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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

Analytical Chemistry Section
Building 402, ARC-East
Beltsville, Maryland 20705

January 18, 1985

MEMORANDUM

SUBJECT: PP# 0F2413/FAP# OH5275
PP# 3F2973/FAP# 3H5378
Thiodicarb (Acetamide/Acetonitrile)
on Milk, Liver and Eggs

FROM: Ronald F. Thomas, Chemist
Analytical Chemistry Section

THRU: Warren R. Bontoyan, Head
Analytical Chemistry Section

THRU: Donald A. Marlow, Chief
Chemical Operations Branch

TO: Michael Firestone, Ph.D., Chemist
RCB, HED-TS-769

A methods trial was requested by RCB, HED for acetamide in chicken liver and acetonitrile in milk and egg white.

Chicken livers were spiked with acetamide at - 0.0, 0.4, and 1.0 ppm. Milk was spiked with acetonitrile at - 0.0, 0.1, and 1.0 ppm. Egg whites were spiked with acetonitrile at 0.0, 0.3, and 0.6 ppm.

The commodities used in this study were obtained from a local supermarket.

Pesticide grade acetonitrile and reagent grade acetamide recrystallized from absolute alcohol were used for spiking.

Method of Analysis: Acetamide in Poultry Liver - SEE ATTACHED RCB METHOD SUMMARY AND ANALYTICAL RESULT FORMS

Acetamide is extracted from poultry liver with acetone. Interfering co-extractives are removed by silica gel column chromatography. Detection and quantification are done by capillary

gas chromatography using a nitrogen phosphorus specific detector. Analysis of four samples can be completed in one-half day. (Note: 1)

Apparatus:

- ° Carlo Erba HRG 5300 Mega Series gas chromatograph (Erba Instruments Inc., Peabody, MA) or equivalent, equipped with a NPD-40 nitrogen-phosphorus detector operated in the N-P mode. Operational parameters were:
- ° Column: Fused silica capillary, 15 meters, 0.32 mm ID, 0.25 um film thickness of bonded Carbowax PEG 20M (Supelcowax 10, Supelco, Inc., Bellefonte, PA).
- ° Injection Volume: 2 ul on-column.
- ° Attenuation set to give 1-cm peak with 0.1 ug/ml acetamide standard.

Gas Flow

Helium carrier	3mL/min.
Helium makeup	35mL/min.
Hydrogen	30mL/min.
Air	350mL/min.

Temperatures:

Injection	Ambient
Detector	250°C
Column	55° to 160°C at 15°C/min, hold at 160°C for 3 min.

Method of Analysis: Acetonitrile in Milk and Egg Whites - SEE ATTACHED RCB METHOD SUMMARY AND ANALYTICAL RESULT FORMS

Acetonitrile is extracted from milk and egg white with methanol. Acetonitrile in the methanol extract is quantified by gas chromatography using a Hall electrolytic conductivity detector (HECD) operated in the nitrogen mode.

Apparatus:

Tracor 565 gas chromatograph (Tracor, Inc., Austin, Texas) equipped with a Tracor 560/700A Hall Electrolytic Conductivity Detector operated in the nitrogen mode.

The method depends on the careful exclusion of acetonitrile contamination in the methanol solvent used to extract acetonitrile from egg white and to dilute the final solution. This contamination can arise via two mechanisms:

1. Acetonitrile present in methanol from the manufacturer: Acetonitrile occurs to varying degrees (up to close to

1 ppm) even in glass distilled, "suitable for residue analysis", grade methanol. Each lot of methanol should be tested chromatographically for the presence of acetonitrile impurity. (note-2)

2. Contamination of methanol with acetonitrile in the laboratory: Since acetonitrile is a commonly used organic component of HPLC mobile phases and multiresidue analyses in PAM I, fairly large amounts of it may be used daily in the residue analysis laboratory. This increases the chance of contaminating initially pure methanol at the sub-part-per-million level, rendering the methanol useless for acetonitrile analysis. We have experienced this in our laboratory. (Note 2)

Because the lack of an on column capillary injection system and the dedication of the Hall Detector to another ACL project, the cleaned-up sample extracts prepared at Beltsville were taken to the Union Carbide laboratory at RTP by ACL chemists for final analysis. The lack of available instrumentation also prohibited ACL's screening of methanol for acetonitrile contamination.

NOTE: 1

The analytical results (see attached RCB Summary Form) indicate the probable presence of a significant quantity of acetamide in either the sample and/or acetone.

RCB told ACL that registrant GC/MS conditions for analyzing acetamide and analytical data using these conditions indicating that acetamide is ubiquitous would be forth coming. However, ACL never received this information.

Note: 2

These statements are exactly as they appeared in the petition method submitted by the registrant.

The ACL analytical results indicate the probable validity of the registrant's statement in that ACL found significant quantities of acetonitrile in the milk and egg white control samples.

RCB Method Summary and Analytical Results Form

Method of Analysis for Acetamide in Poultry Liver

Modifications to method (major or minor):

No Modifications

Special precautions to be taken:

No unusual precautions

Source of analytical reference standards:

Fisher Scientific Products

If derivitized standard used, give source:

NO

Instrumentation for quantitation:

See Report for instruments

Instrumentation for confirmation:

None

If instrument parameters differ from method given, list parameters used:

N/A

Commercial source for any special chemicals or Apparatus:

N/A

Comments:

N/A

Chromatograms:

Submitted

Analytical Results in Chicken Liver Spiked with Acetamide

Do not use control values for recovery corrections.

Do not report control values as 0; if less than limit of detection, report as such.

Sample Identification	Sample Type	PPM Added	PPM Found	% Recovery
Reagent Blank -1	—	0	0.07	—
Reagent Blank -2	—	0	0.07	—
Liver Blank - 1	Liver	0	0.16	—
Liver Blank - 2	Liver	0	0.13	—
Liver - A 0.4 ppm	Liver	0.4	0.34	85
Liver - B 0.4 ppm	Liver	0.4	0.28	70
Liver - A 1.0 ppm	Liver	1.0	0.46	46
Liver - B 1.0 ppm	Liver	1.0	0.62	62
Liver method procedural STD-A 1 ppm	—	1.0	0.75	75
Liver method procedural STD-B 0.4 ppm	—	0.4	0.21	53

RCB Method Summary and Analytical Results Form

Method of Analysis for Acetonitrile in Milk

Modifications to method (major or minor):

None

Special precautions to be taken:

None

Source of analytical reference standards:

Pesticide Grade Acetonitrile

If derivitized standard used, give source:

N/A

Instrumentation for quantitation:

Union Carbide - RTP, N.C.

Instrumentation for confirmation:

N/A

If instrument parameters differ from method given, list parameters used:

N/A

Commercial source for any special chemicals or Apparatus:

N/A

Comments:

N/A

Chromatograms:

Submitted

Method: Method of Analysis For Acetonitrile (metabolite of Thiodicarb) in Milk - dated August 20, 1984

Do not use control values for recovery corrections.

Do not report control values as 0; if less than limit of detection, report as such.

<u>Commodity</u>	<u>Chemical Added</u>	<u>PPM added</u>	<u>PPM found</u>	<u>% Recovery</u>
Reagent Blank	None	0	2.3	---
" "	"	0	1.9	---
Milk Control	"	0	2.6	---
" "	"	0	1.6	---
Milk	Acetonitrile	1.0	4.6	460
"	"	1.0	6.3	630
"	"	1.0	6.4	640
"	"	1.0	4.0	400
"	"	0.1	3.3	330
"	"	0.1	3.4	340

RCB Method Summary and Analytical Results Form

Method of Analysis for Acetonitrile in Egg White

Modifications to method (major or minor):

None

Special precautions to be taken:

None

Source of analytical reference standards:

Pesticide Grade Acetonitrile

If derivitized standard used, give source:

N/A

Instrumentation for quantitation:

Union Carbide - RTP, N.C.

Instrumentation for confirmation:

N/A

If instrument parameters differ from method given, list parameters used:

N/A

Commercial source for any special chemicals or Apparatus:

N/A

Comments:

N/A

Chromatograms:

Submitted

Method: Method of Analysis For Acetonitrile (metabolite of Thiodicarb) in Egg Whites dated August 20, 1984

Do not use control values for recovery corrections.

Do not report control values as 0; if less than limit of detection, report as such.

<u>Commodity</u>	<u>Chemical Added</u>	<u>PPM added</u>	<u>PPM found</u>	<u>% Recovery</u>
Reagent Blank	None	0	1.1	---
" "	"	0	0.7	---
Egg Whites Control	"	0	1.4	---
" "	"	0	0.5	---
Egg Whites	Acetonitrile	0.3	1.1	367
" "	"	0.3	2.2	733
" "	"	0.6	2.1	350
" "	"	0.6	1.1	183
" "	"	0.6	1.1	183
" "	"	0.6	2.0	333
" "	"	0.6	0.9	150