

Shown below are the instruments and the chromatographic conditions used to analyze aerosol sunscreen products by HS GC-MS:

Equipment

Equipment Name	Vendor	Model/Cat. No.
Gas Chromatograph	Agilent (HP)	6890 (G1530A)
Mass Spec. Detector	Agilent	5973 (G1098A)
Headspace Sampler	Agilent	7697A
ZB-624 GC Column	Phenomenex	7KG-G005-27

Headspace Gas Chromatography-Mass Spectrometry (HS GC-MS)

<u>Headspace Unit</u>	Oven: 80 °C Loop: 90 °C Tr. Line: 125 °C Vial equilibration: 25 min Injection: 1 min (1 mL loop) GC cycle time: 35 min Vial size: 10 mL Agitation: 50 shakes/min Fill Pressure: 10 psi	<u>Column</u>	Phenomenex Zebron ZB-624 Cat # 7KG-G005-27 S/N 1078570 60 m x 0.25 mm ID x 1.40 µm film 1.8 mL/min, constant flow
		<u>GC Oven</u>	60 °C for 12.5 min, + 30 °C/min to 240 °C, hold 9.5 min Run time: 28 min
<u>Inlet (Split)</u>	Liner: split with wool Gas: Helium Temp: 200 °C P: 29.6 psi Total flow: 9.5 mL/min Split Ratio: 3:1 Split Flow: 5.4 mL/min	<u>MSD</u>	Transfer line temperature: 250 °C Solvent delay: 0 min MSD off: 17.9 – 20.2 min Scan <i>m/z</i> : 29 – 300
		<u>Library</u>	NIST/EPA/NIH mass spectral library Version 2.0 d (April 26, 2005)

The resulting scan chromatograms were reprocessed by extracting the *m/z* 78 ion (molecular weight of benzene).

For the analysis of lotion products, the equipment is the same. The instrument parameters are follows:

<u>Headspace Unit</u>	Oven: 80 °C Loop: 90 °C Tr. Line: 125 °C Vial equilibration: 25 min Injection: 1 min (1 mL loop) GC cycle time: 35 min Vial size: 10 mL Agitation: 50 shakes/min Fill Pressure: 10 psi	<u>Column</u>	Phenomenex Zebron ZB-624 Cat # 7KG-G005-27 S/N 1078570 60 m x 0.25 mm ID x 1.40 µm film 1.8 mL/min, constant flow
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<u>Inlet (Split)</u>	Liner: split with wool Gas: Helium Temp: 200 °C P: 29.6 psi Total flow: 9.5 mL/min Split Ratio: 3:1 Split Flow: 5.4 mL/min	<u>MSD</u>	Transfer line temperature: 250 °C Solvent delay: 0 min MSD off: 17.9 – 20.2 min SIM <i>m/z</i> 51, 78

Standards/Samples/Spike Preparation for Aerosol and Lotion

Standard (Calibration Curve) Preparation

The benzene reference standard had a concentration of 10.0 mg/mL benzene in DMSO. A benzene stock solution was prepared by transferring 100 μ L of the reference standard solution to a 10-mL volumetric flask and diluting to volume with DMSO (0.100 mg/mL). An intermediate stock solution was prepared by transferring 250 μ L of the stock solution to a 25-mL volumetric flask and diluting to volume with DMSO (0.00100 mg/mL). Aliquots of the intermediate stock solution were transferred to 10-mL volumetric flasks and diluted to volume with DMSO to produce calibration solutions with the following concentrations (Table II).

Table II. Benzene Calibration Solutions Preparation

Solution	Int. Sol'n (mL)	Total (mL)	Concentration (mg/mL)	Concentration (μg/mL or ppm)	In HS vial (μg)	Equivalence in Sample* (μg/g or ppm)
Cal 1	3	10	0.000300	0.300	0.300	6
Cal 2	2	10	0.000200	0.200	0.200	4
Cal 3	1	10	0.000100	0.100	0.100	2
Cal 4	0.5	10	0.0000500	0.0500	0.0500	1
Cal 5	0.25	10	0.0000250	0.0250	0.0250	0.50
Cal 6	0.125	10	0.0000125	0.0125	0.0125	0.25
Cal 7	0.050	10	0.0000050	0.0050	0.0050	0.10
Cal 8	0.025	10	0.0000025	0.0025	0.0025	0.05

* A 0.3-ppm benzene standard solution would be equivalent to 6 ppm benzene in the sample when prepared as stated in this method (0.5 g/10 mL sample preparation)

Sample Preparation – Un-spiked

The sunscreen material was sprayed into a 20-mL vial and then aliquots from the 20-mL vial were used for sample preparations. An un-spiked sample solution was prepared in triplicate by weighing approximately 0.5 g of sunscreen sample into a 10-mL volumetric flask, dissolving and diluting to volume with DMSO.

Sample Preparation – Spiked

Samples spiked with 4 ppm benzene were prepared in triplicate by weighing approximately 0.5 g of sunscreen sample into a 10-mL volumetric flask, adding 2 mL of the intermediate stock solution, then diluting to volume with DMSO.

Samples spiked with 2 ppm benzene were prepared in triplicate by weighing approximately 0.5 g of sunscreen sample into a 10-mL volumetric flask, adding 1 mL of the intermediate stock solution, then diluting to volume with DMSO.

Samples spiked with 0.4 ppm benzene were prepared in triplicate by weighing approximately 0.5 g of sunscreen sample into a 10-mL volumetric flask, adding 0.2 mL of the intermediate stock solution, then diluting to volume with DMSO.

Headspace Vial Preparation

The headspace vials were prepared for analysis by adding 5 mL of water followed by 1 mL of prepared solution.

Blank	5 mL water + 1 mL DMSO
Cal. Solutions	5 mL water + 1 mL Calibration solution
Sample	5 mL water + 1 mL sample solution (spiked or un-spiked)