

Quantitative surface analysis on ²⁸Si-spheres for the redefinition of the kilogram

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Abstract

A novel instrumentation for the quantitative surface analysis of silicon spheres was set up and taken into operation at the PTB. The instrumentation combines X-ray fluorescence spectroscopy and X-ray photoelectron spectroscopy techniques in order to enable the characterization and quantification of the oxide layer and unintentional contaminations.

The instrumentation is equipped with a ball manipulator, giving the opportunity to measure on each point of a spherical sample surface beside common flat samples. Another feature of the instrumentation is a special load lock system, which allows the transportation of a sphere to a mass comparator under vacuum conditions.

The surface characterization is needed to reduce the uncertainties in the determination of the Avogadro and Planck constant. Both values are needed for the new definition of the SI unit kg in terms of fundamental constants and independent from a material artefact. Two monocrystalline, isotopically enriched ²⁸Si-spheres were manufactured for this purpose. Since every silicon surface is covered by a surface layer composed of silicon oxide and a contamination layer, the surface layer mass on the ²⁸Si-spheres has to be determined in order to correct the results of the mass measurement of the spheres. The use of complementary X-ray methods allows minimizing the influence of the surface on the total uncertainty budget of the Avogadro and Planck constants. This is relevant, because a relative standard uncertainty of less than $2 \cdot 10^{-8}$ has to be achieved to make a contribution to the new definition of the kilogram. Corresponding to that, the realization of the redefined kilogram via silicon spheres will also be improved.

Measurements on the ²⁸Si-spheres were carried out several times. The surface was characterized regarding the elementary composition including the chemical binding states of the components and the mass of the surface layer.

Measurement techniques, surface analysis, Avogadro constant, mass realization

1. Introduction

The present definition of the SI unit kilogram by the international prototype of the kilogram is aimed to be replaced by a new definition based on fundamental constants, which is the Planck constant h .

A possible way to define a value for the Planck constant is based on the Avogadro constant N_A . For this reason the Avogadro constant is determined by measurements on two isotopically enriched, monocrystalline ²⁸Si-spheres with a mass of one kilogram. With the knowledge of the molar mass, the lattice parameter of the crystal, the volume, and the mass of the sphere, N_A can be determined [1].

Due to the always present surface layer, correction parameters have to be applied to the mass determination. The mass of the surface layer, which is dominated by the silicon oxide layer, has to be subtracted from the mass value of the sphere. As a result of this correction the measurement uncertainty for the Avogadro constant is reduced, which is crucial because an uncertainty of less than $2 \cdot 10^{-8}$ has to be achieved to make a contribution to the redefinition of the kilogram.

The instrumentation was set up to characterize and quantify the surface layer of silicon spheres with the opportunity to analyse every spot on the surface. Experiments for reproducibility and first measurements on ²⁸Si-spheres were carried out.

2. Methods

2.1. Instrumentation

The instrumentation presented here allows the measurement with X-ray fluorescence spectroscopy (XRF) and X-ray photoelectron spectroscopy (XPS) that rely on the detection of fluorescence photons and photoelectrons respectively (cf. Figure 1). Both are emitted by the sample surface as a reaction to excitation with X-rays.



Figure 1. XRF/XPS-Instrumentation

The excitation source is an Al-K α X-ray tube equipped with a quartz crystal monochromator. The fluorescence radiation is detected by a 60 mm² silicon drift detector while an electron

analyzer with a stripe anode detector is in use for the XPS measurements.

The ball manipulator is an essential part of the instrumentation (cf. figure 2). It allows measurements on every point on the sphere's surface and the change of the measurement geometry. The manipulator contains five axes stacked on top of each other. Beginning from the top, the sphere is borne on three motor-driven PEEK rollers which provide the rotation around an axis lying in the equatorial plane. It follows a vertical linear axis for height adjustment and thereunder another rotational axis. It realizes the rotation of the sphere around its vertical axis with a range of 370°, so an equatorial scan can be carried out. Beneath follows a linear stage of 60 mm range in the horizontal plane allowing adjusting the sample surface in measurement position. The lowest stage is a rotational one for changing the angle of incidence by the rotation around the centre of the chamber. Its range is 100°.

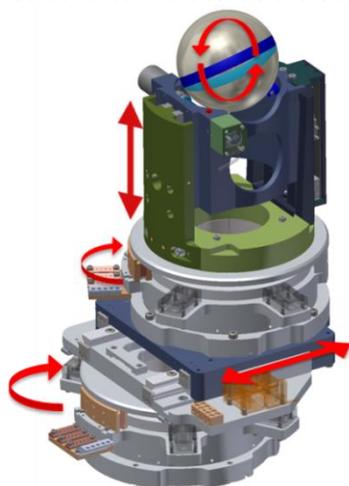


Figure 2. Schematic view of the ball manipulator

Beside spherical samples also flat samples can be measured in the instrumentation with the help of a mount for twelve samples.

The load lock of the instrumentation features a transport system allowing a sphere to move to a mass comparator under vacuum conditions. Thus surface analysis and mass determination can be carried out successively, without altering the surface layer. The transfer is based on a portable vacuum container that is located in the load lock and can be attached to the load lock of the Sartorius CCL1007 mass comparator as well.

2.2. Initial Experiments/Commissioning

Reproducibility and repeatability experiments were carried out with XRF on flat reference samples. For the reproducibility testing the samples were transferred out of the measuring chamber to the load lock between two measuring cycles. Three reproducibility cycles were carried out. Within one cycle every measurement on a given sample was repeated up to nine times to obtain data to determine the repeatability. Also XPS and XRF measurements were conducted on 72 points on the equator of a ²⁸Si-sphere with excitation energy of 1486.6 eV (Al K α). The total measurement time for 72 points was 8 h.

3. Results

The experiments have shown a reproducibility of 0.50 % and a repeatability of 0.47 % standard deviation for the ratio of oxide to silicon. Figure 3 shows a fluorescence spectrum from a single point on the sphere and its deconvolution with detector response functions that were determined by a synchrotron

radiation based calibration [2], fluorescence lines and as well background contributions [3].

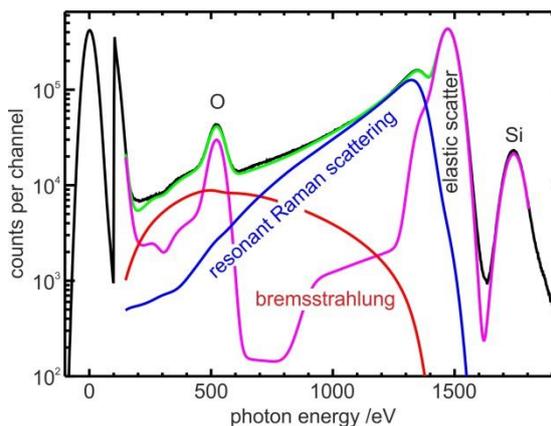


Figure 3. XRF-spectrum excited with Al K α radiation from an X-ray tube

Figure 4 shows XPS results from a measurement around the equator of the sphere. The graph shows beside the O 1s and C 1s peak areas the part of quadrivalent bound Si (SiO₂) of the Si 2p photoemission. The correlation between the Si and the O signal shows that the oxygen signal is dominated by the oxide layer of the sphere. Further contributions of oxygen arise from carbon and water contaminations. The carbon distribution is independent from the other elements. Thus, it can be concluded, that the carbon contaminations exist in a separate surface layer.

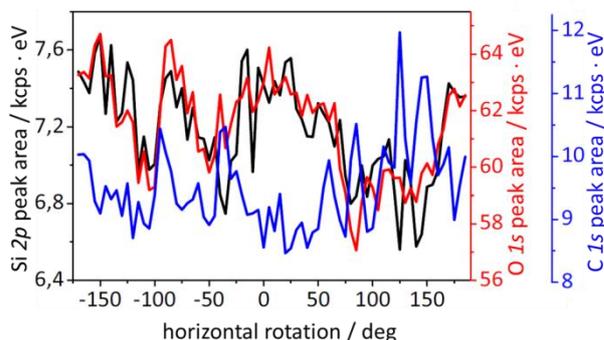


Figure 4. XPS results measured along the equator of a sphere. Only the quadrivalent bound part of the Si 2p photoemission is shown here.

4. Outlook

A new instrumentation for the surface analysis of spherical samples with a link to mass determination is presented. Possible changes in the surface layer can be determined through X-ray methods as well as through mass measurements without altering surface layer. Surface analysis on silicon spheres decreases the measurement uncertainty of the Avogadro and Planck constants and, corresponding to this, a realization of the kg via silicon spheres can be improved. In further investigations the whole surface of the sphere will be measured and quantified concerning the mass deposition of the oxide layer.

References

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