## 1 SCOPE

1.1 This method describes a general procedure for the determination of boric acid and salts of boric acid in toys applicable to item 8 of Part I, Schedule I of the Hazardous Products Act.

## 2 APPLICABLE DOCUMENTS

2.1 Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods. Volume 14.02, ASTM E177-90a, P.79-90, 1998.

2.2 Standard Practice for Intralaboratory quality Control Procedures and a Discussion on Reporting Low-Level Data. Volume 11.01, ASTM D4210-89, P.412-419, 1998.

2.3 John Keenan Taylor, Quality Assurance of Chemical Measurements. Lewis Publishers, INC. 328 p., 1987.

2.4 B. Marchand, “Determination of boric acid and salts of boric acid in toys. Product Safety Laboratory, Project Report No. 2000-0564, September 2000.

2.5 André G. Craan, Anthony W. Myres, and Douglas W. Green, Hazard Assessment of Boric Acid in Toys. Regulatory Toxicology and Pharmacology **26**, 271-280 (1997).

2.6 Standard Operating Procedure (SOP-04) for the Elan 5000 ICP-MS..

## 3 REAGENTS AND APPARATUS

3.1 Boron Standard, 1000 ppm, SCP Science.
3.2 Mix Standards, Cat # ICP-MSCS, High-Purity.
3.3 Certified A.C.S., Boric acid crystals, Fisher Scientific.
3.4 Ethanol, Commercial Alcohols Limited.
3.5 Pro Analysi, Nitric acid 65%, Merck.
3.6 Centrifuge tubes, disposable, 50 and 15 mL, Fisher Scientific.
3.7 Volumetric flasks, 100mL.
3.8 Volumetric pipette, 10 mL PYREX disposable.
3.9 Water Bath, Polystat, Model 12050-00, Circulator, Cole-Parmer.
3.10 Analytical Balance, with a precision of 0.1µg. Mettler AG204.
3.11 ICP-MS Elan 5000, Perkin-Elmer.

## 4 EXPERIMENTAL PROCEDURE

4.1 Weigh about 100 mg of sample into 50 mL centrifuge tubes and add 10 mL of ethanol 0.1% (v/v). Place the tubes in the water bath at 37 °C for 4 hours at a RPM of 120. Dilute the solution to the 50 mL mark with deionized water. Usually, a dilution of 20 times in 1% (v/v) nitric acid is recommended for the samples. If the concentration of boron is higher than the last standard used for the calibration, the sample is diluted again until the concentration is bracketed by two standard levels.

4.2 Prepare the spike solutions by weighing about 15-20 mg of boric acid crystals, mix the powder with about 100 mg of a sample that does not contain boron such as sample #: 92-0050 (modelling clay, RoseArt brand) and add 10 mL of 0.1% ethanol solution in 50 mL centrifuge tubes. Place the tubes in the water bath at 37 °C for 4 hours at a RPM of 120. Dilute the solution to the 50 mL mark with deionized water. Dilute the spike solutions 1000 times in 1% (v/v) nitric acid.

## 5 ANALYSIS

5.1 Prepare a blank (1% (v/v) nitric acid) and a minimum of three working standards in the linear range of the detector of the instrument to obtain a linear calibration curve with a correlation coefficient of at least 0.996. The working standards used to built the calibration curve were as follows: 10 ppb, 20 ppb, 50 ppb and 100 ppb from a 5 ppm boron stock solution.

5.2 The standards and the controls should be analysed using five replicates. For the samples, two or three different aliquots should also be analysed using five replicates.

5.3 Analysis conditions:

Instrument: Elan 5000, Perkin-Elmer
Autosampler: AS-90
Flow Rates (L/min): Plasma:15.00, Auxiliary: 0.800, Nebulizer: 0.951
Gas: Liquid Argon
Plasma power: 1000 W
Replicate time (ms): 1500
Dwell time (ms): 300
Scanning mode: peak hop
Sweeps/reading: 5
Number of replicates: 5
Mass used: 11 m/z

## 6 CALCULATION AND REPORTING

6.1 Calculate the concentration of boron as percent by weight in the test sample according to the following equation:

$$\text{Boron \% (w/w)} = \frac{C \div 1000 \times V \times Df}{10{,}000 \text{ ppm} \times W(g)}$$

where:

C = Concentration of boron in test sample (ppb)
V = Final volume of test sample (50 mL)
Df = Dilution factor (if required)
W = Weight of test sample used (g).

6.2 Calculate the concentration of boric acid ($H_3BO_3$) in the test sample according to the following equation:

$H_3BO_3(\%)$ = Boron (%) X (61.81 g/mol ÷10.81 g/mol)

where:

61.81 = Molecular weight of boric acid
10.81 = Atomic weight of boron

6.3 Calculate the spike solution according to the following equations:

Weight of boric acid ($H_3BO_3$)(mg) X (10.81 g/mol ÷ 61.81 g/mol) = Weight of boron.

$$\frac{\text{Weight of boron (mg)} \times 1000 \text{ mL}}{50 \text{ mL} \times Df} = \text{Concentration of Boron (ppm)}$$

Where:

Df = Dilution factor of 1000

61.81 = Molecular weight of boric acid
10.81 = Atomic weight of boron

6.4 Where the quantity of sample for testing is sufficient and where practical, the result of analysis shall be reported as the average of a minimum of two independent replicate determinations having a precision which should not differ more than the specifications defined in section 8.

6.5 Where applicable, the deviation from the mean of the duplicate determinations or the standard deviation of replicate determinations (s for n > 2) shall be calculated *(Note 1)*, and the result of analysis reported in the following format:

| HPA | Method | Sample No. | Specimen No. | Description | Concentration as Boric Acid % (W/W) |
|---|---|---|---|---|---|
| Item 8 Part I Schedule 1 | C XX.X | 1 | 1A | Boric Acid and salts | x.xx ± 2s |

## 7 QUALITY CONTROL PROCEDURE

7.1 In order to ensure the proper operation of the instrumentation and that the precision and accuracy of the analytical measurements meet the specifications of the method, the following quality control procedures shall be conducted concurrently with the analysis of the test sample.

7.2 The normal and correct operation of the ICP-MS shall be verified according to the following guidelines:

7.2.1 Run the standard operating procedures for ICP-MS (SOP-04) and verify that the measurements are within the tolerance limits of the expected values. If the control measurements fall within acceptable limits, a note shall be entered in the test sample file to the effect that the instrument calibration was found to be "within control". Should the instrument be found in a state of disrepair or out of specifications, the ICP-MS shall immediately be repaired and/or recalibrated to meet the prescribed operating conditions prior to proceeding with the analysis.

7.3 The normal and correct operation of the test method shall be verified according to the following guidelines:

7.3.1 Conduct the analysis of a spike solution of boric acid under identical experimental conditions to that of the test sample. Record the test result for the boric acid in the analytical instrument's QC logbook, and verify that the result is within acceptable limits, a note shall be entered in the test sample file to the

---

*Note 1: The standard deviation (s) of the test results may be calculated according to the following equation, where: $x_i$ is the result of each individual determination, $\bar{x}$ is the average of the replicate determinations and n is thetotal number of replicates.* $\left[ s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \right]$

effect that the test method was found to be "within control". Should the test result of the control sample be found to fall outside the specifications of the method, the entire analytical procedure shall be repeated.

## 8 PRECISION AND BIAS

8.1 *Repeatability*: The closeness of agreement between test results, as obtained by the same analyst with the same instrument under constant operating conditions on identical test material, should, in the normal and correct operation of the test method, not differ more than 6.7 % repeatability limit at a 95% probability level (n=10) for a test value of 0.25% (w/w) boric acid.

95% repeatability limit = $1.960 \sqrt{2}\ CV\%_r$ *(Note 2)* = $2.8\ CV\%_r^2$ = 2.8 x 2.4 = 6.7%

8.2 *Reproducibility*: The variability between two single and independent results, as obtained by different analyst working in the same laboratory on identical test material, should, in the normal and correct operation of the method, not differ more than 12.9% reproducibility limit at a 95% probability level (n=20) for a test value of 0.25% (w/w) boric acid.

95% reproducibility limit = $1.960 \sqrt{2}\ CV\%_R$ *(Note 3)* = $2.8\ CV\%_R$ *(Note 3)* (between analysts) = 2.8 x 4.6 = 12.9%.

8.3 *Bias*: The bias of the test method obtained from the average of a set of test results minus the accepted reference value which is the spike of a sample that does not contain boron on two different days for 12 replicates is -14.4%. The test results should be within the warning limits (±2xs) *(Note 4)* and the control limits (±3xs) *(Note 4)* of the expected value.*(Note 5)* If the result lies outside the control limits, identify and correct the problem and reanalyzed samples if necessary.

## 9 LIMIT OF DETECTION

9.1 The limit of detection (LOD) of this method, as determined by the ICP-MS has been calculated to be 0.00002 % (w/w)) for boric acid using a 10 ppb standard. *(Note 6)*

---

*Note 2: $CV\%_r$= Repeatability coefficient of variation in percent (within a laboratory)- ASTM Test Method E177-90a.*
*Note 3: $CV\%_R$= Reproducibility coefficient of variation in percent (different conditions)- ASTM Test Method E177-90a.*
*Note 4: s = standard deviation*
*Note 5: See applicable documents # 2.3 for the reference.*
*Note 6: ASTM Test method: D4210-89.*

LOD = 2 x 1.645 x s = 3.29 x 0.1311ppb = 0.43 ppb = 0.00002 % (w/w) *(Note 7)*

s = standard deviation obtained from replicate analyses (n=7).

$LOD_{boric\ acid}$= 0.00002% x (61.81 g/mol ÷ 10.87 g/mol) = 0.0001%w/w

## 10 LIMIT OF QUANTIFICATION

10.1 The limit of quantification (LOQ ) of this method, as determined by the ICP-MS has been calculated to be 0.00007 % (w/w) for boric acid using the 10 ppb standard. *(Note 6)* Results below the limit of quantification are reported as less than (< LOQ) the LOQ.

LOQ = 10 x s = 10 x 0.1311ppb = 1.31 ppb = 0.00007 % (w/w) *(Note 7)*

s = standard deviation obtained from replicate analyses (n=7).

$LOQ_{boric\ acid}$ = 0.00007% x (61.81 g/mol ÷ 10.87 g/mol) = 0.0004%w/w

*Note 7: Based on a final volume of 50 mL and a sample mass of 0.1g.*

. . . . . END . . . . . .