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MEMORANDUM

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SUBJECT: Bentazon Method Review-Report No. ECM0173W1-W3

FROM: Aubry E. Dupuy, Jr., Branch Chief Aubry E Dupuy, Jr
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TO: Kevin Costello (7507C)
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The BEAD/Environmental Chemistry Lab has performed an Environmental Chemistry Method Review (ECMR) on Bentazon in water using the method, "Method For The Analysis of Bentazon and Selected Metabolites In Rice Paddy Water By TSP-LC/MS/MS". A similar method in support of registration MRID No. 434319-03 (soil) was tried by ECL but we experienced high instability for Bentazon and its two analytes due to the high volatile salts which were not compatible with our HPLC/MS system. The method used to accomplish the evaluation was submitted by BASF Corporation in support of registration MRID No. 434319-02 (water).

The attached method review report includes three parts:

Part I: Summary and Conclusions

A brief statement of the acceptability of the method or any deficiencies discovered during method review.

Part II: Discussion of Problems Found During Method Review

An in depth discussion of deficiencies and/or problems associated with this method.

Part III: SEP Checklist

Standard Evaluation Procedure (SEP) Checklist review information..

If you have questions concerning this report, please contact Charles Kennedy at (228) 688-2443 or Aubry Dupuy at (228) 688-3212.

cc: Christian Byrne, QA Officer
BEAD/ECL

Charles Kennedy
BEAD/ECL

Environmental Chemistry Method Review Report

Method For The Analysis of Bentazon and Selected Metabolites In Rice Paddy Water By TSP-LC/MS/MS

Report Number ECM0173W1-W3

Final Report

Environmental Chemistry Laboratory
Biological and Economic Analysis Division

Prepared by: Charles Kennedy Charles Kennedy 08/28/01
ECL Chemist Signature Date

Reviewed by: Christian Byrne Christian Byrne 08/28/01
ECL/QA Officer Signature Date

Part I
Summary and Conclusions

We have completed the Environmental Chemistry Method Review (ECMR) "Method For The Analysis of Bentazon and Selected Metabolites In Rice Paddy Water By TSP-LC/MS/MS". The method used to accomplish the reviews was submitted by BASF Corporation in support of registration MRID No. 434319-02.

This report is intended to show that this method does not function on the current LC/MS/MS system at ECL as well as to indicate possible recovery problems with this method.

Part II

Discussion of Problems Found During Method Review

The highest level of concern for this method is that it was optimized for a thermospray source on a Finnigan MAT TSQ=700 equipped with a TSP2 thermospray interface that typically used high salt concentrations and heat for ionization. Even though the nature of the triple quad analyzer is similar in theory and operation to today's triple quad mass analyzers, the source has vastly different properties than today's interface for liquid ion spray. Thermospray sources use high salt to promote ionization, but today's newer interfaces have phased out the carrier liquid as the primary source of ionization and have instead relied on a balance of solvent, high voltage potential and nebulization/aerosol process to confer charge. The source of ionization is quite different and consequently changes the response and chemical properties needed to detect an analyte of interest.

This current method submitted by BASF uses 200 mM ammoium acetate/0.1% formic acid that is inappropriate for a current typical ion spay source. ECB's instrumentation uses a Thermospray interface on a PE SCIEX 300 API LC/MS/MS system. This source best responds to low volatile salts below 20 mM at flows up to 1 mL/min which has similar requirements of ion spray source.

A simlar method in support of registration MRID No. 434319-03 was tried as written with high instability for Bentazon and the two analytes; 8-chlorobentazon, and N-methlybentazon. Bentazon and 8-chlorobentazon are scanned in the negative mode and N-methybentazon is run in the positive MS/MS mode. Initially, both 8-cholorbentazon and N-methlybentazon had a low response which was opposite from BASF methods where these analytes had the strongest response. PE SCIEX was consulted about introducing high salt into the instrumentation and they advised ECB that such high concentrations would not only cause ion suppression, high background, but could possibly damage the mass spectrometer by salt deposition on the inside of the analyzer. BASF was then contacted and concurred they have PE SCIEX instruments and would never run high salt and high flow as stated in the method. Therefore, the concentration of salt was lowered to a arbitrary value of 10 mM ammonium formate with a 300 μL/min flow to the mass spectrometer. All other conditions were set per the method including running both negative and positive MS/MS modes the same as the original method. Initially, the response of N-methylbentzon improved and the other two ions for 8-chlorobentazon and Bentazon stayed about same. The stability of the three ions was also much improved with lower background noise. Eventually, the ion signals of Bentazon, 8-chlorobentazon, and N-methylbentazon dropped to much lower levels and stayed at this level for the remainder of sample testing but stabilized. A possibility is that as the salt was working its way out of the mass spectrometer from the high salt introduction, it passed an optimal point that probably was the correct salt level. The response of the standards was non-linear and fitted only to a quadratic response curve when run. BASF methods had clearly linear responses for all three analytes as is evident in the areas of its three standards. This in itself shows that this BASF method is instrument specific and is hard to achieve a linear response on today's newer instrumentation with this modification. Due to its similarity to the method for surface water, it is considered unacceptable in this present form.

This method needs to be changed at the interface of HPLC and MS for today's newer ion spray source resulting in a linear response and stable ion formation. It also needs to be fine tuned at the cleanup stage to guarantee no loss of analyte through binding on filters by possibly choosing inert filters such as PTFE. It is thought that BASF methods could be acceptable if these modifications were made.

Part III

SEP Checklist

The completed SEP Checklist is attached for review (Attachment 1).

ATTACHMENT 1

ENIVIRONMENTAL CHEMISTRY METHODS (ECMs) PROGRAM STANDARD EVALUATION PROCEDURE (SEP) CHECKLIST BACKGROUND AND INITIAL REVIEW INFORMATION

I. Background Information

A. Title of Method Method For The Analysis Analysis Of Bentazon And Selected Metabolites In Rice Paddy Water By TSP-LC/MS/MS

B. ECS No. ECM 0173W1-W3

C. MID or TRID No. 434319-02

D. Matrix (es) Water

E. Analyte (es) detected N-Methylbentazon, 8-Chlorobentazon

II. Information About the Laboratory

A. Name BASF Corporation

B. Address P.O. Box 13528, Research Triangle Park, NC 27709-3528

C. Telephone No. 1-800-669-2273
D. Name of the Study Director Robert G. Peterson
E. Name of the Lead Chemist Robert R. Bethem
F. Laboratory Validation: Primary X Secondary ______

III. Method Summary Information for Analyte (s) ______
A. Is the Method CLASSIFIED or CONFIDENTIAL No
B. Sample Preparation Water samples (100mL) acidified with approximately 100µl of 6N HCL
C. Sample Extraction Place the SPE column on the vacuum manifold and condition by drawing 2-column volumes of methanol followed by 2-column volumes of HPLC water through the column. Draw the sample through the column and discard all eluates. Elute the column with 8 mL MeOH, collect and concentrate to ~2 mL. Transfer to 10 mL tube and concentrate to 0.3-0.6 mL and dilute to 2.0 mL with HPLC water. Syringe filter a portion of the final extract through 0.45-µm filter into a autoinjector vial.

D. Sample Cleanup C-18 column
E. Sample Derivatization (If Applicable) Not Applicable
F. Sample Analysis
   1. Instrumentation Thermospray Finnigan MAT TSQ=700
   2. Primary Column LC/MS C18 reverse phase column
   3. Confirmatory Column N/A
   4. Detector LC/MS
   5. Other Confirmatory Techniques N/A
   6. Other Relevant Information N/A

G. Detection and Quantitation Limits ______

   1. Limits of Quantitation (LOQ)

      Claimed in Method 1 .0 ppb Estimated 1 .0 ppb

   2. Method Detection Limit (MDL)

      Claimed in Method N/A Estimated 0.3 ppb

H. Recovery (Accuracy) Data Overall recoveries at 1.0, 10.0,100.0 and 250 ppb:.

Bentazon (1.0ppb) = 110%, SD = 1.4, RSD = 1.3%, (10ppb) =108.5%, SD =.71, RSD = .65%, (100ppb) = 112.5%, SD = .71, RSD = .63, (250ppb) = 105%, SD = .00, RSD = .00,
8-chlorobentazon (1.0ppb) =101.1%, SD = 4.1, RSD = 4.1, (10ppb) = 109.5%, SD = 2.1 RSD = 1.9, (100ppb) = 112 %, SD = 1.4, RSD = 1.3, (250ppb) = 89.5%, SD =7.9, RSD = 8.8
N-methylbentazon (1.0ppb) = 91.8%, SD = 4.5, RSD = 4.9, (10ppb) = 97.1%, SD = 1.3 RSD = 1.3, (100ppb) = 95%, SD = .21, RSD = .22, (250ppb) = 81.1%, SD = 6.4, RSD = 7.9

I. Precision Data See Recovery Data (H.) for Precision Data

Detailed Information about the Method	Yes	No	Review Futher
A. Is the Method marked CONFIDENTIAL?		X	
B. Is it the most up-to-date method?	* X		
C. Does the method require spiking with the analyte (s) of intrest?	X		
D. If the method requires spiking explosive or carcinogenic reagents, are proper precautions explained?		X	
E. Is the following information supplied?	Yes	No	Review Futher
1. Detailed stepwise description of			
a. The sample preparation procedure	X		
b. The sample spiking procedure	X		
c. The extraction procedure	X		
d. The derivatization procedure		X	
e. The cleanup procedure	X		

*Only with changes suggested.

f. The analysis procedure	X		
2. Procedures for			
a. Preparation of standards	X		
b. Calibration of instrument	X		
3. List of glassware and chemicals			
a. Are sources recommended	X		
b. Are they commercially available?	X		
4. Name model, etc., of the instrument, column, detector, etc., used			
a. Are sources recommended?	X		
b. Are they commercially available?	X		
5. MDL			
a. Is there an explanation of how it was calculated?		X	
b. Is it a scientifically accepted procedure?	X		
c. Is the matrix blank free of interference(s) at the retention time, wavelength, etc., of the analyte(s) of intrest?	X		
6. LOQ	Yes	No	Review Futher
a. Is there an explanation of how it was calculated?	X		
b. Is it a scientifically accepted procedure?	X		

7. Precision and accuracy data			
a. Were there an adequate number of spiked samples analyzed?	X		
b. Are the mean recoveries between 70-120%?	X		
c. Are the RSDs of the replicates 20% or less at the LOQ, or above?	X		
8. Description and/or explanation of			
a. Areas where problems may be encountered?	X		
b. Steps that are critical?	X		
c. Interferences that may be encountered?		X	
9. Characterization of the matrix(es)	X		

V. Respresentative Chromatograms

A. Are there representative Chromatograms for

1. Analyte(s) in each matrix at the MDL, LOQ, and 10 x LOQ?	X		
2. Method blanks?	X		
3. Matrix blank?	X		
4. Standard curves?	X		
5. Standards that can be used to recalculate some of the values for analyte(s) in the sample chromatograms?	X		

	Yes	No	Review Further
B. Can the responses of the analyte(s) in the chromatograms of the spiking level be accurately measured?	X		

A. Is there a statement of adherence to the FIFRA/GLP?	X		
VII. Independent Lab Validation (ILV)			
A. Was an ILV performed?	X		
B. Did the ILV's percision/accuracy data meet the criteria established on page 3 of the Data Reporting Guidelines (OPP-00405) FRL-4943-5)?	X		
C. Were recommendations of major or min or modifications to the method made by the independent lab performing the ILV? If major modifications were suggested, what were they?		X	
VIII. Completeness			
A. Has enough information been supplied to do a proper review?	X		
B. Has enough information been supplied to do a laboratory evaluation, if requested?	X		
C. Are all steps in the method scientifically sound?	*X		
D. Is a confirmatory method or technique provided?		X	
E. Check the category below which best describes this ECM.			

1. Satisfactory	
2. Major Deficiencies	X
3. Minor Deficiencies	

*Only with changes suggested.

Recommendations

This method needs to be changed at interface of HPLC and MS for today's newer ion spray source resulting in a linear response and stable ion formation. It also needs to be fine tuned at the clean-up stage to guarantee no loss of analyte though binding of filters by possibly choosing inert filters such as PTFE. It is felt this method could be acceptable if these modifications were made.

Name (print) and Signature of Reviewer: Charles D. Kennedy Charles D. Kennedy

Date Initial Review was Assigned: February 20, 2001

Date Initial Review was Completed: February 23, 2001

Date Final Review was Completed: June 29, 2001

Name (s) (print) and Signature (s) of Other Reviewers:

Christian Byrne Christian Byrne