

SEMI F33-0708

TEST METHOD FOR CALIBRATION OF ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETER (APIMS)

This standard was technically approved by the global Gases Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on May 13, 2008. It was available at www.semi.org in June 2008. Originally published in 1998.

NOTICE: This Standard or Safety Guideline has an Inactive Status because the conditions to maintain Current Status have not been met. Inactive Standards or Safety Guidelines are available from SEMI and continue to be valid for use.

1 Purpose

1.1 This test method may provide guidelines for the calibration of the APIMS for measurement of impurities in nitrogen, argon, helium and hydrogen. APIMS is currently the technique of choice for measurements of low level impurities in gas distribution systems and components because it is essentially the only commercially available method capable of ppt impurity analysis and it has a superior response time. This method may provide guidelines for application of other techniques with similar detection limits and response time to APIMS which may not be commercially available at this time.

2 Scope

2.1 This method applies to the analyte calibration of the APIMS for a target impurity range of 100 ppt to as high as 200 ppb impurity range. The actual calibration range should bracket the impurity measurement range of interest, dependent upon the measurement to be conducted. Anything else is outside the range of the calibration.

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 The actual range of calibration will depend upon the type of APIMS used. Counting detection electronics will saturate in the 200,000 CPS to 1,000,000 CPS range, depending upon the make and model. Counting detection will have to use different ions in different concentration regions, depending upon the impurity. The actual calibration procedure will be different for APIMS using analog detection versus counting detection. Interference between impurities can cause limitation in measurements in the presence of multiple impurity species.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI C9.1 — Guide for Analysis of Uncertainties in Gravimetrically Prepared Gas Mixtures

SEMI C15 — Test Method for ppm and ppb Humidity Standards

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

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 *APIMS* — atmospheric pressure ionization mass spectrometer

5.1.2 *CPS* — counts per second

5.1.3 *m/z* — *m* in atomic mass units and *z* in elementary charge units

5.1.4 *NIST* — National Institute of Standards and Technology

5.1.5 *ppb* — molar parts per billion (nmole/mole). The same as ppbv.

5.1.6 *ppm* — molar parts per million (μmole/mole). The same as ppmv.

5.1.7 *ppt* — molar parts per trillion (pimole/mole). The same as pptv.

5.1.8 R^2 — a statistical term expressed as the ratio of the sum of squares of the regression divided by the total sum of the squares.

5.2 Definitions

5.2.1 *zero gas* — nitrogen, argon, helium or hydrogen with an estimated level an order of magnitude, or more, lower than the lowest calibration point for each impurity of interest.

6 Summary of Method

6.1 The calibration of the APIMS is conducted by adding known concentrations of impurities to a zero gas and measuring the corresponding ion intensities. A calibration response factor can be determined by regression analysis.

7 Interferences

7.1 It is essential to confirm that the mass chosen is indeed representative of the species of interest and that other commonly present impurities do not contribute at the same mass. For example: the intensity of the peak at $m/z = 29$ correlates with the concentration of H_2 in N_2 , because of the N_2H^+ formation. However, spurious signal at this peak can arise in two different ways:

1. Contributions of other ions of the same mass, such as $N^{14}N^{15+}$ or $C_2H_5^+$.
2. Contributions of the same ion from different parent species; that is, N_2H^+ due to recombination of matrix gas nitrogen with fragments of H_2O , CH_4 , etc. Before using $m/z = 29$ as a measure of H_2 in N_2 , interference such as these must be understood. This also may apply to other ions.

7.2 High impurity levels can cause clustering with, or quenching of, the other impurity ions and affect the sensitivity of the APIMS for those impurities. This is especially true for impurity levels of 10 ppb and above.

8 Apparatus

8.1 *APIMS* — The APIMS used for impurity detection can be of any type.

8.2 *Impurity Standard* — Any device (either standard cylinder or permeation tube based or of any other type) that can reliably deliver impurity concentrations usually in the range of 100 ppb to 10 ppm with an accuracy of $\pm 5\%$. The standards should be traceable to an applicable national standard, such as NIST.

8.3 *Dynamic Dilution System* — A dilution system that can dilute the output gas of the impurity standard with a zero gas to produce a gas with impurity concentrations in the range of interest.

9 Reagents and Materials

9.1 Zero gas.

9.2 Impurity standard.

10 Safety Precautions

10.1 This method applies to calibration and measurement of impurities in nitrogen, argon, helium and hydrogen. This method does not address the additional safety precautions for APIMS calibration and impurity measurement in hydrogen gas.

11 Test Specimen

11.1 Not applicable.

12 Preparation of Apparatus

12.1 The impurity standard and zero gas should be connected to the dynamic dilution system, which is in turn connected to the inlet of the APIMS. The entire dilution system should be purged until all impurities have stabilized at a constant dilution system flow, for all components in the dilution system. The relative standard deviation for each analyte should be less than 10% for the past 12 hours before the calibration. Constant pressure and flow should be maintained to the APIMS ionization region at all time.

13 Calibration and Standardization

13.1 *Definition of an Impurity Standard* — An impurity ‘standard’ is defined to be any device capable of delivering a flow of known impurity level gas at a controlled pressure (see ¶ 8.2).

13.2 *Examples of Standards* — Some examples of impurity standards and the principles upon which they are based are as follows:

13.2.1 *Cylinder Standards* — The ‘standard’ will include a regulator specified for use with the cylinder. The impurity concentration can be calculated based on that added to the cylinder in preparation. A minimum use pressure must be specified.

13.2.2 Permeation and effusion tube standards. These must include purification means and some means of regulating the outlet pressure. The impurity delivery rate can be calculated based on the weight loss of the tube as a function of time.

13.2.3 Moisture standard methods based on saturation of gas with water vapor at a fixed temperature and pressure. The moisture concentration in the gas may then be calculated from a knowledge of the saturation vapor pressure of water over a plane of the pure phase of ice at the saturation temperature and of the interaction virial coefficients of the gas-vapor mixture. The two-pressure and two-temperature methods are refinements of this approach requiring additional chambers whose temperature and pressure must be known.

13.3 *Dilution of Standards* — For all impurity generation methods, lower concentrations can be generated by dynamic dilution; that is, by combining a known flow of the standard gas with a known flow of zero gas. A diluted standard is acceptable provided:

13.3.1 The zero gas should have an impurity level at least an order of magnitude below the stated level of the analysis (to be verified using the same flow path as during the subsequent analysis, and at the lowest flow rate actually used in the calibration).

13.3.2 The absolute accuracy of the dilution system components are verified by comparison with a reliable flow standard. The frequency of verification must take into account the transport of the instrument and other changes that will affect the dilution system.

13.3.3 The linearity of the dilution system can be demonstrated over the entire range of operation. This last criterion is particularly important whenever some portion of the combined flow is discarded, as mixing problems can easily arise at large dilution factors.

13.4 *Mass Calibration* — The mass scale of the mass spectrometer should be calibrated according to the manufacturer’s instructions over the mass range of interest.

13.4.1 The validity of the mass selected for each impurity must be confirmed (i) by demonstrating that the intensity at the mass increases monotonically with added concentration of the impurity species of interest and (ii) that other usually present impurity species do not make significant contributions to the intensity at that mass. Tables 1 through 4 list the typical masses for various species in argon, nitrogen, hydrogen and helium.