“Application of Neutron Activation Analysis for the characterization of the silicon materials used to determine the Avogadro constant”

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Abstract:

The silicon route is one of the approaches which have been proposed for the redefinition of the kilogram in terms of the Avogadro constant. In this framework, the elemental characterization of the adopted ultra-pure ^{28}Si enriched materials is of fundamental importance to avoid biased results. The aim of this research is the development of an analytical method involving Neutron Activation to investigate with the lowest possible uncertainty, ^{30}Si mole fraction and quantify impurities present within the crystal.

The International prototype of kilogram

Scientific community made great efforts in the last decades to move units of International System of measurement from artifact to fundamental constants of nature.

The redefinition of unit of mass is involved in this activity. In this framework the knowledge of Avogadro constant by counting the atoms present in a quasi perfect silicon sphere highly enriched of the isotope 28 plays a key role.

Aim of the project

In order to quantify Avogadro constant with requested relative uncertainty (< 2 x 10^{-8}) these silicon materials have to be of well known isotopic composition and ideally free from crystal defects. For this reason the contribution to the relative uncertainty due to isotopic composition and defects have to be below 10^{-9} level, in order to use these crystals for a useful evaluation of Avogadro constant.

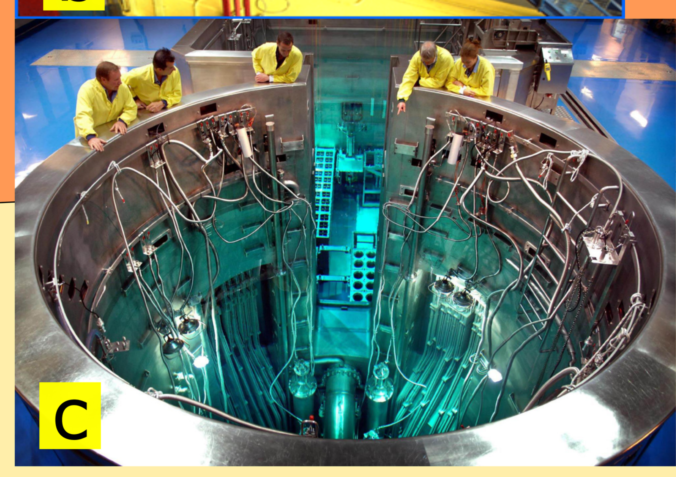
The aim of this project of research is to apply Instrumental Neutron Activation Analysis (INAA) for characterization of these silicon crystals. This analytical technique allows to reach low detection limits for several elements and is not destructive for the sample.

Three areas of investigation:

a Sample of silicon crystal highly enriched of isotope 28

b Irradiation facility at LENA, Pavia. Triga MARK II reactor (250 kW). Nominal flux 1.8x10^{13} cm^{-2} s^{-1}

c Irradiation facility at ANSTO, Sydney. OPAL reactor (20 MW). Nominal flux 6.5x10^{13} cm^{-2} s^{-1}



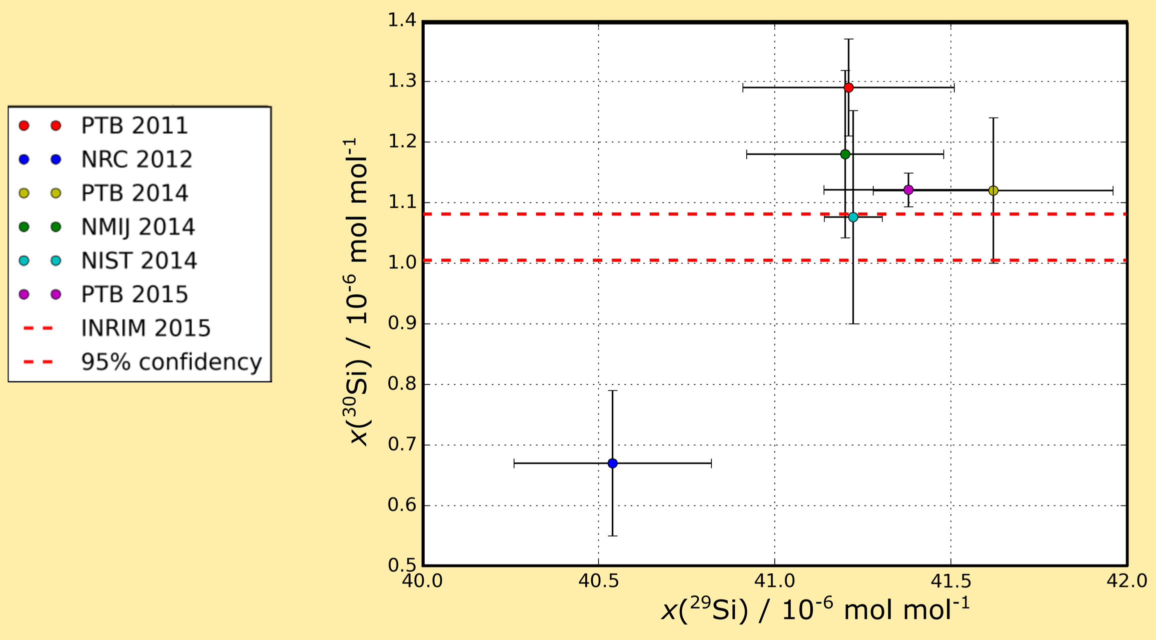
^{30}Si mole fraction

The 30Si mole fraction has been measured by several National Metrology Institutes (NMI) using mass spectrometry. In one case discrepancies have been highligthed.

For this project, a relative Instrumental Neutron Activation Analysis method was performed. A natural silicon crystal of mass and shape similar to the sample to be measured was used as standard reference. The mole fraction of ^{30}Si was quantified by counting gamma-delayed emissions with a HPGe detector. Activation was performed by the neutron reaction $^{30}Si(n,\gamma)^{31}Si$ (2.6 h half-life) and subsequent emission at 1266.1 keV.

The ^{30}Si molar fraction value, 1,043(19) x 10^{-6}, obtained with INAA technique is consistent with NIST, NMIJ and PBT results carried out with VE-IDMS.

a)



b)

	x(29Si) / 10^{-6}	x(30Si) / 10^{-6}	Relative uncertainty
PTB 2011	41,21(15)	1,29(4)	
NRC 2012	40,54(14)	0,67(6)	
PTB 2014	41,62(17)	1,12(6)	
NMIJ 2014	41,2(14)	1,18(69)	
NIST 2014	41,223(41)	1,076(88)	
PTB 2015	41,38(12)	1,121(14)	
INRIM 2015	-	1,043(19)	1,36E-009

a) graphical comparison of 30Si mole fraction value obtained by INAA (red band) with values obtained by other NMI.

b) table of analytical values of isotopic abundance.

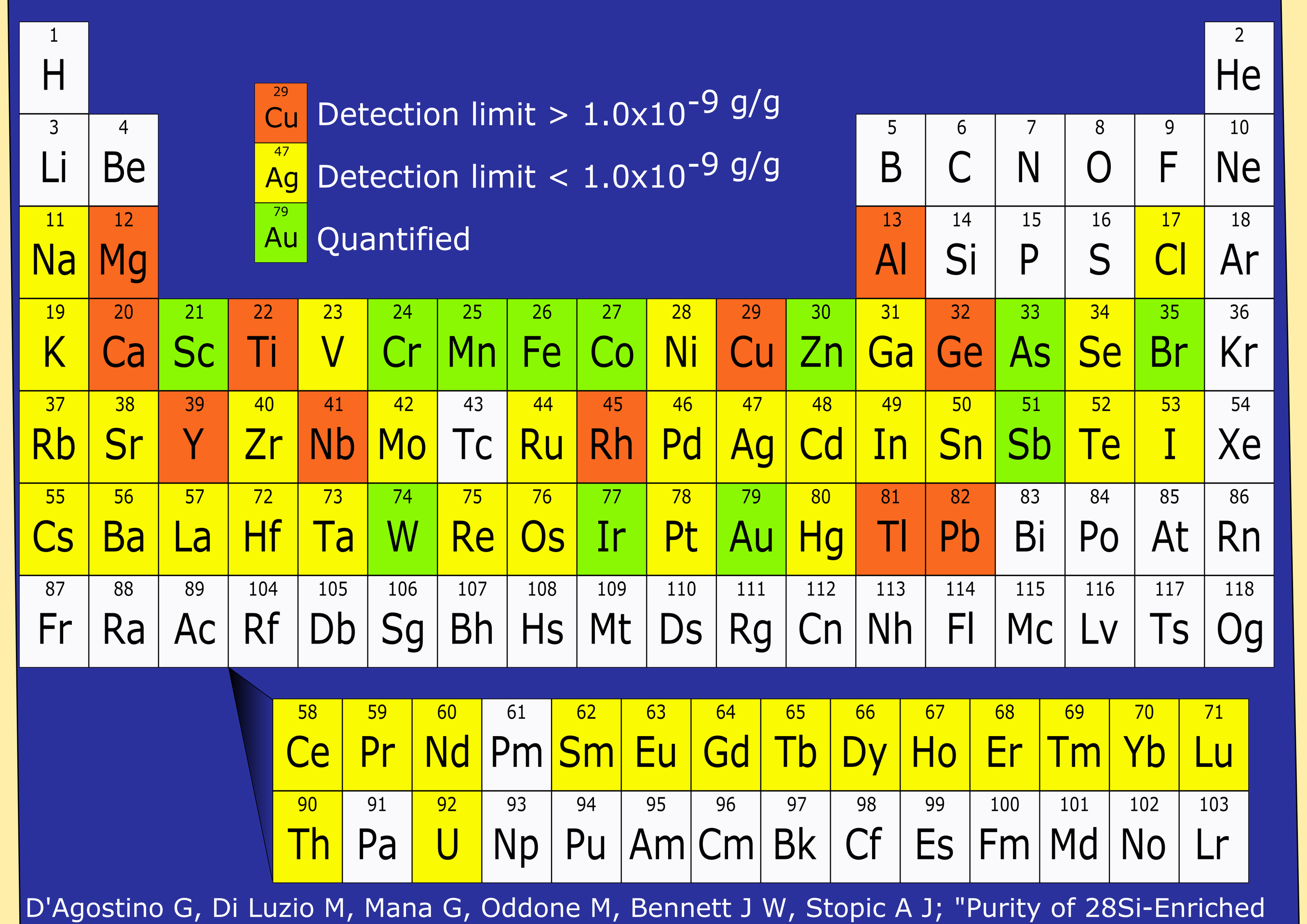
D'Agostino G, Di Luzio M, Mana G, Oddone M, Pramann A, Prata M; "^{30}Si Mole Fraction of a Silicon Material Highly Enriched in ^{28}Si Determined by Instrumental Neutron Activation Analysis", *Analytical Chemistry* **2015**, 87(11): 5716-5722

Impurities

Despite this silicon material is assumed as 'ultra-pure', the elemental contamination was checked with INAA using both the relative method, and the k_0 method.

The k_0 method uses a co-irradiated flux monitor to relate activity of different radioisotopes avoiding the use of several elemental standards. Evaluations of 61 short and long-lived radionuclides were performed at OPAL reactor of ANSTO using k_0 method while evaluation of 5 medium-lived radionuclides activated using fast reactions and relative method was performed at TRIGA reactor.

12 contaminant elements were quantified with mass fractions ranging from 8.53(49) x 10^{-10} of Fe to 7.18(96) x 10^{-15} of Ir. A detection limit was estimated for 54 unquantified elements.



D'Agostino G, Di Luzio M, Mana G, Oddone M, Bennett J W, Stopic A J; "Purity of 28Si-Enriched Silicon Material Used for the Determination of the Avogadro Constant", *Analytical Chemistry* **2016**, DOI: 10.1021/acs.analchem.6b01537

Vacancy-related defects

A preliminary quantification of vacancy-related defects was carried out using a sample of natural silicon crystal.

The sample was filled by Cu at high temperature (750 °C) for 3 h and slowly cooled to precipitate $CuSi_3$ within the void defects following the method as suggested by Spaepen.

5 following cycles of annealing at lower temperature (450 °C) for 2 h were performed to out-diffuse the interstitial Cu.

Relative INAA was exploited to quantify Cu amount through the reaction $^{63}Cu(n,\gamma)^{64}Cu$ and counting ^{64}Cu (12.7 h half-life) gamma emission at 1345.77 keV.

The result of the experiment showed a Cu concentration plateau corresponding to Cu trapped within the sample. From its quantification, an upper limit for the density of vacancies is estimated.