Headspace GC-MSD Analysis of Denaturants In SDA Products

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SDA Products

- Contain specially denatured spirits or rum
- Not intended for ingestion
- Not taxed by TTB
- Require formula approval in most cases
- Must be unfit for beverage purposes
- Cannot recover potable alcohol from article

SDA Background Information

- Title 27 CFR Parts 20 and 21
- General Use Formulas
- 49 different SDA formulas in the regulations
- 92 denaturants listed in the regulations
- Approximately 40% are currently used as denaturants or as ingredients in products

SDA Background Information, Cont'd.

- Routine analyses
- STARS samples
- Compliance samples
- Many gel hand sanitizers
- New innovations
- Least monitored industry

Objectives

- Develop a method to encompass many denaturants in one run
- Ease of use and suitable for denaturants of interest
- Analyze all product types and matrices
- Suitable replacement for previous 5830 GC method and current method

Previous 5830 GC Method

- Developed by Glenn E. Martin and Donald M. Figert and published in JOAC in 1974
- Used Flame Ionization Detector and packed column
- 12 Denaturants were analyzed
- 3 Concentration Levels (2, 4 and 8 % vol.)

Current Denaturant Method

- 6890 Alcohol GC with TCD and packed column for quantitation
- 6890 GCD for screening (qualitative analysis)
- Developed individual methods as needed
- Separate runs for each denaturant
- Never validated nor published

Headspace GC-MSD vs. 5830 GC

- 6890 GC
- MSD
- Capillary Column
- 10 denaturants
- 9 Concentration Levels
- Liquid, gel and solid samples

- 5830 GC
- FID
- Packed Column
- 12 denaturants
- 3 Concentration Levels
- Liquid samples

Headspace Parameters

- Oven temperature = 90 ºC
- Loop temperature = 100 ºC
- Transfer line temperature = 110 ºC
- GC-cycle time = 28 minutes
- Vial equilibration time = 15 minutes
- Pressurization time = 0.20 minute
- Loop fill time = 0.20 minute
- Loop equilibrium time = 0.20 minute
- Injection time = 0.20 minute
- Shake = High

GC-MSD Parameters

- Stationary phase = DB-Wax 0.32 mm i.d. x 30 m, 0.5 µm film thickness
- Initial oven temperature = 31 ^{o}C for 6 minutes
- Temperature ramp to 60 ^{o}C at 25 ^{o}C/min for 1 min; then to 220 ^{o}C at 50 ^{o}C/min for 2 min
- Total run time = 13.36 minutes
- Split ratio = 200:1 with 50 µl sample loop
- MSD scan 25 – 250 amu

Sample Preparation for Headspace GC-MSD Analysis

For liquid and gel samples

Using positive displacement transferpettor:

- Add 200 µL sample or standard to 20 mL headspace vial
- Spike with 100 µL diluted acetone – d_6 (internal standard)

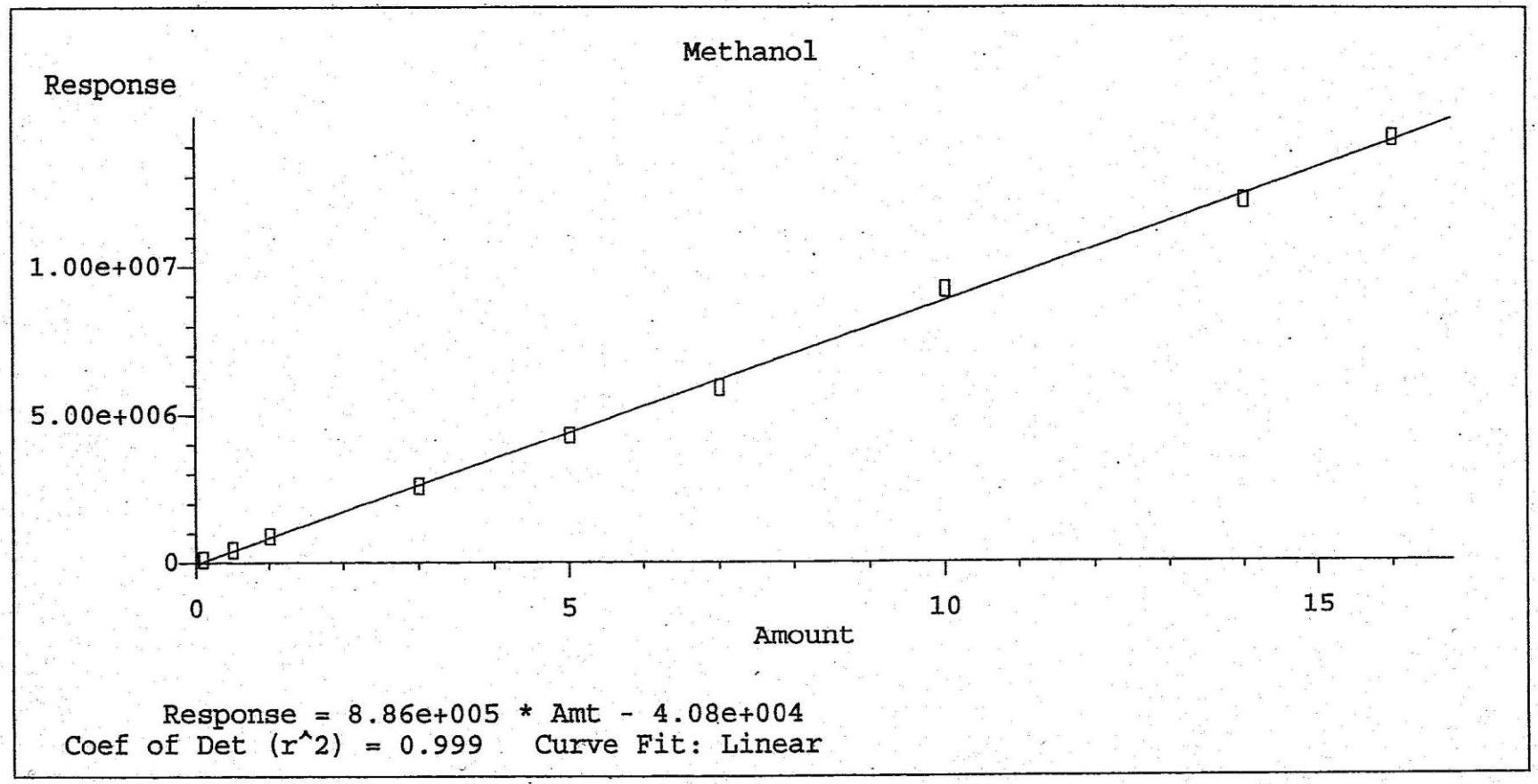
Work Completed

- Analyzed 20 SDA products to date
- Evaluated 10 concentrations ranging from 0.1 – 20% by volume
- 5 replicates of 5 concentration levels and 5 SDA products
- Analyzed data from 12 unknowns (blinds)

Properties of 10 Denaturants and Internal Standard

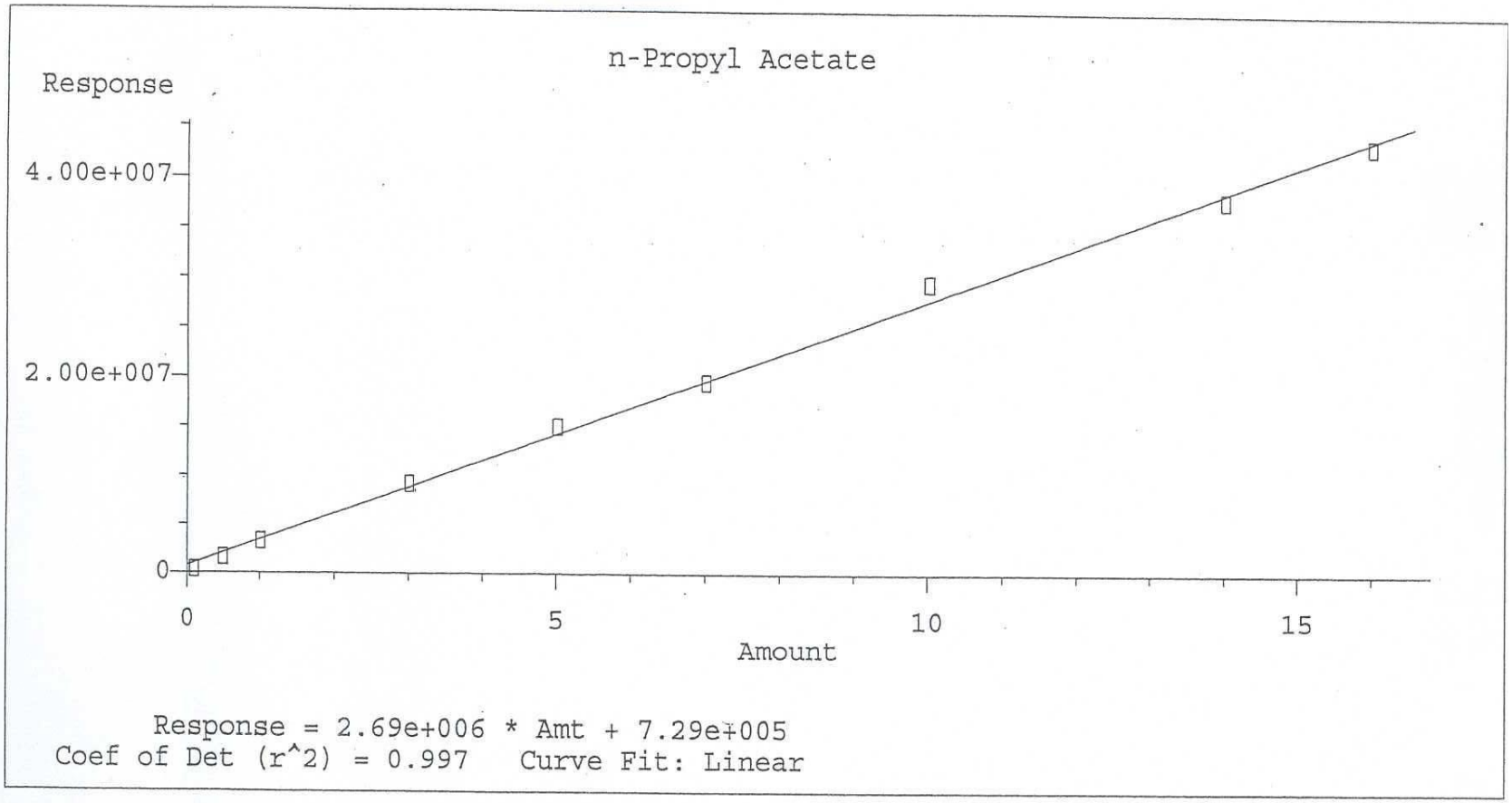
Denaturant	Boiling Point (°C)	Retention Time (min)	Target Ion (m/z)	Qualifier Ions (m/z)
Acetone- d_6 (Internal Standard)	55.5	2.10	46	64,28
Acetone	55.5	2.14	43	39,58
Ethyl Acetate	76.5-77.5	3.18	43	61,70
Heptane	98	1.39	71	43,57
Isopropanol	82.5	4.30	45	43,59
Methanol	64.7	3.42	31	29,32
Methyl Ethyl Ketone	79.5-79.8	3.36	43	29,72
Methyl Isobutyl Ketone	117-118	6.56	43	58,85
n-Propyl Acetate	102	5.54	43	61,73
tert-Butanol	83	3.65	59	41,57
Toluene	110.6	7.27	91	39,65

Calibration Curve of Methanol



Method Name: C:\HPCHEM\1\METHODS\SDA1.M
Calibration Table Last Updated: Wed May 11 14:01:10 2005

Calibration Curve of n-Propyl Acetate



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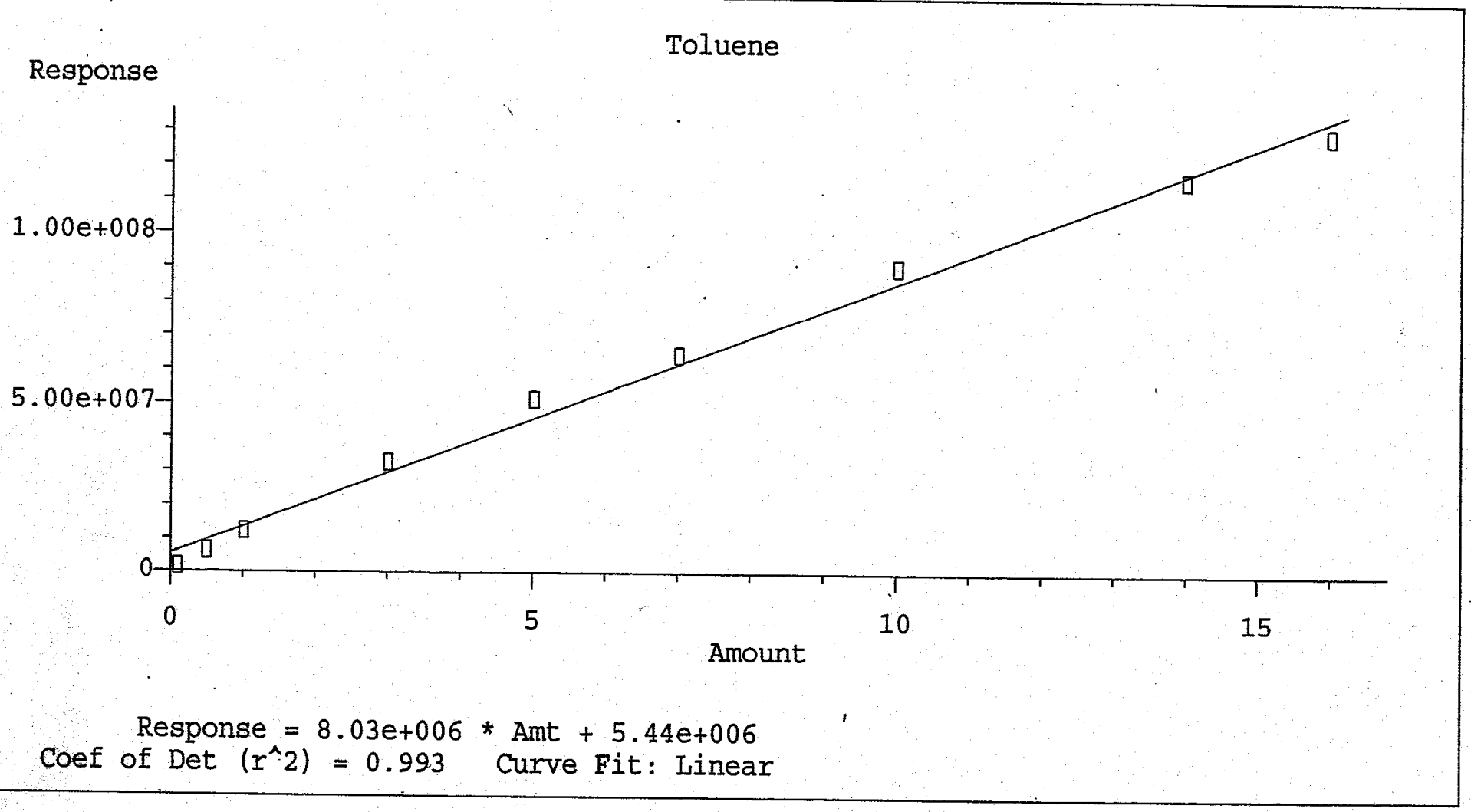
Calibration Table Last Updated: Wed May 11 14:42:23 2005

Calibration Curve of Toluene



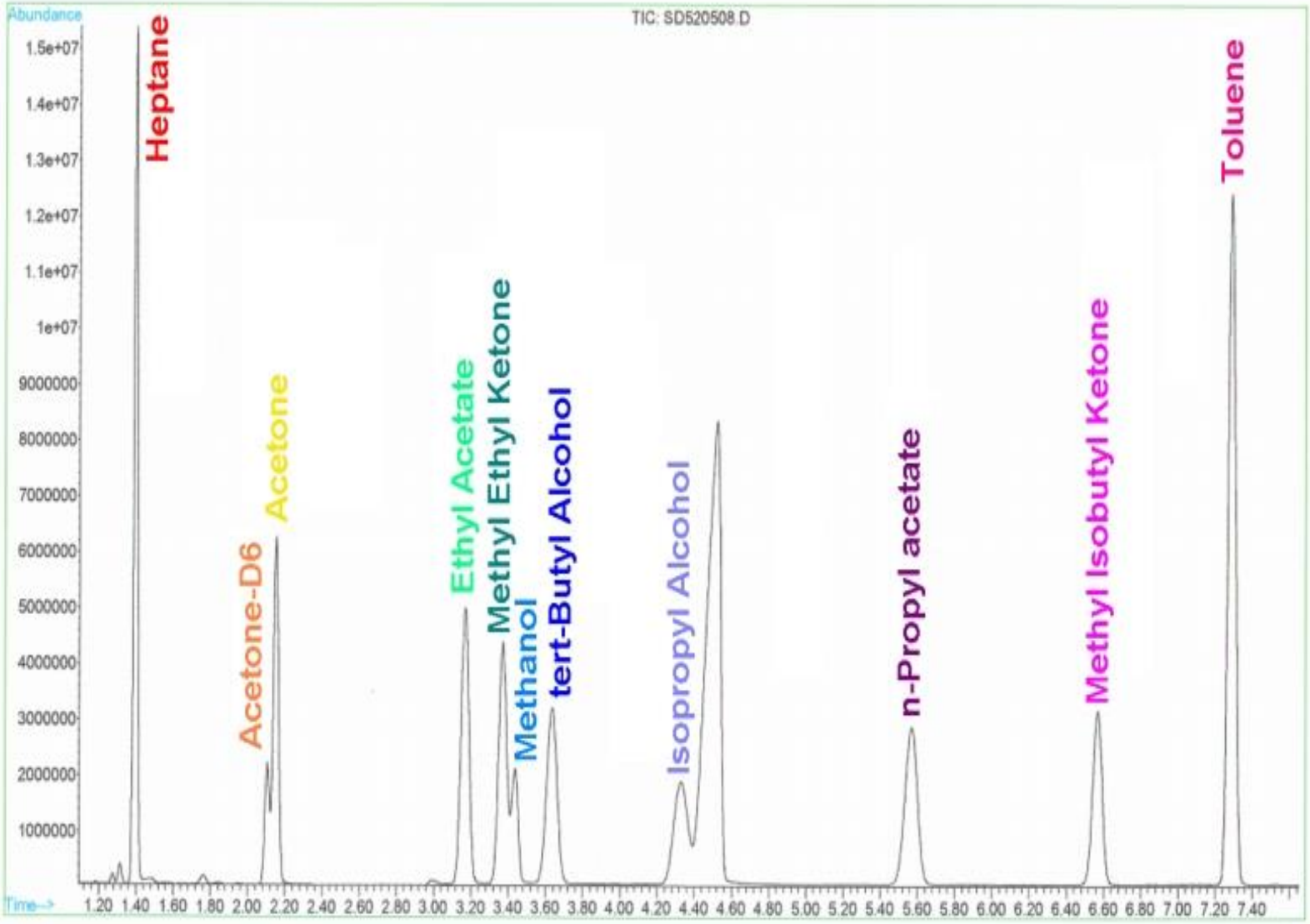
Response = 8.03e+006 * Amt + 5.44e+006
Coef of Det (r^2) = 0.993 Curve Fit: Linear

Method Name: C:\HPCHEM\1\METHODS\SDA1.M

Linear Range of 10 Denaturants

Denaturant	r^2	Linear Range (% vol)	LOQ (% vol)
Acetone	0.998	0.10-16	0.10
Ethyl Acetate	0.997	0.10-16	0.10
Heptane	0.996	0.10-16	0.10
Isopropanol	0.997	3-10	3
Methanol	0.999	0.10-16	0.10
Methyl Ethyl Ketone	0.998	0.10-16	0.10
Methyl Isobutyl Ketone	0.996	0.10-10	0.10
n-Propyl Acetate	0.997	0.10-16	0.10
tert-Butanol	0.998	0.10-16	0.10
Toluene	0.993	0.10-16	0.10

3% Concentration of 10 Denaturants



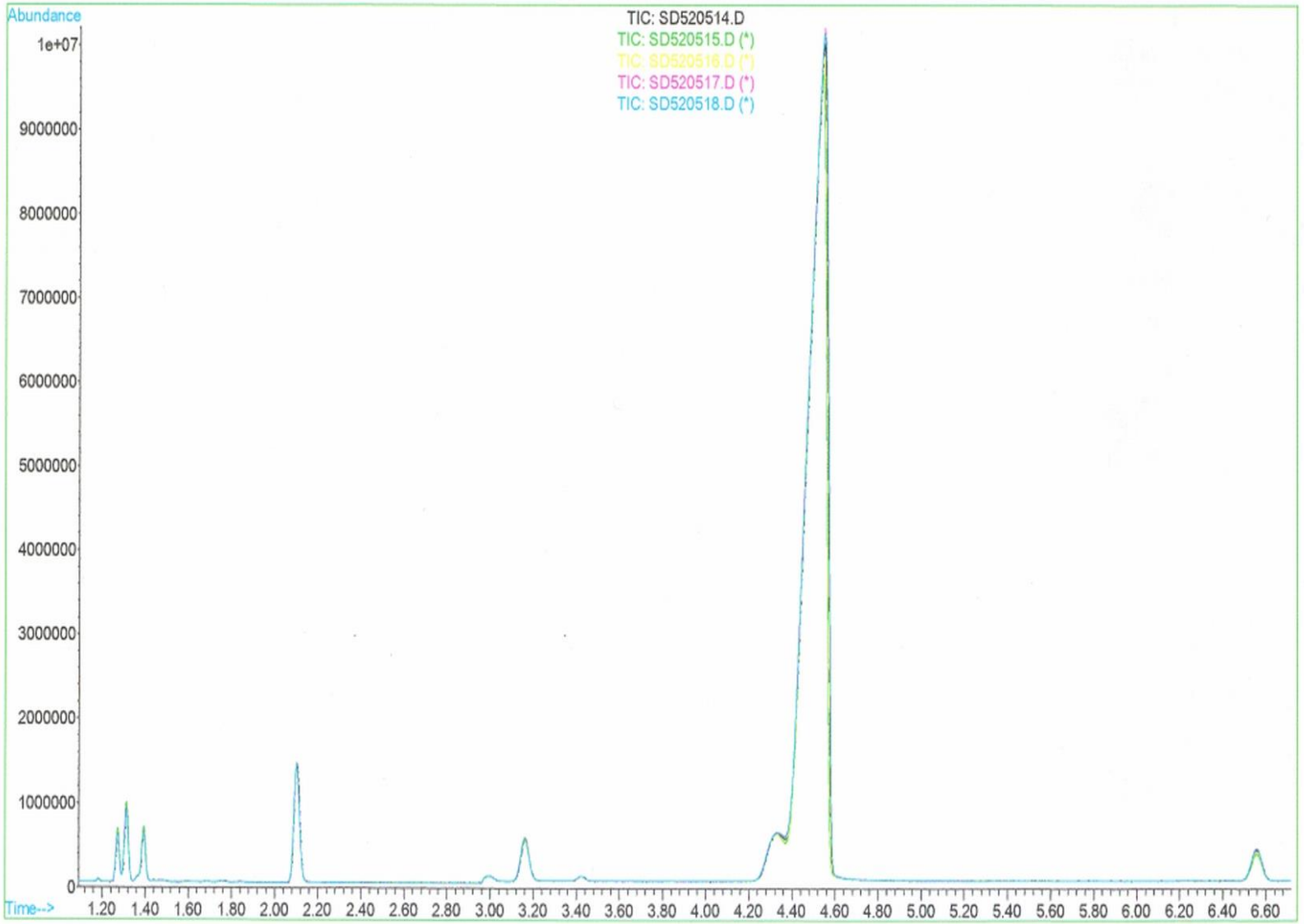
Data For 5 Injections of 1% &10% Standards

Denaturant	Avg. Value 1% Std.	% RSD 1% Std.	Avg. Value 10% Std.	% RSD 10% Std.
Acetone	1.01	2.66	9.83	0.87
Ethyl Acetate	1.05	1.94	9.99	1.87
Heptane	0.84	6.73	9.45	1.93
Isopropanol	Not Calib.	Not Calib.	9.22	1.67
Methanol	1.09	1.71	10.23	1.43
Methyl Ethyl Ketone	1.08	1.81	10.13	2.56
Methyl Isobutyl Ketone	1.36	4.51	10.92	9.47
n-Propyl Acetate	1.16	1.94	10.45	5.55
tert-Butanol	1.26	2.66	10.66	4.78
Toluene	1.08	1.60	9.90	3.54

Data For Sample #40206

Denaturant	Heptane	Ethyl Acetate	Methanol	IPA	MIBK
Per Formula (% vol)	0.97	0.97	N/A	4.62	0.97
Vial #1	1.51	1.22	0.45	4.15	1.58
Vial #2	1.55	1.37	0.47	4.20	1.40
Vial #3	1.49	1.22	0.43	4.25	1.51
Vial #4	1.57	1.29	0.46	3.97	1.73
Vial #5	1.47	1.24	0.45	4.10	1.67
Avg. Value	1.52	1.27	0.45	4.13	1.58
% RSD	2.44	4.50	2.93	2.32	7.38

5 Injections of Sample #40206



Summary

- Method represents the most commonly used volatile denaturants
- Great reproducibility, precision and accuracy
- All 10 denaturants were successfully identified
- Ability to analyze various sample types without matrix interference
- Provides both quantitative and qualitative data

Overlay of Sample #40220 and Distillate

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File        : C:\HPCHEM\1\DATA\32905\SD329052.D
Operator    : Tomika
Acquired    : 29 Mar 2005  17:26      using AcqMethod SDA1
Instrument  :   GC/MS Ins
Sample Name: 40220
Misc Info   :
Vial Number: 2
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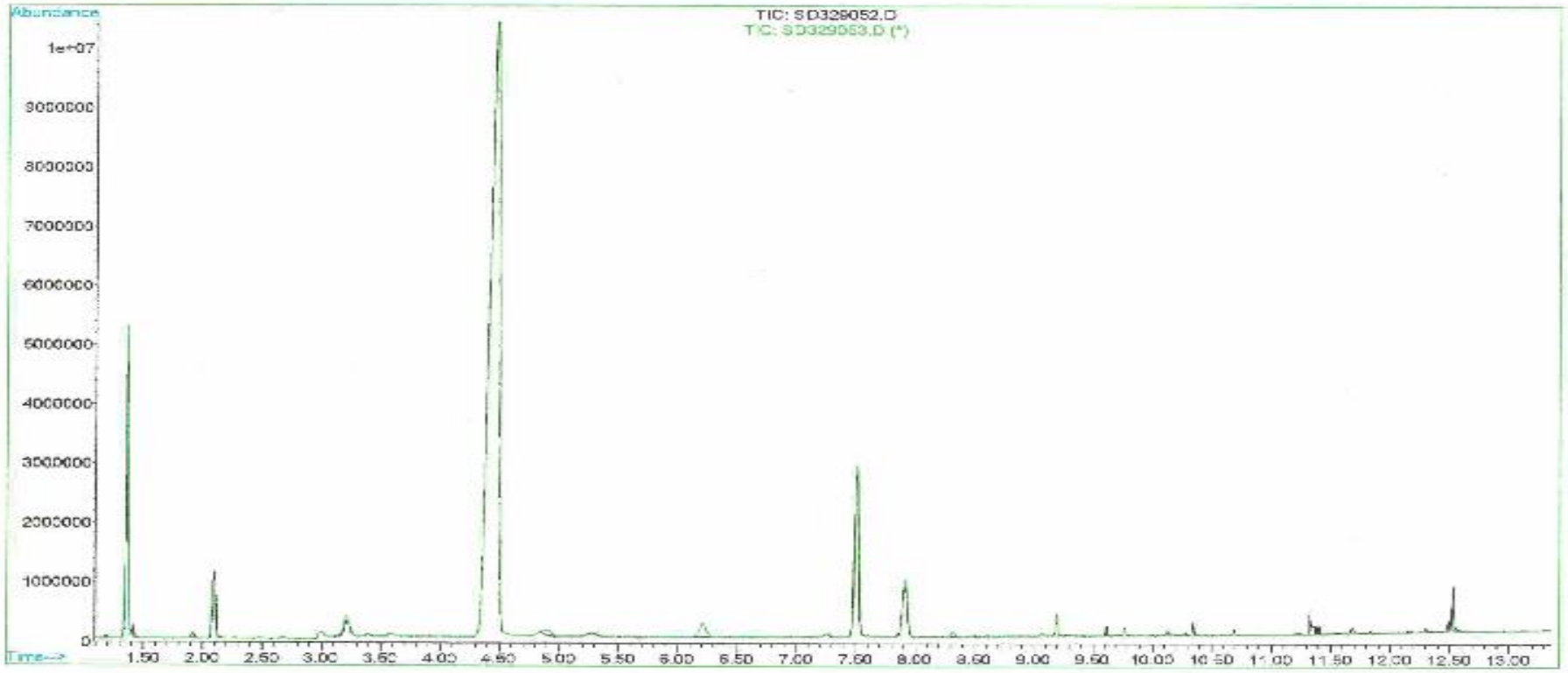

Future Work

- Analyze more SDA products
- Experiment with DB – 624 column (30 m x 0.25 m i.d., 0.25 μm)
- New GC-MSD with Headspace unit (Time dependent vs. Volume dependent)

Acknowledgements

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