TGA-MS

Simultaneous quantification and qualitative composition analysis of vapor effluents?

The analysis request was to analyze the samples by Thermogravimetric Analysis with Mass Spectrometry detection (TGA/MS) using the following sample plan:

- 14-2024 (resin), as received
- 14-2082 (amine), as received
- 50/50 amine/resin mixture by weight
- 10/90 amine/resin mixture by weight
- 10/85/5 amine/resin/citric acid mixture by weight

Each sample listed above was analyzed at both 80°C and 110°C in a nitrogen (N_2) atmosphere. The programs were set up as follows:

- 80°C runs: ambient temperature (25°C to 80°C at the rate of 10°C per minute with a hold at 80°C for 70 minutes)
- 110°C runs: ambient temperature (25°C to 110°C at the rate of 10°C per minute with a hold at 110°C for 70 minutes)

Table 9 includes sample weight loss information for each run.

Table 9: Sample weight loss information

Sample ID	Temperature (°C)	Initial Sample Weight (mg)	Sample Weight Loss (mg)	Sample Weight Loss (%)
14-2024	80	26.14	13.05	50
14-2024	110	40.89	21.79	52
14-2082	80	33.30	0.78	2
14-2082	110	30.15	2.24	7
50/50 amine/resin	80	32.29	8.26	25
50/50 amine/resin	110	41.58	15.71	38
10/90 amine/resin	80	42.22	9.98	24
10/90 amine/resin	110	28.48	4.32	51
10/85/5 amine/resin/citric acid	80	34.09	15.91	47
10/85/5 amine/resin/citric acid	110	37.92	16.74	44

Thank you for choosing MCLinc. This report reviewed and approved by:

Michele Sanders
Laboratory Manager

Kristal Tate
Chemist

Summary

The purpose of this analytical testing was to monitor some commercially relevant samples while heating in the TGA furnace; in particular, looking for the presence of butyldiethanolamine in the outgassing stream from the samples. The three major peaks for butyldiethanolamine are known to be detected by mass spectrometer (MS) at mass/charge ratio (m/z) 130, 88 and 56 atomic mass units (AMU), as shown in the NIST reference spectrum given in Appendix 1.

The analytical testing of samples and mixtures of samples as given in the sample plan of the previous section found none of the three major peaks for butyldiethanolamine, i.e., m/z ratio of 130, 88 or 56 AMU. Evaluation of data from the MS is performed by an analyst trained by the MS manufacturer, Pfeiffer Vacuum.

Summary

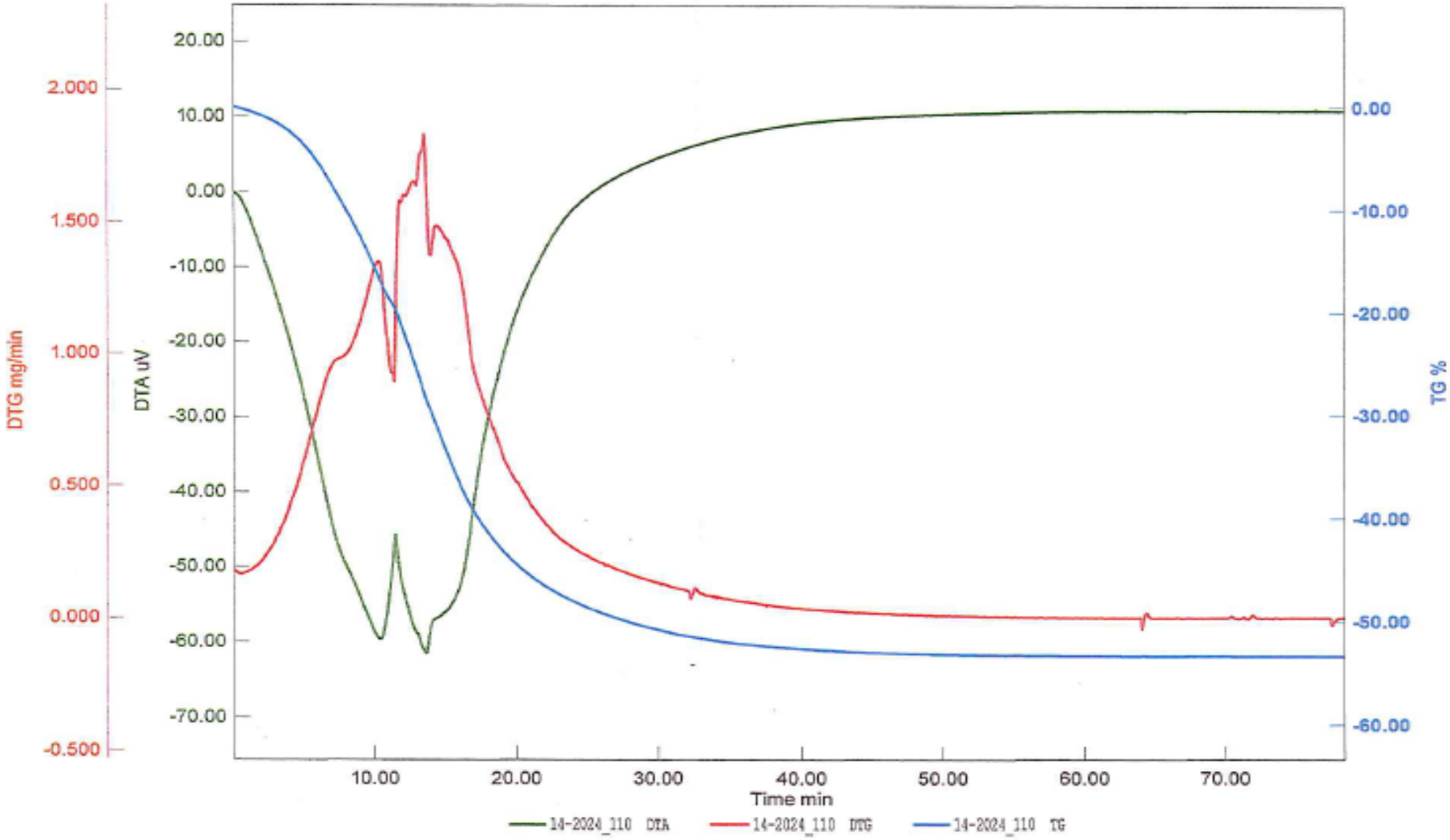
- Composition of effluent vapor can be non-intuitive
  - ester hydrolysis leading to butanol
  - Variable water loss rate; viscosity
- Coupling of TGA & MS makes possible the complete evaluation of the vapor effluent
- TGA/MS is the best possible method for a VOC waiver
- BDEA is non-volatile to the Method 24 threshold when evaluated by TGA/MS

Module:	TG/DTA
Data Name:	14-2024_110
Measurement Date:	9/26/2014
Sample Name:	14-2024_110
Sample Weight:	40.890 mg
Reference Name:	TAI002878A
Reference Weight:	0.000 mg

Temperature Program:

	Cel	Cel	Cel/min	min	s
1*	25	110	10	70	2.5

Comment:
Operator: User
Pan: Alumina

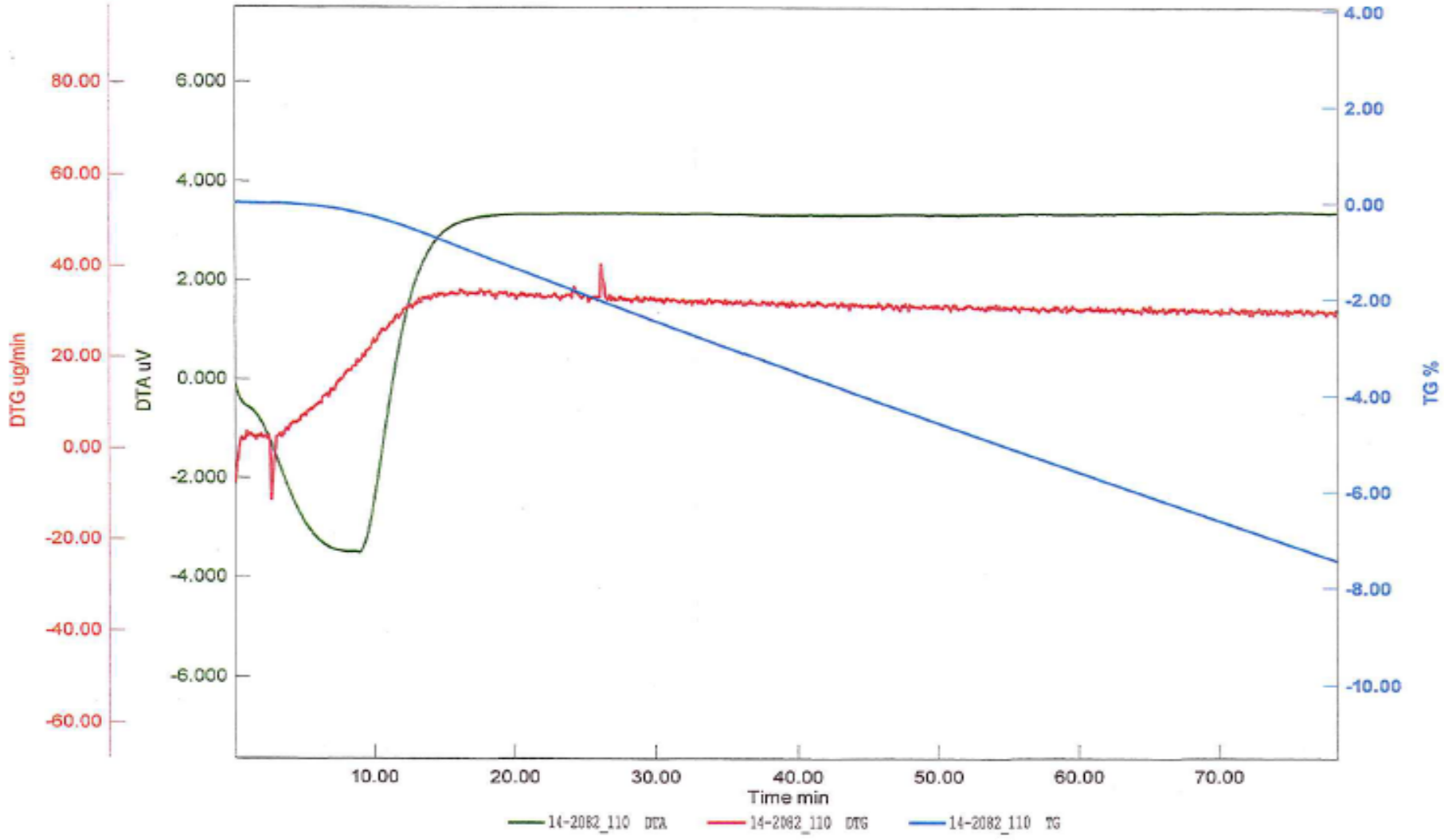


Module:	TG/DTA
Data Name:	14-2082_110
Measurement Date:	9/26/2014
Sample Name:	14-2082_110
Sample Weight:	30.150 mg
Reference Name:	TAI002878A
Reference Weight:	0.000 mg

Temperature Program:

	Cel	Cel	Cel/min	min	s
1*	25	110	10	70	2.5

Comment:
Operator: User
Pan: Alumina

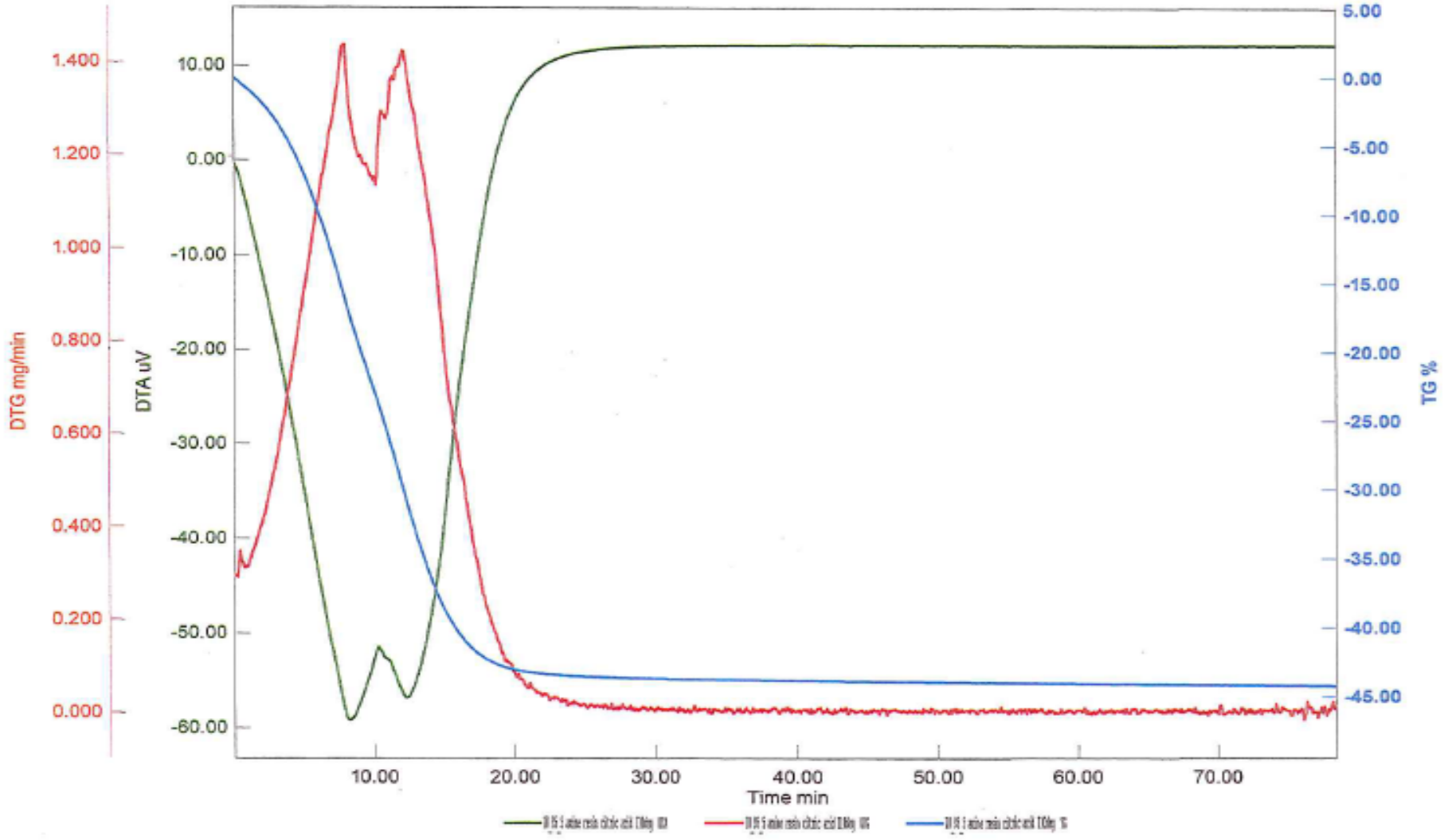


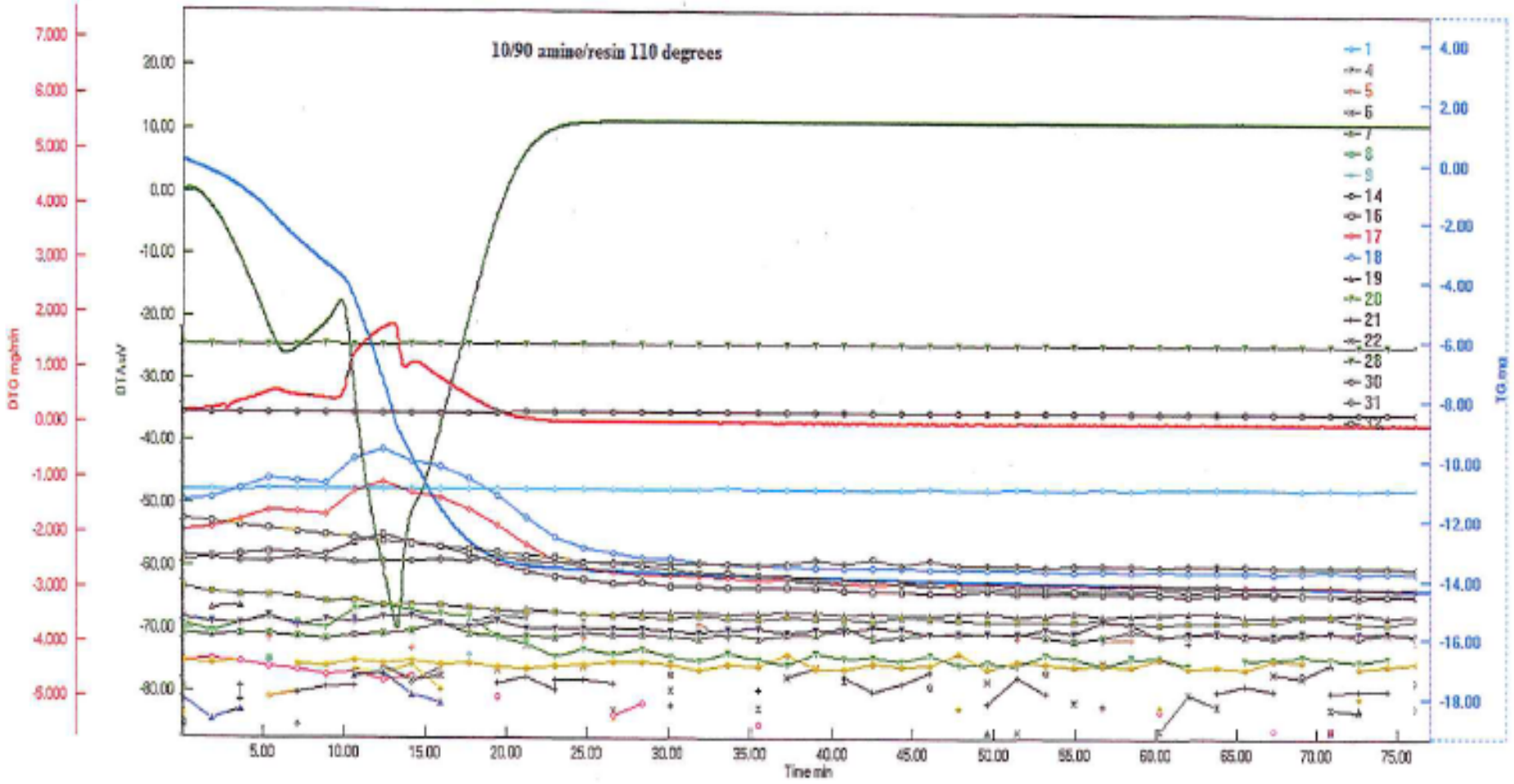
Module: TG/DTA
Data Name: 10_85_5 amine resin citric acid 110deg
Measurement Date: 10/3/2014
Sample Name: 10/85/5 amine/resin/citric acid 110 deg
Sample Weight: 37.920 mg
Reference Name: TAI002878A
Reference Weight: 0.000 mg

Temperature Program:

	Deg Cel	Cel/min	min	s
1*	25	110	10	70 2.5

Comment:
Operator: User
Pan: Alumina




10/90 amino/resin 110 degrees
DTG mg/min
DTA uV
TG mg
Time min
1
4
5
6
7
8
9
14
16
17
18
19
20
21
22
28
30
31

Experimental

The TGA instrument is a Seiko Exstar SII TG/DTA 6300 and the mass spectrometer is a Pfeiffer Vacuum Thermostar unit. The TGA heats the pre-weighed sample at the programmed ramp rate in the delivered atmosphere and records the weight of the sample during the entire heating process. The TGA and MS are connected by means of a silica capillary contained within a heated sample line. The MS detector is under vacuum, thereby pulling the outgassed products of the sample into the MS quadrupole detector.

Each sample is separately analyzed and a blank analysis is performed after each sample to ensure that the system is free of contamination.

The samples were analyzed from ambient temperature to 80°C in 100% Nitrogen (N_2) atmosphere and from ambient temperature to 110°C in 100% Nitrogen (N_2) atmosphere. The furnace ramp rate was 10°C/minute to final temperature (80°C or 110°C) with a 70 minute hold time at the final temperature. Sample results include the TGA profile of the sample, the MS detector output and a table of mass to charge (m/z) components detected from the sample and the run time/temperature that the m/z components were detected. Please note that the Identification column includes possibilities at the given m/z ratio. The MS range was selected up to 200AMU. Some analysis runs had a m/z peak at 20AMU. This peak is unidentified.

TGA and MS spectra are included in Appendix 1. Several TGA graphs are included, % Weight Loss (%TG) versus Run Time (min.), Weight Loss (TG) in mg or ug versus Temperature (°C), and Weight Loss (TG) in mg or ug versus run time (min.). The MS spectrum shows m/z versus Run Time (min) with the key to identifying m/z on the right side of the graph. All figures are from the same analysis run. When m/z peaks were detected, the TGA graph and the MS spectrum were superimposed on one figure to show the relationship between the two.