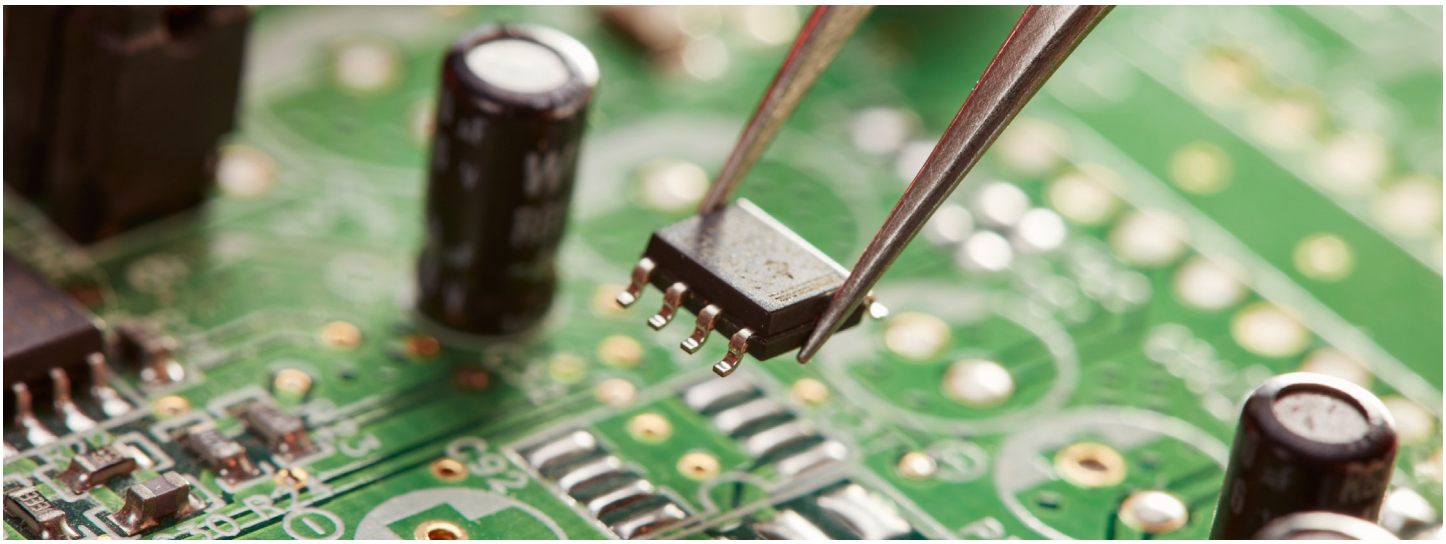
Sample Preparation of Electronic Device Components for Hexavalent Chromium Analysis by IEC Method 62321-7-2:2017



Abstract

The increasing use of consumer and electronic device components worldwide has drawn increased attention to their impact on the environment. The correct disposal of these materials is of critical importance due to the potential for hexavalent chromium contamination of soil and water. Most countries around the world have adopted regulations regarding the Restriction of Hazardous Substances (RoHS). Recently the International Electrotechnical Commission (IEC) has established a new test method, IEC 62321-7-2:2017, to test for hexavalent chromium in many of these products. This new method is a replacement for parts of the corresponding clauses in IEC 62311:2008.

Introduction

The recent passage of IEC 62321-7-2:2017 provides determination of hexavalent chromium in polymers and electronics using colorimetric determination by a UV-Vis Spectrophotometer. Prior to analysis, a sample preparation method using microwave digestion is used. The IEC method has several post digestion steps and requires multiple reagents to be made up prior to the procedure. This application note will establish the correct microwave equipment, options, and program to be followed in order to be in compliance with the method. It will also attempt to make the method easier to follow by alerting the analyst to make up specific reagents prior to starting the procedure.

Instrumentation

The microwave procedure for the IEC method (62321-7-2:2017 e) does not require rigorous conditions. It only requires the samples to reach a temperature of 150 – 160 °C and to hold for 90 minutes. A MARS 6 equipped with standard IR temperature control and the stirring option was used. The samples were prepared in the CEM 55 mL MARSXpress vessel, a simple to use 3 part vessel with vent and reseal capabilities. (See **Figure 1**) Alternatively, a MARS One with 55 mL MARSXpress Vessels or a MARS 6 with EasyPrep or iPrep vessels can also be used for this method.

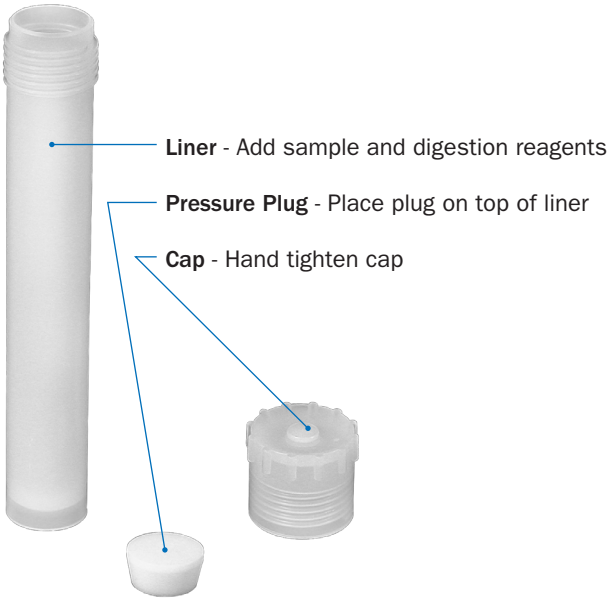


Figure 1: MARSXpress 3-Part Vessel

Procedure

Note:

Prior to the digestion procedure, you will need to grind or cut up samples into small pieces.

Reagents Preparation

You must make up these reagents prior to sample preparation. All reagents used must be reagent grade or better.

Digestion Solution
Dissolve 20 g of NaOH and 30 g of $NaCO_3$ in water in 1 L volumetric flask and dilute to mark with clean deionized water. This should be stored at 20 -25 °C and be made fresh monthly. Test pH prior to use and discard solution if pH is below 11.5.

Phosphate Buffer
Disolve 87.09 g K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of clean deionized water. Transfer to a 1 L volumetric flask and make up to volume with clean deionized water.

Nitric Acid at 35%
Dilute 50 mL of reagent grade HNO_3 to 100 mL with clean deionized water. Store at 20 °C.

Diphenylcarbazide
Dissolve 250 mg 1,5-Diphenylcarbazide in 50 mL of acetone. Store in a brown bottle. Prior to use, check solution for discoloration. Store up to two weeks and if solution becomes discolored discard and prepare a fresh batch.

Sulfuric Acid at 10%
Dilute 10 mL of distilled reagent grade or spectroscopic grade H_2SO_4 with clean deionized water to 100 mL into a volumetric flask.

Other required Reagents

- Toluene (Analytical Grade)
- $MgCl_2$ anhydrous (Analytical Grade)

Microwave Digestion Procedure

1. Weigh approximately 0.15 grams of sample into 55 mL MARSXpress vessel and add magnetic stir bar.
2. Add 10 mL of Digestion Solution
3. Add 5 mL of Toluene (analytical grade)
4. Add 400 mg of $MgCl_2$ (anhydrous) analytical grade
5. Add 0.5 mL of Phosphate Buffer
6. Evenly space vessels into MARSXpress turntable and place into microwave cavity. Create Classic microwave digestion program as defined in **Table 1**.

Table 1: Microwave Digestion Custom Program Settings

Stage	Ramp	Temp (°C)	Hold
1	15 mins	155	60 mins
2	1 sec	155	30 mins

Results

The MARS 6 with MARSXpress vessels can be used to successfully perform the closed vessel microwave digestion portion (62321-7-2:2017 e) of the hexavalent chromium determination sample preparation. As shown in **Figure 2**, the precise power control can easily obtain the necessary digestion conditions required for the duration of the run. Although the method does not call for it, we would recommend the stirring option to help extract all of the hexavalent chromium into the aqueous phase in the vessel prior to separation. Once the microwave portion is complete a post digestion procedure is required, which is outlined in the following section.

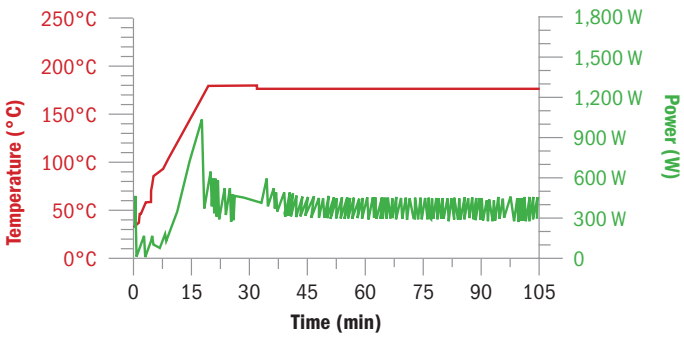


Figure 2: Temperature Curve

The Green power line represents the precise control of the MARS system while the Red Temperature line shows that the samples are being held in the correct temperature range of 150 -160 °C for 90 minutes.

Post Digestion Preparation

1. Cool and transfer solution to a separatory funnel to separate organic phase. Discard organic phase.
2. Filter aqueous phase with a 0.45 µm membrane filter. Rinse the digestion vessel three times with water and filter rinse solution as well. If filter becomes clogged use a larger pore size filter.
3. Rinse inside of flask and filter pad with water and transfer filtrate and rinse solution into a 150 mL beaker with magnetic stir bar.
4. Add Nitric Acid (35%) dropwise while stirring and monitor pH to adjust to 7.5 +/- 0.5.
5. Check to see if sample is clear.

If sample is clear:

1. Develop color
    a. Add 2.5 mL of diphenylcarbazide solution to each beaker.
    b. Slowly add sulfuric acid (10%) to the vessel to adjust pH to 2.0 +/- 0.5.
    c. Transfer the contents quantitatively to a 50 mL volumetric flask and adjust sample volume to 50 mL with deionized water and invert several times.
    d. Let stand 5 – 10 minutes to develop full color.
2. Transfer appropriate portion to a 1 cm absorption cell and measure at 540 nm with colorimetric instrument. Analysis must be complete within 30 minutes of color development.
3. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the color development procedures.
4. From corrected absorbance determine the concentration by referring to calibration curve from IEC method.

If sample is turbid or colored:

Filter the sample with a 0.45 µm membrane filter.

- If sample is colored, filter solution with a C_{18} cartridge syringe before proceeding to develop color.
- If sample is clear after filtration proceed to develop color.

1. Develop color
    a. Add 2.5 mL of diphenylcarbazide solution to each beaker.
    b. Slowly add sulfuric acid (10%) to the vessel to adjust pH to 2.0 +/- 0.5.
    c. Transfer the contents quantitatively to a 50 mL volumetric flask and adjust sample volume to 50 mL with deionized water and invert several times.
    d. Remove 5 mL from the flask and record and measure with colorimetric instrument. This is the background absorption measurement.
    e. Perform background correction by adding 2.5 mL diphenylcarbazide solution to each sample digestion solution.
    f. Mix and add deionized water to adjust volume to 50 mL inverting several times.
    g. Let stand 5 – 10 minutes to develop full color.
2. Transfer appropriate portion to a 1 cm absorption cell and measure at 540 nm with colorimetric instrument. Analysis must be complete within 30 minutes of color development.
3. Correct the absorbance reading by subtracting the reading from the measurement taken above for background absorbance.
4. From corrected absorbance determine the concentration by referring to calibration curve from IEC method.

Discussion

The IEC method 62321-7-2:2017 is a suitable alternative to analysis by ICP; however, great care should be taken to minimize error in each step. Technicians should be well trained in proper analytical technique to minimize sample to sample variability and minimize introduction of error, which could lead to false or inaccurate results.

United States (Headquarters)
800-726-3331
704-821-7015
Fax: 704-821-7894
info@cem.com

France
33 (01) 69 35 57 80
Fax: 33 (01) 60 19 64 91
info.fr@cem.com

Germany, Austria, Switzerland
(49) 2842-9644-0
Fax: (49) 2842-9644-11
info@cem.de

Ireland
+353 (0) 1 885 1752
Fax: +353 (0) 1 885 1601
info.ireland@cem.com

Italy
(39) 35-896224
Fax: (39) 35-891661
info.srl@cem.com

Japan
+81-3-5793-8542
Fax: +81-3-5793-8543
info@cemjapan.co.jp

United Kingdom
(44) 1280-822873
Fax: (44) 1280-822873
info.uk@cem.com

www.cem.com

Flow Chart of
IEC Method 62321-7-2:2017

Reagents Preparation

You must make up these reagents prior to sample preparation. All reagents used must be reagent grade or better.

Digestion Solution
Dissolve 20 g of NaOH and 30 g of $NaCO_3$ in water in 1 L volumetric flask and dilute to mark with clean deionized water. This should be stored at 20 -25 °C and be made fresh monthly. Test pH prior to use and discard solution if pH is below 11.5.

Phosphate Buffer
Disolve 87.09 g K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of clean deionized water. Transfer to a 1 L volumetric flask and make up to volume with clean deionized water.

Nitric Acid at 35%
Dilute 50 mL of reagent grade HNO_3 to 100 mL with clean deionized water. Store at 20 °C.

Diphenylcarbazide
Dissolve 250 mg 1,5-Diphenylcarbazide in 50 mL of acetone. Store in a brown bottle. Prior to use, check solution for discoloration. Store up to two weeks and if solution becomes discolored discard and prepare a fresh batch.

Sulfuric Acid at 10%
Dilute 10 mL of distilled reagent grade or spectroscopic grade H_2SO_4 with clean deionized water to 100 mL into a volumetric flask.

Other required Reagents

- Toluene (Analytical Grade)
- $MgCl_2$ anhydrous (Analytical Grade)

Microwave Digestion Procedure

Weigh approximately 0.15 grams of ground sample into 55 mL MARSXpress vessel and add magnetic stir bar.

To each vessel add:

- Add 10 mL of Digestion Solution
- Add 5 mL of Toluene (analytical grade)
- Add 400 mg of $MgCl_2$ (anhydrous) analytical grade
- Add 0.5 mL of Phosphate Buffer

Evenly space vessels into MARSXpress turntable and place into microwave cavity. Create Classic microwave digestion program as defined below.

Microwave Digestion Custom Program Settings:

Stage	Ramp	Temp (°C)	Hold
1	15 mins	155	60 mins
2	1 sec	155	30 mins

Post Digestion Procedure

1. Cool and transfer solution to a separatory funnel to separate organic phase. Discard organic phase.
2. Filter aqueous phase with a 0.45 µm membrane filter. Rinse the digestion vessel three times with water and filter rinse solution as well. If filter becomes clogged use a larger pore size filter.
3. Rinse inside of flask and filter pad with water and transfer filtrate and rinse solution into a 150 mL beaker with magnetic stir bar.
4. Add Nitric Acid (35%) dropwise while stirring and monitor pH to adjust to 7.5 +/- 0.5.
5. Check to see if sample is clear.

Flow Chart of
IEC Method 62321-7-2:2017