 + 0.196X_{Pt}^{Test} + 4.3963 = 53.85 \text{ (cmol/mol)} \quad \text{-------------} \quad (4)$$

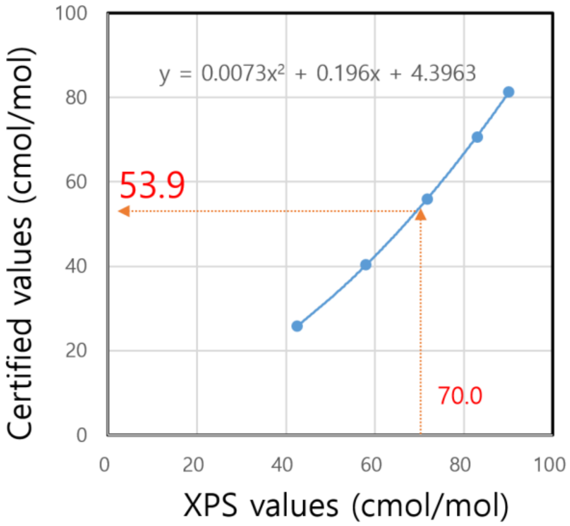

Figure 4. An example of determining the relative mole fraction of Pt in test specimen by using the multiple-point calibration.

(2) Quantification by ARRSF

The mole fractions of alloy films can also be analysed by the relative sensitivity factors determined from certified alloy films. The alloy reference relative sensitivity factors (ARRSF) is determined from the relative ratio of the peak area of Pt (A_{Pt}^{al}) divided by the certified mole fractions of Pt (C_{Pt}^{al}) and the peak area of Ni (A_{Ni}^{al}) divided by the certified mole fractions of Ni (C_{Ni}^{al}). If these two values (A_{Ni}^{al}/C_{Ni}^{al}, A_{Pt}^{al}/C_{Pt}^{al}) are divided by the larger one (A_{Pt}^{al}/C_{Pt}^{al}), the larger one becomes 1 (= $(A_{Pt}^{al}/C_{Pt}^{al})/(A_{Pt}^{al}/C_{Pt}^{al})$) and the smaller one (= $(A_{Ni}^{al}/C_{Ni}^{al})/(A_{Pt}^{al}/C_{Pt}^{al})$) becomes a value less than 1, which is called ARRSF.

$$R_{Pt}^{AR} = (A_{Pt}^{al}/C_{Pt}^{al})/(A_{Pt}^{al}/C_{Pt}^{al}) = 1,\ \ R_{Ni}^{AR} = (A_{Ni}^{al}/C_{Ni}^{al})/(A_{Pt}^{al}/C_{Pt}^{al}) < 1 \quad \text{---------------} \ (5)$$

By using the relative values like this, the uncertainty factors due to changes in measurement conditions can be compensated and the uncertainty in determining the relative sensitivity factors is highly improved.

The mole fraction of Pt in the test alloy films (X_{Pt}^{Test}) can be measured by the ARRSF (R^{AR}) from the peak areas of Pt (A_{Pt}^{Test}) and Ni (A_{Ni}^{Test}) using the following equation.

$$X_{Pt}^{Test} = \frac{A_{Pt}^{Test}}{A_{Pt}^{Test} + (A_{Ni}^{Test}/R^{AR})} \quad \text{---} \ (6)$$

For the application of ARRSFs, an alloy reference film with a mole fraction similar to that of the analysis sample is recommended. ARRSFs have been used for the previous KCs in SAWG for Fe-Ni alloy film in K-67 [2] and Cu(In, Ga)Se$_2$ film in K-129 [3]. In this pilot study, the mole fraction of the test Pt$_x$Ni$_{1-x}$ alloy film was also determined using ARRSFs determined from the Pt$_{0.5}$Ni$_{0.5}$ alloy film.

(3) Quantification by MRRSF

NPL submitted the mole fractions determined by Multi-alloy Reference Relative Sensitivity Factors (MRRSF). The MRRSF (R^{MR}) is determined from the average values of ARRSFs (R^{AR}) determined from the five certified Pt$_x$Ni$_{1-x}$ alloy films as shown in Table 5.

In this method, the mole fractions of Pt (X_{Pt}^{al}) in the five certified Pt$_x$Ni$_{1-x}$ alloy films can be determined from the peak areas of Pt (A_{Pt}^{al}) and Ni (A_{Ni}^{al}) using by the following equation.

$$X_{Pt}^{al} = \frac{A_{Pt}^{al}}{A_{Pt}^{al} + (A_{Ni}^{al}/R^{MR})} \quad \text{---} \ (7)$$

Table 5 shows that the mole fractions of Pt in the Pt$_x$Ni$_{1-x}$ alloy films measured by MRRSF are similar to the certified values because the matrix and sputtering effects are compensated.

Table 5. Example of mole fractions of Pt in the Pt$_x$Ni$_{1-x}$ alloy films measured by MRRSF.

Sample	Peak Area		ARRSF (R^{AR})	Pt Mole Fraction (cmol/mol)	
	A_{Pt}^{al}	A_{Ni}^{al}		XPS	Certified

$Pt_{0.20}Ni_{0.80}$	36,381	26,113	0.2579	26.48	25.8 ± 0.6
$Pt_{0.35}Ni_{0.65}$	47,983	19,205	0.2698	40.19	40.4 ± 0.8
$Pt_{0.50}Ni_{0.50}$	60,678	13,095	0.2737	55.30	55.9 ± 0.6
$Pt_{0.65}Ni_{0.35}$	72,012	8,092	0.2699	70.37	70.6 ± 0.8
$Pt_{0.80}Ni_{0.20}$	77,471	4,702	0.2633	81.52	81.3 ± 0.8
Average (MRRSF, R^{MR})			0.2669		
Standard Deviation			0.0063		
Relative SD (%)			2.3		

In this case, linear fitting is suitable for the quantitative analysis. The first-order equation is derived from the measured mole fractions of Pt (X_{Pt}^{al}) by XPS in the five Pt_xNi_{1-x} alloy reference films as x and the certified mole fractions (C_{Pt}^{al}) of Pt as y, as shown in Figure 5.

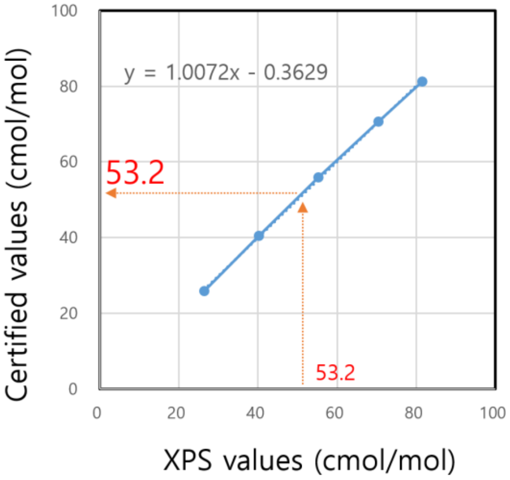

Figure 5. An example of determining the relative mole fraction of Pt in the test specimen by the first-order equation derived from MRRSF.

3.3. Determination of Uncertainty

The Pt mole fraction of the test alloy specimen, i.e. measurand of KRISS, using XPS and PERSF is 53.85 (cmol/mol) expressed in the equation (4). In the quantification of alloy films by second-order multiple point calibration using PERSFs, the combined standard uncertainty (u_c) is calculated from the combination of three standard uncertainties by the following relation, inspired by NIM’s suggestion,

$$u_c^2 = u_{CRM}^2 + u_m^2 + u_{cal}^2 \quad \text{-- (8)}$$

where u_{CRM} is the standard uncertainty in the certification of the five $\mathrm{Pt_xNi_{1-x}}$ alloy reference films. The u_{m} is the standard uncertainty in the determination of mole fraction of the test $\mathrm{Pt_xNi_{1-x}}$ alloy reference film and u_{cal} is the standard uncertainty in the determination of the calibrated mole fraction of the test $\mathrm{Pt_xNi_{1-x}}$ alloy film.

(1) Uncertainty in the certified mole fractions (u_{CRM})

The uncertainty in the certified mole fractions of $\mathrm{Pt_xNi_{1-x}}$ alloy reference films is determined from the average expanded uncertainties [12] of the five $\mathrm{Pt_xNi_{1-x}}$ alloy reference films divided by the coverage factor.

$$u_{\mathrm{CRM}} = \frac{U_{CRM}}{k} = \frac{0.72}{2} = 0.36 \text{ (cmol/mol) -- (9)}$$

(2) Uncertainty in mole fraction measurement of the test $\mathrm{Pt_xNi_{1-x}}$ alloy film (u_{m} (X_{Pt}))

The mole fraction of Pt in the test film (X_{Pt}^{Test}) is determined from the PERSFs of Pt (S_{Pt}) and Ni (S_{Ni}) determined from the pure Pt and Ni films by the following equation,

$$X_{Pt}^{Test} = \frac{A_{Pt}^{Test}/S_{Pt}}{A_{Pt}^{Test}/S_{Pt} + A_{Ni}^{Test}/S_{Ni}} \times 100 \quad \text{(cmol/mol) ------------------------------------- (10)}$$

Where A_{Pt}^{Test} and A_{Ni}^{Test} are the peak areas of Pt $4f_{7/2}$ and Ni $2p_{3/2}$ of the test film, respectively. The standard uncertainty of the mole fraction measurement for the test $\mathrm{Pt_xNi_{1-x}}$ alloy film; u_{m} is determined by the following relation. The uncertainties in the sensitivity factors are not significant here, as they are corrected later during the calibration process. Therefore, the standard uncertainty of X_{Pt}^{Test}; u_{m} is calculated by the combination only with the standard uncertainties of A_{Pt}^{Test}; $u\left(A_{Pt}^{Test}\right)$ and the standard uncertainties of A_{Ni}^{Test} ; $u\left(A_{Ni}^{Test}\right)$.

The standard uncertainty of mole fraction of Pt; u_{m} can be calculated by the general steps of uncertainty propagation at GUM, so the final formula of the standard uncertainty is as following relations:

$$u_{m1}^2 = \left\{\frac{100/S_{Pt}\left(A_{Pt}^{Test}/S_{Pt} + A_{Ni}^{Test}/S_{Ni}\right) - 100\cdot A_{Pt}^{Test}/S_{Pt}^2}{\left(A_{Pt}^{Test}/S_{Pt} + A_{Ni}^{Test}/S_{Ni}\right)^2}\right\}^2 \cdot u^2\left(A_{Pt}^{Test}\right) \quad \text{-------------------------- (11)}$$

$$u_{m2}^2 = \left\{\frac{-100\cdot A_{Pt}^{Test}/(S_{Pt}\cdot S_{Ni})}{\left(A_{Pt}^{Test}/S_{Pt} + A_{Ni}^{Test}/S_{Ni}\right)^2}\right\}^2 \cdot u^2\left(A_{Ni}^{Test}\right) \quad \text{-- (12)}$$

$$u_m = \sqrt{u_{m1}^2 + u_{m2}^2} = 0.34 \text{ (cmol/mol) -- (13)}$$

(3) Uncertainty from calibration equation $u_{\mathrm{cal}}\,(C_{Pt}^{Test})$

The calibration equation can be represented by the following equation:

$$C_{Pt}^{Test} = aX_{Pt}^{Test^{2}} + bX_{Pt}^{Test} + \mathrm{c} \quad \text{--} \quad (14)$$

Where C_{Pt}^{Test} is the corrected relative mole fraction of Pt of the test film, and X_{Pt}^{Test} is the relative mole fraction of Pt of the test film. The equations of uncertainty were derived in Annex A to evaluate the uncertainty of the calibration equation;

$$u_{\mathrm{cal}} = s'\sqrt{\textstyle\sum_{i=0}^{2}\sum_{j=0}^{2} H_{ij} X_{Pt}^{Test(i+j)}} = 0.17\ \text{(cmol/mol)} \quad \text{-------------------------------} \quad (15)$$

Where H_{ij} is each component at the following matrix;

$$\boldsymbol{H} = \begin{bmatrix} 5 & \sum_{i=1}^{5} X_{Pt-i} & \sum_{i=1}^{5} X_{Pt-i}^{2} \\ \sum_{i=1}^{5} X_{Pt-i} & \sum_{i=1}^{5} X_{Pt-i}^{2} & \sum_{i=1}^{5} X_{Pt-i}^{3} \\ \sum_{i=1}^{5} X_{Pt-i}^{2} & \sum_{i=1}^{5} X_{Pt-i}^{3} & \sum_{i=1}^{5} X_{Pt-i}^{4} \end{bmatrix}^{-1} , \text{------------------------ ------------------------} \quad (16)$$

s', residual standard deviation with degrees of freedom (here, ν = 5-2-1=2),

$X_{\mathrm{Pt}}^{Test(i+j)}$, the (i +j)-th power of the relative mole fraction of Pt of the test film,

X_{Pt-i}^{k} , the k-th power of the relative response mole fraction of Pt of the reference film.

(4) Uncertainty budget

The uncertainty budget of the relative mole fraction of Pt(C_{Pt}^{Test} = 53.85 cmol/mol) is shown in Table 6, and the combined standard uncertainty is calculated from the following equation:

$$u_{\mathrm{c}}(C_{Pt}^{Test}) = \sqrt{u_{\mathrm{CRM}}^{2} + u_{\mathrm{m}}^{2} + u_{\mathrm{cal}}^{2}} = 0.52\ \text{(cmol/mol)} \quad \text{----------------------------------} \quad (18)$$

In consequence, the expanded uncertainty:

$$U(C_{Pt}^{Test}) = k \cdot u_{\mathrm{c}}(C_{Pt}^{Test}) = 1.1\ \text{(cmol/mol)} \quad \text{--} \quad (19)$$

The effective degrees of freedom (ν_{eff}) were estimated from the standard uncertainties and the degrees of freedom by the Welch-Satterthwaite formula, as in the following equation.

$$\nu_{eff} = u_{c}^{4} \Big/ \sum_{i=1}^{N} \frac{u_{i}^{4}}{\nu_{i}} \quad \text{---} \quad (17)$$

Table 6. Uncertainty budget for the quantification of the test Pt_xNi_{1-x} alloy film by XPS (KRISS)

Uncertainty component	Quantified values (cmol/mol)

Standard uncertainty, u_{CRM} Standard uncertainty, u_{m} Standard uncertainty, u_{cal}	0.36 0.34 0.17
Combined standard uncertainty u_{c}	0.52
Degree of freedom, ν_{CRM} Degree of freedom, ν_{Pt} Degree of freedom, ν_{CPt}	∞ 4 2
Effective degree of freedom, ν_{eff}	20
Coverage factor, k	2.09
$U = k \cdot u_{\mathrm{c}}$	1.1

4. RESULTS

A. X-ray Photoelectron Spectroscopy (XPS)

Five laboratories used XPS for the quantification of $\mathrm{Pt_xNi_{1-x}}$ alloy films. Table 7 shows the details of the XPS instruments for which the results were retained and the experimental conditions of the participating laboratories.

Table 7. Details of the XPS instruments and the experimental parameters

Laboratory	KRISS	BAM	NIM	NIST	NPL
Maker	Ulvac-PHI	Ulvac-PHI	Thermo Fisher Scientific	Kratos Analytical	Kratos Analytical
Model	VersaProbeII	Quantes	ESCALAB 250Xi	Axis Ultra DLD	AXIS Supra+
Sputtering Ion	Ar+	Ar+	Ar+	Ar+	Ar+ and Ar500+
Impact Energy (keV)	0.5	0.5	0.5	0.5	5 and 10
Sputtering time (min)	12	15	4	>5	-
Incidence Angle (°)	45	45	40	45	45

(1) KRISS obtained the XPS spectra by VersaProbe-II using an Al Kα X-ray source with an electron pass energy of 23.5 eV and an energy step of 0.05 eV. The sample surfaces were sputtered by $\mathrm{Ar^+}$ ions at a beam energy of 500 eV and at an angle of incidence 45° for 12 minutes. Peak areas are determined by integrating the two peak intensities after peak smoothing and background

subtraction by the Shirley method in the colored regions, as shown in Figure 3. The integration range for the area measurement of Pt *4f* peak is from Pt $4f_{7/2}$ + 7 eV to Pt $4f_{7/2}$ - 3 eV, and those for Ni *2p* peak is from Ni $2p_{3/2}$ + 11 eV to Ni $2p_{3/2}$ - 5 eV, respectively. The same analysis conditions were applied to all specimens, and the measurements were repeated five times to minimize the measurement uncertainty. PERSFs were determined from the intensities of the Pt *4f* and Ni $2p_{3/2}$ peaks of the pure Pt and Ni samples. The mole fractions of the Pt_xNi_{1-x} alloy reference films were calculated from the measured PERSFs, and a 2nd-order calibration equation for multiple point calibration was extracted from the measured mole fractions of the Pt_xNi_{1-x} alloy reference films. The mole fraction of the unknown Pt_xNi_{1-x} alloy film was determined from the PERSFs and then corrected from the 2nd-order calibration equation.

(2) BAM obtained the XPS spectra using the Quantes model manufactured by Ulvac-PHI, Inc. The sample surfaces were sputtered by Ar cluster ions at a beam energy of 500 eV and at an angle of incidence 45° for 15 minutes. PERSFs were determined from the intensities of the Pt *4f* and Ni $2p_{3/2}$ peaks of the pure Pt and Ni samples. The mole fractions of the Pt_xNi_{1-x} alloy reference films were calculated from the measured PERSFs, and the calibration equitation was extracted from the measured mole fractions of the Pt_xNi_{1-x} alloy reference films: $y = 0.01207\ x^2 - 0.423\ x + 21.386$. The mole fraction of the unknown Pt_xNi_{1-x} alloy film was determined from the calibration equation.

(3) In the case of NIM, the mole fractions the Pt_xNi_{1-x} alloy reference films were analyzed by the ESCALAB 250Xi (Thermo Fisher Scientific) using a monochromatic Al Kα radiation source with a pass energy of 20 eV and a beam spot diameter of 400 µm. The surface of the films was cleaned by sputtering with 500 eV Ar+ ion beam at an incidence angle of 40°. The mole fractions of the Pt_xNi_{1-x} alloy reference films were calculated from the PERSFs measured from the pure Pt and Ni films. The mole fraction of the unknown Pt_xNi_{1-x} alloy film determined from the PERSFs was corrected to the reported value from the calibration equation.

(4) NIST obtained XPS spectra using the Axis Ultra DLD (Kratos Analytical). The sample surfaces were sputtered with Ar^+ ions at a beam energy of 500 eV and at an angle of incidence 45° from the surface normal over an area of 3 mm x 3 mm for a minimum of 5 minutes. At least six spatially unique measurements were made for each sample. For PERSFs, Pt 4f and Ni 2p counts per second (CPS) (average values and standard deviations) were acquired from the pure Pt and Ni films, respectively. The Pt 4f and Ni 2p CPS (average values and standard deviations) were next acquired for each of the Pt_xNi_{1-x} alloy reference/unknown films and corrected using the PERSFs.

The calibration equation was extracted from the measured Pt 4f mole fractions of the Pt_xNi_{1-x} alloy reference films. The mole fraction value of the unknown Pt_xNi_{1-x} alloy film was determined from the calibration equation. Lastly, the NIST Uncertainty Machine was employed to propagate error for the unknown Pt_xNi_{1-x} alloy film, which was reported in terms of a standard deviation [14]. The reported values for both average and standard deviation of the unknown Pt_xNi_{1-x} alloy film are reported in Table 8.

(5) NPL carried out the experiments using an AXIS Supra+, manufactured by Kratos Analytical. The sample surfaces were cleaned by sputtering with Ar^+ ions at a beam energy of 5 keV, followed by 10 keV Ar_{500}^+ cluster ions at an angle of incidence 45° from the surface normal rastered over an area of approximately 4 mm x 4 mm on the sample. The Pt mole fractions of the Pt_xNi_{1-x} alloy films were calculated using the ratio of intensities for the Ni *2p* peaks and Pt *4d* peaks from the mean AMRSF calculated using the certified reference alloy compositions.

The mole fractions of Pt_xNi_{1-x} alloy films were determined using the MRRSFs and ARRSFs are shown in Table 8. ARRSF will be more quantitative because the matrix effects and sputtering effects can be compensated in the quantitative analysis of alloy films by XPS after sputtering to clean the sample surface.

Table 8. Pt mole fraction [cmol/mol] of the test sample by XPS measurements.

Laboratory	RSF	Reported
KRISS	PERSF	53.9±1.1
BAM	PERSF	54.7±3.2
NIM	PERSF	54.0±1.6
NIST	PERSF	54.1±0.9
NPL	MRRSF	54.1±1.0
Average	-	54.2
Stdev	-	0.3

B. X-ray Fluorescence analysis (XRF)

Three laboratories were involved in the quantification of Pt_xNi_{1-x} alloy films by XRF, as shown in Table 9. NIST and VNIIM used commercial XRF instruments, while PTB used monochromatized synchrotron radiation at the electron storage ring BESSY II in Berlin, Germany.

Table 9. Details of the XRF instruments and the experimental parameters

Laboratory	NIST	PTB	VNIIM
Maker	Bruker	Synchrotron Radiation	Helmut Fischer GmbH
Model	M4 Tornado	BAMline at BESSY II	FISCHERSCOPE X-RAY XDAL 237
X-ray energy (keV)	50	9 & 12	50
Current (uA)	100 (uA)	-	210,000
Exposure time (s)	60	variable	30

(1) NIST used micro XRF (mXRF) for quantitative analysis using a M4 Tornado manufactured by Bruker[1]. It was assumed that the films were thin, which allows for minimal attenuation of the Ni K shell and the Pt L shell photons. This method may not work for films of increased or high variation in thickness without doing a more formal calculation of attenuation.

For the quantitative analysis, the sensitivity factors (S_{pure}) were determined to normalize the measured counts of alloy film into molar ratios using the 100% Pt and Ni films for calibration. The best 100 measurements (those with the lowest statistical variation) out of a total of 200 measurements were used to determine measured counts, for a total of 100 minutes of data collection used for each sample. Measurement counts for two detectors within the instrument were analysed separately and then averaged in the final calibration to adjust for any sample geometry and substrate diffraction effects. Results from both detectors are shown in Figure 6 to show linearity of all results.

Relative mole fractions of Pt for the five Pt_xNi_{1-x} alloy reference films were measured in the unit of cmol/mol. A calibration equation can be derived from the linear fitting of the measured relative mole fractions of Pt of the five Pt_xNi_{1-x} alloy reference films via mXRF and the certified mole fractions provided by KRISS. The calibration curve between mXRF and certified data shows a near perfect linear relation with a slope of 0.9999 ± 0.001 and an offset of 0.002 ± 0.077 for cmol/mol. Due to this high linearity, the measured Pt cmol/mol did not change post-calibration. Uncertainty imposed by calibration contributed only an additional 2% to the overall budget.

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[1] Certain equipment, instruments, software, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement of any product or service by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Approximately 90% of the uncertainty budget is attributed with calculating sensitivity factors for Ni and Pt, with the remaining uncertainty contribution from measurement count variance from the test sample.

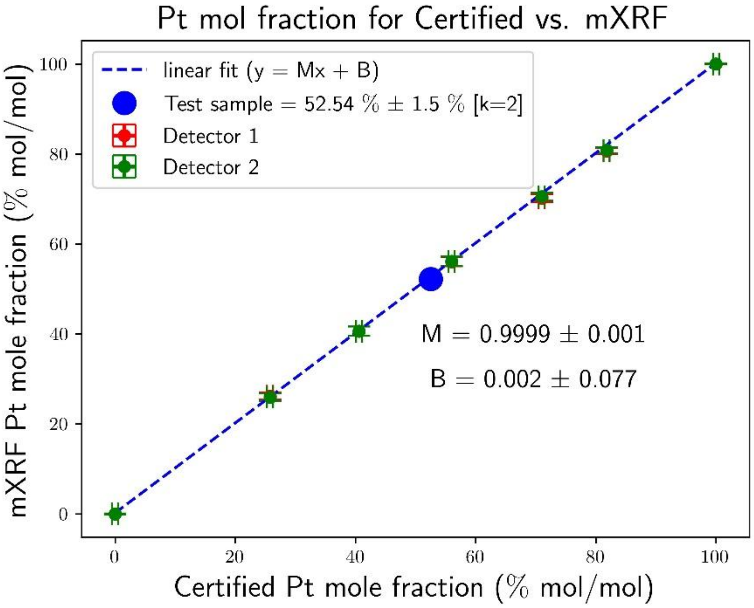

Figure 6. Linear calibration curve for the Certified versus mXRF mole fractions

(2) PTB measured the elemental mole fractions of Pt in Pt_xNi_{1-x} alloy films by reference-free X-ray fluorescence analysis (XRF).[16] Measurements were performed at the wavelength-shifter beamline “BAMline” [17] at the electron storage ring BESSY II in Berlin, Germany. This beamline provides monochromatized synchrotron radiation with high spectral purity. A double crystal monochromator and a double multilayer monochromator were combined to optimize the available spectral purity. For the measurements, Ni-K and Pt-L X-ray fluorescence radiation was selectively excited using monochromatic photon energies of 9 keV and 12 keV, respectively. Based on the analysis of the characteristic Ni-Kα and the Pt-Lα lines, the reference-free XRF approach enables both the quantification of the total mass thickness of the Pt_xNi_{1-x} alloy films (g cm^{-2}) and the mass fractions of Pt and Ni (cg g^{-1} or wt%). Based on the knowledge of the mass fractions and the respective molar masses of Ni (58.69 g mol^{-1}) and Pt (195.09 g/mol), the individual mole fraction (cmol mol^{-1} or mol%) can be derived. The reported combined standard uncertainty values are calculated according to Supplement 1 to the GUM [18], taking into account uncertainty contributions of all relevant experimental, instrumental and fundamental parameters.

It has to be pointed out that the Pt mole fraction can be determined by reference-free X-ray spectrometry without using calibrated reference samples, just relying on calibrated instrumentation and fundamental parameters like fluorescence production cross sections. The uncertainties are dominated by the uncertainties of these cross sections and are higher than for RBS and ICP-MS, but reference-free XRF is an independent traceable method. As shown in Table 10, the reference samples were also measured and the results are in very good agreement, especially with the ICP-MS data where – except for the sample with the lowest Pt content – the variations never exceed 0.1 cmol/mol.

Table 10. Pt mole fraction results [cmol/mol] and expanded uncertainties

Sample	RBS	ID ICP-MS	XRF (PTB)
$Pt_{0.20}Ni_{0.80}$	25.8 ± 0.5	25.8 ± 0.7	23.7 ± 1.8
$Pt_{0.35}Ni_{0.65}$	40.6 ± 0.5	40.2 ± 0.8	40.1 ± 2.3
$Pt_{0.50}Ni_{0.50}$	56.0 ± 0.5	55.9 ± 0.7	55.9 ± 2.4
$Pt_{0.65}Ni_{0.35}$	71.0 ± 0.5	70.4 ± 0.4	70.4 ± 2.0
$Pt_{0.80}Ni_{0.20}$	81.8 ± 0.5	81.1 ± 0.4	81.0 ± 1.5
Test film	-	-	52.8 ± 2.5

(3) VNIIM obtained the XRF data using the FISCHERSCOPE X-RAY XDAL 237 manufactured by Helmut Fischer GmbH. Five measurement points were selected to evaluate the coating’s heterogeneity of the samples. One is the center of the specimen, and four points are in a circle of 6 mm in diameter. The relative Pt mole fractions of the five Pt_xNi_{1-x} alloy reference films were measured. According to the technical protocol, expanded uncertainties U (k=2, P=0.95) of these values are 0.5 %. The calibration equitation was extracted from the linear fitting of Pt Lα peak’s intensity of five Pt_xNi_{1-x} alloy reference samples and the pure Pt film on the mole fraction of them determined from RBS. The reported mole fraction of the test specimen was determined by applying the measured Pt Lα peak’s intensity of the test sample to the calibration equitation.

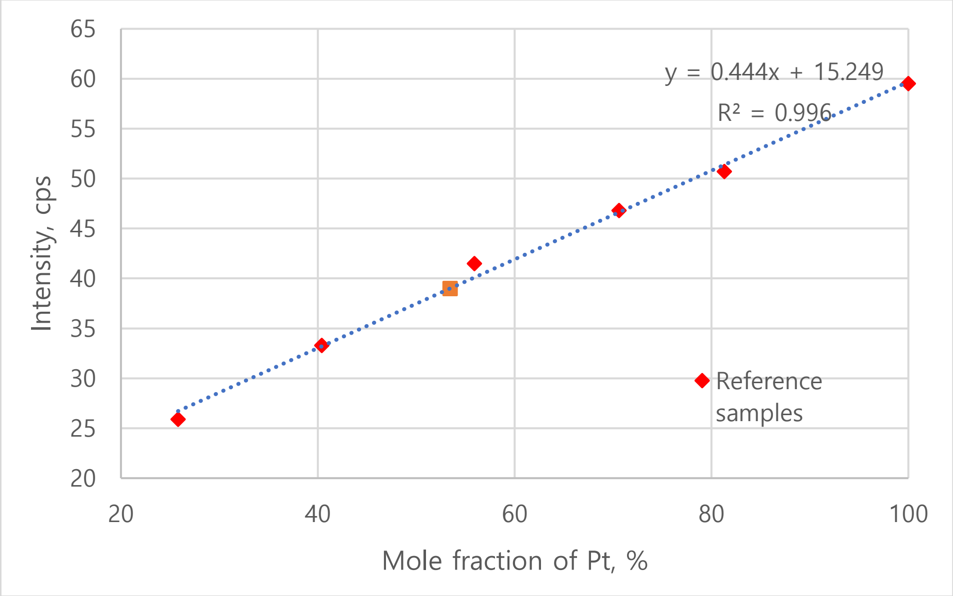

Figure 7. Dependence of Pt Lα peak's intensity from mole fraction of Pt

Table 11 summarizes the XRF mole fractions of the test specimen. It shows an average mole fraction of 52.9 cmol/mol and a standard deviation of 0.5 cmol/mol.

Table 11. CCQM-P248 Pt mole fraction results obtained by XRF.

Institute	Pt mole fraction [cmol/mol]
NIST	52.4±1.5
PTB	52.8±2.5
VNIIM	53.4±2.4
Average	52.9
Standard Deviation	0.5

C. Scanning Electron Microscopy / Energy Dispersive X-ray Spectrometry (SEM/EDX)

DFM measured the elemental mole fractions of Pt in Pt_xNi_{1-x} alloy films by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). Measurements were performed with a Hitachi FlexSEM 1000 II SEM/EDX. This method does not require the extraction of PERSFs. Five areas were mapped out for each sample with the EDX acquisition: middle of the sample, top left, top right, bottom left and bottom right. Each scan area was 1.3 mm by 1.0 mm in size. The elements Pt, Ni, Si, and C were found in the samples. C comes from contamination, and Si from the substrate. Average atomic percentages of all elements were extracted, and the Pt mole fractions were calculated as x = [Pt]/([Pt]+[Ni]).

The calibration curve was produced via linear fitting from the measured and certified average mole fractions of the reference films. This was used to calculate the corrected mole fraction of the test sample. The uncorrected mole fraction was found to be 48.67 cmol/mol, and the corrected mole fraction was found to be 52.39 cmol/mol. If the standard deviation and *k* value are applied, the expanded uncertainty is 0.94 cmol/mol.

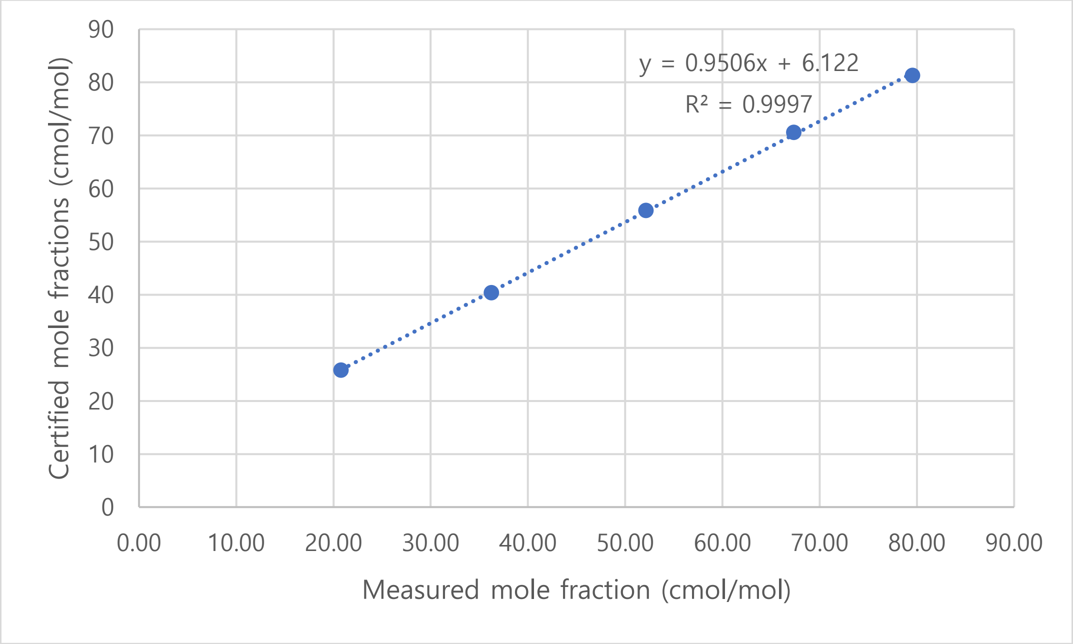

Figure 8. Linear calibration for the mole fractions measured by SEM/EDX and the certified values.

5. DISCUSSIONS

The mole fractions and the expanded uncertainties of the Test Pt_xNi_{1-x} alloy thin film measured by the participating laboratories using XPS, XRF and SEM/EDX are plotted in Figure 9 as a simulation of a key comparison to ensure the equivalency in the measurement capability of national metrology institutes for the quantification of Pt_xNi_{1-x} alloy thin films.

The reference value (blue solid line) of the pilot comparison was determined by the arithmetic mean method. The uncertainty (U_{ref}) of the reference value (red broken line) was calculated from the standard uncertainty of the individual laboratory values (x) and a coverage factor (*k*) of 2.262.

$$u_{ref} = s(x_i) \text{ -- } (18)$$

$$U_{ref} = ku_{ref} \quad \text{--} \quad (19)$$

Here, the standard uncertainty of the reference value u_{ref} is determined from the standard deviation of the reported mole fractions and i indicates the individual laboratories.

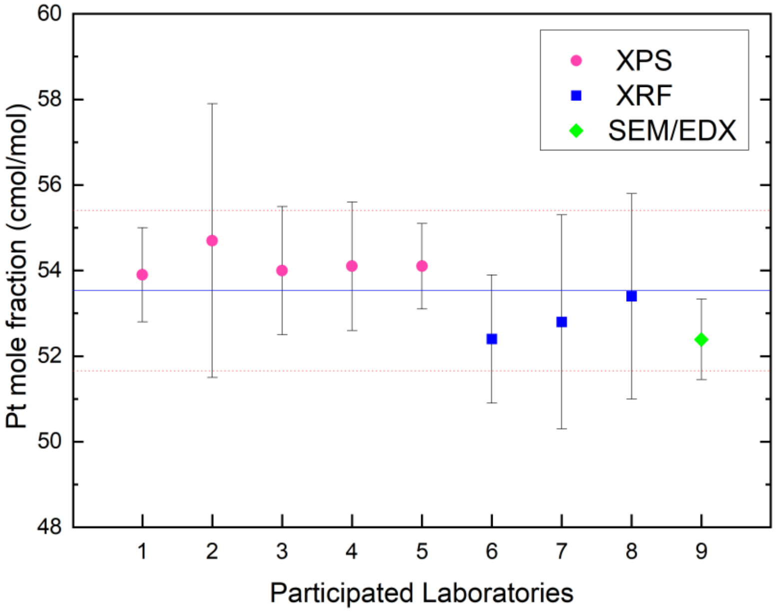

Figure 9. The reported mole fractions and expanded uncertainties as the results of P248

Figure 9 shows that the mole fractions measured by XPS are somewhat larger than those measured by XRF and SEM/EDX. The reason for this discrepancy seems to be the matrix effect of XPS. As shown in Figure 6, 7, and 8, the matrix effect can be ignored in XRF and SEM/EDX. For this reason, the use of ARRSFs or MRRSFs may be better than PERSFs for the quantitative analysis of binary alloy films showing severe matrix effects.

5. CONCLUSION

CCQM P248 pilot study to determine the mole fractions of Pt_xNi_{1-x} alloy thin films was performed by CCQM SAWG. Eight laboratories, including seven NMIs and one DI, participated in this pilot study using XPS, XRF and SEM/EDX.

In the case of XPS, the second-order multiple-point calibration equation using PERSFs is applied as a new method to determine the mole fractions of binary alloy films. However, due to the severe matrix effect, the mole fractions of the Pt_xNi_{1-x} alloy thin films measured by this method showed larger values than those by XRF and SEM/EDX. The mole fractions determined by MRRSFs and ARRSFs with XPS measurements were smaller than by multiple-point calibration with PERSFs.

In this study, the averaged mole fractions of the five reference Pt_xNi_{1-x} alloy thin films measured by RBS and ICP-MS as the certified values. The RBS values agreed well with those measured by ICP-MS within a 1.1 % difference.

The result of P248 shows that the reported average mole fraction is close to the certified value within the uncertainty level. The quantitative analysis of the Pt_xNi_{1-x} alloy thin film system can be a good subject for CCQM key comparison.

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References

[1] Seah M P, Unger W E S, Wang H, Jordaan W, Gross Th, Dura J A, Moon D W, Totarong P, Krumrey, M, Hauert R, and Zhiqiang M 2009 *Surf. Interface Anal.* 41 430-439.

[2] Kim K J, Wirth T, Hodoroaba V-D, Gross T, Unger W, Jordaan W, Van Staden M, Prins S, Kim J W, Moon D W, Wang H, Song X, Zhang L, Fujimoto T and Kojima I, 2010 *Metrologia* 47 Tech. Suppl. 08011.

[3] Kim K J, Kim A S, Jang J S, Suh J K, Wirth T, Hodoroaba V D, Unger W, Joyce R. Araujo J R, Archanjo B S, Galhardo C E, Damasceno J, Achete C A, Wang H, Wang M, Bennett J, Simons D, Kurokawa A, Terauchi S, Fujimoto T, Streeck C, Beckhoff B, Spencer S and Shard A, 2016 *Metrologia* 53 08011.

[4] Sobina E, Prinz C, Landi S M, Santos B P S, Damasceno J C, Kuznetsov O, BİLSEL M, Sadak A E and Wang H, 2023 *Metrologia* 60 08007.

[5] Kim K J, Yu H, Lee S M, Kwon J H, Ruh H, Radnik J, Archanjo B S, Annese E, Damasceno J C, Achete

C A, Yao Y, Ren L, Gao H, Windover D5, Matsuzaki H, Azuma Y, Zhang L, Fujimoto T, Jordaan W A, Reed B, Shard A G, Cibik L, Gollwitzer C and Krumrey M, 2023 *Metrologia* 60 08010.

[6] Seah M P, Spencer S J, Bensebaa F, Vickridge I, Danzebrink H, Krumrey M, Gross T, Oesterle W, Wendler E, Rheinländer B, Azuma Y, Kojima I, Suzuki N, Suzuki M, Tanuma S, Moon D W, Lee H J, Cho H M, Chen H Y, Wee A T S, Osipowicz T, Pan J S, Jordaan W A, Hauert R, Klotz U, Marel C, Verheijen M, Tamminga Y, Jeynes C, Bailey P, Biswas S, Falke U, Nguyen N V, Chandler-Horowitz D, Ehrstein J R, Muller D and Dura J A 2004 *Surf. Interface Anal.*, 36 1269 – 1303.

[7] Yoshitake M and Yoshihara K 1989 *Surf. Interface Anal.*17 711-718.

[8] Kim K J, Moon D W, Park C J, Simons D, Gillen G, Jin H and Kang H J 2007 *Surf. Interface Anal.*39 665-673.

[9] Kim K J, Simons D and Gillen G 2007 *Appl. Surf. Sci.*253 6000 – 6005.

[10] Kim K J, Moon D W, Hayashi T, Fujimoto T, Heo S, Jeong C S, Jordaan W, Staden M V, Prins S, Kang H J, Kim J H, Gross T, Procop M, Schmidt D, Wirth T, Unger W E S, Wang H and Song X P, 2009 *Metrologia* 46 Tech. Supple. 08006.

[11] Kim T G, Heo S W, Min W J, Han T H, Yim Y H, Yu H and Kim K J, 2021, *Metrologia* 58 065004.

[12] EURACHEM/CITAC Guide CG4, “Quantifying Uncertainty in Analytical Measurement,” 3rd Ed. p116, 2012.

[13] Walpole R E, Myers R H, Myers S L and Ye K, “Probability and Statistics for Engineers and Scientists” 9th Ed. PERSON, 2014, 504-509.

[14] https://uncertainty.nist.gov/

[15] JCGM 102:2011, Supplement 2 to the “Guide to the expression of uncertainty in measurement” – Extension to any number of output quantities.

[16] Beckhoff B, 2008 *J. Anal. At. Spectrom.* 23, 845 - 853.

[17] Riesemeier H *et al.* 2005 *X-Ray Spectrom.* 34, 160 -163.

[18] JCGM 101:2008, Evaluation of measurement data – Supplement 1 to the “Guide to the expression of uncertainty in measurement” – Propagation of distributions using a Monte Carlo method.

Annex A: The uncertainties in measurement assisted by 2nd-order linear regression (LR)

In many cases of measurement, the determined values are obtained after calibrating the instrument and applying correction factors derived from ordinary high-order linear regression(LR) methods. In this case, the uncertainty equations derived with 2nd-order linear regression methods applying GUM Supplement-2 [13,15] are summarized below.

The general form of the 2nd-order regression equation is as follows;

$$y = b_0 + b_1 x + b_2 x^2 \tag{A1}$$

where *x* is the response value of the measurement target, *y* is the determined value of the measurement target and, b_0, b_1 and b_2 are coefficients of 2nd-order LR.

The derived total combined standard uncertainty ($u_c(y)$) could be divided by two terms; such as uncertainties due to repeatability of target ($u_{c1}(y)$) and due to calibration line ($u_{c2}(y)$).

$$u_c^2(y) = u_{c1}^2(y) + u_{c2}^2(y)\,, \tag{A2}$$

Where the standard uncertainty due to repeatability of target ($u_{c1}(y)$) is determined by Equation A3 and the standard uncertainty due to calibration line ($u_{c2}(y)$) is determined by Equation A4.

$$u_{c1}^2(y) = (s')^2 \frac{1}{p}\,, \tag{A3}$$

$$u_{c2}^2(y) = (s')^2 \sum_{i=0}^{2} \sum_{j=0}^{2} H_{ij}\, x^{(i+j)}\,, \tag{A4}$$

Where *p* is the times of measurement (here, *p*=5) and *s'* is residual standard deviation of reference with the unit of reference quantity;

$$s' = \sqrt{\frac{\sum_{i=1}^{n} \{y_i - (b_0 + b_1 x_i + b_2 x_i^2)\}^2}{n-3}} \tag{A5}$$

and *n* is number of references, in our case it is 5. The H_{ij} is component of *i*-row and *j*-column of the following response matrix;

$$\boldsymbol{H} = (\boldsymbol{X}^T \boldsymbol{X})^{-1}. \tag{A6}$$

Where, x_i is *i*-th response value and

$$\boldsymbol{X} = \begin{bmatrix} 1 & x_1 & x_1^2 \\ 1 & x_2 & x_2^2 \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ 1 & x_5 & x_5^2 \end{bmatrix}, \tag{A7}$$

The Equation A6 of the matrix, ***H*** can be further described as shown in following formula;

$$\boldsymbol{H} = \begin{bmatrix} n & \sum_{i=1}^{n} x_i & \sum_{i=1}^{n} x_i^2 \\ \sum_{i=1}^{n} x_i & \sum_{i=1}^{n} x_i^2 & \sum_{i=1}^{n} x_i^3 \\ \sum_{i=1}^{n} x_i^2 & \sum_{i=1}^{n} x_i^3 & \sum_{i=1}^{n} x_i^4 \end{bmatrix}^{-1} \tag{A8}$$

Annex B: The uncertainty budget of VNIIM

Table 1. Uncertainty budget of mole fraction of Pt in the test sample

Type	Source of uncertainty	Evaluation		Standard uncertainty		Sensitivity coefficient		Contribution to uncertainty	
		value	unit	u_i	unit	c_i	unit	c_iu_i	unit
A	Type A standard uncertainty of the test sample measurements	53.4	%	0.53	%	1.0	-	0.53	%
A	Type A standard uncertainty of the linear calibration equation	53.4	%	1.0	%	1.0	-	1.0	%
B	Type B standard uncertainty	53.4	%	0.36	%	1.0	-	0.36	%
Combined standard uncertainty								1.2	%
Expanded uncertainty ($k = 2$, $P = 0.95$)								2.4	%