Background Statement for SEMI Draft Document 4768
NEW STANDARD: TEST METHOD FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) OF SILICON

Note: This background statement is not part of the balloted item. It is provided solely to assist the recipient in reaching an informed decision based on the rationale of the activity that preceded the creation of this document.

Note: Recipients of this document are invited to submit, with their comments, notification of any relevant patented technology or copyrighted items of which they are aware and to provide supporting documentation. In this context, “patented technology” is defined as technology for which a patent has issued or has been applied for. In the latter case, only publicly available information on the contents of the patent application is to be provided.

An increasing demand for poly-Si as raw material for manufacturing mono- and multicrystalline Si resulted from the strong growth of the PV industry in the past years. Suppliers of this material correspondingly increased and are still increasing their capacity and new suppliers enter the market. By this an also increasing demand for trace element analysis of poly-Si was and will be generated

• for controlling the manufacturing processes for poly-Si, and
• for testing the specification negotiated between suppliers and customers.

For simplifying the interface between suppliers, customers and analytical laboratories it appears advisable to standardize analytical methods and procedures for achieving a common understanding of these methods and a common reference for values defined in product specifications. Neutron Activation Analysis (NAA) is a most sensitive method for the detection of trace elements in Si and is well established in the semiconductor industry. Therefore it was suggested to develop a standard for a test method for NAA for poly-Si.

The SNARF for the test method for NAA for poly-Si was approved by the Silicon Wafer Committee in its meeting in San Francisco on July 15, 2009. The Silicon Wafer Committee offered in this meeting to transfer the responsibility for this activity to the PV Committee. This was accepted by the PV Committee in its meeting in Hamburg on September 22, 2009. Doc. 4768 was developed subsequently by a small working group, discussed in the Int’l Analytical Test Methods TF and was approved for ballot by the PV Committee in its meeting in Berlin on March 9, 2010 to be adjudicated at the PV Committee meeting in San Francisco in July 2010. Check www.semi.org/standards for the latest meeting schedule.
SEM Draft Document 4768
NEW STANDARD: TEST METHOD FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) OF SILICON

1 Purpose

1.1 Neutron Activation Analysis (NAA) is a highly sensitive method for multi-element quantitative and qualitative analysis of various materials. In particular, it is an established method in the semiconductor industry for analyzing and qualifying poly-silicon (poly-Si), the feedstock for growing semiconductor grade single crystalline silicon (c-Si) as well as silicon wafers, regarding trace element contamination. The increasing demand for feedstock Si in the photovoltaic industry resulted in a higher volume of production of poly-Si and in developing alternative methods for purifying raw Si, resulting in materials that are generically called solar grade silicon (sog-Si) in the present document. This material may occur in a variety of shapes, like chunks, powder, and granules.

1.2 The growing volume of production of poly-Si and sog-Si requires also an increase of quality control for these materials, for which Instrumental Neutron Activation Analysis (INAA) is one method of choice. INAA is an NAA where the analysis is conducted directly on the irradiated samples, in contrast to Radiochemical NAA (RNAA) where the irradiated samples are subjected to chemical separation for removing interfering species or for concentrating the radioisotope of interest. Currently INAA is performed by laboratories using different irradiation sources and conditions, electronic equipment and preparation methods, and it is applied to a wide morphological variety of Si. Standardizing INAA for application to silicon will remove differences in the analytical approach and will establish a common reference for the analyses.

2 Scope

2.1 The test method covers the INAA of Si produced by chemical vapor deposition (CVD) or metallurgical purifying processes.

2.2 Samples to be analyzed may occur in single crystalline, polycrystalline, or multicrystalline form, as powder, granules, chunks, or wafers.

2.2.1 The test method refers to the analysis of the bulk of the materials. Analysis of the surface or surface near regions of samples may be performed according to the test method by additional sample preparation and avoiding carefully surface contamination during sample extraction, handling and preparation.

2.2.2 The test method does not refer to the analysis of thin amorphous, polycrystalline or micromorph Si films.

2.2.3 The test method is not intended for but may be applied to the analysis of samples of Si that were intentionally contaminated with high concentrations of specific elements after checking the impact on safety, LOD and t_{50}.

2.3 The test method covers only the activation of appropriate trace element nuclides by thermal or epithermal neutrons.

2.4 The test method is intended for analyzing a wide range of trace elements (see Appendix 1). This requires in general irradiation times longer than the lifetime of the decay of activated \(^{31}\text{Si}\) and waiting times before performing the analysis until the activity of \(^{31}\text{Si}\) has sufficiently decreased.

NOTICE: This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users of this standard to establish appropriate safety and health practices and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 Si with high concentrations of other elements may require specific attention regarding the level of tolerable radioactivity.

3.2 Only elements with isotopes that are converted in an appropriate radioactive nuclide by irradiation with neutrons can be detected by INAA (see Appendix 1). The nuclides of most elements lighter than Si have very short
decay lifetimes after irradiation with thermal or epithermal neutrons. Their analysis is not covered by this test method, it requires different procedures.

3.3 High concentrations of As, Sb, and P may impact the LOD, depending on total neutron irradiation flux. P enhances the background in the entire γ-spectrum due to β-radiation, As and Sb also enhance the background of the γ-spectrum, but mainly in the energy range below their γ-lines. In addition, As and Sb may block the radiation counter because of their high activity. Following concentrations should not be exceeded for reliable determination of other elements: As, Sb < 1E13 at/cm³, P < 1E16 at/cm³ for best LOD.

NOTE 1: Analysis of samples with higher concentrations is possible, but impact on LOD and safety has to be taken in account. As, P, and to some extent Sb are used as dopants in the semiconductor industry and are intentionally added during crystal growth. Therefore their concentration in an ingot can be estimated with sufficient accuracy. For completely unknown samples it is recommended to perform a preview INAA analysis with short irradiation time for assessing the concentration of potentially interfering elements.

3.4 The analysis of thin PV wafers is possible, but little bulk material may be left after removing the surface damage of such wafers. Sampling of several wafers may be required to achieve the mass necessary for analysis, depending on the LOD requested and irradiation time.

4 Referenced Standards and Documents

4.1 SEMI Standards

SEMI C28 — Specifications and Guidelines for Hydrofluoric Acid
SEMI C35 — Specifications and Guideline for Nitric Acid

4.2 ISO Standard


4.3 ASTM Standard

D1193 — Standard Specification for Reagent Water

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

(Refer to SEMI’s Compilation of Terms (COT) for a list of the most current terms and their definitions.)

5.1 Acronyms

5.1.1 ADC — analog to digital converter
5.1.2 CRM — certified reference material
5.1.3 DI water — de-ionized water
5.1.4 INAA — instrumental neutron activation analysis
5.1.5 LDPE — low density polyethylene
5.1.6 LN₂ — liquid nitrogen
5.1.7 LOD — limit of detection
5.1.8 MCA — multichannel analyzer
5.1.9 NAA — neutron activation analysis
5.1.10 PE — polyethylene
5.1.11 PFA — perfluoralkoxy

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2 International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211 Geneva 20, Switzerland
3 ASTM International, 100 Barr Harbour Drive, PO Box C700, West Conshohoken, PA 19428-2959, USA
5.1.12 PP — polypropylene

5.2 Definitions

5.2.1 ambient background — radiation resulting from sources outside of sample recorded by detector.

5.2.2 energy resolution — width of peak in $\gamma$-spectrum at $1/e$ of its maximum.

5.2.3 full-energy peak detection efficiency $\varepsilon_p$ — probability of detecting a $\gamma$-photon emitted by the $\gamma$-source, dependent on energy of $\gamma$-photon, distance between source and detector, and the shape of the source.

5.2.4 irradiation capsule — container in which sample is kept during irradiation.

5.2.5 irradiation time $t_{irr}$ — duration of irradiation.

5.2.6 short time irradiation — irradiation for a time $\leq$ maximum irradiation time allowed for PE foil.

5.2.7 lifetime $t_{1/2}$ — time after which a nuclide activity has decayed to 50 % of its starting value.

5.2.8 long time irradiation — irradiation longer than short time irradiation.

5.2.9 measuring time $t_c$ — duration of recording of $\gamma$-spectrum. An additional index $i$ is used, such as $t_{ci}$ with $i = 1, 2, \ldots$ for several measurements.

5.2.10 minimal waiting time $t_{w0}$ — time after end of irradiation until the activity of Si matrix has decayed to $\leq 1$ MBq, typically $t_w \geq 36 \text{ h}$.

5.2.11 relative detector efficiency — ratio of the peak area of the 1.33 MeV line of a calibrated $^{60}$Co $\gamma$-source divided by the total source disintegrations during dead time corrected $t_m$ to the efficiency of a 3x3NaI(Tl) scintillation detector at 25 cm.

5.2.12 relative intensity, of $\gamma$-ray peak — probability of $\gamma$-ray peak occurring at decay of isotope.

NOTE 2: Unstable isotopes can emit $\gamma$-radiation with several well defined energies. The relative intensity denotes the frequency of $\gamma$-rays emitted with the different energies.

5.2.13 waiting time $t_w$ (sometimes also called decay time) — time after end of irradiation until start of measurement. An additional index $i$ is used, such as $t_{wi}$ with $i = 1, 2, \ldots$ for several measurements.

6 Summary of Method

6.1 The history of the sample is checked regarding potentially interfering trace elements and a decision regarding the necessity of a preview analysis is made.

6.2 The sample is prepared before irradiation according to its structure (chunk, granule, wafer or powder) and put in an appropriate container.

6.3 The sample is irradiated with thermal neutrons by an appropriate neutron source for a time as required for the intended LOD.

6.4 The sample is prepared after irradiation according to its structure.

6.5 A spectrum of the emitted $\gamma$-rays is taken.

6.6 The spectrum is evaluated with appropriate software and the concentrations of the impurities are calculated with the $k_0$-method or by using the activation equation (see Appendix 2) after corrections for neutron flux variations, self absorption, ambient background radiation, and set-up dead time were applied.

7 Interferences

7.1 Sodium — Due to the reaction $^{28}\text{Si}(n, p+\alpha)^{24}\text{Na}$, which is a reaction with fast neutrons, an apparent Na concentration may be measured that is higher as originally present in the sample. The effect of this interference depends on the irradiation source’s neutron spectrum.

7.2 Abundance of isotopes — has to be known for the sample for being able to calculate the total concentration of an element in Si. Different isotopes of an element react differently with neutrons or not at all. Typically calculations assume a natural abundance of isotopes.
7.3 Peak interferences — Closely adjacent peaks in γ-spectra of nuclides of specific elements may overlap, inhibit the identification of the nuclide, and detrimentally impact the quantitative analysis. In such cases alternative lines, if present, should be used for the quantitative analysis. Identification of nuclides may be ascertained by correlating the peak area obtained by measurements performed after different waiting times based on the known lifetimes of the nuclides.

8 Ambient

8.1 Laboratory — consisting of a part for chemical sample treatments and a part for the measurement apparatus. It has to be certified by local overseeing agency for handling radioactive materials.

8.2 Operators — certified for handling radioactive materials according to local legislation.

9 Apparatus

9.1 Irradiation System

9.1.1 Neutron Source — nuclear research reactor with constant flux of thermal neutrons. Sources differ in neutron flux and neutron spectrum. Preferably mainly slow, thermal neutrons with a small contribution of fast neutrons should be used. Typically neutron fluxes of appropriate reactors are in between 5E12 and 2E14 n/(sec cm²). The spatial flux variations of the neutron beam have to be known, then they can be taken into account. They impact the accuracy of the analysis results.

NOTE 3: The spatial flux variations at the irradiation positions are usually known to the operator of the reactor. If not known or in critical cases multiple radiation monitors can be used for probing the spatial flux variations.

9.1.2 Irradiation Stage — specific to the irradiation source used.

9.2 Detector and Electronics

9.2.1 γ-detector — intrinsic Ge detector or Li-drifted Ge detector (GeLi) cooled with liquid nitrogen, pre-amplifier included, for detecting γ-rays. The intrinsic efficiency of this detector for detecting γ-rays should be > 20%.

9.2.2 Dewar vessel — for LN₂ for cooling detector.

9.2.3 Electronics — consists of power supply for γ-detector, amplifier, ADC, MCA, PC.

9.2.3.1 Power supply for γ-detector — voltage according to detector used.

9.2.3.2 Main amplifier

9.2.3.3 ADC — ≥ 12 bit

9.2.3.4 MCA — ≥ 4000 channels (stand-alone or board for PC).

9.2.3.5 PC — hard- and software interface appropriate for MCA.

9.3 Balance — calibrated and certified, with accuracy ≤ 1% of weight of “sample”, for determining the weight of the sample, the weight of the neutron flux monitor and for controlling stock removal by etching of sample.

10 Reagents and Materials

10.1 Irradiation capsule — typical Al, AlMg, or high purity graphite alloy for long time irradiation, as provided by reactor, polymer for short time irradiation.

10.2 Neutron flux monitor — 4N Zr or better, for longtime irradiation, 4N Zr or 3N Au for short time irradiation, foil or wire.

10.3 Hydrofluoric acid (HF) — purity Grade 1 or better (SEMI C28).

10.4 Nitric acid (HNO₃) — purity Grade 1 or better (SEMI C35).

10.5 Water — DI water according to ASTM D1193, type IV

NOTE 4: Grade 1 quality as well as DI water are sufficient because impurity in the acid solutions are not radioactive or are only deposited on sample surface, which is removed before measurement of γ-radiation.
10.6 Containers for etching and cleaning — inert with respect to acids used, not glass or silica, adapted to sample size.

10.7 Sample carriers — inert with respect to acids used, not glass or silica.

10.8 Tweezers — preferably PFA; metal tweezers must not be used.

10.9 silica container — for powder and granular Si, size adjusted to irradiation capsule.

10.10 Gloves — for handling of radioactive samples one way, typically latex, for HF treatment of samples acid resistant gloves.

10.11 Wash bottle or squeeze bottle — LDPE.

10.12 Film tube — PE.

10.13 Sample bottle — PFA or LDPE.

10.14 CRM — appropriate for detector and distance of sample to detector.

10.15 Liquid nitrogen — as commercially available.

11 Safety Precautions

11.1 Regional and international safety precautions regarding handling of aggressive chemicals.

11.2 Regional and international safety precautions and regulations regarding handling of radioactive materials.

11.3 Regional and international safety precautions and regulations regarding handling of liquid nitrogen.
12 Test Specimen

12.1 *Size* — to be adjusted to irradiation capsule.

12.2 *Sample minimum mass* — depending on required LOD and neutron flux, see Appendix 1.

12.3 *Number of samples per irradiation capsule* — according to size of samples and capsule, several samples per capsule are possible, no impact on measurement result.

12.4 *Si powder* — needs additional package in irradiation capsule.

12.5 *Granular Si* — needs additional package in irradiation capsule.

13 Sample Preparation

13.1 Treatment of samples for long time irradiation before irradiation.

13.1.1 Treatment of chunks before irradiation.

13.1.1.1 Record sample parameters: mass, size.

NOTE 5: Size is required for determining the full-energy peak detection efficiency. For samples with irregular shape an effective size has to be estimated.

13.1.1.2 Remove surface damage and contamination by acid etching (HF/HNO₃/H₂O solution), if required.

13.1.1.3 Rinse in DI water and dry.

13.1.1.4 Record sample parameters: mass.

13.1.1.5 Optional: Seal in PE foil for shipment to reactor.

13.1.1.6 Put in irradiation capsule at reactor for irradiation.

13.1.2 Treatment of powder and granular Si before irradiation.

13.1.2.1 Put powder or Si granules in silica container.

13.1.2.2 Record sample parameters: mass, approximate grain size.

13.1.2.3 Optional: seal silica container in PE foil for shipment to reactor.

13.1.2.4 Seal in irradiation capsule at reactor for irradiation.

NOTE 6: The term “put” means that the container does not have to be waterproof in the present context, in contrast to the term “seal”, which requires a waterproof container or capsule. However, it is recommended not to fuse the sample in a quartz ampoule.

13.1.3 Treatment of wafers before irradiation.

13.1.3.1 Record sample parameters: mass.

13.1.3.2 Remove surface damage by acid etching if required.

13.1.3.3 Split wafer in pieces.

13.1.3.4 Record sample parameters: mass, size.

13.1.3.5 Wrap as many pieces as required in Al sheet, mark Al sheet if required.

13.1.3.6 Optional: Seal in PE foil for shipment to reactor.

13.1.3.7 Put in irradiation capsule at reactor for irradiation.

13.2 Treatment of samples for short time irradiation before irradiation.

13.2.1 Polymer irradiation capsules may be used instead of Al or graphite irradiation capsules, if sample size allows this.

13.2.2 For powder and granular samples no silica container is required, sealing in PE foil or container is sufficient.

13.2.3 Irradiation capsule may be not necessary.
13.3 Treatment of samples after irradiation, before measurement:

13.3.1 Rinse in DI water.

13.3.2 Remove surface contamination by acid etching (HF/HNO₃/H₂O solution).

13.3.3 Rinse in DI water and dry.

13.3.4 Record sample parameters: mass, size.

13.3.5 Seal chunks and wafers in PE foil for preventing contamination of detector with radioactive material. Put granular or powder samples in container made of polymeric material.

14 Preparation of Apparatus

14.1 Standard procedure: equipment powered and ready for measurement for 24 h / 7 days.

14.2 LN₂ for cooling the detector has to be replenished regularly.

14.3 In case of start-up after shut down or change of set-up of electronics, follow procedure as described by supplier of detector, and check and adjust, if needed, signal baseline restoration at output of amplifier with oscilloscope. This also should be performed when deterioration of energy resolution is observed.

15 Calibration and Standardization

15.1 The balance for weighing samples and neutron flux monitor has to be calibrated and certified in regular intervals by an accreditation agency.

15.2 The Ge-detector and related electronics have to be calibrated regarding full-energy peak efficiency, energy and energy resolution in regular intervals using certified radioactive references⁴ and the results of the calibration have to be recorded. The calibration has to be performed for each distance used between sample and detector, as well as after any change in the settings of the electronics or after it was switched off.

15.3 Dead time has to be measured

15.3.1 after changing the settings of the electronics, and/or

15.3.2 for ADC with automated dead time correction when dead time ≥ 10 %.

NOTE 7: Dead time measurement can be performed e.g. with the help of a pulse generator or by changing the distance between sample and detector.

15.4 Measurement of background radiation has to be performed in regular intervals or when suspicious results occur, e.g. due to contamination of detector.

16 Procedure

16.1 Check history of sample regarding potentially interfering trace element concentrations, and decide whether preview analysis is required.

16.2 Perform preview analysis, if required, according to the following procedure. If preview analysis is not required, skip this step.

16.3 Prepare sample as described in ¶¶ 13.1 and 13.2.

16.4 Irradiate sample with thermal neutrons, typically longer than several hours, depending on LOD required, purity of sample and economic considerations.

16.5 Record duration and end time of irradiation.

16.6 Prepare sample as described in ¶ 13.3.

16.7 Put sample in front of detector in a distance in agreement with calibration and dead time of detector.

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⁴ Debertin, K., Helmer, G., Gamma and X-ray Spectrometry with Semiconductor Detectors, North Holland, Amsterdam, 1988
16.8 Measure sample a first time after \( t_w \leq t_{w0} \) by recording the spectrum (count rate vs energy) of the \( \gamma \)-rays emitted by the sample. This first measurement has to be started close to \( t_{w0} \), in particular for elements with short lifetimes, and before 7 d after end of irradiation.

16.9 Repeat measurement as often as required, but at least once, so that \( t_w > 7 \) d. Repeating the measurement improves the LOD and allows better identification of critical elements based on their characteristic lifetimes.

16.10 Measure neutron flux monitor in parallel to first sample measurement by recording the spectrum of the \( \gamma \)-rays emitted by it.

16.11 Correct for spatial flux variations of neutrons and self-absorption if necessary.

16.12 Evaluate recorded spectra of sample and neutron flux monitor regarding element identification, element concentration and detection limit considering detector efficiency, sample weight and time evolved after irradiation.

16.13 Assess the accuracy of the concentrations.

16.14 Report the results according to § 18.

17 Calculations or Interpretation of Results

17.1 Calculation of LOD — according to ISO 11929-7:2005.

17.2 Determination of element concentrations:

17.2.1 Determine area under peak with software as assessed in Blaauw et al.\(^5\) or equivalent. Special care has to be applied regarding separation of multiple peaks.

17.2.2 Identify isotope associated with individual peaks.

17.2.3 Calculate isotope activity at the end of irradiation taking into account \( t_w \) and \( t_m \) as well as detector efficiency \( \varepsilon \) and the relative intensities of the \( \gamma \)-rays investigated. Correct for ambient background as well as dead time.

17.2.4 Determine element concentration according to \( k_0 \)-method\(^6\) or by using the activation equation, considering the irradiation time (see Appendix 2).

18 Reporting Results

18.1 Information to be reported mandatorily:

18.1.1 Origin and identification of sample.

18.1.2 Sample parameters: mass, estimated removed layer thickness (mass difference of samples before and after etching in relation to estimated surface area).

18.1.3 All deviations, e.g. too little mass.

18.1.4 Measurement results:

18.1.4.1 Concentration of elements detected and its error per sample.

18.1.4.2 LOD per element and either per sample or per maximum of all samples in one irradiation lot.

18.2 Information to be reported optionally

18.2.1 Irradiation parameters: reactor, position of sample in reactor during irradiation, thermal and epithermal neutron flux, irradiation time.

18.2.2 Measurement parameters: \( t_w \)'s, \( t_m \)'s.

18.2.3 Sample parameters: size

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\(^6\) De Corte, F., Simonits, A., Atomic Data and Nuclear Data Tables, 85 (2003) 47
19 Precision and Accuracy

19.1 Accuracy — based on results of ¶ 16.2. Si reference materials are not available.

19.2 Precision — of detector and electronics, dependent on regular, sufficiently frequent calibration. Irradiation is controlled by a neutron flux monitor.

NOTE 8: For a general introduction to NAA, its interferences, systematic and statistical errors see DeSoete et al.?

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APPENDIX 1
RADIOACTIVE NUCLIDES FOR INAA

NOTICE: The material in this appendix is an official part of SEMI (doc#) and was approved by full letter ballot procedures on (date of approval).

A1-1 Elements that can be detected in Si by INAA

A1-1.1 Criteria

A1-1.1.1 Almost all elements have radioactive isotopes/nuclides after irradiation with thermal neutrons. Those unstable isotopes decay by emitting particles (electrons, positrons, protons, and $\alpha$) and/or photons ($\gamma$-rays). The decay of the radioactivity is characterized by a nuclide specific lifetime, after which the activity has decayed to 1/2 of its value at the start, and, in case of $\gamma$-rays, by nuclide specific $\gamma$-ray energy.

A1-1.1.2 Nuclides suitable for use in INAA have to have a sufficiently long lifetime in order to be still present in sufficient concentrations after a waiting time that is needed for reducing the activity of the Si matrix to a level that a) allows safe handling of the samples, and b) avoids interference with the radiation emitted by the trace elements to be analyzed. This excludes most of the lighter elements with mass < 23 because of their short lifetime.

A1-1.1.3 Table A1-1 lists the elements and their nuclides that can be used for INAA with a good LOD.

A1-1.2 Additional elements — additional elements such as Ti (nuclides Sc-47/48, $t_{1/2} = 3.35$ d/43.6 h) and Ni (nuclide Co-58, $t_{1/2} = 70.86$ d) can be determined by using reaction channels of fast neutrons, but detection limits strongly depend on the specific neutron spectrum at the used irradiation position of the neutron source.

Table A1-1 Radioactive Nuclides for INAA

<table>
<thead>
<tr>
<th>Element</th>
<th>Nuclide</th>
<th>Lifetime $t_{1/2}$</th>
<th>Normalized LOD $1/\text{at/cm}^3$</th>
</tr>
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<tbody>
<tr>
<td>Na</td>
<td>$^{24}\text{Na}$</td>
<td>15.02 h</td>
<td>(see 7.1)</td>
</tr>
<tr>
<td>K</td>
<td>$^{42}\text{K}$</td>
<td>12.36 h</td>
<td>3E14</td>
</tr>
<tr>
<td>Ca</td>
<td>$^{47}\text{Ca}$</td>
<td>4.54 d</td>
<td>1E15</td>
</tr>
<tr>
<td>Sc</td>
<td>$^{46}\text{Sc}$</td>
<td>83.83 d</td>
<td>5E09</td>
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<td>27.7 d</td>
<td>1E12</td>
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<tr>
<td>Fe</td>
<td>$^{59}\text{Fe}$</td>
<td>44.50 d</td>
<td>5E13</td>
</tr>
<tr>
<td>Co</td>
<td>$^{60}\text{Co}$</td>
<td>5.27 a</td>
<td>1E11</td>
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<tr>
<td>Cu</td>
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<td>12.70 h</td>
<td>2E14</td>
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<td>119.80 d</td>
<td>1E12</td>
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</tr>
<tr>
<td>Element</td>
<td>Nuclide</td>
<td>Lifetime $t_{1/2}$</td>
<td>Normalized LOD $\text{at/cm}^3$</td>
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<tr>
<td>---------</td>
<td>---------------</td>
<td>--------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Te</td>
<td>$^{131}\text{Te}/^{131}\text{I}$</td>
<td>8.02 d</td>
<td>$5 \times 10^1$</td>
</tr>
<tr>
<td>Cs</td>
<td>$^{134}\text{Cs}$</td>
<td>2.06 a</td>
<td>$1 \times 10^1$</td>
</tr>
<tr>
<td>Ba</td>
<td>$^{137}\text{Ba}$</td>
<td>11.80 d</td>
<td>$2 \times 10^2$</td>
</tr>
<tr>
<td>La</td>
<td>$^{140}\text{La}$</td>
<td>40.28 h</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Ce</td>
<td>$^{141}\text{Ce}$</td>
<td>32.50 d</td>
<td>$1 \times 10^2$</td>
</tr>
<tr>
<td>Pr</td>
<td>$^{142}\text{Pr}$</td>
<td>19.13 h</td>
<td>$1 \times 10^2$</td>
</tr>
<tr>
<td>Nd</td>
<td>$^{147}\text{Nd}$</td>
<td>10.98 d</td>
<td>$2 \times 10^2$</td>
</tr>
<tr>
<td>Sm</td>
<td>$^{153}\text{Sm}$</td>
<td>46.70 h</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Eu</td>
<td>$^{152}\text{Eu}$</td>
<td>13.33 a</td>
<td>$2 \times 10^2$</td>
</tr>
<tr>
<td>Gd</td>
<td>$^{155}\text{Gd}$</td>
<td>18.56 h</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Tb</td>
<td>$^{160}\text{Tb}$</td>
<td>72.30 d</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td>Ho</td>
<td>$^{164}\text{Ho}$</td>
<td>26.8 h</td>
<td>$3 \times 10^2$</td>
</tr>
<tr>
<td>Yb</td>
<td>$^{169}\text{Yb}/^{175}\text{Yb}$</td>
<td>32.02 d/4.2 d</td>
<td>$3 \times 10^2$</td>
</tr>
<tr>
<td>Lu</td>
<td>$^{177}\text{Lu}$</td>
<td>6.71 d</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Hf</td>
<td>$^{183}\text{Hf}$</td>
<td>42.40 d</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Ta</td>
<td>$^{182}\text{Ta}$</td>
<td>115.00 d</td>
<td>$5 \times 10^3$</td>
</tr>
<tr>
<td>W</td>
<td>$^{187}\text{W}$</td>
<td>23.90 h</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Re</td>
<td>$^{186}\text{Re}$</td>
<td>3.78 d</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Os</td>
<td>$^{185}\text{Os}$</td>
<td>93.60 d</td>
<td>$5 \times 10^3$</td>
</tr>
<tr>
<td>Ir</td>
<td>$^{192}\text{Ir}$</td>
<td>73.83 d</td>
<td>$5 \times 10^3$</td>
</tr>
<tr>
<td>Pt</td>
<td>$^{195}\text{Pt}$</td>
<td>4.02 d</td>
<td>$2 \times 10^3$</td>
</tr>
<tr>
<td>Au</td>
<td>$^{198}\text{Au}$</td>
<td>2.70 d</td>
<td>$5 \times 10^3$</td>
</tr>
<tr>
<td>Hg</td>
<td>$^{207}\text{Hg}$</td>
<td>46.59 d</td>
<td>$1 \times 10^3$</td>
</tr>
<tr>
<td>Th</td>
<td>$^{233}\text{Th}/^{233}\text{Pa}$</td>
<td>27.00 d</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td>U</td>
<td>$^{239}\text{U}/^{239}\text{Np}$</td>
<td>2.36 d</td>
<td>$2 \times 10^3$</td>
</tr>
</tbody>
</table>

1) Irradiation conditions: mass*$\Phi_{\text{th}}$ = $1 \times 10^{14}$ g/cm$^2$, $t_{\text{irr}}$ = 1 d, measurement conditions: $t_w = 5$ d, $t_e = 8$ h, $t_{w2} = 10$ d, $t_{c2} = 24$ h, relative detector efficiency $\varepsilon = 0.4$ for sample placed directly on detector cap.

A1-2 Limits of detection for trace elements in Si

A1-2.1 The actual LOD’s for the different elements investigated are calculated after the measurement according to 17.1.

A1-2.2 However, it is advised for economical reasons to adjust the irradiation time according to the LOD’s expected for an investigation.

A1-2.3 The LOD for the different elements depends on several parameters: sample mass, neutron flux density, irradiation time, the cross section of the elemental isotopes for capturing a neutron and the lifetime of the nuclides.

A1-2.4 In the fourth column of Table A1-1 standardized LOD’s for the elements with appropriate nuclides are displayed for common irradiation and measurement conditions. The LOD for other conditions may then be estimated by using the coefficient $C$, which is proportional to the LOD for a given nuclide:

$$C = (m_s \Phi_b \varepsilon (1 - e^{-\lambda t_{\text{irr}}}) e^{-\lambda t_e} (1 - e^{-\lambda t_{w2}}))^{-1}$$  \hspace{1cm} (A1-1)$$

with sample mass $m_s$, flux density of thermal neutron $\Phi_b$, irradiation time $t_{\text{irr}}$, detector efficiency $\varepsilon$, measuring time $t_e$, and decay constant $\lambda = (\ln 2)/t_{1/2}$.

A1-2.5 The irradiation time $t_{\text{irr}}$ required for achieving a requested LOD for a specific element may then be calculated by comparing $C$ for the intended investigation with $C$ of the reference irradiation conditions.

A1-2.6 This estimation does not take in account the smooth background in the $\gamma$-ray spectrum due to the radioactivity of the sample.
APPENDIX 2
CALCULATION OF ELEMENT CONCENTRATION

NOTICE: The material in this appendix is an official part of SEMI (doc#) and was approved by full letter ballot procedures on (date of approval).

A2-1 Activation equation
A2-1.1 The mass $m_x$ of a trace element $x$ with the atomic weight $M_x$ in Si may be calculated by applying the activation equation

$$A_0 = m_x \frac{N_x a_x (\Phi_{th} \sigma_{th} + \Phi_{epi} \sigma_{epi})}{M_x} (1 - e^{-\lambda t_{irr}})$$  \hfill (A2-1)

This equation describes the activity $A_0$ of an element at the end of the irradiation with an irradiation time $t_{irr}$, with the Avogadro number $N_A$, the abundance $a_x$ of the isotope investigated of the element $x$, the thermal and epithermal neutron fluxes $\Phi_{th}$ and $\Phi_{epi}$, the cross sections for the corresponding reaction $\sigma_{th}$ and $\sigma_{epi}$ (also called resonance integral), and the decay constant $\lambda$ for the isotope $x$. The activity $A(t)$ at a given time $t$ after the irradiation is then

$$A(t) = A_0 e^{-\lambda t}$$  \hfill (A2-2)

and the measured activity after the waiting time $t_w$ is

$$A(t_w) = \frac{N_{p,x}}{\varepsilon_{p,x} C_t} = A_0 e^{-\lambda t}$$  \hfill (A2-3)

with the measured peak area $N_{p,x}$ for the isotope $x$, the full-energy peak efficiency $\varepsilon_{p,x}$, the counting factor $C$ (see Eq. A2-8), and the measuring time $t_c$. This allows then with equation A2-1, the tabulated values for $\sigma$ and the neutron flux $\Phi$ as measured by the monitor to calculate the concentration of the trace element investigated. The concentration $\rho_x$ of trace element $x$ is then obtained by

$$\rho_x = \frac{m_x}{m_s} = \frac{N_{p,x} e^{-\lambda t_c} M_s}{m_s c_{p,x} C t_c N A a_x (\Phi_{th} \sigma_{th} + \Phi_{epi} \sigma_{epi}) (1 - e^{-\lambda t_{irr}})}$$  \hfill (A2-4)

A2-2 $k_0$ – Method
A2-2.1 Alternatively the concentration $\rho_x$ of a trace element $x$ may be calculated by the standardized $k_0$-method\(^9\) by using the following equations

$$\rho_x (\frac{\text{mg}}{g}) = \frac{A_x}{A_m} \frac{1}{k_{0,m}(x)} \frac{f + Q_{0,m}(\alpha)}{f + Q_{0,x}(\alpha)} \varepsilon_{p,m} \varepsilon_{p,x} 10^6$$  \hfill (A2-5)

with the specific activities $A_x$ and $A_m$ for the sample and the flux monitor, respectively, the experimentally determined correction factor $k_{0,m}(x)$, the ratio $f$ of thermal and epithermal neutron flux $\Phi_{th}/\Phi_{epi}$, the factors $Q_{0,m}(\alpha)$ and $Q_{0,x}(\alpha)$ characterizing the neutron flux as well as the reaction rates, and the full-energy peak detection efficiencies $\varepsilon_{p,m}$ and $\varepsilon_{p,x}$ for the monitor and the trace element $x$, respectively, and a correction factor $\alpha$ (see Eq. A2-10).

A2-2.2 The specific activities $A_x$ and $A_m$ are calculated according to

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\(^8\) N.E. Holden, Neutron scattering and absorption properties, in CRC Handbook of Chemistry and Physics, 1999

\(^9\) De Corte, F. Simonits, A., Vademecum for k$_0$-Users, DSM Research, Geleen, 1994
with the measured net peak areas \(N_{p,x}\) and \(N_{p,m}\) corrected for pulse loss and true coincidences for the trace element and the monitor, the measuring time \(t_c\), the saturation factor \(S\), the decay factor \(D\), the counting factor \(C\), the sample mass \(W\) in g, and the monitor mass \(w\) in g.

A2-2.3 The factors \(S\), \(D\), \(C\) of ¶ A2-2.2 are defined as

\[
S = 1 - e^{-\lambda_D}
\]  
(A2-8)

\[
D = e^{-\lambda_c}
\]  
(A2-9)

\[
C = \frac{1 - e^{-\lambda_c}}{\lambda_c}
\]  
(A2-10)

A2-2.4 The experimentally determined \(k_0\)-factor of analyte \(x\) versus monitor \(m\) is defined as

\[
k_{0,m}(x) = \frac{M_m \alpha \sigma_{0,x} \gamma_x}{M_x \alpha \sigma_{0,m} \gamma_m}
\]  
(A2-11)

with the atomic weight \(M\), the abundance \(\alpha\), the cross section \(\sigma_0\) for neutron capture and \(\gamma\)-emission at an neutron energy of 2200 m/s, and the absolute \(\gamma\)-intensity for the analyte \(x\) and the monitor \(m\). \(k_{0,m}(x)\) can also be calculated with the help of the tabled values\(^a\) by

\[
k_{0,m}(x) = \frac{k_{0,0}(x)}{k_{0,0}(m)}
\]  
(A2-12)

A2-2.5 The Q-factors for the analyte \(x\) and the monitor \(m\) are defined as

\[
Q_{0}(\alpha) = \left\{ \left( \frac{0.429}{0.55^\alpha (2\alpha + 1)} \right) \right\} (1eV)^\alpha
\]  
(A2-13)

with the effective resonance energy \(E_r\) in eV, a correction factor \(\alpha\) for the neutron flux rate for an approximately \(1/E^{1+\alpha}\) distribution, and \(Q_0\) as the ratio of the resonance integral \(I_0\) and the cross section \(\sigma_0\):

\[
I_0 = \int_{0.55eV}^{\infty} \frac{\sigma(E)}{E} dE
\]  
(A2-14)

A2-2.6 The energy dependent full-energy peak efficiencies \(\varepsilon_{p,x}\) and \(\varepsilon_{p,m}\) are determined during calibration for the nuclides and monitor elements investigated.

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