1 of 1

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Separation and Identification of Carboxylic Acids in MALT
Samples from the Headspace Gases in Hanford Tank 103C

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SUMMARY

Samples of headspace gases from Westinghouse Hanford Company (WHC) waste storage tank 103C were analyzed by gas chromatography/mass spectrometry by Pacific Northwest Laboratory staff. The samples were obtained using a cryo-trap sampler designed by WHC and known as the Mobile Analytical Laboratory Trap (MALT). The samples, which were obtained in September 1989, were available in large amounts (200 mL). The specific targets for this analysis were n-butyric, i-butyric, n-valeric, and i-valeric organic acids. Of the acids targeted, only n-butyric was found, and only trace amounts of it were detected with a detection limit below 1 ppm in the extract. The levels found were so low as to cause difficulty in quantitation. All concentrations reported here are for the methanol extract solutions and not the concentrations in the headspace of tank 103C. To calculate concentrations in the headspace, the MALT sampling volume and the methanol rinse volume must be obtained from the MALT personnel at WHC.

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CONTENTS

SUMMARY	iii
INTRODUCTION	1
DESCRIPTION OF EXPERIMENT	3
Standards and Solutions	3
Sample Preparation	3
GC/MS Parameters	4
RESULTS	5
DISCUSSION AND CONCLUSION	9

TABLES

1	Retention Times	4
2	Recovery and Detection Limits for WHU 9	8
3	Recovery and Detection Limits for WHU 9	8

FIGURES

1	Methodology Scheme for the Separation of Carboxylic Acids in MALT Samples	2
2	Chromatogram of Samples and Spiked Samples	6
3	Mass Spectra of Butanoic Acid in WHU 10 and from Wiley Standard Library	7

INTRODUCTION

Noxious-odor-exposure incidents have resulted in the need to characterize the vapor space in Westinghouse Hanford Company (WHC) tank 103C. Low-molecular-weight carboxylic acids typically have a noxious odor and are suspected degradation products in some of the WHC waste storage tanks at Hanford. Pacific Northwest Laboratory^(a) conducted experiments for WHC to characterize low-molecular-weight carboxylic acid in provided samples. In this report, a methodology is described to detect low-molecular-weight carboxylic acids in cryo-trap extract samples used to sample the headspace from tank 103C. The cryo-trap sampler was designed by WHC and is currently referred to as Mobile Analytical Laboratory Trap (MALT). The MALT sampler was designed by WHC and is not discussed in this report.^(b) Specifically, n-butyric, i-butyric, n-valeric, and i-valeric acids were targeted for this method. Figure 1 shows the flow chart of the separation scheme developed to isolate the carboxylic acid fraction.

The applicability of this method is demonstrated with WHU-9 and WHU-10 MALT extract samples obtained in September 1989 from WHC. These two samples were available in large amounts (200 mL) as compared to MALT samples recently obtained from Phase 0 sampling (30 mL). Results indicated that these samples contained only trace amounts of n-butyric acid with a detection limit below 1 ppm in the extract. All concentrations reported here are for the methanol extract solutions and not the concentrations in the headspace of tank 103C. To calculate concentrations in the headspace, the MALT sampling volume and the methanol rinse volume must be obtained from the MALT personnel at WHC.

(a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

(b) W. U. Ulbricht. Report on 241-C Tank Farm Air Sampling Results of 1989, WHC-SD-WM-RPT-019. Dated June 1991.

Figure 1. Methodology Scheme for the Separation of Carboxylic Acids in MALT Samples

DESCRIPTION OF EXPERIMENT

Before analysis by gas chromatography/mass spectrometry (GC/MS), it was necessary to remove water and other interfering constituents from the samples. Spiked samples were also extracted to determine the method's recovery efficiency. Samples were prepared using both sodium hydroxide and sodium bicarbonate to determine if any differences occurred in the recoveries when using these two bases.

STANDARDS AND SOLUTIONS

Stock Solution	Chem Services n-butyric, i-butyric, n-valeric, and i-valeric acids, 100 μ L, were diluted in 10 mL methanol:water (80:20).
Spiking Solution	Stock Solution, 1 mL, was diluted into 10 mL methanol:water (80:20).
NaOH solution	0.1 M
NaHCO ₃ solution	0.1 M
H ₂ SO ₄ solution	0.1 M

SAMPLE PREPARATION

1. A spiked sample was prepared by adding 200 μ L of spiking solution to 25 mL of sample. This gave roughly 200 μ g/25 mL or an 8 ppm spike.
2. A 25-mL aliquot of sample was made basic (to test strip) with either the NaOH or NaHCO₃ solution. Only the NaOH solution was used with the WHU 10 sample.
3. The base/neutral constituents were extracted with 20 mL of pentane. The pentane extract was retained for further study.
4. The extracted sample with 20 mL of added water was rotary-evaporated to about 20 mL to remove methanol and other volatiles. The distillate was retained for further study.

5. The sample was acidified (to test strip) with the H₂SO₄ solution.
6. A 3.5-g quantity of NaCl was dissolved in the sample to aid in "salting out" the organic acids and to speed the phase separation.
7. The sample was extracted twice with 2 mL of ethyl acetate.
8. The ethyl acetate extracts were combined and diluted to 5 mL.
9. The ethyl acetate extracts were assayed by GC/MS. The retention times are listed in Table 1.

GC/MS PARAMETERS

Column: J&W, DB-1, 30 m x 0.32 mm, 5.0 µm
 Injector: 220°C
 Transfer line: 220°C
 Injection: 1 µL splitless
 Oven: 40°C for 1 min., 32°C/min to 70°C for 4 min, 12°C/min to 260°C for 6.23 min
 Mass Spec: EM at 2000 eV, on at 5.5 min, scan from 35 to 260 amu.

Table 1. Retention Times

<u>Component Identification</u>	<u>Retention Time</u>
IsoPropyl Acetate(a)	6.24 minutes
n-Propyl Acetate(a)	7.77
Glyme(a)	8.44
i-Butyric acid	8.67
n-Butyric acid	9.38
i-Valeric acid	10.8
n-Valeric acid	11.7
Alkane	15.1
Unknown	23.3
Tributyl phosphate	23.6

(a) Impurities in experiment solvent, not from sample.

RESULTS

Of the organic acids targeted, only n-butyric acid was found. Calculations were performed on an Excell spreadsheet using conventional external standard formulae.

$$\text{Conc.} = (8 \text{ ppm} \times \text{Area of Sample}) / (\text{Area of Standard} \times \text{Recovery})$$

WHU 9	0.27 ppm
WHU 9	0.39 ppm, when not using the excessive recovery value
WHU 10	0.46 ppm

In the WHU 9 sample, the n-butyric acid was identified in the hydroxide extracted sample, but the level of n-butyric acid was too low for positive identification in the bicarbonate extracted sample. Figure 2 presents chromatographs of hydroxide extracted WHU 9, and Figure 3 compares the mass spectrum from the chromatograph of WHU to a standard spectrum found in the computer based spectra library.

Detection limits were set at 2.5 times the noise in the total ion chromatographs. They are listed in the attached tables and were generally below 1 ppm. The extracted ion chromatograph (EIC) was used for quantifying n-butyric acid. It was present at a level below the detection limit as determined by the total ion chromatograph (TIC). The detection limits by EIC were not determined.

Figure 2. Chromatogram of Samples and Spiked Samples

From WHU 10
Chromatograph

From Wiley Spectra
Library

Figure 3. Mass Spectra of Butanoic Acid in WHU 10 and from Wiley Standard Library

The recoveries, results, and detection limits are in Tables 2 and 3.

Table 2. Recovery and Detection Limits for WHU 9

<u>Recovery of Spikes</u>				
<u>Name</u>	<u>Recovery by Hydroxide</u>		<u>Recovery by Bicarbonate</u>	
i-Butyric acid	60%		72%	
n-Butyric acid	142%		156%	
i-Valeric acid	86%		86%	
n-Valeric acid	95%		102%	

<u>Detection Limits(a)</u>				
<u>Name</u>	<u>Hydroxide Extracted</u>		<u>Bicarbonate Extracted</u>	
	<u>Peak Height</u>	<u>Det. Limit</u>	<u>Peak Height</u>	<u>Det. Limit</u>
i-Butyric acid	38 mm	1.05 ppm	42 mm	0.95 ppm
n-Butyric acid	95	0.42	91	0.44
i-Valeric acid	91	0.44	83	0.48
n-Valeric acid	80	0.50	79	0.51

Table 3. Recovery and Detection Limits for WHU 10

<u>Recovery of Spikes</u>		
<u>Name</u>	<u>Recovery by Hydroxide</u>	
i-Butyric acid	79%	
n-Butyric acid	86%	
i-Valeric acid	93%	
n-Valeric acid	95%	

<u>Detection Limits(a)</u>		
<u>Name</u>	<u>Hydroxide Extracted</u>	
	<u>Peak Height</u>	<u>Det. Limit</u>
i-Butyric acid	49 mm	0.82 ppm
n-Butyric acid	66	0.61
i-Valeric acid	100	0.40
n-Valeric acid	94	0.43

(a) Based on a spike of 8 ppm and $2.5 \times \text{Noise} = 5 \text{ mm}$ (height of noise on original printout)

DISCUSSION AND CONCLUSION

Trace levels of n-butyric acid were detected in both samples, but the levels found were so low as to cause difficulty in quantitation. None of the other organic acids targeted in this experiment were found.

Detection limits were at or below 1 ppm. The level of n-butyric acid found was below the TIC detection limit of 0.4 ppm for the WHU 9 sample and 0.6 ppm for the WHU 10 sample.

The recoveries of analytes ranged from 60% to 156% in these experiments. No reasonable explanation can be given for the excessive n-butyric acid recoveries found in the WHU 9 sample by both extraction methods.

We would like to examine the extracts and distillates retained during the clean-up portion of this experiment. There are potentially other compounds to be found in these fractions.

The record of this research is recorded in Laboratory Notebook #BNW 53692 stored in building 329, room 3.

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