

SEMI PV74-0216 (Reapproved 0221) TEST METHOD FOR THE MEASUREMENT OF CHLORINE IN SILICON BY ION CHROMATOGRAPHY

This Standard was technically approved by the Photovoltaic Global Technical Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on December 10, 2020. Available at www.semiviews.org and www.semi.org in February 2021; originally published August 2016.

1 Purpose

1.1 The quality of polysilicon is very important for the user. More and more granular silicon is being produced and used to produce polysilicon for use in the photovoltaic industry. Research shows that more chlorine remains in granular silicon than in chunk silicon. Chlorine remaining in the silicon affects the quality. Thus, it is necessary to develop a method to measure the chlorine in silicon.

1.2 This Test Method can facilitate unification of protocols and test results among worldwide laboratories used for monitoring or qualifying chlorine in silicon.

2 Scope

2.1 This Standard provides a test method for measuring the chlorine in silicon by ion chromatography (IC).

2.2 This Test Method can be used for various rod, chunk, granule, and chip sizes for polysilicon to determine the chlorine content. Forms of silicon other than granular need to be pulverized, in particle size range of 200 to 3000 μm . The detection limit for routine analysis is 1.0 ppmw.

2.3 The relative units ppbw and ppmw are used for impurity concentration values in this Test Method. For conversion to other units, see SEMI AUX022.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 None.

NOTE 1: Take the utmost care to ensure all contact to the sample containers are pure; rinse containers with copious amounts of deionized (DI) water and use nitrogen to blow clean.

4 Referenced Standards and Documents

4.1 *ASTM Standards*¹

ASTM D1193 — Standard Specification for Reagent Water

ASTM E122 — Standard Practice for Calculating Sample Size to Estimate, with Specified Precision, the Average for a Characteristic of a Lot or Process

4.2 *Other Documents*

SEMI AUX022 — Conversion of Units for Impurity Concentrations in Silicon

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

5 Terminology

5.1 Refer to SEMI Standards Compilation of Terms (COTs) for a list of the most current terms and their definitions.

¹ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, <http://www.astm.org>

5.2 Abbreviations and Acronyms

5.2.1 *IC* — ion chromatography

5.2.2 *ppmw* — part per million weight

5.2.3 *ppbw* — part per billion weight

5.3 Definitions

5.3.1 *certified reference material (CRM)* — a NIST traceable single or multi-element solution standard.

5.3.2 *granular silicon* — nearly spherical granules (200 to 3000 μm) of silicon as produced in a fluidized bed reactor.

5.3.3 *method blank* — a solution of acid prepared using the preparation method without a specimen or test sample used to establish the contribution of trace chlorine contamination from the laboratory environment, reagents or labware to the background.

5.3.4 *standard samples* — samples prepared to known concentrations of the analytes, typically 0.1 ppma, 0.2 ppma, 0.5 ppma and 1 ppma to provide a chlorine standard for the IC instrument.

6 Summary of Test Method

6.1 *Release* — When heated to 1500°C the silicon sample melts (melting point of silicon is 1414°C) and releases chlorine in the form of SiCl_4 vapor at the melting point.

6.2 *Absorption* — Using argon as a purge gas through the tube, the chlorine in the form of SiCl_4 is carried through two bubblers in series filled with ultrapure water.

6.3 *Measurement* — After absorbing and decomposing the SiCl_4 in the scrubbers, the two aqueous solutions are analyzed by IC.

7 Apparatus

7.1 *IC* — Ion chromatography instruments.

7.2 *Electronic Balance(s)* — 0.1 mg accuracy for weighing silicon samples.

7.3 *High Temperature Tube Furnace* — For heating the silicon sample to at least 1500°C.

7.4 *Sample Container* — Quartz boat for holding the silicon sample that is able to hold at least 2 g of sample.

7.5 *Sample Tube* — Made of Al_2O_3 , used for melting the silicon samples.

7.6 *Bubblers* — 10 mL capacity used for scrubbing of the exhaust gas.

7.7 *Ultrasound Equipment* — Eluents sonicated for an IC instrument.

8 Reagents and Materials

8.1 *Ultrapure Water* — Unless otherwise indicated, reagent water should be conformant to ASTM D1193.

8.2 *Argon Gas* — 99.999% (V/V) minimum.

8.3 *Standard Solution* — 1000 ppmw (mg/kg) Cl solution, certified reference material (CRM).

9 Safety Precautions

9.1 Users of the tube high temperature furnace must be trained, in accordance with the operating rules, to avoid injury.

10 Sampling

10.1 This Test Method is intended for sampling of silicon lots. Typically, one 5 kg bag from a lot is selected for sampling. The sample is taken from this bag, and the chlorine values analyzed are assumed representative of the lot. Statistical techniques, such as process capability ratios, are used to determine actual sampling plans for manufacturing processes. A choice of sampling plans is found in ASTM E122. For referee purposes, a sampling plan shall be agreed upon before conducting the test. Contamination during the sampling procedure is a critical concern and shall be avoided.