**Responses and changes made 2020/06/30**

Manuscript ID: #877

Title: Development of a combined XRF/XPS surface analysis system for surface layer quantification of 28Si-spheres
Correspondence Author: Yu-Hsin Wu

Dear Dr Ogushi,

We appreciate very much the valuable comments from the reviewers. We have made revisions according to their suggestions. Here are the responses after each item and use blue-colored font. For convenience we are also sending a version with revisions highlighted in yellow in the manuscript.

In this re-submitted version, we add 4 co-authors from PTB. This is due to we had a lot of discussions with PTB before submitting the previous version. We think that list them as co-authors is necessary for us. Please forgive my carelessness so that they are not on the author list from the beginning.

**Referee’s comment**

Reviewer A:

The followings are minor editorial comments.

Page 1

1. Abstract, Line 1

 “the national measurement laboratory (NML)” is the name of your institute? Not

 CMS/ITRI?

2. Introduction, Left column, Line 2

 “Planck constant” should be changed to “the Planck constant”.

3. Introduction, Left column, Line 3

 “h = 6.626 070 15\*10-34 J s” should be changed to “*h* = 6.626 070 15×10-34 J s”.

4. Introduction, Left column, Line 4

 “new definitions” should be changed to “new definition”.

5. Introduction, Left column, Line 9

 Please consider the change “from Physikalisch-Technische Bundesanstalt (PTB)”

 to “from Physikalisch-Technische Bundesanstalt (PTB, Germany)”.

Page 2

6. Right column, Last line

 Please consider the change “The construction work including the assembly,,,” to

 “The construction work includes the assembly,,,.

Page 3

7. Left column, 2nd paragraph

 Please consider the use of “Pa” instead of “mbar”.

8. Right column, Line 17

 Could you please add some sentences to describe the method used for the

 calibration of the SiO2 reference samples at PTB?

Response:

Thanks for your opinion. We have made the corrections of point 1-7 according to your opinion and change the name to CMS/IRI. For the 8th, we have added some sentence in Chapter 4, right column, line 20 as

 “To quantify the mass deposition of oxygen of the five SiO2 reference samples with thickness ranging from 2 nm to 10 nm, the samples were measured in PTB’s laboratory for at synchrotron radiation BESSY II in Berlin. The monochromatized synchrotron radiation of 684 eV photon energy was used to irradiate the sample. With the calibrated photodiode and SDD to collect the signal of incident beam and the fluorescence. The mass deposition of the oxygen can be directly determined.”

Reviewer C:

Concern 1:

Current primary methods developed by National Metrology Institutes for new kilogram realizations includes Kibble Balance, Joule Balance and XRCD. Kibble balance has been mentioned in this manuscript as “comparing electrical power to mechanical power”, but Joule Balance was not included by the authors. The referee would like to recommend the author adding the Joule Balance method in Introduction and several references accordingly, such as:

Li, Z., Zhang, Z., Lu, Y., Hu, P., Liu, Y., Xu, J., ... & Wang, D. (2017). The first determination of the Planck constant with the joule balance NIM-2. Metrologia, 54(5), 763.

Li, Z., Bai, Y., Xu, J., Lu, Y., Hu, P., Liu, Y., ... & He, Q. (2020). The upgrade of NIM-2 joule balance since 2017. Metrologia.

Concern 2:

It is confused to understand the following sentence located above the equation (2) on Page 2: “… and compared with the fluorescence intensities O kα and Si kα measured by….”, since there are two distinguishable K-edge characteristic peaks with different intensities and energies for Silicon when excited by X-ray photons with energy higher than 1840 eV. The author may want to provide explanation why Kα1 and Kα2 peaks of Silicon were combined in the system design and measurement considerations.

Concern 3: Please provide more details about how to transfer the mass deposition of oxygen determined by XRF and the ratio among O, Si and C determined by XPS into the measured results of their mass.

Concern 4:

Please provide more details about the XRF detector, including its energy resolution, active energy range, the material of the detector, etc. And, does the material of the silicon drift detector impacts the spectrum measurements? (Since the excitation X-ray photons may be scattered, although very small, into the spectrometer and generate fluorescence of the materials of the detector; and, X-ray photon escaping issues during spectra measurements) If so, what correction methods are available and will be employed?

Concern 5:

The expressions regarding the Kα fluorescence of different elements in the whole manuscript such as “the fluorescence intensities O kα and Si kα” may be re-worded into “the intensities of Oxygen Kα and Silicon Kα (or, Kα2 and Kα1) fluorescence” for more clear understanding.

Concern 6:

The grammar and spellings must be carefully checked during the revision.

Response:

Thanks for your opinion.

1. The reference have been added in reference [6].
2. In order to make the expression clearer, we made the following corrections in section 3.1, line 13 as

 “The combined XRF/XPS surface analysis system is used to measure the fluorescence intensities of oxygen and silicon to obtain the intensity ratio between O kα (525 eV) and Si kα (1740 eV) from the 5 SiO2 reference samples. ”

 K-alpha emission is composed of two spectral lines, Kα1 and Kα2. The Kα1 emission

 is higher in energy than the Kα2 emission. A larger number of electrons follow the

 Kα1 transition (L3 → K) relative to the Kα2 (L2 → K) transition which causes the ratio of the intensities of Kα1 and Kα2 is very close to 2:1. Kα1 and Kα2 are close enough in wavelength that an average of the two wavelengths, Kα, is used in XRF.

3. We have added some sentence to illustrate how to transfer the mass deposition measured by XRF to XPS in section 3.2, right column, line 19 as

 “The ratio between the elements measured by XPS is proportional to the number of atoms of each elements. With the mass deposition of oxygen determined by XRF, the number of oxygen atoms per unit area can be obtained. ”

For further details of surface characterization, please refer to the reference [16] M. Müller, B. Beckhoff, E. Beyer, E. Darlatt, R. Fliegauf, G. Ulm, M. Kolbe, Quantitative surface characterization of silicon spheres by combined XRF and XPS analysis for the determination of the Avogadro constant, *Metrologia* 54 (2017) pp. 653-662.

4. We have added more details related to SDD in chapter 4, left column, line 18 as

“The Bruker SDD (silicon drift detector) X-flash fluorescence detector with a

windowless detecting area of 30 mm².”

and chapter 4, right column, line 14 as

“The response function and detector efficiency of the SDD has been calibrated

in the energy range from 100 eV to 1850 eV. The response function of the SDD

is measured by changing the energy of the incident beam from the

monochromatized synchrotron radiation and will be used to be convoluted with

the theoretical model of bremsstrahlung and resonant Raman scattering.”

 The material of the detector influences the detector efficiency due to its

 absorption coefficients. For the details on how to evaluate the detector response

 and efficiency, please refer to the reference [25]F. Scholze, M. Procop,

 Modelling the response function of energy dispersive X-ray spectrometers with

 silicon detectors, X-ray Spectrometry, 38 (2009) pp.312– 321.

5. We made the following corrections in section 3.1, line 13 as

 “The combined XRF/XPS surface analysis system is used to measure the fluorescence intensities of oxygen and silicon to obtain the intensity ratio between O kα (525 eV) and Si kα (1740 eV) from the 5 SiO2 reference samples.”

 This wording “O kα” and “Si kα” are easier for readers to understand.

6. Thanks for your opinion. I have checked the manuscript before re-submission.

Reviewer D

Main comments:

Besides the information and technology from PTB, as a research paper, it is difficult for readers to find out something new what the authors did.

Minor comments:

1. The title of the paper

It is better to use a slash as “a combined XRF/XPS surface analysis system” instead of “a combined XRF XPS surface analysis system”.

2. Page 1, 4th line of the section of “1. Introduction”

The plural form “the new definitions came” should be singular form “definition”.

3. Page 1, 6th and 7th lines of the section of “1. Introduction”

It is better to mention the name of the method, the Kibble balances.

4. Page 1, 8th and 9th lines of the section of “1. Introduction”

The abbreviation “XRCD” should be stated clearly here and used below instead of “the x-ray-crystal-density method”.

5. Page 1, the first sentence of the 1st paragraph of the section “2. The surface layer model of the 28Si-enriched sphere”

The meaning of this sentence is unclear. Counting the number of Si atoms in a 28Si-enriched sphere is to determine the Plank constant. Based on the new Plank constant, XRCD will be used to determine the mass of the Si sphere to realize the new kilogram. Please refer to some other papers, such as Metrologia 54, pp 718.

6. Page 1, the first sentence of the 2nd paragraph of the section “2. The surface layer model of the 28Si-enriched sphere”

Other than COx and C, hydrocarbon were also estimated to be a main constituent of the carbonaceous layer.

7. Page 4, 12th line

What is QPA method? The complete expression should be stated.

Response:

Thanks for your opinion.

This paper is mainly focused on the methodology of surface layer quantification, and how to build up and integrate the XRF/XPS surface analysis system according to the information given to us by PTB. The subsequent work including software and hardware integration and XRF data fitting methods will be independently developed by us. This will be a part where we will have more differences from PTB, but we expect to publish these contents in future articles.

Regarding the point 1-6, we have made corrections and add the reference in [11].For point 7, we added the description of the QPA method in Chapter 5, line19 as

“The transmission function T(KE) of the XPS spectrometer is required to be estimated using the quantiﬁed peak-area approach (QPA) method by measuring Au 4f, Au 4d, Au 4p3/2, Ag 3d, Ag 3p3/2,Cu 3p,Cu 2p3/2,Ge 3p and Ge 2p3/2 standard peak areas from reference samples with the pass energy of 40 eV and 80 eV. ”

We hope that our responses to the reviewer’s comments are satisfactory and the revised version of the manuscript be accepted for publication. We appreciate your help in handling our manuscript for publication in ACTA IMEKO.

Sincerely yours,

Yu-Hsin Wu

(YH.Wu@itri.org.tw)