SAND2013-7071C

Exceptional service in the national interest

Sandia National Laboratories

Acetic Acid as a Degradation Product or Inventory of Ethylene-Vinyl Acetate (EVA)

JOWOG 2013, AWE

September 9-12, 2013

Lance L. Miller, Robert Bernstein, Gregory V. White II, John L. Schroeder, and James M. Hochrein

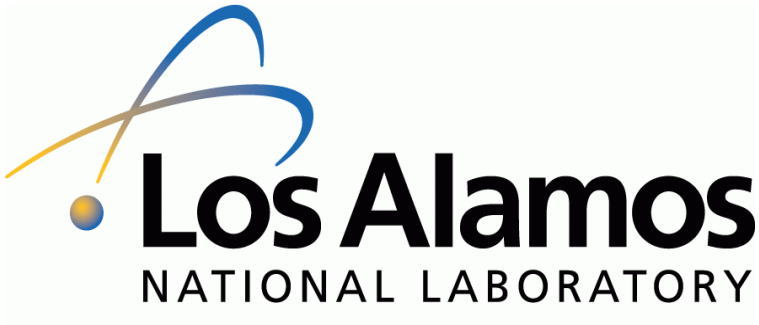
Materials Science and Engineering Center

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

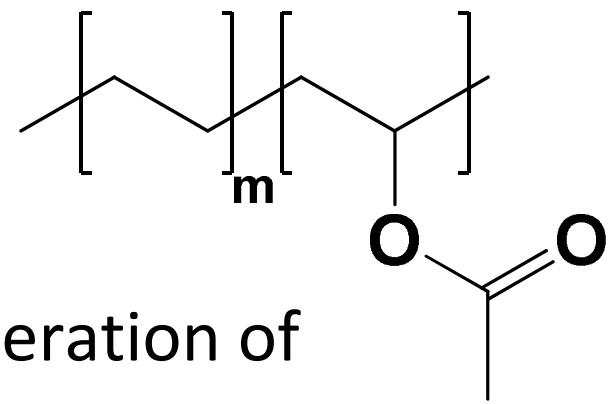
Collaboration

Sandia National Laboratories



Introduction

- Ethylene-vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate.



- Of great concern with EVA is the generation of acetic acid as the material ages.

Introduction (cont.)

- Is the acetic acid leftover from the formation of the polymer and trapped in the EVA matrix? Or is it generated with time/aging?
  - The heating associated with accelerated aging could be driving the acetic acid out of the EVA 'inventory'.
  - If true, predictions and degradation models for EVA would need to be modified.
- The purpose of this research is to understand acetic acid in EVA; inventory vs. generation; rates of formation/quantification

Methodology – sample preparation

- Obtain samples of unaged and aged EVA.
  - Perform a solvent extraction to pull any acetic acid out of the EVA matrix.
- 8 samples were used including:
  - EVA "goo" → Celanese DUR-O-SET® E-200 HV
  - EVA at zero point → "goo" thermally cured
  - Cast EVA → water removal from zero point with vacuum oven
  - 40°C aged EVA → Cast EVA aged 564 days at 40°C
  - 65°C aged EVA → Cast EVA aged 564 days at 65°C
  - 80°C aged EVA → Cast EVA aged 526 days at 80°C
  - 124°C aged EVA → Cast EVA aged 564 days at 124°C
  - 138°C aged EVA → Cast EVA aged 526 days at 138°C

EVA samples

- "Zero Point" EVA is the raw Celanese material thermally cured The curing process includes:
  - Raw material poured into flat glassware.
  - One day in oven at 80°C.
  - Two hours in oven at 138°C.
  - Two weeks at 80°C.
- "Cast" EVA is "Zero Point" EVA vacuum baked at 40°C.
  - This is done primarily to remove water.
- All aged samples were aged starting with "Cast" EVA.

Methodology – sample preparation

- 50 milligrams of each EVA sample was placed into a separate scintillation vial and 10mL of Methylene Chloride was added as the solvent.
  - The mixture was left seaked for 72 hours.
- The remaining liquid was then extracted and filtered into sample vials for analysis.

Methodology – sample analysis

- A Waters GCT Premier Gas Chromatograph/Mass Spectrometer was used to analyze the samples.

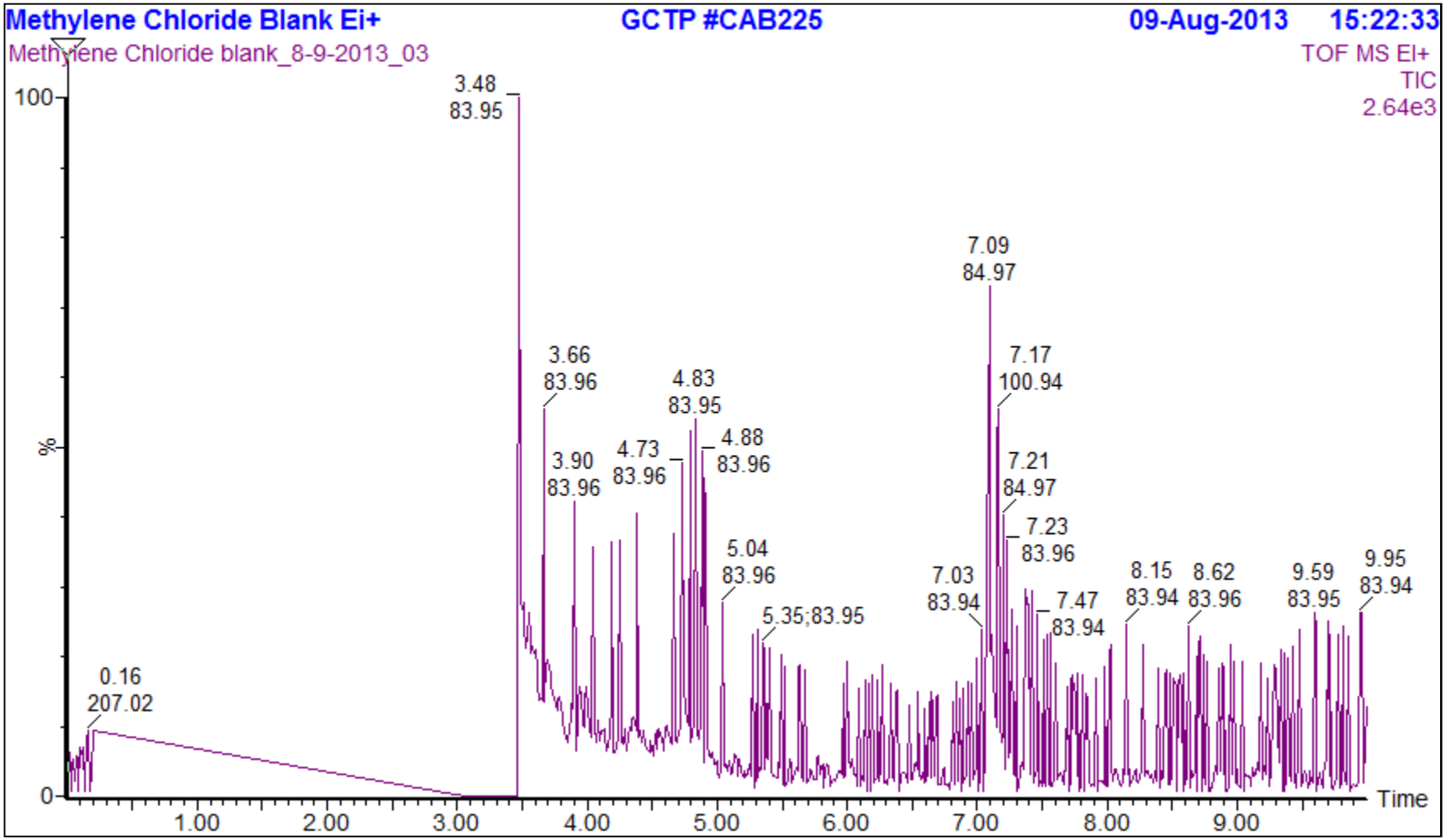
- A calibration curve was generated using known standards of acetic acid in methylene chloride of 1pg/µL, 10pg/µL, 50pg/µL, 100pg/µL, 500pg/µL, and 1ng/µL
- The EVA samples, standards as quality control and methylene chloride blanks were ran in series.
- Five total sample sets were performed.

Methodology - instrument

- GC method:
  - 30 meter/.25mm diameter/.25µm film J&W HP-FFAP column
  - 1µL injection
  - Initial temperature at 70°C with 15°C ramp per minute up to 200°C

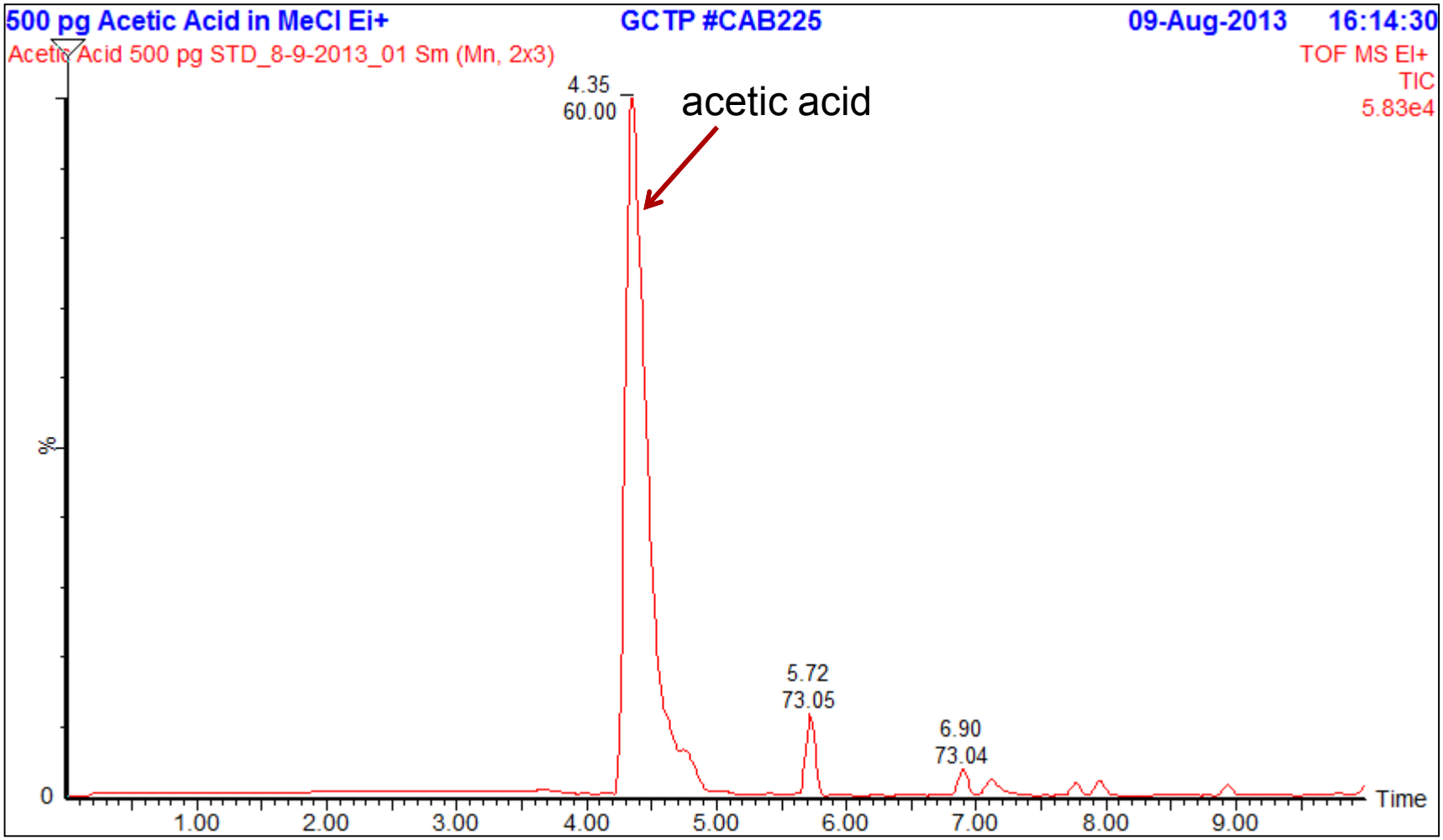
- Time of Flight Mass Spectrometry in positive electron ionization mode was used.

Results - representative methylene chloride blank



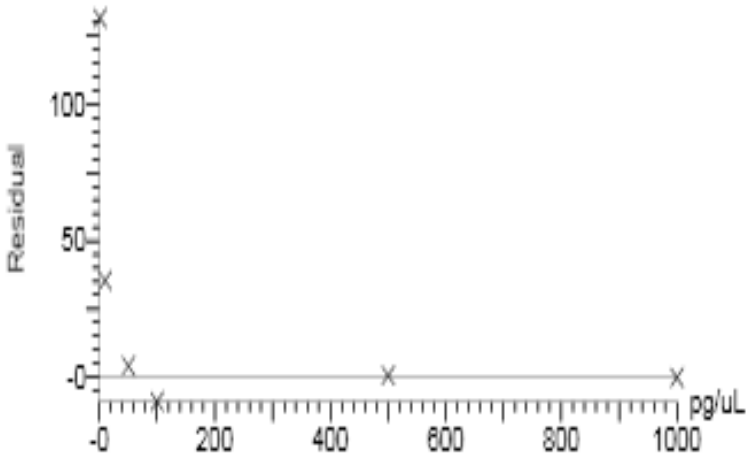
Scaled chromatogram is normal for instrument noise and methylene chloride trace

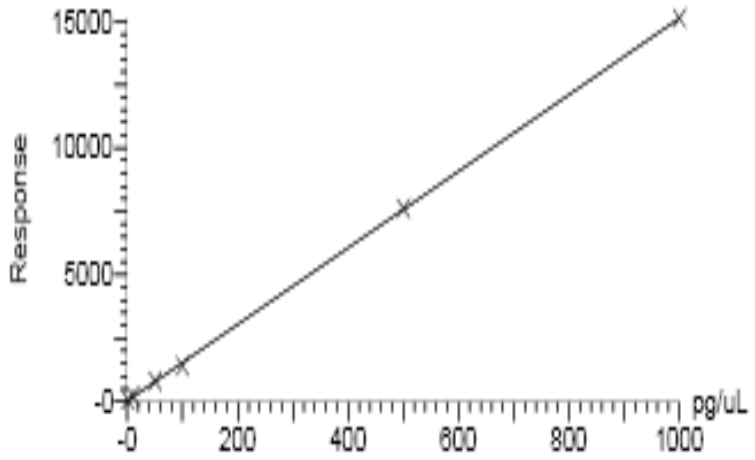
Results - representative acetic acid peak



Results - representative calibration curve

Compound name: acetic_acid_EIpos
Correlation coefficient: r = 0.999934, r^2 = 0.999868
Calibration curve: 15.1046 * x + 22.7918
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: Null, Axis trans: None





Results – quantification table

This column give the calculated pg/µL from the calibration curve.

Compound name: acetic_acid_Elpos
Correlation coefficient: r = 0.999934, r^2 = 0.999868
Calibration curve: 15.1046 * x + 22.7918
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: Null, Axis trans: None

	#	Name	Type	Std. Conc	RT	Area	IS Area	Response	Detecti...	pg/uL
1	1	Acetic Acid 1 pg STD_8-9-...	Standard	1.000	4.37	57.786		57.786	MM	2.3
2	2	Acetic Acid 10 pg STD_8-9...	Standard	10.000	4.37	227.289		227.289	MM	13.5
3	3	Acetic Acid 50 pg STD_8-9...	Standard	50.000	4.36	809.138		809.138	MM	52.1
4	4	Acetic Acid 100 pg STD_8-...	Standard	100.000	6.51	1397.856		1397.856	MM	91.0
5	5	Acetic Acid 500 pg STD_8-...	Standard	500.000	4.34	7614.127		7614.127	MM	502.6
6	6	Acetic Acid 1 ng STD_8-9-...	Standard	1000.000	4.35	15119.329		15119.329	MM	999.5
7	7	Methylene Chloride blank_...	Blank		4.38	1.395		1.395	MMI	
8	8	Cast EVA_8-12-2013_01	Analyte		4.39	142.949		142.949	MM	8.0
9	9	Zero Point EVA_8-12-2013...	Analyte		4.37	673.823		673.823	MM	43.1
10	10	40C EVA_8-12-2013_01	Analyte		4.37	82.999		82.999	MM	4.0
11	11	Acetic Acid 10 pg QC_8-12...	QC	10.000	4.36	207.557		207.557	MM	12.2
12	12	65C EVA_8-12-2013_01	Analyte		4.46	21.577		21.577	MMI	
13	13	124C EVA_8-12-2013_01	Analyte		4.37	204.316		204.316	MM	12.0
14	14	Cast EVA 2_8-12-2013_01	Analyte		4.54	42.228		42.228	MM	1.3
15	15	Zero Point EVA 2_8-12-20...	Analyte		4.33	901.200		901.200	MM	58.2
16	16	EVA GOO_8-12-2013_01	Analyte		4.35	881.637		881.637	MM	56.9
17	17	Acetic Acid 100 pg QC_8-1...	QC	100.000	4.36	1658.417		1658.417	MM	108.3
18	18	80C EVA_8-12-2013_01	Analyte		4.29	338.302		338.302	MM	20.9
19	19	138C EVA_8-12-2013_01	Analyte		4.36	541.191		541.191	bb	34.3

Results

- Five total sample sets were performed with each giving near identical results
  - The results were averaged to calculate total acetic acid

Material Sample	Material Treatment	Total acetic acid extracted from 50mg sample
EVA goo	No treatment	561 ng
EVA at zero point	Cured with thermal treatment	524 ng
Cast EVA	Vacuum baked at ~40°C	41 ng
40°C aged EVA	Cast EVA aged 564 days at 40°C	23 ng
65°C aged EVA	Cast EVA aged 564 days at 65°C	<10 ng
80°C aged EVA	Cast EVA aged 526 days at 80°C	176 ng
124°C aged EVA	Cast EVA aged 564 days at 124°C	105 ng
138°C aged EVA	Cast EVA aged 526 days at 138°C	312 ng

Conclusions

- Acetic acid is seen in the methylene chloride extraction from the raw material as well as the cured material.
- Most of the extractable acetic acid is driven off during the vacuum bake casting process to remove water.
- It appears acetic acid generation is then taking place and is extractable in the aged material.
  - During the aging process for these materials, nothing was done to ensure no loss of gaseous species.
  - Therefore, the quantification of total acetic acid generated by the material is unknown. This study was only able to identify any remaining acetic acid that could be extracted.

Future Work

- Start with equal mass unaged samples.
  - Age the samples while ensuring a sealed volume to collect all generated acetic acid.
  - Thereby making quantification of acetic acid generated during aging possible.