Determination of Benzene in Sunblock Employing Static Headspace Sampling

Application Note

Consumer Products

Authors

Anne Jurek
Applications Chemist
EST Analytical
Cincinnati, OH

Abstract

Benzene is classified as a Group A, known human carcinogen, by the Environmental Protection Agency. Benzene is commonly used in the manufacturing of detergents, pharmaceuticals, and dyes. Due to its toxicity, manufacturers take precautions to remove the benzene before products are released to the public. Recently, it has been found, that there can be large amounts of Benzene in sunscreen. This application will examine how to test assorted sunscreen products for Benzene using static headspace sampling.

Introduction:

According to the Occupational Safety and Health Administration (OSHA), exposure to Benzene over an eight-hour period should be limited to one part per million. Since sunscreen is applied over a large surface area every two hours for full sun protection, any small amount of Benzene in the product can exceed these limits. Thus, it is important to ensure that the sun protection being used is free of Benzene or that the levels are extremely low.

Manufacturers need to be able to determine if there is Benzene in their products. There are a variety of techniques to do this. One of these methods is static headspace. Static headspace is used to sample volatile compounds in complex matrices. For this reason, it is an ideal technique for the detection of Benzene in sunscreen. This application will examine sunscreen samples in order to determine if there is Benzene contamination using the Flex Series Autosampler and static headspace sampling.

Experimental:

The Flex Series Autosampler was configured with a 2.5mL headspace syringe for the 1mL sample injection while a 20mL headspace vial tray and a six-position incubator/agitator were employed for the sample preparation. The Flex was installed on Gas Chromatograph/Mass Spectrometer (GC/MS) for separation and analysis. A 30m x 0.25mm x 1.4µm 624 column was mounted in the GC while the MS was run in Selective Ion Monitoring (SIM) mode. Sample preparation and analysis was optimized and the experimental parameters for the Flex Series Autosampler and GC/MS are outlined in Tables 1 and 2.

Autosampler	FLEX
Preheat	
Syringe Heater Parameters	Enabled
Syringe Heater Temp.	100ºC
Wait for Temp.	Yes

Incubator Heater Parameters	Enabled
Incubator Heater Temp.	100ºC
Wait for Temp.	Yes
Incubate/Agitate	
Accessory	Incubator
Mode	Incubate and Agitate
Incubate Duration	20min
Incubate Temp	100ºC
Agitate Duration	20min
Agitation Mode	Orbital
Agitation Speed	500rpm
Sampling Parameters	Sample Directly from Vial in Incubator
Wait	
Wait Input	GC Ready
Headspace Fill	
Headspace Syringe	2.5mL
Needle Depth	20mm
Sample Volume	1000µL
Sample Rate	100µL/sec
Syringe Temp.	100ºC
Post Sample Delay	1 sec
GC Injection	
Injection Target	Single Injection Port 1
Injection Depth	205mm
Injection Volume	1000µL
Injection Rate	500µL/sec
Post Injection Delay	1 sec
GC Cycle Time	20min
GC Start Signal Timing	After Injection
Headspace Sweep Needle	
Syringe Pump Count	3
Syringe Pump Volume	1500µL
Syringe Pump Rate	500µL/sec
Wait	
Wait Time	5min

Table 1: Headspace Experimental Parameters

GC/MS	Parameter
Inlet	Split/Splitless
Inlet Temp.	220ºC
Inlet Head Pressure	24.912 psi
Mode	Split
Split Ratio	5:1
Column	Rxi-624Sil MS 30m x 0.25mm I.D. 1.4µm film thickness
Oven Temp. Program	60ºC hold for 12.0 min, ramp 40ºC/min to

	240ºC, hold for 0.5 min, 16.5 min run time
Column Flow Rate	1.0 mL/min
Gas	Helium
Total Flow	9.0mL/min
MS Transfer Line Temp.	180ºC
Source Temp.	230ºC
Quad. Temp.	150ºC
Acquisition Mode	SIM
SIM Ions1.00 to 16.5min	52, 77, 78, 83, 84
Cycle Time	6.73Hz
Solvent Cut Time	1.0min

Table 2: GC/MS Experimental Parameters

Neat Benzene and Benzene-d6 were procured. The Benzene and Benzene-d6 neat chemicals were diluted to 100µg/mL in dimethyl sulfoxide (DMSO). The Benzene-d6 standard was used as the Internal Standard (IS) with a concentration of 2µg/mL while the eight-point Benzene calibration curve was prepared with a range of 0.05 to 10µg/mL. Standards were prepared in a 20mL headspace vial with a 5mL volume of DMSO spiked with IS and Benzene standard. Using the outlined parameters, a calibration curve was established. Once the calibration curve was determined, seven replicate precision and accuracy samples were prepared by adding 0.5g of Benzene free sunblock to 4.4mL DMSO and spiking the sample with the 100µL Benzene-d6 IS. The samples were tested at a low and a mid-point of the calibration curve. Table 3 summarizes the calibration and precision and accuracy results.

Compound	Curve %RSD	Curve Response Factor	Curve Linear Regression	Precision (0.1µg/ mL) %RSD	Accuracy (0.1µg/ mL) %Recovery	Precision (2µg/ mL) %RSD	Accuracy (2µg/ mL) %Recovery
Benzene	13.99	1.185	0.999	3.14	111.43	1.02	93.71

Table 3: Calibration Curve, Precision and Accuracy Results Summary

In order to test sunscreen, several brands of spray and lotion sunblock were obtained. Each sunscreen was tested in triplicate in order to verify the accuracy of the results. The sunscreen samples were created by adding 0.5g of the sunblock to a 20mL headspace vial, adding 4.4mL of DMSO and 100µL of IS. The results are displayed in Table 4. Figure 1 is an Extracted Ion Chromatogram (EIC) of the 2µg/L standard.

Sunblock	Run 1	Run 2	Run 3	Avg.	Std. Dev.	%RSD	Active Ingredients
Brand A Spray	3.3	3.4	3.4	3.367	0.047	1.40	Avobenzone 3%, Homosalate 10%, Octisalate 5%, Octocrylene 10%
Brand A Lotion	ND	ND	ND	NA	NA	NA	Avobenzone 2.5%, Homosalate 6%, Octisalate 4.5%, Octocrylene 8%
Brand B Spray	ND	ND	ND	NA	NA	NA	Avobenzone 3%, Homosalate 15%, Octisalate 5%, Octocrylene 4%, Oxybenzone 6%

Brand B Lotion	ND	ND	ND	NA	NA	NA	Avobenzone 3%, Homosalate 8%, Octisalate 5%, Octocrylene 4%
Brand C Lotion	ND	ND	ND	NA	NA	NA	Avobenzone 3%, Homosalate 10%, Octisalate 5%, Octocrylene 5%
Brand D Spray	ND	ND	ND	NA	NA	NA	Avobenzone 2%, Homosalate 7%, Octocrylene 5%

ND- Below Detection Limit

NA - Not Applicable

Table 4:

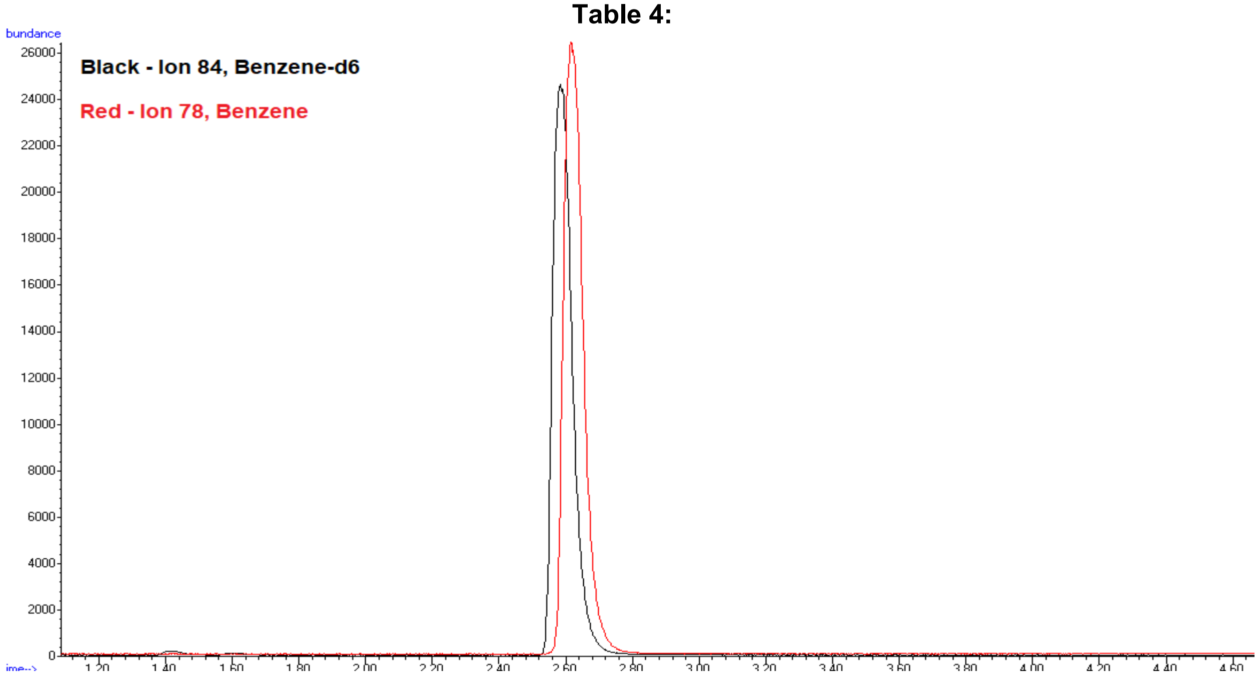

Figure 1: EIC of the 2μg/mL Benzene Standard

Conclusions:

Static headspace sample provided linear, accurate and reproducible data. For the sunscreens tested, most of them were below the detection limit. However, one of the sunscreen spray samples had over three parts per million of Benzene in it. This level of Benzene is known to be cancerous and the fact that sunscreen is reapplied throughout the day, it could be toxic. The problem of Benzene in sunscreen needs to be addressed by the manufacturers and buyers should know what product they are buying and if it is safe. Manufacturers can easily determine the Benzene in their products by using the static headspace procedure outlined in this application.

References:

1. VALISURE DETECTS HIGH LEVELS OF KNOWN HUMAN CARCINOGEN BENZENE IN SEVERAL SUNSCREEN PRODUCTS AND REQUESTS FDA ACTIONS, May 25, 2021, https://www.valisure.com/blog/valisure-news/valisure-detects-benzene-in-sunscreen/

2. Benzene PDF, Retrieved 7/1/21, https://www.epa.gov/sites/production/files/2016-09/documents/benzene.pdf

3. Federal Register, Benzene, Standard number 1910.1028, publication date, 9/11/87, https://www.osha.gov/laws-regs/federalregister/1987-09-11#:~:text=December%2010%2C%201987.-,Abstract%3A%20Amendment%20of%20existing%20standard%20for%20Occupational%20Exposure%20to%20Benzene,(STEL)%20of%205%20ppm.

For More Information

For more information on our products and services, visit our website www.estanalytical.com/products.

EST analytical