TEST METHOD

Effective: 28 June 2010 DOWM 102452-E10B
Supersedes: DOWM 102452-E10A

Additives in Gas Phase Polyethylene by Extraction and UV Spectrophotometry

1. Scope

This method is applicable to the analysis of the following additives in gas phase polyethylene over the following ranges:

Analyte	Applicable Range
	% (w/w)
Irganox 1010	0.01 – 0.07
Irganox 1076	0.01 – 0.09
Butylated Hydroxy Toluene (BHT)	0.002 – 0.07

2. Principle

Ground gas phase polyethylene pellets are refluxed with solvent or granular polyethylene resin is mixed with a solvent to extract additives from the polyethylene. The absorbance of the resulting solution is measured using a UV spectrophotometer. The concentration of additive in the original sample, in % (w/w), is determined by comparison to external standards using a calibration curve.

3. Safety

Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents and procedures before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: OPERATION MANUALS, MATERIAL SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

4. Interferences

4.1. The method determines Total Irganox 1010 and Irganox 1076. The method does not differentiate between active and corresponding reaction (oxidation) products.

4.2. This method is not applicable for resins containing a combination of antioxidants or other additives that will interfere with the UV absorption band at 283 nm. Specifically, you cannot analyze Irganox 1010, Irganox 1076 and BHT in the same sample.

4.3. Dust or contamination of spectrophotometer cuvettes are possible interferents. Cuvettes should be cleaned and dust removed before analyzing samples or blanks.

4.4. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate method.

5. Apparatus

5.1. Analytical balance: capable of weighing to the nearest 0.001-g, Mettler model AB204S, available from Mettler-Toledo Inc., P.O. Box 71, 69 Princeton-Hightstown Road, Hightstown, NJ 08520, or equivalent.

5.2. UV-visible spectrophotometer: Agilent model 8453 Diode Array spectrophotometer, available from Agilent Technologies, 3200 Hillview Avenue, Palo Alto, CA 94304.

5.3. Quartz glass cuvettes: 10-mm pathlength, for Agilent model 8453 Diode Array Spectrophotometer, available from Agilent Technologies, or equivalent.

5.4. Computing Integrator: Chemstation with Rev A.09xx software, available from Agilent Technologies, or equivalent.

5.5. Grinding Mill: available from Wiley

5.6. Hotplate: available from Fisher Scientific, 2000 Park Lane Drive, Pittsburgh, PA 15275, or equivalent.

5.7. Erlenmeyer flasks: 250-mL size, glass, available from Fisher Scientific, or equivalent.

5.8. Volumetric flasks: Class A, 100- and 250-mL volumes, available from Fisher Scientific, or equivalent.

5.9. Condensors: glass, water-cooled with 24.40 standard taper, available from Fisher Scientific, or equivalent.

5.10. Magnetic stirrer and stir bars, available from Fisher Scientific, or equivalent.

5.11. Filter paper: Whatman #4 or #41, available from Fisher Scientific, or equivalent.

5.12. 200 micron mesh

5.13. Waring Blender: or other lab blender, available from Fisher Scientific, or equivalent.

5.14. Volumetric flasks with stoppers: 100-mL and 500-mL volumes, available from Fisher Scientific, or equivalent.

5.15. Timer: analog, available from Fisher Scientific, or equivalent.

5.16. Volumetric pipets: Class A, 1-, 3-, 5-, 7- and 9-mL volume, available from Fisher Scientific, or equivalent.

5.17. Transfer pipet: 10-mL volume, available from Fisher Scientific, or equivalent.

6. Reagents

6.1. Cyclohexane: (HPLC grade), or equivalent, available from Fisher Scientific, or equivalent.

6.2. Acetone: (HPLC grade) or equivalent, available from Fisher Scientific, or equivalent.

6.3. Isopropanol (HPLC grade) or equivalent, available from Fisher Scientific, or equivalent

6.4. Butylated Hydroxy Toluene (BHT) available from Fisher Scientific, or equivalent

6.5. Irganox 1010, available from Ciba Specialty Chemicals Incorporated, Additives Division, 4002 Basel, Switzerland, or equivalent (Note 20.2).

6.6. Irganox 1076, available from Ciba Specialty Chemicals Incorporated, or equivalent (Note 20.2).

Note: Irganox 1010, Irganox 1076 and BHT from the production plant is considered equivalent.

7. Reagent Solutions

7.1. Stock Standards (Individual 1.0 mg/mL Stock Standards for Irganox 1010, Irganox 1076 and BHT in cyclohexane)

Note: Individual standards must be prepared for each of the antioxidants for which this method applies since they all have an absorbance at 283 nm

7.1.1. Place a 250-mL volumetric flask on the balance and tare the balance.

7.1.2. Add 0.25 g ± 0.1 g of one of the antioxidants to the tared volumetric flask and record the weight to the nearest 0.01-g.

7.1.3. Dissolve the antioxidant in the flask (Section 7.1.2) with cyclohexane added to the volumetric flask. Dilute the contents of the flask to volume using cyclohexane and mix well.

7.1.4. Calculate the concentration of antioxidant in the stock standard solution as follows:

$$C_{ss,i} = \frac{W_i}{V_{ss}} \times \frac{1000\text{mg}}{1\text{g}}$$

Where:

$C_{SS,i}$ = Concentration, in mg/mL of component of interest, i in the Calibration Stock Solution

W_i = Weight, in grams, of component of interest, i in the Calibration Stock Solution (Section 7.1.2)

V_{SS} = Volume of prepared Stock solution (250 mL)

i = component of interest (Irganox 1010, Irganox 1076 or BHT)

7.2. Calibration Standards:

Refer to the following table for volumes of the Antioxidant Stock Solution to use to prepare a series of at least five Calibration Standards (in addition to the blank) bracketing your expected results:

Calibration Standard #	Volume, in mL, of Antioxidant in the Stock Solution	Volumetric Flask Size, in mL	Dilution Solvent	Nominal Concentration of Antioxidant in the calibration standard, in mg/mL
Blank	0	100	cyclohexane	0
1	1.0	100	cyclohexane	0.01
2	7.5	**250**	cyclohexane	0.03
3	5.0	100	cyclohexane	0.05
4	7.0	100	cyclohexane	0.07
5	9.0	100	cyclohexane	0.09
6	10.0	100	cyclohexane	0.10

7.3. Calculate the concentration of Irganox 1010, Irganox 1076 or BHT in each calibration standard as follows:

$$C_{Cal,i,j} = \frac{V_{SS,i,j} \times C_{SS,i}}{V_{i,j}}$$

Where:

$C_{Cal,,i,j}$ = Concentration, in mg/mL of component of interest, i in the Calibration Solution j
$V_{SS,i,j}$ = Volume, in mL of Stock Standard, i in Calibration Solution j
$C_{SS,i}$ = Concentration, in mg/mL of component of interest, i in the Calibration Stock Solution (Section 7.1)
i = component of interest (Irganox 1010, Irganox 1076 or BHT)
j = Calibration Solution number

8. Analysis Conditions

Spectrophotometer:	Hewlett-Packard 8453
Range:	190 to 1100 nm
Interval:	1 nm
Integration Time:	1 second
Standard Deviation:	ON
Data Analysis:	
Data Type	Absorbance
Display Spectrum:	240 - 320 nm (UV side)
Wavelength:	283 nm
Prompt for sample information:	Off
Prompt for standard information:	On
Concentration Unit:	mg/mL
Calibration Curve	Linear (Beer's Law)

9. Instrument Start Up

9.1. Turn on the power for the computer and wait for the CAG Bootp program to start up.

9.2. Turn on power to the HP 8453 UV/VIS

9.3. Double click on "**UV-Vis**" icon.

9.4. The "**UV-Visible Chemstation**" window will appear. Click "**OK**."

9.5. A "**Warning**" window may appear. Select the option that will have both lamps on.

9.6. Click "**File**" and select "**Load Method.**"

9.7. "**Save Method**" window may appear. Click "**NO**."

9.8. Select the method applicable to the antioxidant to be analyzed.

Note: Remember to use the correct method if the extraction was done using a 40/60 cyclohexane/isopropanol solvent mixture.

9.9. The "**Warning**" window may appear. Select the option that will have both lamps on.

9.10. The "**Standards**" window may appear. Select "**Discard.**"

9.11. Instrument is now ready to run a blank.

10. Instrument Shutdown

10.1. Turn off the deuterium and tungsten lamps by using the taskbar and selecting "Instrument" selecting "**Lamps**" and selecting both lamps to be "**Off**." Then select "**OK**."

10.2. From the "**File**" menu select "**Exit Chemstation**."

10.3. From the "**Start**" menu select "**Shutdown**" then "**Shutdown the Computer**" and click "**Yes**."

10.4. Turn the power off for the computer and HP 8453 Diode Array Spectrophotometer.

11. Calibration

11.1. Load the appropriate spectrophotometer method for Irganox 1010 or Irganox 1076 or BHT and discard any existing calibration standard information as follows:

11.1.1. From the taskbar, click "**View**" and then select "**Standards.**"

11.1.2. Highlight all standards and click "**delete**."

11.2. Analyze the "blank" (Section 7.2 or 7.3) according to the conditions outlined in Section 8.

11.3. Analyze each of the calibration standards (Section 7.2) according to the conditions outlined in Section 8, as follows

11.3.1. Begin with the lowest concentration standard and rinse the cuvette three times with this standard

11.3.2. Fill the cuvette with the standard and ensure the outside of the cuvette is clean and dry.

11.3.3. Place the cuvette in the sample holder of the spectrophotometer and select the "**Standard**" button.

11.3.4. Enter the name of the standard, actual concentration and the concentration units.

11.3.5. Remove the cuvette from the sample holder; discard the solution and clean the cuvette.

11.3.6. Repeat Steps 11.3.1 through 11.3.5 for the remaining calibration standards.

11.4. Once all the standards have been analyzed, click "**Calibrate**" and "**Show Coefficients**."

11.4.1. Check the correlation coefficient value. If less than 0.995, repeat the calibration.

11.4.2. When the correlation coefficient value is greater than 0.995, go to the "**File**" menu and select "**Save Method As….**"

11.4.3. If the filename is correct, click "**OK.**" Click "**Yes**" to replace the existing method.

11.5. If manual calculations are required, construct a calibration graph by plotting the absorbance of each antioxidant versus the concentration of the antioxidant in a spreadsheet program such as Excel. Calculate the slope and intercept of the calibration curve for each component.

$$y_{i,j} = m_i x_{i,j} + b_i$$

where:

$y_{i,j}$ = the absorbance of the antioxidant of interest i, in calibration standard j (Section 11.3)
i = the antioxidant of interest
j = the calibration standard of interest (j = 1, 2, 3)
$x_{i,j}$ = the concentration (mg/mL) of the antioxidant of interest i, in calibration standard j (Sections 7.2 and 7.3)
m_i = the slope (counts × mL/mg) of the linear regression line for antioxidant of interest i
b_i = the intercept (counts) of the linear regression line for the antioxidant of interest i

11.5.1. Check the correlation coefficient value. If less than 0.995, repeat the calibration.

12. Quality Assurance Check-Standard Analysis

12.1. Load the appropriate method as follows:

12.1.1. Click "**File**" from the main menu bar and select "**Load Method**."

12.1.2. Select the method applicable to the antioxidant to be analyzed and click "**OK**."

12.1.3. A message will appear asking to either append or discard existing standards. Choose "**Discard**."

12.1.4. From the task bar, click "**View**" then select "**Samples.**"

12.2. Analyze a solvent blank (**use the correct blank for the method chosen**).

12.2.1. Rinse the cuvette three times with cyclohexane. Fill the cuvette with the blank solution to the level marker.

12.2.2. Place the cuvette into the sample cell holder and secure it by lowering the lever arm to the lowest position located on the left side of the sample holder.

12.2.3. Begin the blank measurement by clicking the "**Blank**" button once at the lower left corner of the computer screen.

12.2.4. The instrument will now scan the blank and a spectrum will appear on the screen.

12.2.5. Release the cuvette from the sample holder and dispose of the blank in the appropriate waste container. Clean and dry the cuvette.

12.3. Analyze a QC reference sample as follows:

12.3.1. Obtain the appropriate reference sample (containing Irganox 1010 or Irganox 1076).

12.3.2. Weigh 5.0 g ± 0.1 g to the nearest 0.01-g directly into a small mouth 250-mL Erlenmeyer flask. Record the weight of sample added to the nearest 0.01-g.

Sample weight is a critical parameter and must not be outside of the specified tolerance

12.3.3. Add 50mL ± 1mL of cyclohexane to the flask as well as some boiling beads.

12.3.4. Place the flask on a pre-heated hot plate and attach a condenser. After the solvent begins to boil, start timing the reflux for 15 ± 2 minutes.

Reflux time is a critical parameter and must not be outside of the specified tolerance

12.3.5. Remove the flask from the hot plate, stopper the flask and let the sample cool to room temperature for 15 - 20 minutes.

12.3.6. Filter the sample with Whatman # 4 filter paper and retain the filtrate for analysis.

12.3.7. Rinse the cuvette three times with the filtrate. Fill the cuvette with filtrate to the level marker.

12.3.8. Secure the cuvette in the sample cell holder.

12.3.9. Select the "**Sample**" button from the lower left corner of the screen or by pressing the "**Sample**" button on the front of the spectrometer to acquire the sample spectrum.

12.3.10. Calculate antioxidant concentration, in % (w/w) (Section 15.1),.and record the data on a Control Chart

Note: If the QC sample result is outside of the control limits on the Control Chart, the result is classified as a failing result. In this case, reanalyze another reference sample.

12.3.11. If a second failing result is obtained, a recalibration may be required

13. Sample Preparation

Note: Pure cyclohexane is the appropriate extraction solvent for most products. However, if the density is too low and the melt index too high, pure cyclohexane will dissolve the polymer itself and make an accurate reading of the additive impossible using the method described in this procedure. If this occurs, use a "40% cyclohexane / 60% Isopropanol" solvent mixture instead of the pure cyclohexane as the extraction solvent for the standards, samples and blank measurement.

13.1. Granular Resin (for BHT dry blended on granules, or for Irganox 1076 in granules)

13.1.1. Fill a stainless steel cup with granular resin and add to the Waring lab blender. Blend the resin for at least 1 minute.

13.1.2. Place a 250-mL Erlenmeyer flask on the balance and tare the balance.

13.1.3. Add 5.0 g ± 0.1 g of the ground resin to the tared Erlenmeyer flask and record the weight to the nearest 0.01-g.

Sample weight is a critical parameter and must not be outside of the specified tolerance

13.1.4. Add 50 mL ± 1 mL of cyclohexane to the flask containing the ground sample.

13.1.5. Place the flask on the magnetic stirrer and place a stir bar into the flask.

13.1.6. Stir the contents at room temperature for 15 minutes ± 2 minutes.

Reflux time is a critical parameter and must not be outside of the specified tolerance

Note: Stir at a rate that provides good agitation without splashing

13.1.7. Filter the sample using Whatman #4 or #41 filter paper

13.1.8. Analyze the sample as described in Section 14, Procedure.

13.2. Pelleted Resin

13.2.1. Ensure the interior of the Wiley mill is clean and free of contamination.

13.2.2. Place the hopper, mesh and sample cup on the mill and then turn on the power switch

13.2.3. Use a total of about 50g of sample introducing about 10g of sample at a time.

13.2.4. Once the entire sample is ground-up, turn off the Wiley mill and remove the sample from the cup. Vacuum the Wiley Mill and ensure there is no sample remaining.

13.2.5. Weigh 5.0 g ± 0.1g to the nearest 0.01-g directly into a small mouth 250-mL Erlenmeyer flask having a 24/40 standard taper ground glass joint.

Sample weight is a critical parameter and must not be outside of the specified tolerance

13.2.6. Add 50 mL ±1 mL of cyclohexane to the flask containing boiling beads and attach to the condenser refluxing apparatus then place on the pre-heated hot plate.

13.2.7. Reflux for 15 minutes ± 2 minutes after the solvent begins to boil.

Reflux time is a critical parameter and must not be outside of the specified tolerance

13.2.8. Turn off the hot plate and let sample cool for 5 minutes before removing it from the refluxing apparatus. Let it cool at room temperature for an additional 15 minutes

13.2.9. Filter the sample with Whatman #4 or #41 filter paper and then analyze the filtrate as described below in Section "Analysis."

14. Procedure

14.1. From the task box, select "**Samples.**"

14.2. Place the blank solvent in a clean and dry cuvette and rinse twice.

Note: The blank solution should be the same as the standard and sample solvent matrix.

14.3. Place the cuvette containing the blank solvent into the sample cell holder and secure it by lowering the lever arm to the lowest position located on the left side of the sample holder.

14.4. Begin the blank measurement by clicking the "**Blank**" button once at the lower left corner of the screen. The instrument will scan the blank and a spectrum will appear on the screen. After confirming the blank spectrum is OK, close blank spectrum box.

14.5. Remove the cuvette from the sample holder by releasing the lever on the lower left hand side and dispose of the contents in the appropriate waste container.

14.6. Obtain the filtrate from sample preparation described previously and fill the cuvette with the sample filtrate, rinsing the cuvette twice with the filtrate before filling with the aliquot to be analyzed.

14.7. Place the cuvette in the sample cell holder and secure.

14.8. Select the "**Sample**" button from the lower left corner of the screen to acquire the sample spectrum.

14.9. After the sample has been scanned the concentration will be displayed in mg/mL in the sample/result table.

14.10. Calculate the % concentration by weight of antioxidant present using the calculation in Section 15 and report the data to the third decimal place.

15. Calculation

15.1. Determine the concentration in % (w/w) of antioxidant in the sample as follows:

$$AO_{i,\%(w/w)} = \frac{C_i \times V_{sol}}{Wt} \times \frac{1\,g}{1000\,mg} \times 100$$

Where:

$AO_{i,\%(w/w)}$ = Concentration, in % (w/w) of Antioxidant i
C_i = Concentration, in mg/mL of antioxidant i, in mg/mL (Section
V_{sol} = Volume of extraction solvent
Wt = sample weight in grams (nominally 5 grams)
i = antioxidant, either Irganox 1010, Irganox 1076 or BHT

15.2. Dilute the sample as follows if the absorbance of the extract solution is off scale:

15.2.1. Pipet 2.0 mL of the extract into a 10.0-mL volumetric flask.

15.2.2. Dilute to volume with cyclohexane and mix well.

15.2.3. Determine the concentration of the diluted sample and calculate the concentration of antioxidant in the sample as follows:.

$$AO_{i,\%(w/w)} = \frac{C_i \times V_{sol}}{Wt} \times \frac{10\ mL}{2\ mL} \times \frac{1\ g}{1000\ mg} \times 100$$

Where:

$AO_{i,\%(w/w)}$ = Concentration, in % (w/w) of Antioxidant i
C_i = Concentration, in mg/mL of antioxidant i, in mg/mL (Section
V_{sol} = Volume of extraction solvent
Wt = sample weight in grams (nominally 5 grams)
i = antioxidant, either Irganox 1010 or Irganox 1076 or BHT
10 mL = total volume of the diluted sample
2 mL = amount of extract that was diluted

16. Precision (Note 20.4 and 20.5)

Precision data for Irganox 1010, Irganox 1076 and BHT is summarized in the following table.

Analyte	n	Degrees of Freedom	$t_{\Sigma df}$	Average Conc	Standard Deviation s	Pooled Standard Deviation s_{pooled}	95% Prediction Interval at a 95% Confidence Level	Expected Range of Future results on similar samples
				% (w/w)	% (w/w)	% (w/w)	± % (w/w)	% (w/w)
Irganox 1010	132	122	1.980	**0.029**		0.0010	0.0020	0.027 to 0.031
Irganox 1076	64	54	2.005	**0.055**		0.0014	0.0028	0.052 to 0.058
BHT	10	9	2.262	**0.029**	0.0026		0.0059	0.023 to 0.035

17. Recovery

Individual single samples of Gas Phase Polyethylenes were analyzed for Irganox 1010, Irganox 1076 and BHT by a primary reference method (DOWM 102408) and results compared to those obtained using this method. Results are summarized in the following table:

Analyte	Reference Method Total Dissolution LC	Extraction UV/VIS method	Recovery
	% (w/w)	% (w/w)	%
Irganox 1010	0.0312	0.0292	93.6
Irganox 1076	0.0528	0.0551	104.4
BHT	0.0333	0.0286	85.9

Recoveries were based on comparison of results from the Extraction, UV/VIS method to those obtained by a reference method (Total Dissolution LC, DOWM 102408).

18. Linearity

The method is linear for Irganox 1010, Irganox 1076 and BHT in gas phase polyethylene over the following ranges:

Analyte	Applicable Range
	% (w/w)
Irganox 1010	0.01 – 0.07
Irganox 1076	0.01 – 0.09
Butylated Hydroxy Toluene (BHT)	0.002 – 0.07

Figures 2, 3 and 4 show calibration curves for Irganox 1010, Irganox 1076 and BHT respectively.

19. Reporting

Report antioxidant concentration as % (w/w) to the third decimal place.

20. Notes

20.1. The accuracy of balances and pipets should be confirmed on a regular basis and documentation of the check should be kept.

20.2. Antioxidants included in this method are listed by trade name in the table below. Generic names and alternative trade names are also provided.

Trade Name	Generic Name
Irganox 1010 Anox PP 20	Tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane
Irganox 1076 Anox PP18 Arenox 76	Octadecyl 3,5-di-tert-butyl-4-hydroyhydrocinnamate
BHT	Butylated Hydroxy Toluene

20.3. In accordance with good laboratory practices, it is strongly suggested that the precision and accuracy of the method be re-determined if another set of equipment is to be used or the method is to be used in another laboratory.

20.4. Precision data for Irganox 1010 and Irganox 1076 was determined from multiple analyses [n] of single samples of Gas Phase Polyethylene, by ten different operators, over a period of several months. Precision data was grouped by operator and pooled

The estimated prediction interval at the 95% confidence level of a future final result determined on a similar sample is calculated as:

$$\pm\, t_{\Sigma(n-1)} \times s_{pooled}$$

where

$t_{\Sigma(n-1)}$ = t-value for the total number of degrees of freedom
s_{pooled} = the pooled standard deviation of the pooled data

20.5. Precision data for BHT was determined from multiple analyses [n=10] of a single samples of Gas Phase Polyethylene, over a period of two days.

The stated prediction intervals at the 95% confidence level is calculated as:

$$\pm t_{(n-1)} \times s$$

where

$t_{(n-1)}$ = t-value at n-1 degrees of freedom,
s = the pooled standard deviation of the validation data

The stated prediction intervals at the 95% confidence level relates to future final results determined on similar samples. This assumes a normal distribution of results and equal variability between locations.

****

Figure 1
Typical U.V. Curves for Irganox 1076/Irganox 1010 BHT

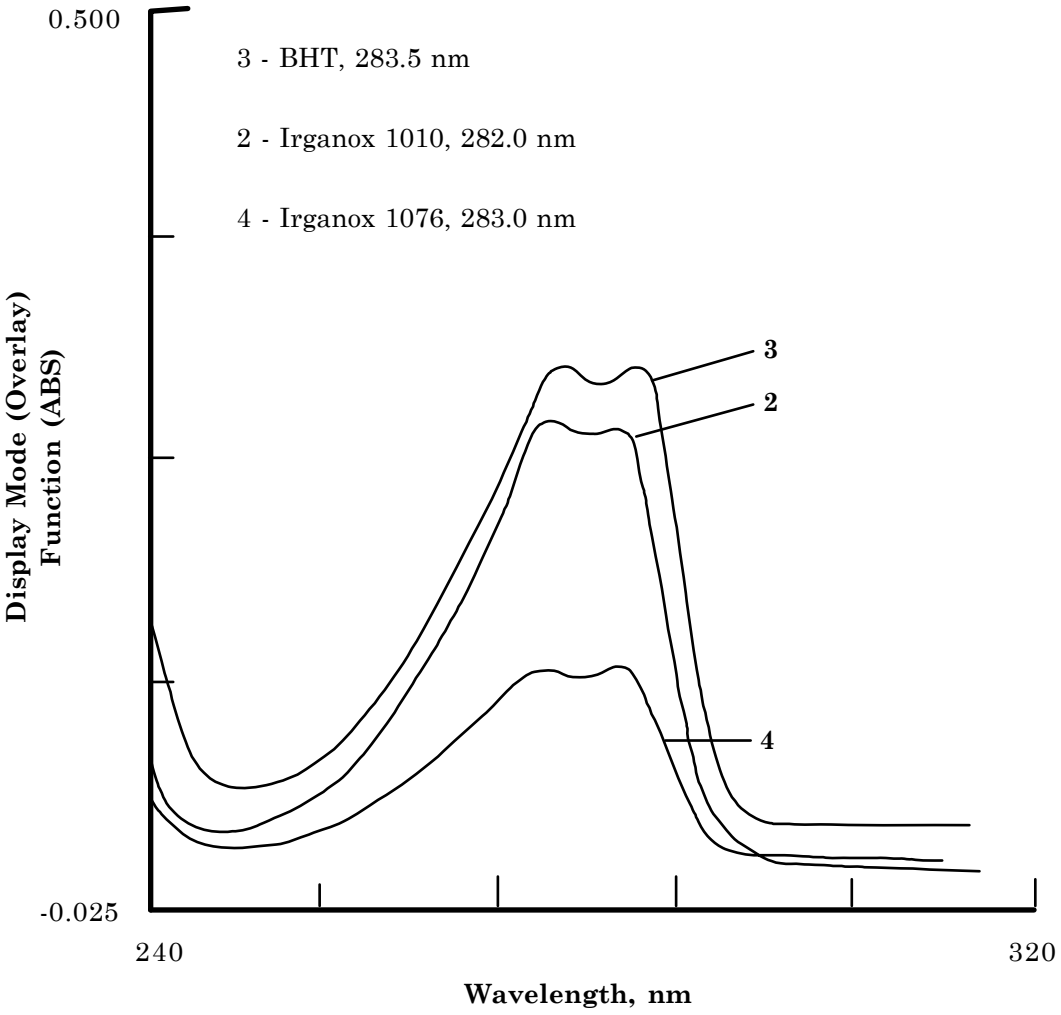


Figure 2

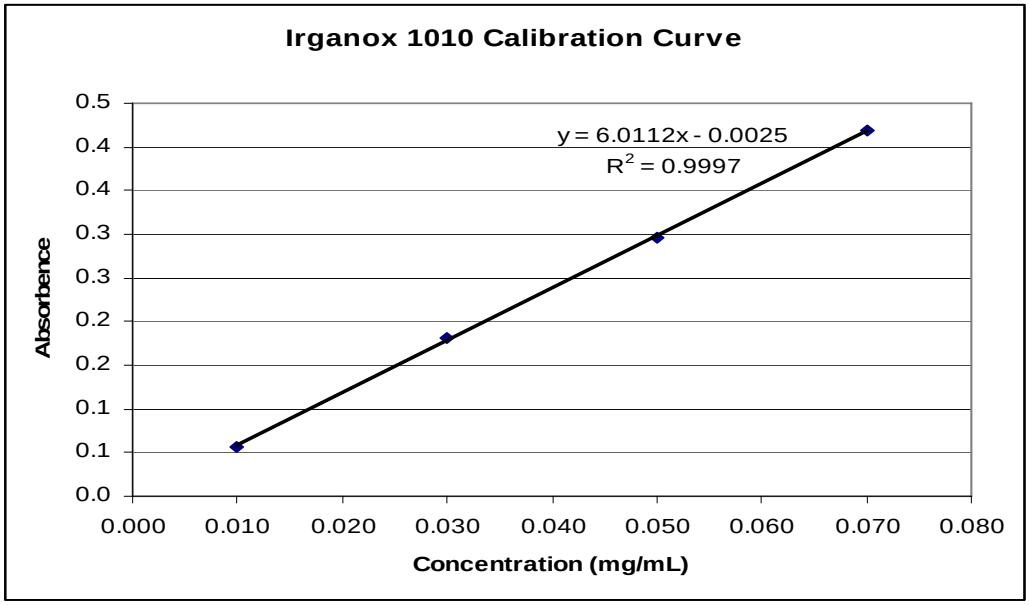


Figure 3

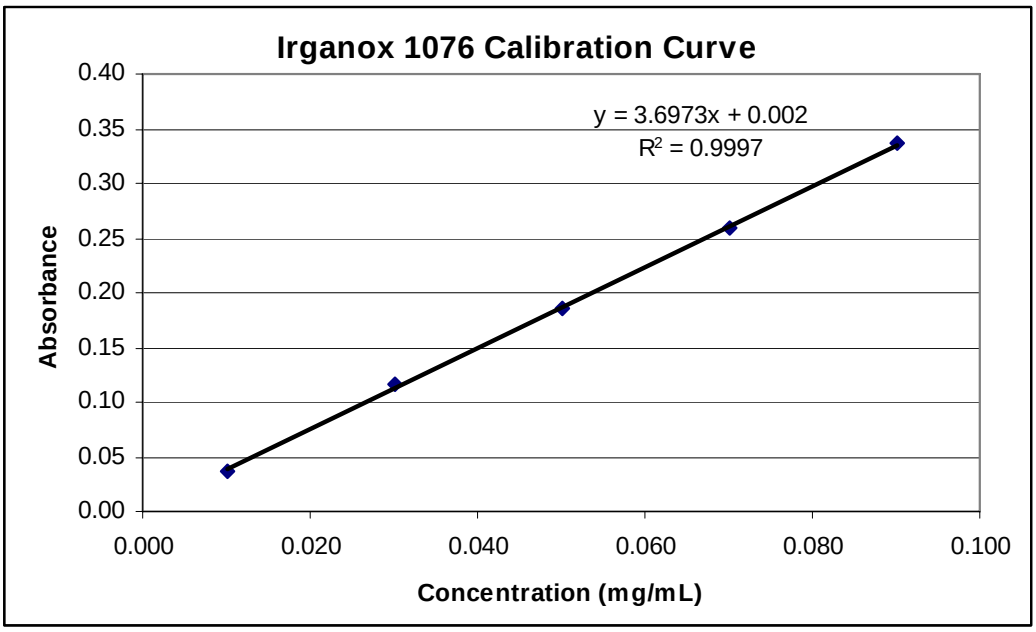
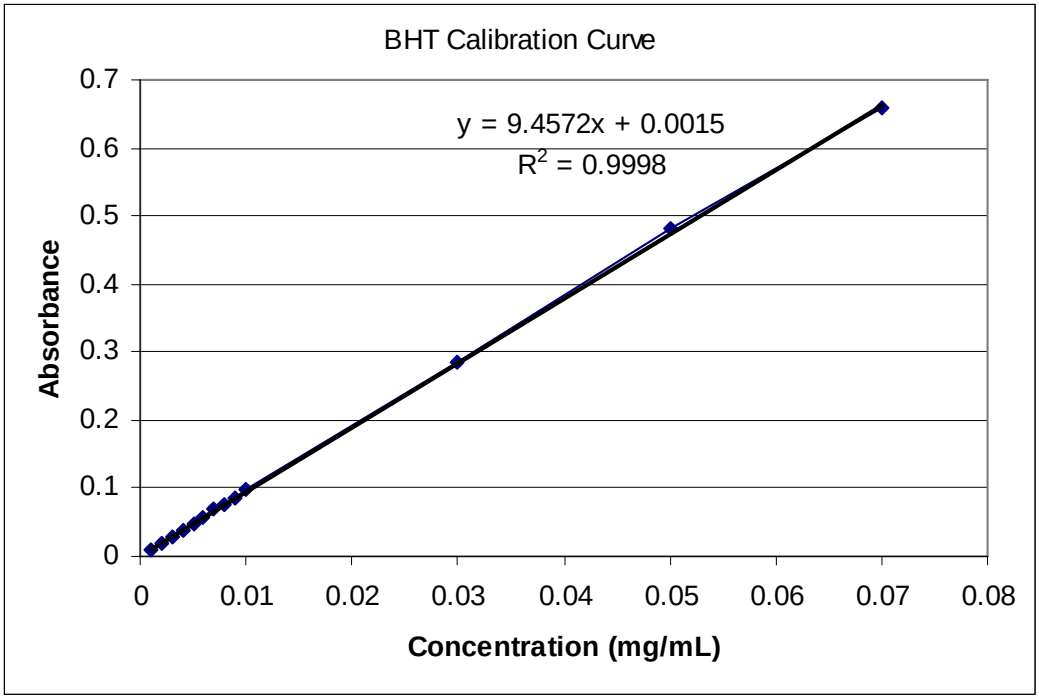


Figure 4


BHT Calibration Curve
y = 9.4572x + 0.0015
R2 = 0.9998
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
Concentration (mg/mL)