Test Procedure TP-SA-064
Edition: October 2019

Residual Benzene Content

Applicable Products: Non-Benzene Polymerized Carbopol® Polymers, Pemulen™ Polymeric Emulsifiers and Noveon® AA-1 Polycarbophil

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Scope:

This procedure describes the analysis of benzene in non-benzene polymerized Carbopol® polymers, Pemulen™ polymeric emulsifiers and Noveon® AA-1 polycarbophil.

Abstract:

A sample of the polymer is shaken with a 16.6% dimethyl sulfoxide (DMSO) in water mixture. The sample vial is placed in a headspace analyzer for equilibration at 80°C for 45 minutes. A one mL sample of the headspace is transferred to a gas chromatograph. A flame ionization detector is used to measure the response of benzene. The area response is compared to the response for a series of standards and the benzene concentration in the sample is calculated.

Safety Precautions:

1. Wear safety goggles and gloves and follow good laboratory practices.
2. Polymer dust is irritating to the respiratory passages and inhalation should be avoided.
3. Benzene is a flammable liquid and a known carcinogen.
4. Dimethyl sulfoxide (DMSO) is combustible and may be harmful if inhaled or absorbed through the skin
5. See the MSDS for additional safety and handling information.

Interferences:

Any component eluting at the same retention time as benzene would influence the result. These interferences could be present in the sample or the DMSO used to extract. Isopropyl acetate, iso-octane, and cyclohexene elute at similar times as benzene. Demonstrating these chemicals do not co-elute with benzene on the analytical column used under the conditions and flow rate employed should be accomplished prior to performing analyses.

Apparatus:

1. Gas chromatograph with capillary column capability and flame ionization detector.
2. Headspace sampler with 1 mL sample loop.
3. Data processing station.
4. **PRIMARY COLUMN:** Restek RTX-1701 column, 30 meter x 0.53 mm with 3 µm film thickness (or equivalent).
5. **CONFIRMATION COLUM:** Restek RTX-1 column, 30 meter by 0.53 mm with 3 µm film thickness and Restek RTX-1701 column, 30 meter x 0.53 mm with 3 µm film thickness connected with a Restek Presstight® connector (or equivalent)
6. 22 ml headspace vials.
7. Mechanical shaker.
8. Teflon-lined septum with crimp top for headspace vials.
9. 50 µl syringe.
10. Manual aluminum seal crimper tool.
11. Analytical balance capable of ±0.0001 g accuracy.
12. Automatic burette.
13. 2 mL GC autosampler vials with Teflon-lined screw cap.
14. 1 L volumetric flask.
15. Graduated cylinder, 250 mL.
16. Pipette bulb.

Reagents:

1. Benzene, ACS certified.
2. Water, HPLC grade or similar solvent-free water.
3. Dimethyl sulfoxide (DMSO), ACS certified.

Instrument Set-up:

GC CONDITIONS (**Primary Column**):

Prior to the analysis of samples or standards, the following chromatographic conditions should be set:

Detector Temperature	250°C
Injection Port Temperature	140°C
Oven Conditions	
Initial Temperature	40°C
Initial Time	10 minutes
Ramp Rate	30°C/min
Final Temperature	240°C
Final Time	5 minutes
Carrier Flow	5 ml/min helium (35

	cm/sec velocity) programmed in constant pressure mode.
Split ratio	0.5:1

GC CONDITIONS (**Confirmation Column**):

Prior to the analysis of samples or standards, the following chromatographic conditions should be set:

Detector Temperature	250°C
Injection Port Temperature	200°C
Oven Conditions	
Initial Temperature	50°C
Initial Time	7.5 minutes
Ramp Rate 1	50°C/min
Final Temp 1	40°C
Hold Time 1	7 minutes
Ramp Rate 2	30°C/min
Final Temperature 2	240°C
Final Time 2	5 minutes
Carrier Flow:	9 PSI for 15 minutes then 20 PSI for remainder of run programmed in ramped pressure mode.
Split ratio	0.5:1

HEADSPACE PARAMETERS:

Equilibrium Time	45 minutes
Equilibration Temperature	80°C
Transfer Line Temperature	105°C
Valve Oven Temperature	105°C
Vial Pressure	10 psig
Loop Fill Pressure	7 psig
Injection Volume	1 mL
Mixer Option (if equipped)	Off

Calibration:

1. Add 1 mL DMSO, accurately weighed, to a 2 mL GC autosampler vial. Screw cap onto vial.
2. Using a 50 µl syringe, add 20 µl benzene, accurately weighed, through the septum.
3. Label vial **Primary Standard**.
4. Add 1 mL DMSO, accurately weighed, to a 2 mL GC autosampler vial. Screw cap onto vial.
5. Add 20 µl of the Primary Standard, accurately weighed, to the vial in step 4. Label the vial **Secondary Standard**.
6. Add 10 mL DMSO, accurately weighed, to a 22 mL headspace vial. Seal the Teflon-lined butyl rubber septum on the vial with an aluminum crimp cap.
7. Add 30 µl of the Secondary Standard, accurately weighed, to the vial in step 6. Label the vial **Working Standard**.
8. Prepare 3 standards and a blank in 22 mL headspace vials. To each, weigh 0.0500 ± 0.0010 g polymer. Record the weights.
9. Using an automatic burette, add 6 mL of 16.6% v/v DMSO in water mixture (See Special Instruction 1) to each of the vials from step 8.
10. To one of the vials, using a 50 µl syringe, add 10 µl **Working Standard**. Accurately weigh.
11. Cap and seal vial with a Teflon-lined butyl rubber septum. Label as **Calibration Standard 1**.
12. Repeat steps 10 and 11, adding 20 µl and 50 µl to two of the vials from step 9. Label as **Calibration Standard 2** and **Calibration Standard 3.**
13. The fourth vial from step 8 is labeled as **Blank**. No Working Standard is added. Place all standards and the blank on the shaker for one hour.

Calibration Standard Preparation Summary

	Polymer g ± 0.0010	16.6% DMSO in water (mL)	Working Standard (µl)
Calibration Standard 1	0.0500	6	10
Calibration Standard 2	0.0500	6	20
Calibration Standard 3	0.0500	6	50
Blank	0.0500	6	0

14. Set instrument up according to operational parameters and analyze the samples on the gas chromatograph.
15. Analyze the **Blank** and **Calibration Standards.**

Sample Procedure:

1. Tare a 22 mL headspace vial.
2. Add 0.05 g of sample to be tested to the vial. Record the weight to the nearest 0.0001 g.
3. Using the automatic burette, add 6 mL 16% DMSO in water to the vial.
4. Cap and seal vial with a Teflon-lined butyl rubber septum.
5. Place on the orbital shaker for one hour.
6. Confirm the headspace analyzer and gas chromatograph parameters specified for the analysis have been input.
7. The data processing station can be set-up to calculate the results and report as ppm benzene. See CALCULATIONS section for manual calculation of results.

Calculations:

A. Calculation of standard concentrations:

Primary Standard (P):

P (g/g) = A/B

where A = Weight of benzene (g)
B = total wt Primary Std. (g) (combined wt of benzene + DMSO)

Secondary Standard (S):

S (g/g) = (C/D) P

where C = Weight of Primary Std. (g)
D = total wt Secondary Std. (g)
P = benzene concentration in Primary Std. (g/g)

Working Standard (W):

W (g/g) = (E/F) S

where E = Weight of Secondary Std. (g)
F = total wt Working Std. (g)
S = benzene concentration in Secondary Std. (g/g)

Calibration Standard (CS):

CS (mg/kg) = (G*H) (1,000,000/0.05)

where G = Weight of Working Std. (g)
H = benzene concentration in Working Std. (g/g)

B. Calculation of response factor for benzene:
(Determine response factor for each of the Calibration Standards).

RF = CS (mg/kg) / (I-J)

where CS (mg/kg) = Calibration Standard (mg/kg) from step A
I = CS (mg/kg) Benzene peak area
J = Blank peak area

C. Repeat calculation for two remaining Calibration Standards. Calculate the average of the three response factors.

D. Calculation of benzene (mg/kg) in sample

Benzene (mg/kg) =

Avg. RF * Sample Peak Area

Special Instructions:

1. 16.6% v/v DMSO: To a 1 liter volumetric flask, add 166 mL DMSO. Dilute to the mark with HPLC water and mix.
2. If a peak is observed at the retention time of benzene using the primary column, the sample should be re-analyzed using the confirmation column and associated parameters. The calibration and sample preparation parameters are the same with the confirmation column as with the primary column.

References:

- *Current edition of the United States Pharmacopeia/National Formulary (USP/NF) <467>*
- *Current edition of the European Pharmacopeia 2.4.24.*