FINAL REPORT ACTION ITEM CHECK-OFF LIST

Chemical Name: Tetrabromobisphenol-A
Trade Name(s): BA-59P
CAS No: 79-94-7
Lab Study ID No: Wildlife 439C-130 Determination of the Dissociation Constant of Tetrabromobisphenol-A

☒ Reviewed for possible:
- ☐ FIFRA 6 (a) (2) and/or
- ☐ TSCA Section 8 (e) reporting

☐ Copy of FIFRA 6 (a) (2) and/or TSCA Section 8 (e) letter to the following Agency(ies), if applicable:
- ☐ EPA-FIFRA
- ☐ EPA-TSCA
- ☐ California [FIFRA 6 (a) (2)s]
- ☐ Other States [FIFRA 6 (a) (2)s]: _____

☐ Confidentiality Statement page addressed, signed, and dated in FIFRA reports.

☐ GLP Compliance page signed and dated in FIFRA reports.

☐ Flagging Statement page addressed, signed and dated in FIFRA reports This looks like a copy and not the original.

☒ Copy of report submitted to the Agency(ies) in conjunction and/or sup[ie] following: However, need to determine if reviewed for MSDS and if scanned. Thanks! JAS
- ☐ TSCA Consent Order/Agreement
- ☐ FIFRA Registration or Re-registration
- ☐ California Registration
- ☒ EU Notification — Submitted to UK via ACI
- ☐ Japanese METI Notification
- ☐ Japanese MAFF Notification
- ☐ Canadian (DSL) Notification
- ☐ FIFRA 6 (a) (2) Submission
- ☐ TSCA 8 (e) Submission
- ☐ TSCA 8 (d) Data-Call-In
- ☐ PMN Submission
- ☐ Other: _____

☒ Study Report reviewed for MSDS information.

☒ Copy of Cover & Summary report pages to Business Unit MSDS information center (domestic and international). Dieter & Peter Information not generally placed on MSDS 4/4/03

☒ All information regarding the chemical and the study report entered into the IUCLID Toxicity Data Base.

☐ Scanned final report, date:_____.

☐ Study file merged with final report file and sent to WIL for archiving, date:_____.

DETERMINATION OF THE DISSOCIATION CONSTANT OF TETRABROMOBISPHENOL-A

WILDLIFE INTERNATIONAL, LTD. PROJECT NUMBER: 439C-130

U.S. EPA Product Properties Test Guidelines, OPPTS 830.7370, *Dissociation Constants in Water*
OECD Guideline for Testing of Chemicals, 112, *Dissociation Constants in Water*

AUTHORS:

Frank J. Lezotte, B.S.
Willard B. Nixon, Ph.D.

STUDY INITIATION DATE: September 25, 2001

STUDY COMPLETION DATE: August 7, 2002

Submitted to:

American Chemistry Council's
Brominated Flame Retardant Industry Panel
1300 Wilson Boulevard
Arlington, VA 22209

Wildlife International, Ltd.

8598 Commerce Drive
Easton, Maryland 21601
(410) 822-8600

GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

SPONSOR: American Chemistry Council's
Brominated Flame Retardant Industry Panel

TITLE: Determination of the Dissociation Constant of Tetrabromobisphenol A

WILDLIFE INTERNATIONAL, LTD. PROJECT NUMBER: 439C-130

STUDY COMPLETION: August 7, 2002

This study was conducted in compliance with Good Laboratory Practice Standards as published by the U.S. Environmental Protection Agency in 40 CFR Part 160 and/or 792, 17 August 1989, and OECD Principles of Good Laboratory Practice (ENV/MC/CHEM (98) 17) with the following exceptions:

The reference substance was not characterized in accordance with Good Laboratory Practice Standards.

The reference substance was not identified in the protocol.

STUDY DIRECTOR:

Frank J. Lezotte, B.S.
Chemist
Wildlife International, Ltd.

8-7-02
DATE

← original Signature

QUALITY ASSURANCE STATEMENT

This study was examined for compliance with Good Laboratory Practice Standards as published by the U.S. Environmental Protection Agency in 40 CFR Part 160 and/or 792, 17 August 1989 and OECD Principles of Good Laboratory Practice (ENV/MC/CHEM (98) 17). The dates of all inspections and audits and the dates that any findings were reported to the Study Director and Laboratory Management were as follows:

		DATE REPORTED TO:	
ACTIVITY:	DATE CONDUCTED:	STUDY DIRECTOR:	MANAGEMENT:
Test Substance Preparation and Definitive Test Titration	September 26, 2001	September 28, 2001	October 4, 2001
Data and Draft Report	October 2 and 3, 2001	October 3, 2001	October 4, 2001
Sample Preparation	January 10, 2002	January 10, 2002	January 28, 2002
Data And Draft Report	February 20-22, 2002	February 22, 2002	March 4, 2002
Final Report	August 7, 2002	August 7, 2002	August 7, 2002

Kimberly A. Hoxter

Kimberly A. Hoxter, B.S.
Quality Assurance Representative

8-7-02
DATE

REPORT APPROVAL

SPONSOR: American Chemistry Council's
Brominated Flame Retardant Industry Panel

TITLE: Determination of the Dissociation Constant of Tetrabromobisphenol A

WILDLIFE INTERNATIONAL, LTD. PROJECT NUMBER: 439C-130

STUDY DIRECTOR:

Frank J. Lezotte, B.S.
Chemist

8-7-02
DATE

MANAGEMENT:

Willard B. Nixon, Ph.D.
Director of Analytical Chemistry

8/7/02
DATE

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SUMMARY

SPONSOR:	American Chemistry Council's Brominated Flame Retardant Industry Panel
SPONSOR'S REPRESENTATIVE:	Ms. Wendy Sherman
LOCATION OF STUDY, RAW DATA AND A COPY OF THE FINAL REPORT:	Wildlife International, Ltd. Easton, Maryland 21601

WILDLIFE INTERNATIONAL, LTD. PROJECT NUMBER:	439C-130
TEST SUBSTANCE:	Tetrabromobisphenol A (TBBPA)
STUDY:	Determination of the Dissociation Constant of Tetrabromobisphenol A
TEST DATES:	Experimental Start (OECD) – September 25, 2001 Experimental Start (EPA) – January 25, 2002 Experimental Termination – February 8, 2002

SUMMARY:	The pK_a of Tetrabromobisphenol A was determined to be 9.40 (K_a=3.98 x 10^{-10}).

INTRODUCTION

Tests were performed to determine the dissociation constant of Tetrabromobisphenol A (TBBPA). This study was conducted by Wildlife International, Ltd. for American Chemistry Council's Brominated Flame Retardant Industry Panel at the Wildlife International, Ltd. analytical chemistry facility in Easton, Maryland. These tests were performed based on the procedures in the OECD Guideline for Testing of Chemicals, 112, *Dissociation Constants in Water* (1) and Product Properties Test Guidelines, OPPTS 830.7370, *Dissociation Constants in Water* (2). The experimental portion of this study began September 25, 2001 and was completed February 8, 2002. Raw data generated by Wildlife International, Ltd. and a copy of the final report are filed under Project Number 439C-130 in archives located on the Wildlife International, Ltd. site.

OBJECTIVE

The objective of this study was to determine the dissociation constant(s) of Tetrabromobisphenol A.

EXPERIMENTAL DESIGN

The direct titration method typically used for determining the dissociation constant K (expressed as its log value, pK) of Tetrabromobisphenol A in water was not found to be suitable due to the extremely low aqueous solubility of this compound. Instead, a High Performance Liquid Chromatography (HPLC) method developed at Wildlife International, Ltd was used. The test substance was purified by normal phase HPLC with fraction collection to obtain the purest available form of the test material as specified in the guideline. Test solutions each containing 50 μg/L nominal concentration of Tetrabromobisphenol A were prepared over a pH range from 6.0 to 12.0, at 0.5 pH intervals. Both the dissociated and undissociated components of Tetrabromobisphenol A were determined for each test solution by HPLC with ultraviolet detection. A calibration curve was prepared from external standards of Tetrabromobisphenol A to determine the test substance concentrations in samples.

MATERIALS AND METHODS

This study was conducted following procedures outlined in the protocol "Determination of the Dissociation Constant of Tetrabromobisphenol A". The protocol was based on procedures found in the OECD Guideline for Testing of Chemicals, Method 112 (1); and U.S. EPA Product Properties Test Guidelines, OPPTS 830.7370 (2).

Test Substance

The test substance consisted of a composite of Tetrabromobisphenol A samples received from three manufacturers. The material's identity and date received from each of the manufacturers is given below:

Manufacturer	Lot/Batch	Date Received	Wildlife International, Ltd. Identification Number
Albemarle Corporation	25938C-1	July, 27 2000	5318
Great Lakes Chemical Corporation	008JG21C	July 25, 2000	5315
Bromine Compounds Ltd.	000135	August 17, 2000	5354

The composite test substance was assigned Wildlife International, Ltd. identification number 5381 and was stored under ambient conditions. The composite test substance was shipped to Albemarle Corporation for characterization and purity analyses (Appendix 1). The conclusion of the characterization was that the composite test article was Tetrabromobisphenol A with a purity of 98.91%.

Stocks/Standards Preparation

The test material used for the study was isolated and purified from the industry composite test substance using normal phase High Performance Liquid Chromatography operated in a preparatory mode. The guidelines specify that the purest available form of the substance should be used for the study and preparative liquid chromatography was determined to be the most suitable procedure to isolate this compound from its process related impurities. A stock solution of Tetrabromobisphenol A test material was prepared by weighing 0.01004 g of the purified test substance, transferring it to a 100-mL class A volumetric flask, and diluting to volume in methanol. This primary stock solution contained 0.100 mg/mL of Tetrabromobisphenol A. This stock solution was used to fortify the samples and prepare the calibration standards.

Calibration standards containing Tetrabromobisphenol A ranging in concentration from 50.0 to 500 μg/L were prepared in a solution of 50% methanol : 50% water and analyzed with the verification sample set. Preparation of the calibration standards was performed by diluting aliquots of the appropriate stock solution as follows:

Stock Concentration mg/mL	Aliquot (µL)	Final Volume (mL)	Standard Concentration (µg/L)
0.100	50.0	100	50.0
0.100	150	100	150
0.100	250	100	250
0.100	350	100	350
0.100	500	100	500

Verification Compound

The verification compound, 1,4-Dihydroxynaphthalene, was received from TCI America on January 30, 2002, assigned Wildlife International, Ltd. identification number 5884, and stored under ambient conditions. The reference substance, a gray powder, was identified as: 1,4-Dihydroxynaphthalene, CAS Number 571-60-8, Lot Number. OGK01. The label indicated a purity of 95%.

A stock solution of 1,4-Dihydroxynaphthalene was prepared by measuring 1.0527 g of the reference substance. The test substance was transferred to a 100-mL class A volumetric flask, and adjusted to volume using methanol. This primary stock solution contained 10.0 mg a.i./mL of 1,4-Dihydroxynaphthalene. The primary stock solution was serially diluted with methanol using volumetric pipettes and volumetric flasks. The resultant stock solution was used to fortify the method verification samples and prepare the calibration standards.

Calibration standards containing 1,4-Dihydroxynaphthalene ranging in concentration from 1.00 to 15.0 mg a.i./L were prepared in a solution of 10% methanol: 90% water and analyzed with the verification sample set. Preparation of the calibration standards was performed by diluting aliquots of the appropriate stock solution as follows:

Stock Concentration mg a.i./mL	Aliquot (µL)	Final Volume (mL)	Standard Concentration (mg a.i./L)
1.00	100	100	1.00
1.00	300	100	3.00
1.00	600	100	6.00
1.00	900	100	9.00
1.00	1200	100	12.0
1.00	1500	100	15.0

Solvents, Reagents, and pH Buffer Solutions

All solvents used were HPLC grade or equivalent. Reagents used were ACS grade or equivalent. NANOpure® water (equivalent to ASTM Type II Designation D1193-91) was used in the preparation of pH buffer solutions (3). PH Buffer solutions were prepared using stock solution of Sodium Monophosphate, Borate, Potassium Dihydrogen Phosphate and Potassium Chloride standardized with the requisite amount of either 0.1 M NaOH or 0.2 M NaOH. Preparation of stock buffer solutions is described in Table 3.

Analytical Method

The method used for the analysis of the method verification samples was based upon methodology developed by Wildlife International, Ltd.

Samples of pH buffer solutions (Table 3) were fortified with the appropriate Tetrabromobisphenol A or 1, 4-Dihydroxynaphthalene stock solution and transferred to separatory funnels. Twenty mL of hexane was added to each sample, the samples were stoppered and shaken for approximately one minute, and the phases were permitted to separate. The organic (upper) layer was collected and the extraction was repeated with a second 20 mL aliquot of hexane. The organic layers from each sample were combined with the first extract of the respective sample. For samples with a pH of greater than 5, the aqueous fraction was acidified to approximately pH 3, returned to the separatory funnel and extracted as described above. Samples were rotary evaporated to approximately 0.50 – 1.0 mL using a water bath maintained at approximately 40°C. Samples were then evaporated to dryness under a gentle stream of nitrogen. The requisite volume of the appropriate dilution solvent was volumetrically added to each roundbottom flask

and swirled to dissolve residues. Aliquots from each extract were transferred to autosampler vials and submitted for HPLC/UV analysis.

Concentrations of Tetrabromobisphenol A and 1,4-Dihydroxynaphthalene in the samples were determined using high performance liquid chromatography with UV detection. The instrument, a Hewlett Packard Model 1100 High Performance Liquid Chromatograph (HPLC) was equipped with an Agilent Series 1100 Variable Wavelength Detector operated at 286 nm for Tetrabromobisphenol A and 242 nm for 1, 4-Dihydroxynaphthalene. Chromatographic separations were achieved using a YMC-Pack ODS AM column (150 mm x 4.6 mm, 3 μm particle size). Instrumental parameters for the analysis of Tetrabromobisphenol A are summarized in Table 1 and the instrumental parameters for the analysis of 1, 4-Dihydroxynaphthalene are summarized in Table 2.

Calibration Curves

Calibration standards of Tetrabromobisphenol A in a solution of 50% methanol : 50% water, ranging in concentration from 50.0 to 500 µg/L were analyzed with the sample set during the analyses of the test substance. Five concentrations of calibration standards were analyzed with the set of samples. Calibration standards of 1, 4-Dihydroxynaphthalene in a solution of 10% methanol : 90% water, ranging in concentration from 1.00 to 15.0 mg a.i./L were analyzed with the sample set during the analyses of the reference substance. Six concentrations of calibration standards were analyzed with the set of samples. Linear regression equations were generated using the peak area responses versus the respective concentrations of the calibration standards. The representative calibration curve for the analysis of Tetrabromobisphenol A is presented in Figure 1. The representative calibration curve for the analysis of 1,4-Dihydroxynaphthalene is presented in Figure 7. The concentration of the test substance and reference substance in the respective samples was determined by substituting the peak area responses of the samples into the linear regression equation. Representative chromatograms of low and high Tetrabromobisphenol A calibration standards are presented in Figures 2 and 3, respectively. Representative chromatograms of low and high 1,4-Dihydroxynaphthalene calibration standards are presented in Figures 8 and 9, respectively. Examples of calculations are presented in Table 4.

Limit of Quantitation (LOQ)

The limit of quantitation (LOQ) for the analyses of Tetrabromobisphenol A in aqueous buffer solutions was set at 20.0 µg /L based upon the product of the lowest calibration standard (50.0 µg/L) and the dilution factor of the samples (0.400). The limit of quantitation (LOQ) for the analyses of 1,4-Dihydroxynaphthalene was set at 1.00 mg a.i. /L based upon the product of the lowest calibration standard (1.00 mg a.i./L) and the dilution factor of the samples (1.00).

Determination of pK_a

pK_a determinations were made for samples with measured concentrations greater than 20%, and less than 80% of the nominal concentration. For an acidic test substance, an acid dissociation constant (K_a) and pK_a may be determined using the following equation:

$$pK_a = pH - \log([B]/[HB])$$
$$\text{Antilog}(-pK_a) = K_a$$

Where: pH = pH of test solution at any point
[B] = concentration of ionized species
[HB] = concentration of un-ionized species

The pK_a for organic phase samples was calculated using this equation where:

pH = pH of test solution at any point
[B] = Nominal Concentration (µg/L) - Measured concentration in the organic phase (µg/L)
[HB] = Measured concentration in the organic phase (µg/L)

The pK_a for aqueous phase samples was calculated using this equation where:

pH = pH of test solution at any point
[B] = Measured concentration in the aqueous phase (µg/L)
[HB] = Measured concentration in the organic phase (µg/L)

Examples of calculations are presented in Table 4.

RESULTS

For the initial pK_a determination, triplicate samples of Tetrabromobisphenol A were prepared at a concentration of 40.0 µg a.i./L in degassed NANOpure® water and titrated against standardized 0.02 N hydrochloric acid. However, due to the low aqueous solubility of the test substance, the titration method was deemed not suitable for the determination of pK_a for Tetrabromobisphenol A and an alternative method developed at Wildlife International Ltd, was employed.

Solutions of fifty µg TBBPA/L were prepared over a pH range from 6.0 to 12.0, at pH 0.5 intervals, using a stock solution containing Tetrabromobisphenol A test material in methanol. Ten mg a.i./L solutions were prepared over a pH range from 6.0 to 12.0, at pH 0.5 intervals, using a stock solution containing 1,4-Dihydroxynaphthalene in methanol. Tetrabromobisohenol A and 1,4-Dihydroxynaphthalene samples were extracted with hexane and analyzed by HPLC analysis with UV detection. Values of dissociation constant were calculated for samples with measured concentrations greater than 20% and less than 80% of the nominal concentration. Tetrabromobisphenol A pK_a values calculated for organic phase samples at pH of 9.5 and 10.0, were 9.37 and 9.43, respectively with a mean pK_a of 9.40 and a mean K_a of 3.98×10^{-10} (Table 5). Values for 1,4-Dihydroxynaphthalene pK_a calculated for organic phase samples at pH of 9.0, 9.5 and 10.0, were 9.28, 8.88, and 9.56, respectively with a mean pK_a of 9.24 and a mean K_a of 5.75×10^{-10} (Table 7). The literature value for the pK_a of 1,4-Dihydroxynaphthalene is 9.37 (4). Based on the concept of mass balance, the aqueous phase of the Tetrabromobisphenol A samples were acidified, extracted and analyzed to confirm organic phase results. The Tetrabromobisphenol A pK_a values calculated for aqueous phase samples at pH of 9.5 and 10.0, were 9.34 and 9.46, respectively with a mean pK_a of 9.40 and a mean K_a of 3.98×10^{-10} (Table 6). Because re-acidification of the 1,4-Dihydroxynaphthalene aqueous phase samples causes the samples to degrade, pK_a values were not calculated for aqueous phase samples.

REFERENCES

1. **Organisation for Economic Cooperation and Development.** 1981. Guideline for Testing of Chemicals, 112: *Dissociation Constants in Water.*

2. **U.S. Environmental Protection Agency.** 1996. Product Properties Test Guidelines, OPPTS 830.7370, *Dissociation Constants in Water.* Washington, D.C.

3. **American Society for Testing and Materials.** 1991. Standard Specification for Reagent Water. D1193-91, ASTM Section II Water and Environmental Technology, Vol. 11.01:45-47.

4. **Lange's Handbook of Chemistry, Fourteenth Edition.** 1992. p. 8.38.

Table 1

Typical HPLC Operational Parameters for the Analysis of Tetrabromobisphenol A in pH Buffer Solutions

INSTRUMENT:	Hewlett-Packard Model 1100 High Performance Liquid Chromatograph (HPLC) equipped with an Agilent Series 1100 Variable Wavelength Detector			
ANALYTICAL COLUMN:	YMC-Pack ODS-AM (150 × 4.6 mm, 3-µm particle size)			
STOP TIME:	15 minutes			
FLOW RATE:	1.000 ml/min			
SOLVENT A:	0.1% H_3PO_4			
SOLVENT B:	CH_3CN			
GRADIENT ELUTION PROFILE:	Time (min)	%A	%B	Flow (mL/min)
	0.01	90.0	10.0	1.000
	1.00	90.0	10.0	1.000
	8.00	5.0	95.0	1.000
	10.00	5.0	95.0	1.000
	10.10	90.0	10.0	1.000
	15.00	90.0	10.0	1.000
OVEN TEMPERATURE:	40°C			
INJECTION VOLUME:	150.0 µL			
TETRABROMOBISPHENOL A RETENTION TIME:	Approximately 11.7 minutes			
PRIMARY ANALYTICAL WAVELENGTH:	286 nm			

Table 2

Typical HPLC Operational Parameters for the Analysis of 1,4-Dihydroxynaphthalene in pH Buffer Solutions

INSTRUMENT:	Hewlett-Packard Model 1100 High Performance Liquid Chromatograph (HPLC) equipped with an Agilent Series 1100 Variable Wavelength Detector			
ANALYTICAL COLUMN:	YMC-Pack ODS-AM (150 × 4.6 mm, 3-µm particle size)			
STOP TIME:	13 minutes			
FLOW RATE:	1.000 ml/min			
SOLVENT A:	0.1% H_3PO_4			
SOLVENT B:	CH_3CN			
GRADIENT ELUTION PROFILE:	Time (min)	%A	%B	Flow (mL/min)
	0.01	90.0	10.0	1.000
	1.00	90.0	10.0	1.000
	8.00	5.0	95.0	1.000
	8.10	90.0	10.0	1.000
	13.00	90.0	10.0	1.000
OVEN TEMPERATURE:	40°C			
INJECTION VOLUME:	25.0 µL			
1,4-DIHYDROXYNAPHTHALENE RETENTION TIME:	Approximately 7.69 minutes			
PRIMARY ANALYTICAL WAVELENGTH:	242 nm			

Table 3

pH Buffer Solution Preparations

PH Buffer Solution	Buffer	Buffer Volume (mL)	NaOH Concentration (M)	NaOH Volume (mL)	Final Volume NANOpure® water (mL)
6.0	KH_2PO_4	50.0	0.100	5.7	100
6.5	KH_2PO_4	50.0	0.100	15.2	100
7.0	KH_2PO_4	50.0	0.100	29.6	100
7.5	KH_2PO_4	50.0	0.100	41.2	100
8.0	KH_2PO_4	50.0	0.100	46.8	100
8.5	H_3BO_3	50.0	0.100	10.3	100
9.0	H_3BO_3	50.0	0.100	21.3	100
9.5	H_3BO_3	50.0	0.100	34.4	100
10.0	H_3BO_3	50.0	0.100	43.9	100
10.5	H_3BO_3	50.0	0.200	26.0	100
11.0	Na_2HPO_4	50.0	0.100	4.1	100
11.5	Na_2HPO_4	50.0	0.100	11.3	100
12.0	KCl	25.0	0.200	6.0	100

Table 4

Example Calculations for a Representative Sample

The analytical result, percent recovery and pK_a for sample number 439C-130-9.5-1, with a nominal concentration of 50.0 µg/L in pH 9.5 pH buffer solution was calculated using the following equations:

$$\text{Concentration of Tetrabromobisphenol A sample (µg/L)} = \frac{\text{peak area - (y-intercept)}}{\text{slope}} \text{ x dilution factor}$$

$$\text{Percent of nominal concentration} = \frac{\text{Measured concentration of sample (µg/L)}}{\text{Nominal concentration of sample (µg/L)}} \text{ x 100}$$

$$pK_a = pH - \log \frac{\text{(Nominal concentration of sample (µg/L) - Measured concentration of sample (µg/L))}}{\text{Measured concentration of sample (µg/L)}}$$

Peak Area = 4.86217
Y-Intercept = 0.0518
Slope = 0.0898
Initial Volume (V_i) = 10.0 mL
Final Volume (V_f) = 4.00 mL
Dilution Factor (V_f/V_i) = 0.400
pH = 9.5

$$\text{Concentration of Tetrabromobisphenol A in sample (µg/L)} = \frac{4.86217 - 0.0518}{0.0898} \text{ x } 0.400$$

Concentration of Tetrabromobisphenol A in sample (µg/L) = 21.4

$$\text{Percent of nominal concentration} = \frac{21.4 \text{ µg/L}}{50.0 \text{ µg/L}} \text{ x 100}$$

Percent of nominal concentration = 42.9%

$$pK_a = 9.5 - \log \frac{(50.0 \text{ µg/L} - 21.4 \text{ µg/L})}{21.4 \text{ µg/L}}$$

pK_a = 9.37

Table 5

Method Recoveries for Tetrabromobisphenol A in Organic Phases

Sample		Tetrabromobisphenol A Concentration (µg/L)				
Number (439C-130-)	pH Adjustment	Fortified	Measured[1,3]	Percent Recovery[3]	pK_a[2,3]	Mean pK_a
6.0-1	6.0	50.0	51.5	103	--	
6.5-1	6.5	50.0	58.4	117	--	
7.0-1	7.0	50.0	56.1	112	--	
7.5-1	7.5	50.0	55.5	111	--	
8.0-1	8.0	50.0	52.8	106	--	
8.5-1	8.5	50.0	57.2	114	--	
9.0-1	9.0	50.0	44.6	89.1	--	
9.5-1	9.5	50.0	21.4	42.9	9.37	9.40 SD=0.0424 $K_a=3.98 \times 10^{-10}$
10.0-1	10.0	50.0	10.6	21.2	9.43	
10.5-1	10.5	50.0	< LOQ	--	--	
11.0-1	11.0	50.0	< LOQ	--	--	
11.5-1	11.5	50.0	< LOQ	--	--	
12.0-1	12.0	50.0	< LOQ	--	--	

[1] The limit of quantitation (LOQ) was 20.0 µg/L based upon the product of the lowest calibration standard (50.0 µg/L) and the dilution factor of the samples (0.400).

[2] pKa values were determined for each sample with a percent recovery between 20 and 80 %.

[3] Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

Table 6

Method Recoveries for Tetrabromobisphenol A in Aqueous Phases

Sample		Tetrabromobisphenol A Concentration (µg/L)				
Number (439C-130-)	PH Adjustment	Fortified	Measured[1,3]	Percent Recovery[3]	PK_a[2,3]	Mean PK_a
6.0-2	6.0	50.0	< LOQ	--	--	
6.5-2	6.5	50.0	< LOQ	--	--	
7.0-2	7.0	50.0	< LOQ	--	--	
7.5-2	7.5	50.0	< LOQ	--	--	
8.0-2	8.0	50.0	< LOQ	--	--	
8.5-2	8.5	50.0	< LOQ	--	--	
9.0-2	9.0	50.0	< LOQ	--	--	
9.5-2	9.5	50.0	31.0	62.0	9.34	9.40 SD=0.0849 $K_a=3.98 \times 10^{-10}$
10.0-2	10.0	50.0	37.1	74.3	9.46	
10.5-2	10.5	50.0	40.4	80.9	--	
11.0-2	11.0	50.0	44.7	89.4	--	
11.5-2	11.5	50.0	39.6	79.2	--	
12.0-2	12.0	50.0	41.7	83.4	--	

[1] The limit of quantitation (LOQ) was 20.0 µg/L based upon the product of the lowest calibration standard (50.0 µg/L) and the dilution factor of the samples (0.400).

[2] pKa values were determined for each sample with a percent recovery between 20 and 80 %.

[3] Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

Table 7

Method Recoveries for 1,4-Dihydroxynaphthalene in Organic Phases

Sample		1,4-Dihydroxynaphthalene Concentration (mg a.i./L)				
Number (439C-130-R-)	pH Adjustment	Fortified	Measured[1,3]	Percent Recovery[3]	pK_a[2,3]	Mean pK_a
6.0-1	6.0	10.0	2.35	23.5	--	
6.5-1	6.5	10.0	7.13	71.3	--	
7.0-1	7.0	10.0	8.88	88.8	--	
7.5-1	7.5	10.0	8.16	81.6	--	
8.0-1	8.0	10.0	9.19	91.9	--	
8.5-1	8.5	10.0	8.63	86.3	--	
9.0-1	9.0	10.0	6.55	65.5	9.28	9.24 SD=0.342 $K_a=5.75 \times 10^{-10}$
9.5-1	9.5	10.0	1.93	19.3	8.88	
10.0-1	10.0	10.0	2.67	26.7	9.56	
10.5-1	10.5	10.0	< LOQ	--	--	
11.0-1	11.0	10.0	< LOQ	--	--	
11.5-1	11.5	10.0	< LOQ	--	--	
12.0-1	12.0	10.0	< LOQ	--	--	

[1] The limit of quantitation (LOQ) was 1.00 mg a.i./L based upon the product of the lowest calibration standard (1.00 mg a.i./L) and the dilution factor of samples (1.00).

[2] pKa values were determined for each sample with a percent recovery between 20 and 80 %.

[3] Results were generated using Excel 2000 in full precision mode. Manual calculations may differ slightly.

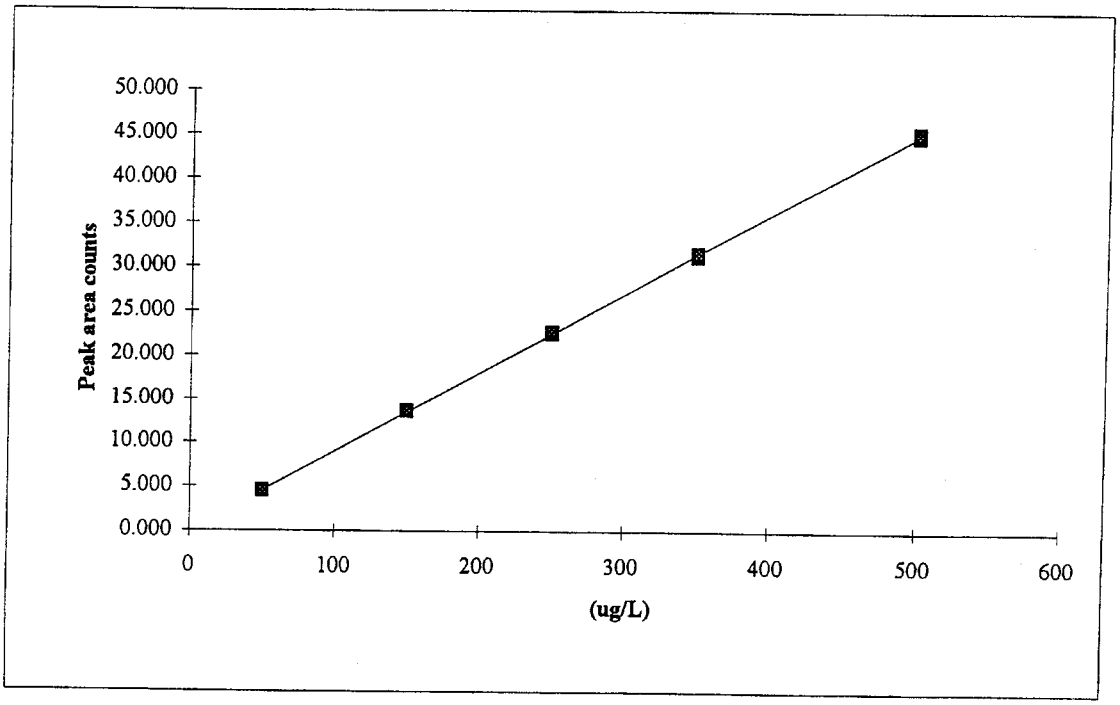


Figure 1. Representative Calibration Curve for Tetrabromobisphenol A.

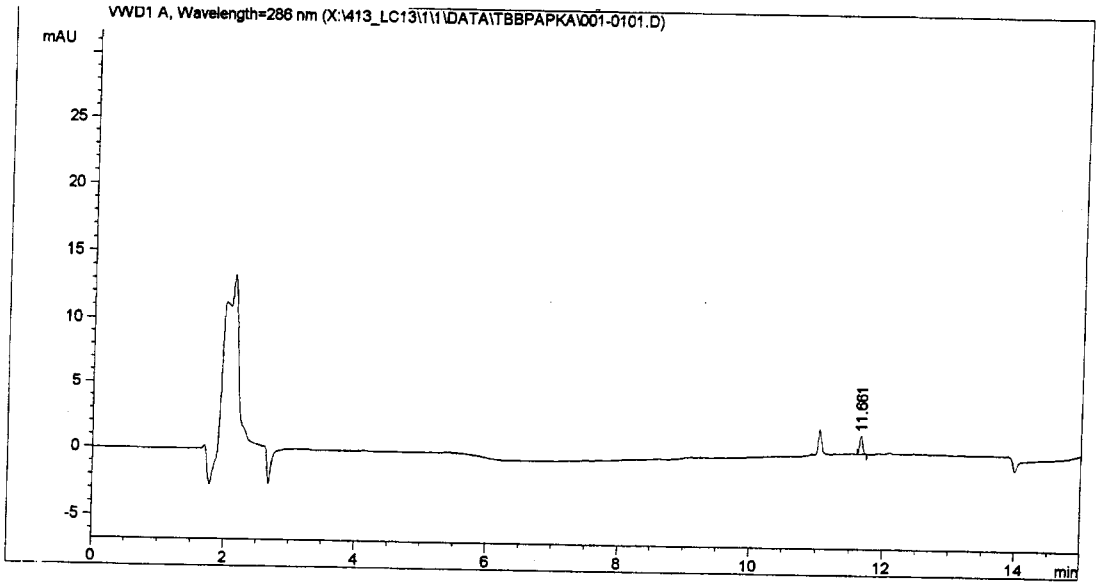


Figure 2. Representative Chromatogram of a Low-Level (50.0 µg/L) Tetrabromobisphenol A Calibration Standard.

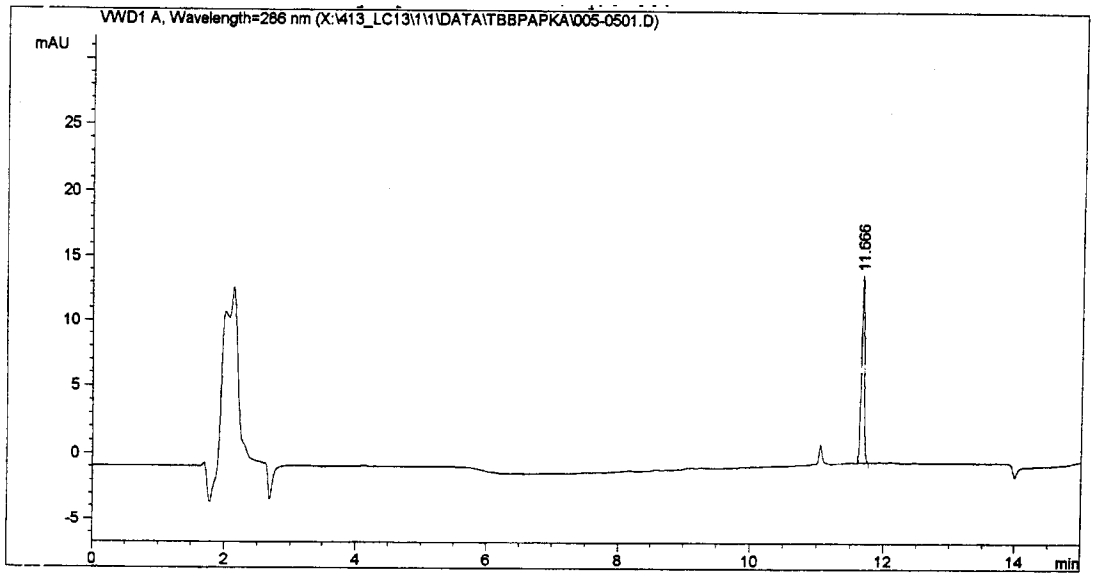


Figure 3. Representative Chromatogram of a High-Level (500 μg/L) Tetrabromobisphenol A Calibration Standard.

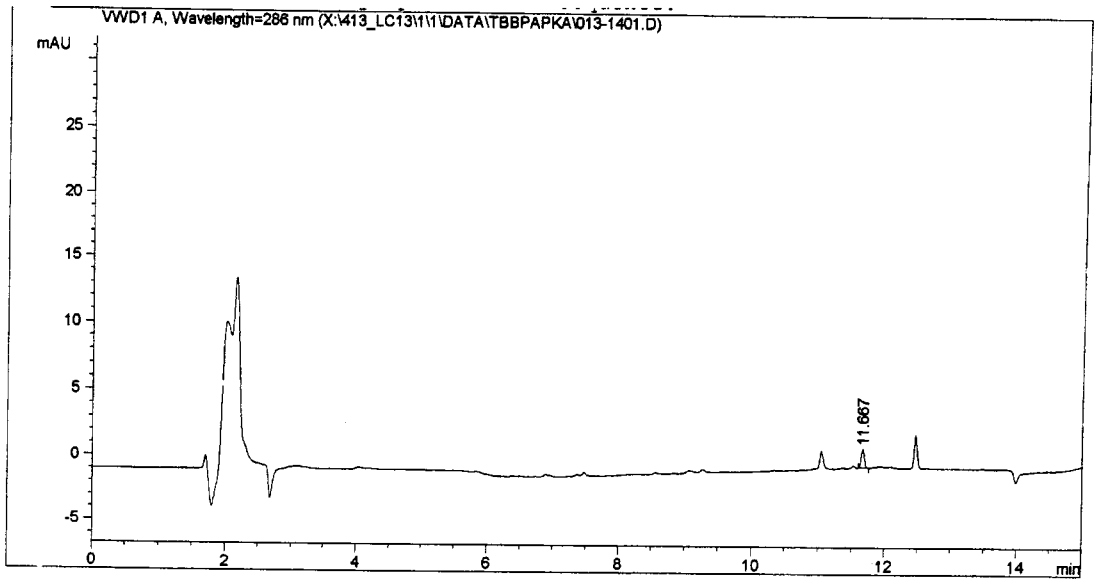


Figure 4. Representative Chromatogram of an Organic Phase Tetrabromobisphenol A Sample at pH 9.5 (439C-130-9.5-1, 50.0 μg/L nominal).

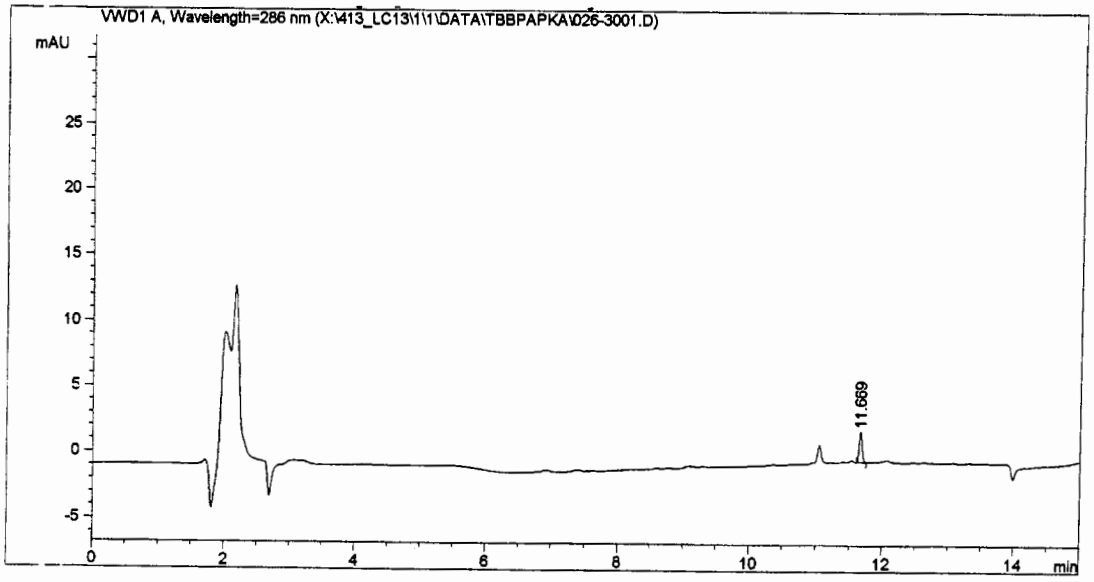


Figure 5. Representative Chromatogram of an Aqueous Phase Tetrabromobisphenol A Sample at pH 9.5 (439C-130-9.5-2, 50.0 μg/L nominal).

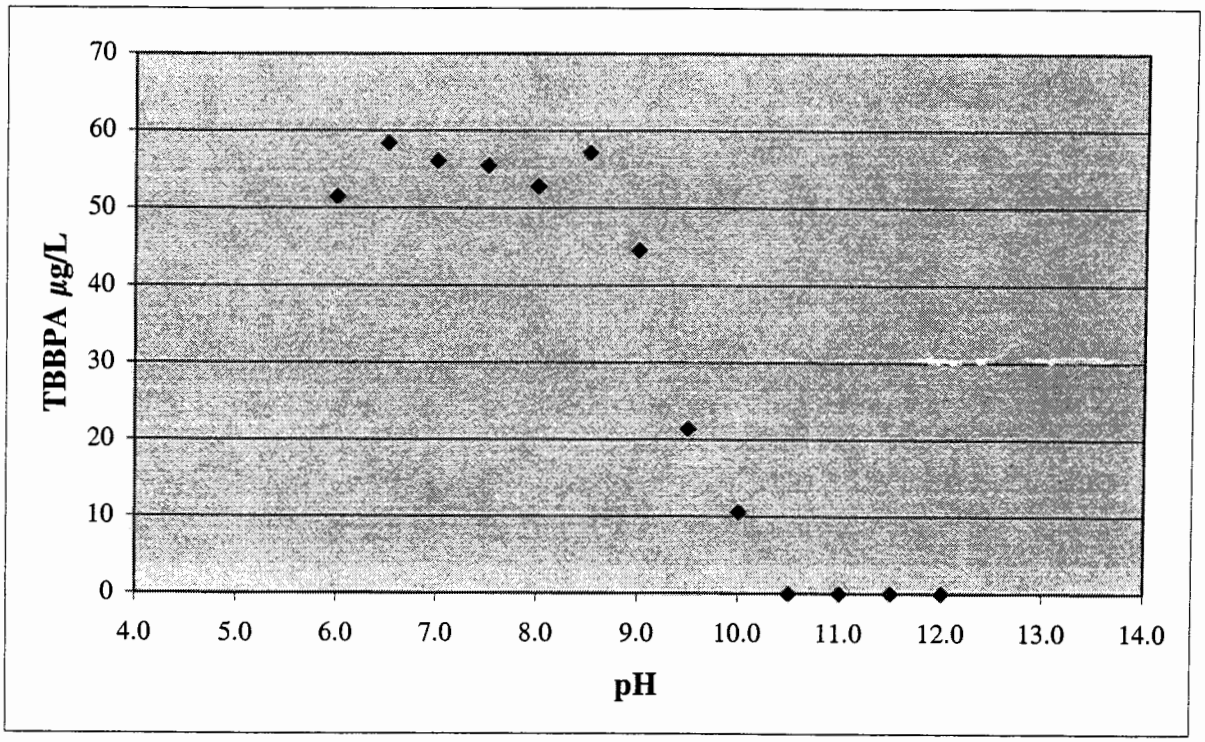


Figure 6. Representative Plot of Concentration as a Function of pH for Tetrabromobisphenol A.

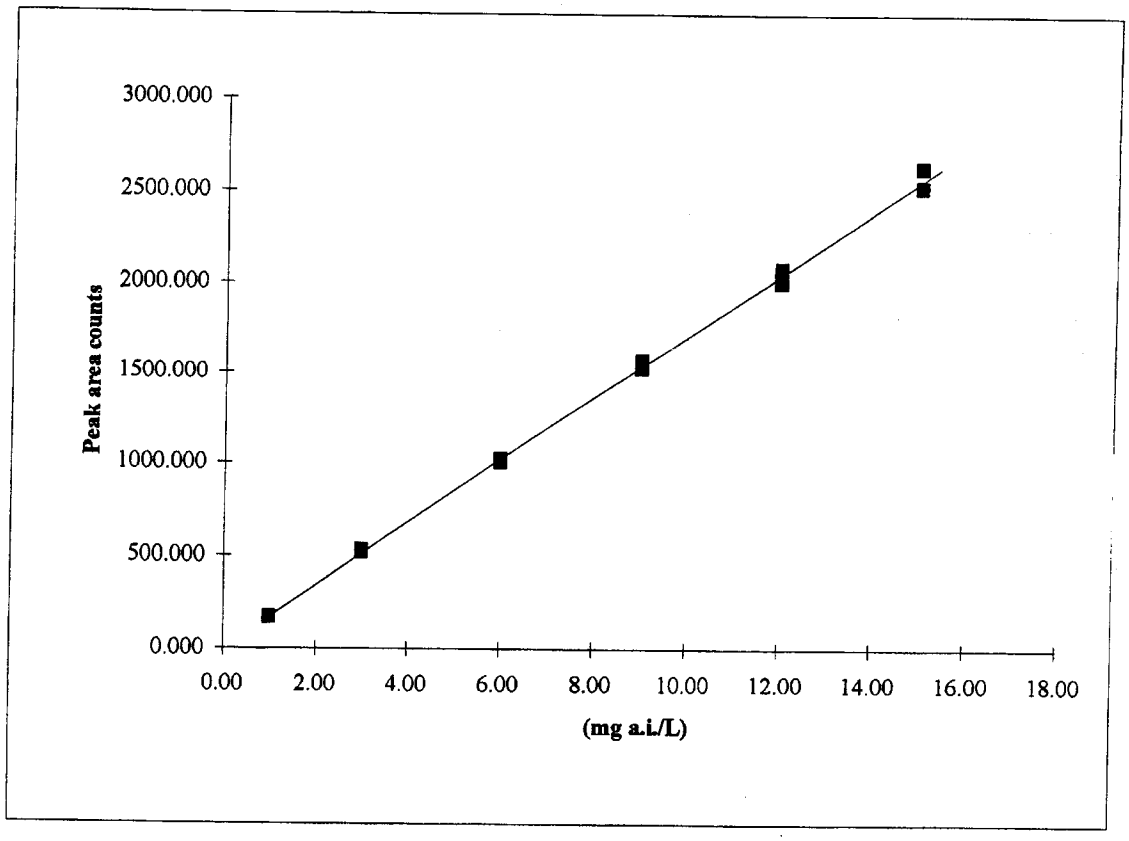


Figure 7. Representative Calibration Curve for 1,4-Dihydroxynaphthalene.

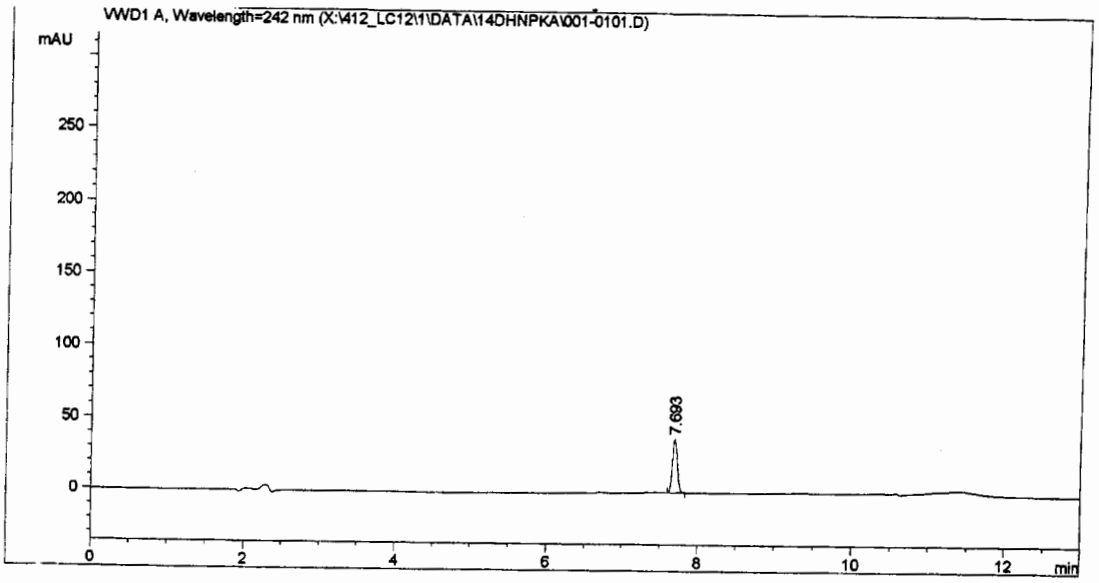


Figure 8. Representative Chromatogram of a Low-Level (1.00 mg a.i./L) 1,4-Dihyroxynaphthalene Calibration Standard.

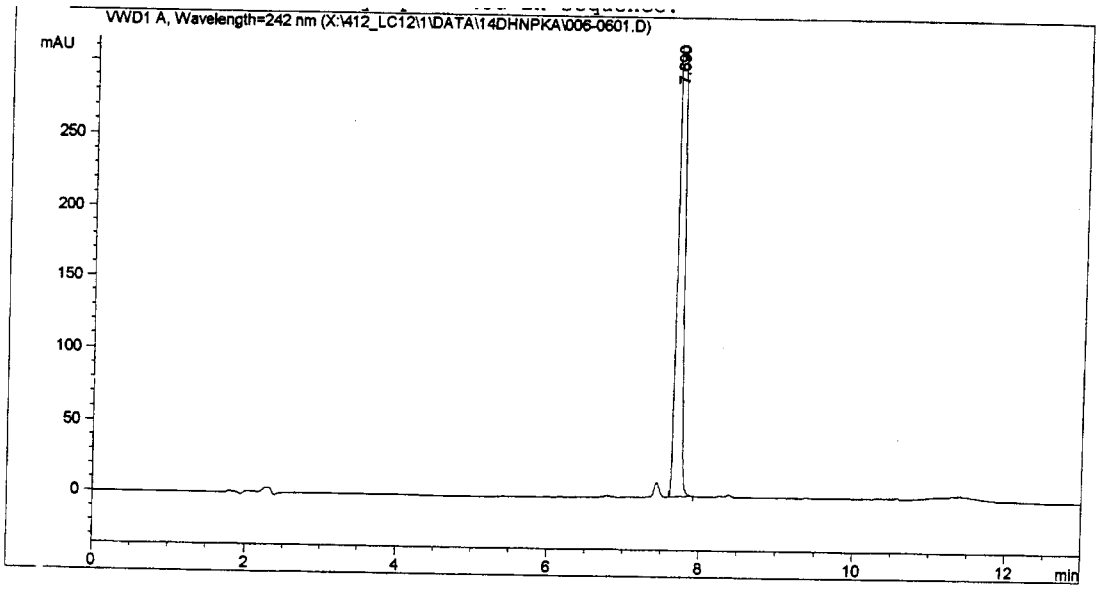


Figure 9. Representative Chromatogram of a High-Level (15.0 mg a.i./L) 1,4-Dihydroxynaphthalene Calibration Standard.

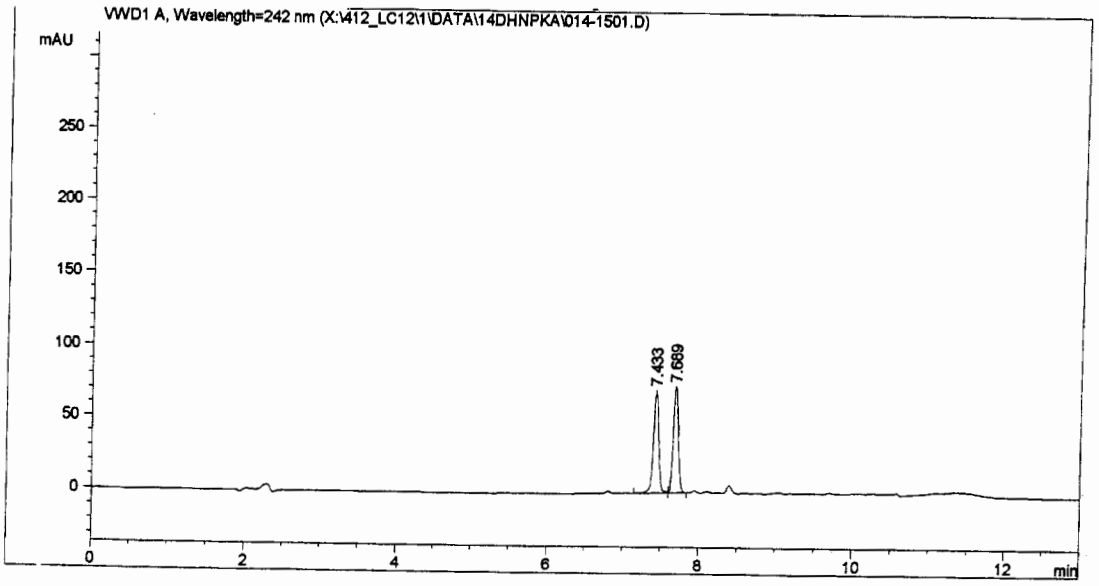


Figure 10. Representative Chromatogram of an Organic Phase 1,4-Dihydroxynaphthalene Sample at pH 9.5 (439C-130-R-9.5-1, 10.0 mg a.i./L nominal).

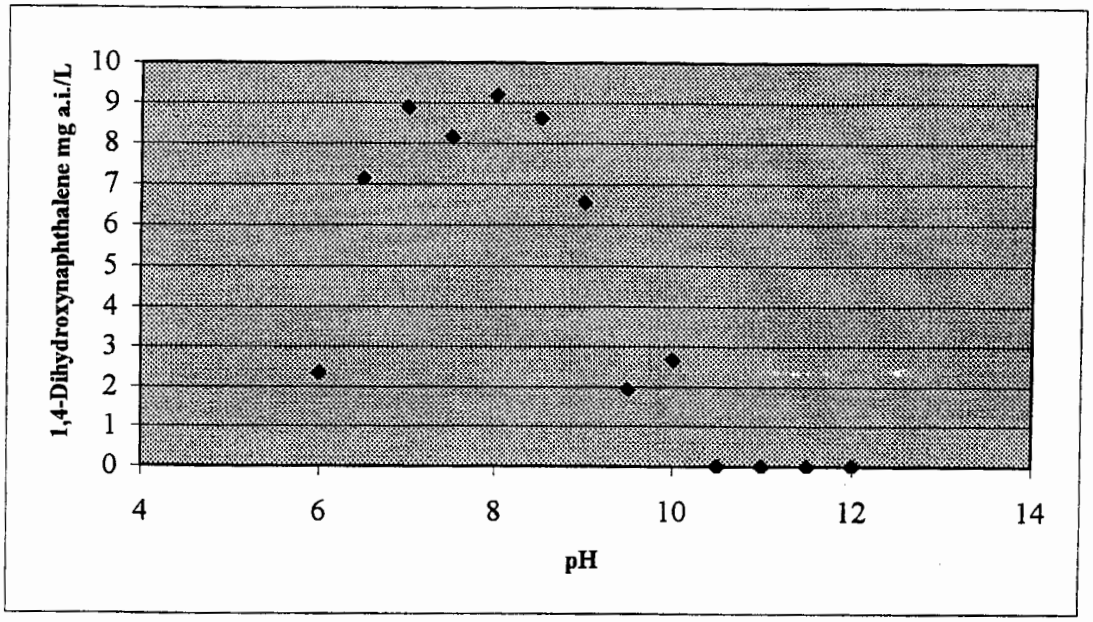


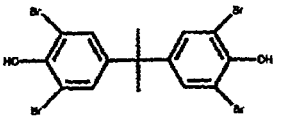
Figure 11. Representative Plot of Concentration as a Function of pH for 1,4-Dihydroxynaphthalene.

Appendix 1

Certificate of Analysis

CONCLUSIONS AND TEST ARTICLE ANALYTICAL DATA. 1.

CHEMICAL NAME: Tetrabromobisphenol-A
C.A.S. No.: 79-94-7
MOLECULAR FORMULA: $C_{15}H_{12}Br_4O_2$
PHYSICAL FORM: White Powder
CHEMICAL STRUCTURE:



ANALYSIS	RESULTS			ANALYSIS DATES	ANALYST
FT-IR	The sample FT-IR spectrum matched that of the reference spectrum. All spectra are on file with the original data.			01/04/01	W. T. Cobb
HPLC					
Sample	Purity (area% TBBPA)	Average	Difference (%) from average		
top center	98.92	98.91	<5%	01/05/01	J. S. Arroyave
middle center	98.89	98.91	<5%	01/05/01	J. S. Arroyave
bottom center	98.91	98.91	0	01/05/01	J. S. Arroyave
			Difference		
pre-study	98.91 (average)			01/05/01	J. S. Arroyave
day zero	98.95		< 5%	05/09/01	J. S. Arroyave
end-of-study	98.91		< 5%	05/09/01	J. S. Arroyave

CONCLUSION: Based on these analytical data, the test article identity was confirmed as tetrabromobisphenol-A. The composite sample was shown to be homogeneous with a purity of 98.91%. The test article was stable during the study.

Conclusions and Test Article Data. 2.

Characterization of Test Article by HPLC (Area%)

	Top Center	Middle Center	Bottom Center	Average
Tetrabromobisphenol-A	98.92	98.89	98.91	98.91
o,p'-Tetrabromobisphenol-A	0.05	0.05	0.06	0.05
2,4,6-Tribromophenol	<0.01	<0.01	<0.01	<0.01
Tribromobisphenol-A	1.03	1.06	1.03	1.04

Conclusions and Test Article Data. 3. Stability of Test Article

Sample Analysis by HPLC (area%)

	Pre-Study Sample	Day Zero Sample	End-Of-Study Sample
Terabromobisphenol-A	98.91 (average)	98.95	98.91
o,p'-Tetrabromobisphenol-A	0.05	0.04	0.03
2,4,6-Tribromophenol	<0.01	0.02	0.01
Tribromobisphenol-A	1.04	1.00	1.04

Appendix 2

Protocol, Amendment and Deviations

PROTOCOL

DETERMINATION OF THE DISSOCIATION CONSTANT OF TETRABROMOBISPHENOL A

U.S. EPA Product Properties Test Guidelines 830.7370
Dissociation Constants in Water

OECD Guideline for Testing of Chemicals, 112
Dissociation Constants in Water

Submitted to

American Chemistry Council's
Brominated Flame Retardant Industry Panel
1300 Wilson Boulevard
Arlington, Virginia 22209

Wildlife International, Ltd.

8598 Commerce Drive
Easton, Maryland 21601
(410) 822-8600

September 6, 2001

Wildlife International, Ltd.

DETERMINATION OF THE DISSOCIATION CONSTANT OF TETRABROMOBISPHENOL A

SPONSOR:	American Chemistry Council's Brominated Flame Retardant Industry Panel 1300 Wilson Boulevard Arlington, Virginia 22209
SPONSOR'S REPRESENTATIVE:	Ms. Wendy Sherman
TESTING FACILITY:	Wildlife International, Ltd. 8598 Commerce Drive Easton, Maryland 21601
STUDY DIRECTOR:	Frank Lezotte, Chemist Wildlife International, Ltd.
LABORATORY MANAGEMENT:	Willard B. Nixon, Ph.D. Director of Analytical Chemistry

FOR LABORATORY USE ONLY

Proposed Dates:

Experimental Start Date: 9-25-01	Experimental Termination Date: 10-6-01
Project No.: 439C-130	Int/Date: 9-25-01
Test Substance No.: 5381	~~Receipt~~ Date: 9-11-2001

PROTOCOL APPROVAL

STUDY DIRECTOR	DATE 9-25-01
LABORATORY MANAGEMENT	DATE 9/25/01
SPONSOR'S REPRESENTATIVE	DATE September 10, 2001

PROTOCOL NO.: 439/090601/112/SUB439

Wildlife International, Ltd.

INTRODUCTION

Wildlife International, Ltd. will determine the dissociation constant of Tetrabromobisphenol A in water at 20°C. The study will be conducted at the Wildlife International, Ltd. analytical chemistry facility in Easton, Maryland. The study will be performed following procedures in the OECD Guideline for Testing of Chemicals, 112, *Dissociation Constants in Water* (1) and Product Properties Test Guidelines, OPPTS 830.7370, *Dissociation Constants in Water* (2). Raw data for all work performed at Wildlife International, Ltd. and a copy of the final report will be filed by project number in archives located at Wildlife International, Ltd. or at an alternative location to be specified in the final report.

OBJECTIVE

The objective of this study is to determine the dissociation constant(s) of Tetrabromobisphenol A (TBBPA) in water at 20°C.

EXPERIMENTAL DESIGN

The titration method is typically used to determine the dissociation constant K (expressed as its log value, pK) of a test substance in water. This method may not be suitable for this low solubility compound and other analytical techniques may be investigated and utilized including spectrophotometric and conductometric procedures.

MATERIALS AND METHODS

Test Substance

The test substance consisted of a composite of TBBPA samples received from three manufacturers. The material's identity and date received from each of the manufacturers is given below:

Manufacturer	Lot/Batch	Date Received	Wildlife International Ltd. Identification Number
Great Lakes Chemical Corporation	008JG21C	July 25, 2000	~~5381~~ 5315 9-25-01
Albemarle Corporation	25938C-1	July 27, 2000	5318
Bromine Compounds, Ltd.	000135	August 17, 2000	5354

The composite test substance was assigned Wildlife International Ltd. identification number 5381 and is being stored under ambient conditions.

PROTOCOL NO.: 439/090601/112/SUB439

Wildlife International, Ltd.

The attached form **IDENTIFICATION OF TEST SUBSTANCE BY SPONSOR** (Appendix I) is to be used to provide available information. The Sponsor is responsible for information on the purity and composition of the test substance, as well as all information related to the safe handling of the test substance. The Sponsor also agrees to accept any unused test substance or test substance containers remaining at the end of the study.

Reagents

Water that meets ASTM Type II standards (ASTM D 1193-91) will be used (3). Other solvents may be used for preparation of stock solutions and reference standards. All solvents will be ACS reagent grade or better.

Test Procedure

A preliminary study will be performed to determine the type of titrant (HCl or NaOH) if not already known, the approximate equivalence point, and the concentration of the titrant to be used. The water used for preparation of the titrant solutions will be degassed to remove carbon dioxide prior to preparation of the titrants. A reference substance (e.g., citric acid) may be used to verify calibration of the procedure. A test solution will be prepared at a concentration not to exceed the lesser of 0.01M or half the saturation concentration in distilled water. A minimum amount of co-solvent may be used to aid solubility. The type of titrant will be determined from the pH of the test solution (i.e., < pH 7 - NaOH; > pH 7 - HCl). The test substance will be titrated with either a 0.1 N or 0.01 N solution of titrant. A titration curve will be prepared by plotting the pH of the test solution versus the milliliters (mL) of titrant added. The center point of the inflection in the titration curve will be used as the approximate equivalence point. The concentration of the titrant to be used for the definitive determination will be calculated by determining the milliliters used for titration to the equivalence point as follows:

Normality of Titrant = (0.1N titrant) X (mL of titrant used/20 mL)

For the definitive study, the test chemical, in a solution not to exceed the lesser of 0.01M or half the saturation concentration, will be titrated if feasability has been demonstrated. The solution will be maintained at 20 ± 1°C. A minimal amount of water miscible co-solvent may be added to facilitate solution. The pH of the solution and milliliters of titrant (to nearest 0.1 mL) added will be recorded after

Wildlife International, Ltd.

each addition of titrant. At least ten incremental additions will be made before the equivalence point. A plot of pH versus milliliters of titrant will be generated. Values of pK will be calculated for a minimum of ten points on the titration curve. Titration will be carried out past the equivalence point. The equivalence point is defined as that section of the titration curve in which a small addition of titrant results in a large change in pH. The test chemical will be titrated a minimum of three times. The dissociation constant (K) and pK (log(K)) will be determined as follows:

$pK_a = pH - \log([B]/[HB])$ for acidic test substances

$pK_a = pH - \log([HB]/[B])$ for basic test substances

Antilog $(pK_a) = K_a$

where pH = pH of test solution at any point
[B] = concentration of ionized species
[HB] = concentration of un-ionized species

The mean and standard deviation of values will be reported. When the average pK_a values of the replicates differ by more than ± 0.1 log units, additional determination will be made. A plot of pH versus volume of standard base or acid will be included along with appropriate tabulated values.

If the direct titrimetric approach proves not to be possible, a description of the alternative procedure will be added by protocol amendment.

Sample Handling and Safety

The Sponsor will identify any special handling or safety precautions to be used with the above referenced test substance. All normal precautions with respect to handling and storage will be taken.

Sample and Test Substance Retention

Upon completion of testing, portions of the test substance used as part of this study will be disposed of in accordance with federal, state and local regulations. Any unused portion of the test substance will be returned to the Sponsor.

Wildlife International, Ltd.

RECORDS TO BE MAINTAINED

Records to be maintained for data generated by Wildlife International, Ltd. will include, but not be limited to:

1. A copy of the signed protocol.
2. Identification and characterization of the test substance, if provided by the Sponsor.
3. Dates of initiation and completion of the study.
4. Dates of experimental start and termination.
5. Storage conditions of the test substance.
6. Test substance use log.
7. Concentration calculations and records of solution preparation.
8. Titrator operating conditions.
9. Statistical calculations.
10. Test conditions.
11. A copy of the final report.

FINAL REPORT

A final report of the results of the study will be prepared by Wildlife International, Ltd. The report will include, but not be limited to the following, when applicable:

1. Name and address of the facility performing the study.
2. Dates upon which the study was initiated and completed.
3. A statement of compliance signed by the Study Director addressing any exceptions to Good Laboratory Practice Standards.
4. Purpose and procedure, as stated in the approved protocol, including all amendments and deviations to the protocol.
5. A copy of the protocol and protocol amendments.
6. The test substance identification, including name, chemical abstract number or code number, purity, composition, empirical formula, molecular formula, manufacturer's lot/batch number, dissociation in water, method of analysis, and any other information provided by the Sponsor.
7. Description of the test method or reference to the method used along with any modifications made.
8. Titrant volumes, measured values of pKa and plots of pH versus titrant volumes.
9. Description of any problems experienced and how they were resolved.

Wildlife International, Ltd.

10. A statement prepared by the Quality Assurance Unit listing the dates that study inspections and audits were made and findings reported to the Study Director and Management.

CHANGING OF PROTOCOL

Planned changes to the protocol will be in the form of written amendments signed by the Study Director and the Sponsor. Amendments will be considered as part of the protocol and will be attached to the final protocol. Any other changes will be in the form of written deviations filed with the raw data. All changes to the protocol will be indicated in the final report.

GOOD LABORATORY PRACTICES

This study will be conducted in accordance with Good Laboratory Practice Standards for EPA (40 CFR Part 160 and/or 792) and OECD Principles of Good Laboratory Practices (ENV/MC/CHEM (98) 17). Each study conducted by Wildlife International, Ltd. is routinely examined by the Wildlife International, Ltd. Quality Assurance Unit for compliance with Good Laboratory Practices, Standard Operating Procedures and the specified protocol. A statement of compliance with Good Laboratory Practices will be prepared for all portions of the study conducted by Wildlife International, Ltd. The Sponsor will be responsible for compliance with Good Laboratory Practices for procedures performed by other laboratories.

Wildlife International, Ltd.

REFERENCES

1. **Organisation for Economic Cooperation and Development.** 1981. Guideline for Testing of Chemicals, 112: *Dissociation Constants in Water.*

2. **Product Properties Test Guidelines.** 1996. OPPTS 830.7370. *Dissociation Constants in Water.*

3. **American Society for Testing and Materials.** 1991. Standard Specification for Reagent Water. D1193-91, ASTM Section II Water and Environmental Technology, Vol. 11.01: 45-47.

Wildlife International, Ltd.

APPENDIX I

IDENTIFICATION OF TEST SUBSTANCE BY SPONSOR

To be Completed by Sponsor

I. Test Substance Identity (name to be used in the report): Tetrabromobisphenol-A

Reference Standard (if applicable): N/A

Test Substance Sample Code or Batch Number: Wildlife International, Ltd. No.5381

Test Substance Purity (% Active Ingredient): 98.91% Expiration Date: August 1, 2002

II. Test Substance Characterization

Have the identity, strength, purity and composition or other characteristics which appropriately define the test substance and reference standard been determined prior to its use in this study in accordance with GLP Standards? X Yes ___ No

III. Test Substance Storage Conditions

Please indicate the recommended storage conditions at Wildlife International, Ltd..

Ambient temperature; protect from light and moisture

Has the stability of the test substance under these storage conditions been determined in accordance with GLP Standards? X Yes ___ No

Other pertinent stability information:

N/A

IV. Toxicity Information:

Mammalian: Rat LD50 > 5 g/kg Mouse LD50: > 10 g/kg

Aquatic:	Invertebrate Toxicity (EC/LC50)	Fish Toxicity (LC50)
	N/A	N/A

Other Toxicity Information (including findings of chronic and subchronic tests):

V. Classification of the Compound:

_____Insecticide _____Herbicide _____Fungicide

_____Microbial Agent _____Economic Poison

Other: Halogenated flame retardant

Project Number 439C-130

Wildlife International, Ltd.

The original document has been misplaced. This copy now serves as the original document. JH 1-30-02

AMENDMENT TO STUDY PROTOCOL

STUDY TITLE: Determination of the Dissociation Constant of Tetrabromobisphenol A

PROTOCOL NO.: 439/090601/112/SUB439 **AMENDMENT NO.:** 1

SPONSOR: American Chemistry Council's Brominated Flame Retardant Industry Panel **PROJECT NUMBER:** 439C-130

SPONSOR STUDY NO.: NA **EFFECTIVE DATE:** September 25, 2001

AMENDMENT: Test Procedure, Page 5

Change: The dissociation constant (K) and pK (log(K)) will be determined as follows:

To: The dissociation constant (K) and pK (-log (K)) will be determined as follows:

REASON: pK is defined as the negative log of the dissociation constant.

AMENDMENT: Test Procedure, Page 5

Change: $pK_a = pH - \log ([HB]/[B])$

To: $pK_b = pH - \log ([HB]/[B])$

REASON: the subscript identifies the pH of the test substance. Since the formula listed is for basic test substances, the value obtained would be a pK_b.

AMENDMENT: Test Procedure, Page 5

Change: Antilog $(pK_a) = K_a$

To: Antilog (-pK) = K

REASON: The dissociation constant is defined as the antilog of the negative pK value. Additionally, since the pK value can be either acidic or basic the formula should be stated in generic terms.

Reviewed by QA GHC 10-4-01

Project Number 439C-130

Wildlife International, Ltd.

STUDY DIRECTOR	DATE 10-4-01
LABORATORY MANAGEMENT	DATE 10/4/01
SPONSOR'S REPRESENTATIVE	DATE 7/30/02

07/30/2002 09:52 FAX 410 822 8915 WILDLIFE INT LTD 002

Project Number 439C-130

Wildlife International, Ltd.

The original amendment has been misplaced. This copy now serves as the original document. FA 7-30-02

AMENDMENT TO STUDY PROTOCOL

STUDY TITLE: Determination of the Dissociation Constant of Tetrabromobisphenol A

PROTOCOL NO.: 439/090601/112/SUB439 **AMENDMENT NO.:** 2

SPONSOR: American Chemistry Council's Brominated Flame Retardant Industry Panel **PROJECT NUMBER:** 439C-130

SPONSOR STUDY NO.: NA **EFFECTIVE DATE:** January 8, 2002

AMENDMENT: Test Procedure, Page 5

ADD:

A second analytical procedure will be performed to collaborate the dissociation constant obtained by the titration procedure. The test substance will be purified using normal phase high performance liquid chromatography (HPLC) with fraction collection. Fifty ppb nominal concentration solutions of the purified test substance will be prepared over a pH range of 2 to 12. Each aqueous solution will be extracted twice with hexane. The extraction solvent is evaporated, the sample is reconstituted in 50% methanol: 50% water, and analyzed by HPLC. For samples at pH ≥ 6, the remaining aqueous phase will be acidified, re-extracted with hexane, and processed as described above.

REASON:

Confirmation of the dissociation constant determined by the titration procedure.

STUDY DIRECTOR — DATE 1-8-02

LABORATORY MANAGEMENT — DATE 1/8/02

Wendy K. Sherman
SPONSOR'S REPRESENTATIVE — DATE 7/30/02

KH 1-8-02

Wildlife International, Ltd.

DEVIATION TO STUDY PROTOCOL

STUDY TITLE: Determination of the Dissociation Constant of Tetrabromobisphenol A

PROTOCOL NO.: 439/090601/112/SUB439 **DEVIATION NO.:** 1

SPONSOR: American Chemistry Council's Brominated Flame Retardant Industry Panel **PROJECT NO.:** 439C-130

DATE OF DEFACTO DEVIATION: September 26, 2001

DEVIATION: The titrant used in the definitive test was prepared at an incorrect concentration. The proper titrant concentration should have been 0.01N hydrochloric acid. The titrant used was 0.02N. hydrochloric acid.

REASON: Calculation error

IMPACT: Since at least ten data points were collected prior to the equivalence point of the titrations, there is no impact to the study.

STUDY DIRECTOR
Frank J. Lezotte, B.S.

10-4-01
DATE

LABORATORY MANAGEMENT
Willard B. Nixon, Ph.D.

11/4/01
DATE

Wildlife International, Ltd.

DEVIATION TO STUDY PROTOCOL

STUDY TITLE: Determination of the Dissociation Constant of Tetrabromobisphenol A

PROTOCOL NO.: 439/090601/112/SUB439 **DEVIATION NO.:** 2

SPONSOR: American Chemistry Council's Brominated Flame Retardant Industry Panel **PROJECT NO.:** 439C-130

DATE OF DEFACTO DEVIATION: January 25, 2002

DEVIATION: Fifty ppb nominal concentration solutions were prepared over a pH range of 6 to 12.

REASON: Previous data indicated that the pKa would be greater than 7. The pH solutions less than 6 were not necessary for the determination of pKa.

IMPACT: Since the pKa was greater than 7, there was no impact to the study.

STUDY DIRECTOR
Frank J. Lezotte, B.S.

2-28-02
DATE

LABORATORY MANAGEMENT
Willard B. Nixon, Ph.D.

2/28/02
DATE

Appendix 3

Personnel Involved in the Study

The following key Wildlife International, Ltd. personnel were involved in the conduct or management of this study:

1. Willard B. Nixon, Ph.D., Director, Analytical Chemistry
2. Raymond L. VanHoven, Ph.D., Scientist
3. Timothy Z. Kendall, M.S., Supervisor
4. Frank J. Lezotte, B.S., Chemist