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Microfiche No.		
OTS0001071		
New Doc ID		Old Doc ID
FYI-OTS-0794-1071		
Date Produced	Date Received	TSCA Section
12/07/81	07/14/94	FYI
Submitting Organisation		
MONSANTO CO		
Contractor		
Document Title		
INITIAL SUBMISSION: 2-MERCAPTOBENZOTHIAZOLE ENVIRONMENTAL MONITORING WITH COVER LETTER DATED 07/25/84		
Chemical Category		
2-MERCAPTOBENZOTHIAZOLE		

7/21-0794-00107/



WI-94-001071
INIT 07/14/94

Monsanto



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MONSANTO POLYMER PRODUCTS CO.
800 N. Lindbergh Boulevard
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July 25, 1984

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Dr. Louis Borghi
Staff Scientist
Dyna-Mac Corporation
11140 Rockville Pike
Rockville, MD 20852

Dear Dr. Borghi:

Attached is a copy of the environmental monitoring study on mercapto-benzothiazole (MBT) which we promised previously to forward to you when it became available.

The study concluded that levels of MBT in surface water samples collected from 18 sites in the eastern United States were all less than 10 micrograms per liter.

Please feel free to call if you have any questions.

Sincerely,

Bernard J. Hill
Product Acceptability Manager
Rubber Chemicals

Attachment

cc: J. R. Condray

15.1878/SS.1

December 7, 1981

**2-MERCAPTOBENZOTHIAZOLE
ENVIRONMENTAL MONITORING**

TO :

The following is an abbreviated report summarizing our efforts to date to determine environmental surface water concentrations of 2-mercaptobenzothiazole.

SUMMARY

A method of analysis for 2-mercaptobenzothiazole (2-MBT) has been developed with a limit of detection of 1 µg/L using environmental surface water. Maximum recovery of 2-MBT from spiked surface water samples is obtained when the samples are analyzed the same day as they are spiked. Under these conditions, mean percent recoveries of 40.2, 72.5 and 82.0 were obtained with spiking levels of 1, 5, and 10 µg/L, respectively.

The mean concentration of MBT in surface waters in the United States is less than the detection limit based upon samples from 18 sites. Recovery of MBT from field and laboratory spiked samples obtained as part of the sample collection procedure averaged 9 percent at the 1.0 µg/L level. This low level of recovery is attributed to chemical degradation of MBT after spiking and prior to analysis. On the basis of this information, it is not possible to assign a precise limit of detection. It is thought to be at least 10 µg/L. A recovery of 82 percent was observed during method validation at a spiking level of 10 µg/L. It is concluded that concentrations of MBT in surface water are less than 10 µg/L. Further method validation is needed to eliminate the uncertainty concerning the limit of detection.

MATERIALS AND METHODS

Surface water samples were collected from 18 sites in the eastern U.S. as part of the National Aquatic Monitoring Program. Detailed maps and a description of sampling methodology can be found in the 1981 method and protocol. Sample collection at each site provided three replicate samples, a field blank, a field spike and a lab spike. (Lab spikes were not prepared for the sites 05, 09, and 13 due to sample breakage or loss.) One sample (#5) at each site was spiked in the field at a concentration of 1.27 µg/L for quality assurance purposes. Samples were preserved by adjusting the pH to 3.5 immediately after collection.

The water samples were analyzed according to a validated method approximately 1 week after collection. The method includes adsorption

onto SEP-PAK filters, desorption into acetonitrile, concentration, and quantification by HPLC with a UV detector. The detection limit for MBT was found to be 1 µg/L in natural waters (Appendix I, Table 1, see comments in Results sections on detection limit).

RESULTS AND DISCUSSION

A summary of MBT concentration in water samples collected at 16 sites in the United States as well as the average percent recovery of MBT from laboratory and field spikes is presented in Table 1. MBT was not detected in any of the 88 water samples or 18 field blanks collected. The limit of detection, previously determined during method validation was reported to be 1 µg/L. However, the average percent recovery of surface water samples spiked in the field and in the laboratory was observed to be 6 and 12 percent, respectively. Percent recoveries of 40, 72 and 82 were observed for spiking levels of 1.02, 5.1 and 10.2 µg/L using river water during method validation (Appendix I-Table 1). The reason for the low percent recovery of MBT from the water samples is not known, but may be due to the chemical instability of MBT in water and biodegradation. Water samples during method validation were analyzed within 4-6 hours after being spiked. The samples were analyzed 1-7 days after the samples were spiked. During this interval, it appears that MBT was chemically transformed, or sorbed to particulates or glassware. The precise limit of detection of this method cannot be determined at the present. Additional method validation is needed using spiked natural water samples which are allowed to age for specific periods of time.

CONCLUSION

This product is only moderately toxic to aquatic organisms and does not appear to present a concern to the aquatic environment.

TABLE 1. MEASURED HBT CONCENTRATION IN SURFACE WATERS

Site	Mean Concentration (ppb)	Lab + Spike Average % Recovery
03 Delaware Bay*	< 1.20	11.5
04 Delaware River*	< 1.02	5.5
05 Chesapeake Bay*	< 1.4	5 ^a
06 Potomac River*	< 1.4	8.5
07 Eastern Lake Erie**	-	-
08 San Francisco Bay*	< 1.02	0
09 Southern Lake Michigan**	< 1.02	0 ^a
10 Northern Lake Michigan**	< 1.02	14.0
11 Lake Huron**	< 1.02	15.5
12 Lake Superior**	< 1.02	20.0 ^a
13 Mississippi River, Memphis**	< 1.02	0
14 Mississippi River, Alton**	< 1.40	11.5
15 Mississippi River, St. Paul**	< 1.02	18.0
16 Missouri River**	< 1.40	4.5
17 Illinois River**	< 1.02	13.0
18 Eastern Lake Erie**	< 1.02	0.5
19 Charles River*	< 1.02	16.5
20 Lake Sylvan**	< 1.02	0
21 Lake Oneida**	< 1.02	7.0

- ** Freshwater Sites
* Estuarine/Saltwater Site
^a Field spike only
- No samples collected

APPENDIX I

- Method Validation
- Summary of Data Pertaining to Limit of Detection

TABLE 1.° METHOD VALIDATION DATA

Spike (µg/L)	Amount Found (µg/L)	Percent Recovery (Accuracy)	Standard Deviation	° R.S.D. (Precision)
2-Mercaptobenzothiazole				
1.02	0.410	40.2	0.03	8%
5.09	3.69	72.5	0.66	18%
10.18	8.32	82.0	1.8	22%

0 0 0 0

ANALYSIS REPORT

To: _____

From: _____

Comments:

1. The detection limits are calculated from the lowest validated level (in Miami River water). For the 2-MBTZ, validation was attempted at the 0.4 µg/L level and the mean recovery was only 8%. Therefore, the 1.02 µg/L level (40% recovery) was taken as the lowest validated level. Since recovery was so poor, even at this level, it was thought that spiking the samples at slightly above this level would give a better estimation of the matrix effects that would be encountered in the actual samples and a better estimation of what the detection limit actually is would be gained. As can be seen from the data, the 2-MBTZ was lost from most of the field spiked samples and overall recovery from both lab and field spikes was extremely poor, resulting in detected levels below the lowest validated level. Since 80% recovery was attained for 2-MBTZ at the 1.02 µg/L level from distilled water, the sample matrix obviously plays a large role in recovery of spikes, probably due to reactivity and/or instability of the compound. It is thought that this data is at least one piece of evidence that if the 2-MBTZ were present in the aquatic environment at the 1 µg/L level, it would not exist (at least in its present form) for more than a few weeks.

CONTINUED

Analyst _____

Results Checked By _____

00009

2. Sample sites 5, 9, and 13 did not have a lab spike. This is due to the fact that one of the bottles from site 5 was broken in transit, one of the samples sent for site 9 was a group 1 bottle and contained methylene chloride and so was not analyzed and the site 13 samples were prepared for analysis before it was realized that none of them had been spiked. On all of the other samples, bottle 1 was used as a lab spike.
3. In some cases the integrator named a peak 2-mercaptobenzothiazole when this was not the case. Close scrutiny of the spikes revealed 2 separate peaks or a broad leading edge denoting 2 fused peaks - not a single larger peak which would tend to confirm identity.

STATISTICAL ANALYSIS OF SPIKES:

2-Mercaptobenzothiazole

	Lab Spikes	Field Spikes
Average Recovery	12.3%	6%

CONTINUED

SAMPLE CALCULATION:

The complete methodology, calibration, validation and method of calculation is contained in Report - "Method for the Determination of and 2-Mercaptobenzothiazole in Natural Waters for - National Aquatic Monitoring Program."

Figure 1 shows the calibration curves, correlation factors and the response factors for 2-mercaptobenzothiazole.

Calculation of Sample Concentration:

$$C_{(a)} = \frac{(A_{(a)}) (VF_{(a)})}{RF_{(s)}}$$

where $C_{(a)}$ = Concentration of the analyte ($\mu\text{g/L}$)

$A_{(a)}$ = Area Counts of the analyte

$RF_{(s)}$ = Response Factor of standard (Area Counts/ $\mu\text{g/L}$)

$VF_{(a)}$ = Volume Factor of analyte ($\frac{\text{Volume of extract (1 ml)}}{\text{Volume of Sample}}$)

Calculation of Spike Concentration:

(assume $VF_{(a)} = 0.001$)

a = 2-mercaptobenzothiazole

$$C_a = \frac{A_{(a)} (0.001)}{42.565}$$

$$C_a = \frac{(50,712 \text{ Area Counts}) (0.001)}{42.565 \frac{\text{Area Counts}}{\mu\text{g/L}}}$$

$$C_a = 1.19 \mu\text{g/L}$$

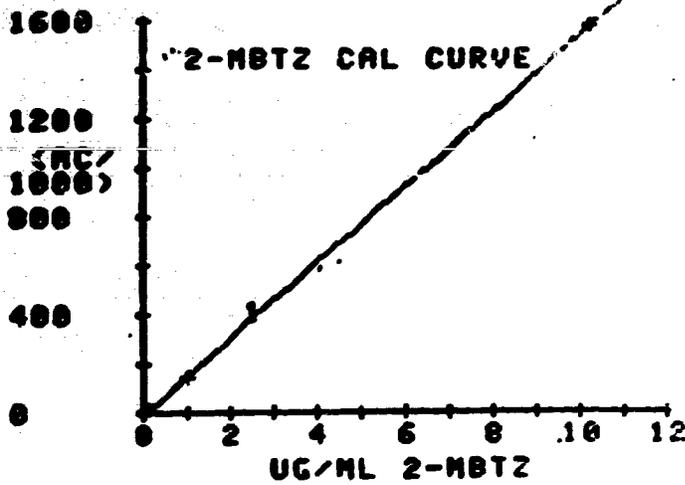
FIGURE 1

2-MERCAPTOBENZOTHIAZOLE
CALIBRATION CURVE DATA

I	X(I)	Y(I)
1	0.1020	13.2340
2	1.0200	144.1040
3	10.1800	1575.0930

ADV: LINEAR REG: CODE 1
SOURCE/DF SS MS F
TOTAL 21501420.0
REG 11501349.2.1 999.9
RESID 1 70.8 70.8
R SQUARE = 1.000

$$\hat{Y} = -0.273 + 155.481 X$$



APPENDIX II

- Sample numbers ending in -1 were spiked in the laboratory at 2.04 $\mu\text{g/L}$.
- Sample numbers ending in -5 were spiked in the field at 1.27 $\mu\text{g/L}$
- The limit of detection, based on laboratory validated spiking of river water is 1.02 $\mu\text{g/L}$. However, the limit of detection used in this report is 10 $\mu\text{g/L}$ because of the low recoveries observed for the field spiked samples.

ANALYSIS REPORT FORM

Date 1/10/81 Analyte 2-mercaptobenzothiazole
 Analyst(s) _____ NBP # _____

Type of Sample
 (check one)
 Water
 Sediment

Study No.	Log No.	Amount Found (ppb)	Comments	
			Spike	% Recovery
	WFB-5-14-81-12-G2-1	<1.02		
	W-5-14-81-12-G2-1	1.02 (0.40)*	2.04	20
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02		
	WFB-5-7-81-13-G2-1	<1.02	1.27	0
	W-5-7-81-13-G2-1	<1.02		
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0
	WFB-5-4-81-14-G2-1	<1.40		
	W-5-4-81-14-G2-1	1.40 (0.47)*	2.04	23
	-2	<1.40		
	-3	<1.40		
	-4	<1.40		
	-5	<1.40	1.27	0
	WFB-5-12-81-15-G2-1	<1.02		
	W-5-12-81-15-G2-1	<1.02	2.04	0
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	1.02 (0.46)*	1.27	36

Reviewed by: _____

Comments: _____
 *Concentration of 2-mercaptobenzothiazole detected in excess of the amount spiked into the sample.

ANALYSIS REPORT FORM

Date 7/2/81 Analyte 2-Mercaptobenzothiazole Type of Sample

Analyst(s) _____ NBP # _____ (check one)

 Water
 Sediment

Study No.	Log No.	Amount Found (ppb)	Comments	
			Spike	% Recovery
	WFB-5-12-81- 08-G2-1	<1.02		
	W-5-12-81-08- G2-1	<1.02	2.04	0
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0
	WFB-5-17-81- 09-G2-1	<1.02		
	W-5-17-81-09- G2-1	G-1 Bottle shipped - not analyzed		
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0
	WFB-5-15-81- 10-G2-1	<1.02		
	W-5-15-81- 10-G2-1	<1.02 (0.58)*	2.04	28
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0
	WFB-5-15-81- 11-G2-1	<1.02		
	W-5-15-81-11- G2-1	<1.02 (0.47)*	2.04	23
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02 (0.104)*	1.27	8

Reviewed by: _____

Date: _____

Comments: *Concentration of 2-mercaptobenzothiazole detected in excess of
the amount spiked into the sample.

ANALYSIS REPORT FORM

Date 1/1/80 Analyte 2-mercaptobenzothiazole
 Analyst(s) _____ NBP # _____

Type of Sample
 (check one)
 Water
 Sediment

Study No.	Log No.	Amount Found (ppb)	Comments	
			Spike	% Recovery
	WFB-5-6-81-03			
	-G2-1	<1.20		
	W-5-6-81-03-			
	G2-1	<1.20 (0.33)*	2.04	16
	-2	<1.20		
	-3	<1.20		
	-4	<1.20		
	-5	<1.20 (0.89)*	1.27	7
	WFB-5-7-81-04			
	-G2-1	<1.02		
	W-5-7-81-04-			
	G2-1	1.02 (0.12)*	2.04	6
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02 (0.06)*	1.27	5
	WFB-5-5-81-05			
	-G2-1	<1.4		
	W-5-5-81-05-			
	G2-1	Bottle Broken in Transit		
	-2	<1.4		
	-3	<1.4		
	-4	<1.4		
	-5	<1.4 (0.32)*	1.27	25
	WFB-5-5-81-06			
	-G2-1	<1.4		
	W-55-81-06-			
	G2-1	<1.4 (0.34)	2.04	17
	-2	<1.4		
	-3	<1.4		
	-4	<1.4		
	-5	<1.4	1.27	0

Reviewed by: _____

Date: _____

Comments: _____
 *Concentration of 2-mercaptobenzothiazole detected in excess of the amount spiked into the sample.



ANALYSIS REPORT FORM

Date 7/2/81 Analyte 2-Mercaptobenzothiazole Type of Sample
 Analyst(s) _____ NBP # _____ (check one)
 Water
 Sediment

Study No.	Log No.	Amount Found (ppb)	Comments	
			Spike	% Recovery
	WFB-5-4-81- 16-G2-1	<1.40		
	W-5-4-81-16- G2-1	<1.40 (0.19)*	2.04	9
	-2	<1.40		
	-3	<1.40		
	-4	<1.40		
	-5	<1.40	1.27	0
	WFB-5-11-81- 17-G2-1	<1.02		
	W-5-11-81-17- G2-1	<1.02 (0.26)*	2.04	13
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02		
	WFB-5-16-81- 18-G2-1	<1.02		
	W-5-16-81-18- G2-1	<1.02 (0.02)*	2.04	1
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0
	WFB-5-9-81-19- G2-1	<1.02		
	W-5-9-81-19- G2-1	<1.02 (0.31)*	2.04	15
	-2	<1.02	These samples showed large peaks in the area of 2-MBTZ but spikes of the extracts showed these peaks not to be 2-MBTZ	
	-3	<1.02		
	-4	<1.02		
	-5	<1.02 (0.23)*	1.27	18

Reviewed by: _____

Date: _____

Comments: *Concentration of 2-mercaptobenzothiazole detected in excess of the amount spiked into the sample.

ANALYSIS REPORT FORM

Date 7/2/01 Analyte 2-mercaptobenzothiazole
 Analyst(s) _____ NBP # _____

Type of Sample
 (check one)
 Water
 Sediment

Study No.	Log No.	Amount Found (ppb)	Comments	
			Spike	% Recovery
	W-5-16-01-20-02-1	<1.02		
	W-5-16-01-20-02-1	<1.02	2.04	0
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0
	W-5-10-01-21-02-1	<1.02		
	W-5-10-01-21-02-1	<1.02 (0.28)*	2.04	14
	-2	<1.02		
	-3	<1.02		
	-4	<1.02		
	-5	<1.02	1.27	0

Reviewed by: _____

Date: _____

Comments: *Concentration of 2-mercaptobenzothiazole detected in excess of the amount spiked into the sample.



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