How to Meet the Analytical Requirements of NJ Low Level TO-15

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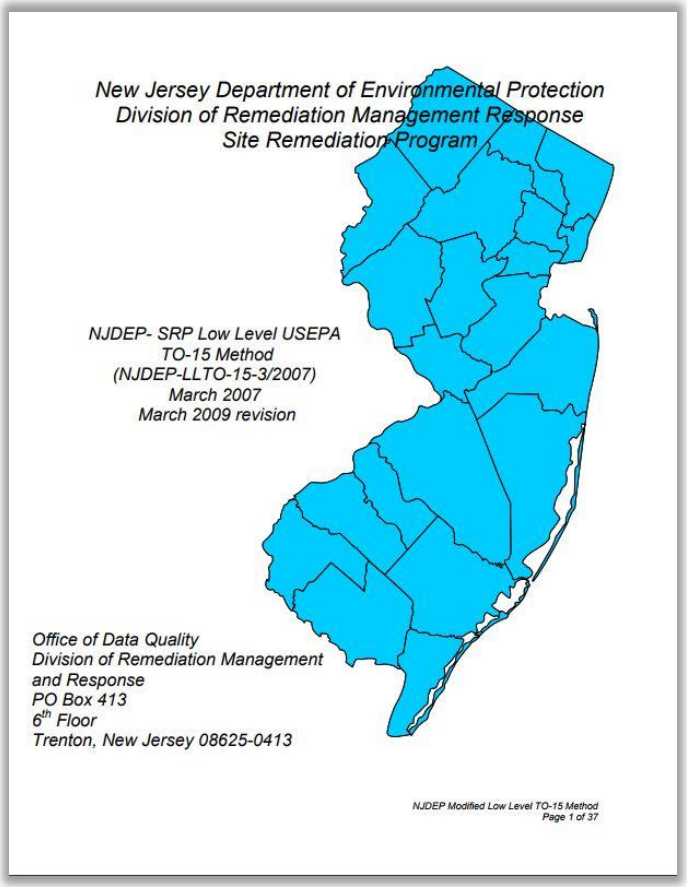
NJ Low Level (LL) TO-15

- Basically a variant of U.S. EPA Method TO-15
- Some minor tweaks targeted to "provide for a lower reporting limit…"
- A little more "prescriptive…"


New Jersey Department of Environmental Protection
Division of Remediation Management Response
Site Remediation Program

NJDEP- SRP Low Level USEPA
TO-15 Method
(NJDEP-LLTO-15-3/2007)
March 2007
March 2009 revision

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Division of Remediation Management
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NJDEP Modified Low Level TO-15 Method
Page 1 of 37

Tweaks:

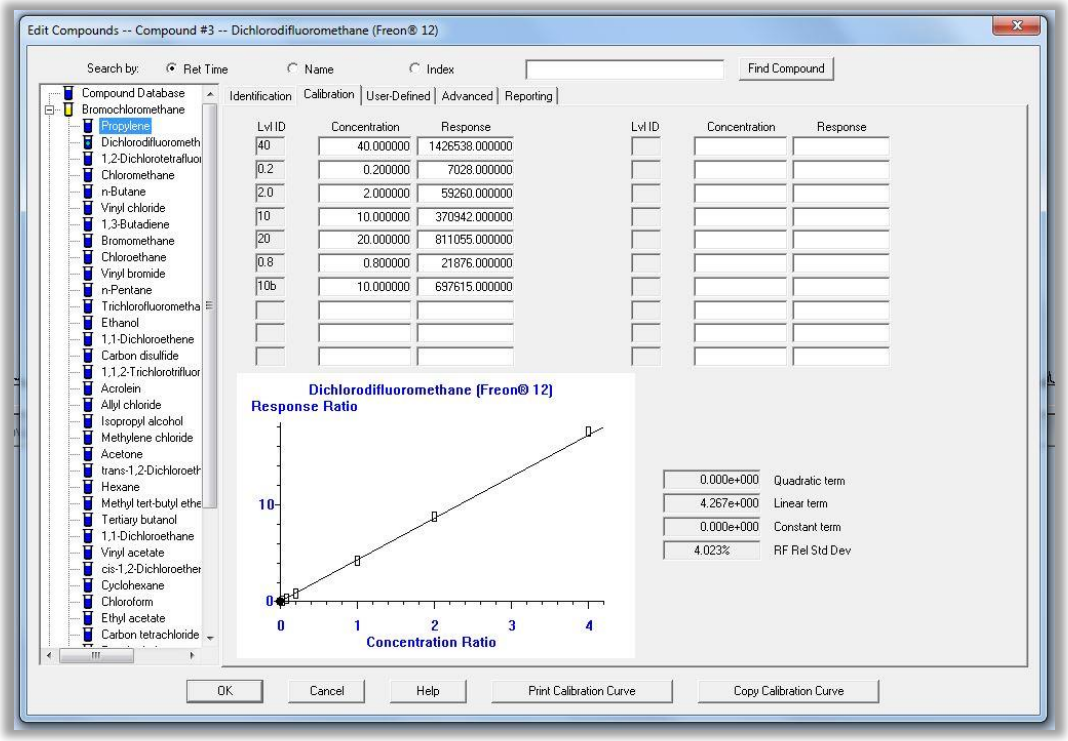
- Holding times
- Canister types and regulators
- Method detection limits
- Reporting limits
- Clean canister certification levels
- GC-MS tuning and instrument performance check requirements
- GC-MS techniques
- Standard type and concentrations
- Initial and continuing calibration standards
- Laboratory control samples
- Limitation regarding the source of make-up air

Focus for Today

- Most of the tweaks are straight-forward/self-explanatory
- Focus on analytical side
- In particular the calibration from 0.20 ppbv to 40 ppbv

0.20 to 40 ppbv Calibration Range

- Single biggest complaint I have received regarding NJ LL TO-15
- Multiple variables involved in calibration:
  - Blanks
  - ISTDs
  - STDs

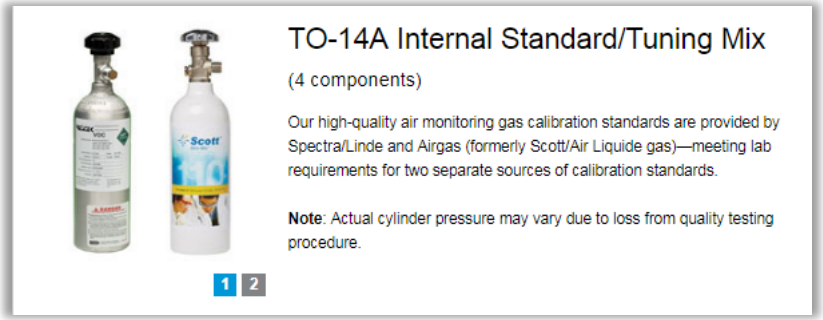


Foundation for Everything

- 12 cleaning cycles at 80 °C
- Humidified (35% RH) ***AIR*** sweep gas
- Filled with filtered "zero" ***air***

ISTDs

- Requires bromochloromethane, chlorobenzene-d5 and 1,4- difluorobenzene
- The required concentration of each of the internal standards is 10 ppbv



ISTDs on a Markes CIA Advantage

- Markes ships the CIA Advantage with a 1 mL sampling loop for ISTD delivery
- My nominal injection volume is 250 mL
  - Beyond this chloromethane misbehaves (i.e., breakthrough)
- You would need a 2.5 ppbv ISTD to achieve the required 10 ppbv of ISTDs
  - This is a custom standard Restek would gladly provide you, but why not “KISS”

Giving my CIA Advantage an "advantage"

- I replaced my 1 mL sampling loop with a 5 mL loop
  - I am sure Markes will do this for you

- Now I dilute my ISTDs down to 500 ppbv into a 6 L canister and achieve 10 ppbv with the 5 mL loop

Why is this an advantage?

- No need for custom ordered standards
- You only have a 18 L of your 110 L standard attached to the system
  - If I have a leak, I am only out 18 L of expensive standard
  - I can attach a mini-regulator and tightly control the pressure delivered to the system despite changes in canister pressure
- Tighter RSDs on internals
  - ±10 µL swing from injection to injection on a 1.0 mL sample represents 1 %
  - Now that same swing only = 0.2%

One Final Note on ISTDs

- Whether you run a Markes or Entech, ISTDs are the foundation of your calibration curve as you are using the %RSD of the RRF

- Inject larger volumes of lower concentrations on both units
  - Example: 7100 customer called and complained of poor linearity. They disclosed they were using a 25 mL volume on ISTDs. We bumped the ISTDs up to 100 mL and the customer was happy

63 VOCs

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75 Comp TO15 + NJ Mix (75 components)

Our high-quality air monitoring gas calibration standards are provided by Spectra/Linde and Airgas (formerly Scott/Air Liquide gas)—meeting lab requirements for two separate sources of calibration standards.

Note: Actual cylinder pressure may vary due to loss from quality testing procedure.

1 2

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10 Comp NJ Subset Test Mix (10 components)

Our high-quality air monitoring gas calibration standards are provided by Spectra/Linde and Airgas (formerly Scott/Air Liquide gas)—meeting lab requirements for two separate sources of calibration standards.

Note: Actual cylinder pressure may vary due to loss from quality testing procedure.

1 2

Label	Compound	Retention Time	Label	Compound	Retention Time
1	Propylene	1.21	41	Trichloroethylene	8.05
2	Dichlorodifluoromethane (Freon® 12)	1.25	42	1,4-Difluorobenzene*	8.18
3	1,2-Dichlorotetrafluoroethane (Freon® 114)	1.37	43	1,2-Dichloropropane	8.90
4	Chloromethane	1.43	44	Bromodichloromethane	9.07
5	n-Butane	1.45	45	Methyl methacrylate	9.45
6	Vinyl chloride	1.49	46	1,4-Dioxane	9.44
7	1,3-Butadiene	1.51	47	cis-1,3-Dichloropropene	10.11
8	Bromomethane	1.82	48	Toluene	10.46
9	Chloroethane	1.94	49	Tetrachloroethene	11.05
10	Vinyl bromide	2.06	50	trans-1,3-Dichloropropene	11.21
11	n-Pentane	2.10	51	4-Methyl-2-2pentanone (MIBK)	11.19
12	Trichlorofluoromethane (Freon® 11)	2.09	52	1,1,2-Trichloroethane	11.45
13	Carbon disulfide	2.64	53	Dibromochloromethane	11.7
14	1,1-Dichloroethene	2.64	54	1,2-Dibromoethane	12.01
15	1,1,2-Trichlorotrifluoroethane (Freon® 113)	2.72	55	2-Hexanone (MBK)	12.58
16	Ethanol	2.68	56	Chlorobenzene	12.91
17	Acrolein	3.09	57	Chlorobenzene-d5*	12.89
18	Allyl chloride	3.25	58	n-Nonane	12.99
19	Methylene chloride	3.4	59	Ethylbenzene	13.02
20	Isopropyl alcohol	3.45	60	m-Xylene	13.28
21	Acetone	3.51	61	p-Xylene	13.27
22	trans-1,2-Dichloroethene	3.62	62	o-Xylene	14.06
23	Hexane	3.75	63	Bromoform	14.05
24	Methyl tert-butyl ether (MTBE)	3.82	64	Styrene	14.07
25	Tertiary butanol	4.13	65	Cumene	14.53
26	1,1-Dichloroethane	4.58	66	4-Bromofluorobenzene[t]	14.96
27	Vinyl acetate	5.16	67	n-Propyl benzene	15.24
28	cis-1,2-Dichloroethene	5.56	68	2-Chlorotoluene	15.44
29	Cyclohexane	5.83	69	1,1,2,2-Tetrachloroethane	15.42
30	Bromochloromethane*	5.90	70	4-Ethyltoluene	15.45
31	Chloroform	6.12	71	1,3,5-Trimethylbenzene	15.62
32	Carbon tetrachloride	6.22	72	1,2,4-Trimethylbenzene	16.28
33	1,1,1-Trichloroethane	6.37	73	1,3-Dichlorobenzene	16.74
34	Tetrahydrofuran	6.36	74	1,4-Dichlorobenzene	16.92
35	Ethyl acetate	6.46	75	Benzyl chloride	17.41
36	2-Butanone (MEK)	6.70	76	1,2-Dichlorobenzene	17.64
37	2,2,4-Trimethylpentane	6.84	77	1,2,4-Trichlorobenzene	20.28
38	Benzene	7.03	78	Hexachlorobutadiene	20.29
39	Heptane	7.07	79	Naphthalene	20.72
40	1,2-Dichloroethane	7.40			

* Internal standard
[t] Tuning standard
Courtesy of NJ

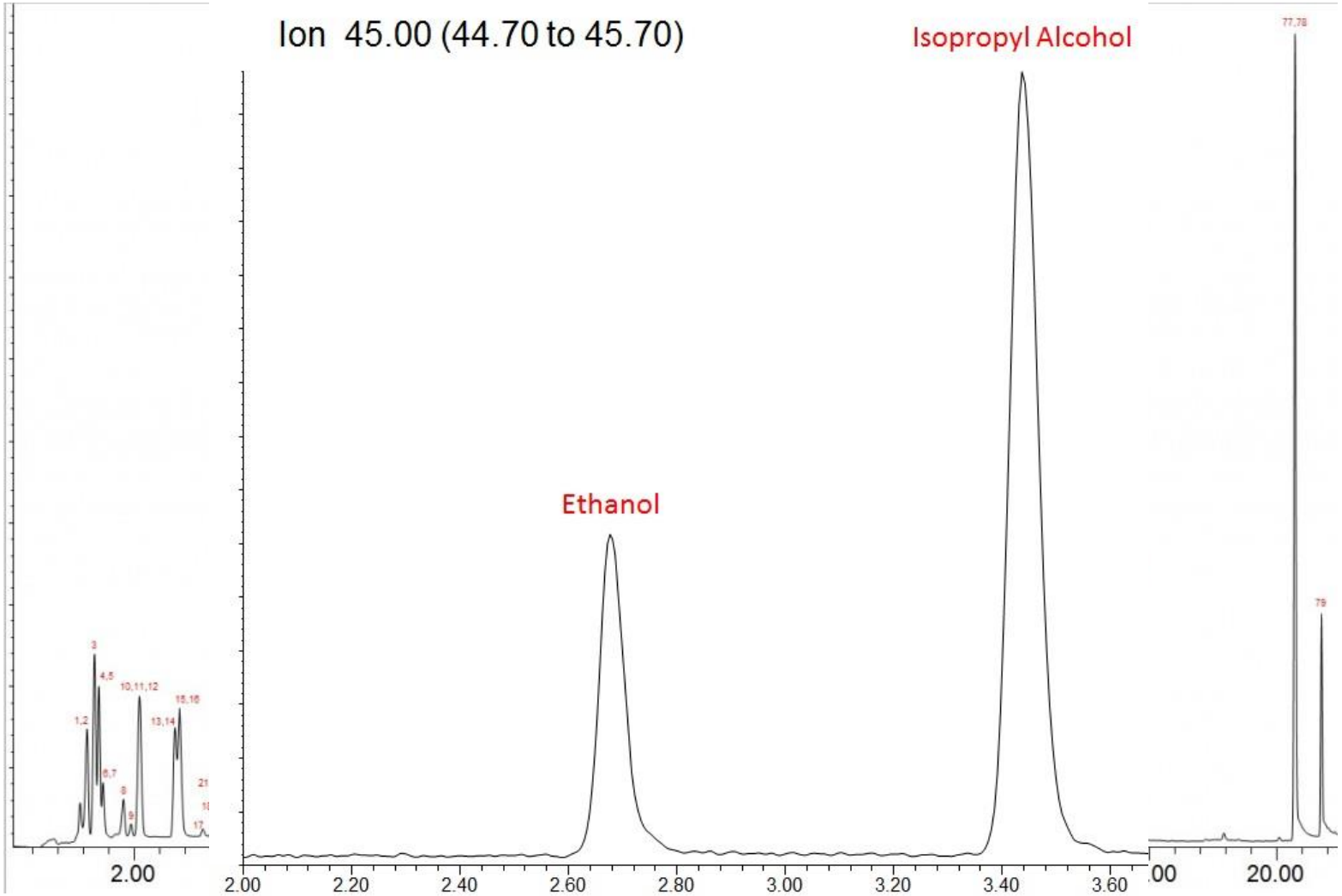
Analytical Parameters

Markes CIA Advantage™ Parameters	
General Settings	
Mode	MFC Sampling IS First
Standby Split On	True
Standby Split Flow	5 mL/min
Flow Path Temperature	200 °C
GC Cycle Time	22.17 min
Minimum Carrier Pressure	5.0 psi
Pre Sampling	
Leak Test	True
Sample Purge Time	1.0 min
Sample Purge Flow	50 mL/min
Add Internal Standard	True
Loop Fill Time	1 min
Loop Equilibrate Time	0 min
Loop Inject Time	1
Loop Inject Flow	5 mL/min
Sampling	
Sample By Volume	True
Sample Quantity	250 mL
Sample Flow	100 mL/min
Use Dedicated Purge Channel	False
Post Sampling Purge Time	1.0 min
Post Sampling Purge Flow	50.0 mL/min
Enable CIA Post Sampling Purge	True
Trap Settings	
Trap Purge	1.0 min
Trap Purge Flow	50 mL/min
Trap Low	40 °C
Trap High	300 °C
Trap Heating Rate	Max
Trap Hold	3.0 min
Split On	True
Split Flow	7.5 mL/min
Post Desorb Purge Time	1.0 min
Post Desorb Purge Flow	100 mL/min

Agilent 7890B/5977A GC-MS Parameters	
Column	
Rtx-VMS, 30 m, 0.25 mm ID, 1.40 µm (cat.# 19915)	
Oven	
32 °C (hold 5 min) to 150 °C at 8 °C/min to 230 at 33 °C	
Carrier Gas	
Type	Helium
Mode	Constant Flow
Flow Rate	2.0 mL/min
Linear Velocity	51.15 cm/sec
Detector	
Type	Single Quadrupole MS
Mode	Scan
Transfer Line Temp.	250 °C
Source Temp.	230 °C
Quad Temp.	150 °C
Electron Energy	70 eV
Tune Type	BFB
Ionization Mode	EI

- My system had a sweet spot injection volume around 250 mL
- This volume was largely dictated by chloromethane.

Rtx-VMS 30 x 0.25 x 1.40



Calibration Curve

- 5-point minimum from 0.20 to 40 ppbv
- No single canister calibration with varying volumes!!!
  - Introduces varying volumes of H20
    - Impacts collection efficiency on preconcentrator traps
    - Impacts mean free path on MS (i.e., sensitivity changes)
    - Impacts chromatography, which can cause inconsistent integrations
  - Besides, multiple canisters affords multiple calibrations before all the standards are consumed

Proof is in the pudding…

- I ran one 6-point curve by analyzing 250 mL of 0.2, 0.8, 2.0, 10, 20, and 40 ppbv canisters
- I then ran one 6-point curve by varying the volume injected on the same 20 ppbv standard prepared above
  - 2.5, 10, 25, 125, 250, 500 mL
- Same concentrations delivered (in theory)

Proof is in the pudding…

Compound	Variable Volume	Constant Volume	Compound2	Variable Volume2	Constant Volume2
Propylene	25	5.0	1,2-Dichloroethane	18	11
Dichlorodifluoromethane (Freon® 12)	25	11	Trichloroethylene	89	8.2
1,2-Dichlorotetrafluoroethane (Freon® 11)	23	9.2	1,2-Dichloropropane	13	13
Chloromethane	49	15	Bromodichloromethane	15	14
n-Butane	31	14	Methyl methacrylate	26	18
Vinyl chloride	38	12	1,4-Dioxane	15	22
1,3-Butadiene	14	11	cis-1,3-Dichloropropene	23	8.8
Bromomethane	30	10	Toluene	7.5	4.8
Chloroethane	28	26	4-Methyl-2-2pentanone (MIBK)	22	10
Vinyl bromide	34	10	Tetrachloroethene	13	15
n-Pentane	24	14	trans-1,3-Dichloropropene	29	9.2
Trichlorofluoromethane (Freon® 11)	22	12	1,1,2-Trichloroethane	16	12
Ethanol	14	7.4	Dibromochloromethane	16	15
1,1-Dichloroethene	25	14	1,2-Dibromoethane	20	12
Carbon disulfide	13	16	2-Hexanone (MBK)	37	6.4
1,1,2-Trichlorotrifluoroethane (Freon® 1)	35	14	n-Nonane	28	13
Acrolein	24	15	Ethylbenzene	7.8	16
Allyl chloride	18	14	Chlorobenzene	10	15
Isopropyl alcohol	25	18	m- & p-Xylene	32	14
Methylene chloride	9.5	20	o-Xylene	16	15
Acetone	31	6.3	Styrene	25	20
trans-1,2-Dichloroethene	23	10	Bromoform	16	23
Hexane	5.8	12	Cumene	18	14
Methyl tert-butyl ether (MTBE)	32	12	n-Propyl benzene	21	12
Tertiary butanol	35	29	1,1,2,2-Tetrachloroethane	10	15
1,1-Dichloroethane	18	4.7	4-Ethyltoluene	29	11
Vinyl acetate	27	14	1,3,5-Trimethylbenzene	26	16
cis-1,2-Dichloroethene	24	12	2-Chlorotoluene	15	17
Cyclohexane	30	11	1,2,4-Trimethylbenzene	26	18
Chloroform	19	6.7	1,3-Dichlorobenzene	28	11
Ethyl acetate	21	14	1,4-Dichlorobenzene	37	13
Carbon tetrachloride	7.8	11	Benzyl chloride	50	23
Tetrahydrofuran	28	13	1,2-Dichlorobenzene	37	12
1,1,1-Trichloroethane	19	12	Hexachlorobutadiene	25	18
2-Butanone (MEK)	10	11	1,2,4-Trichlorobenzene	31	20
Isooctane	88	18	Naphthalene	28	29
Heptane	26	23			
Benzene	34	15	**Average**	**26**	**13**
			Missing NJ LL TO-15 Criteria	**11**	**0**

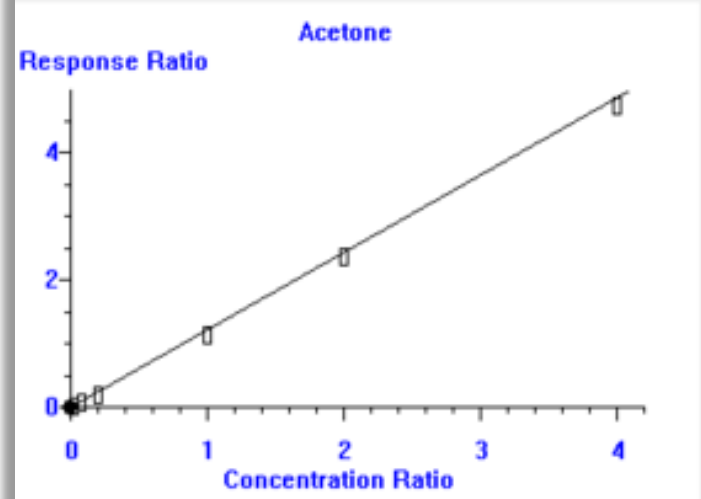
Conclusions

- Make a canister for each calibration level and keep the injection volume the same
- Just like any other analytical method out there

Blanks, blanks, blanks…

Lvl ID	Concentration	Response
0.20	0.201000	9876.000000
0.8	0.800000	31420.000000
2.0	2.010000	79518.000000
10	10.060000	435406.000000
20	20.000000	884642.000000
40	40.000000	1805571.000000

Lvl ID	Concentration	Response



0.000e+000	Quadratic term
1.213e+000	Linear term
0.000e+000	Constant term
17.551%	RF Rel Std Dev

Remaining Analytical Requirements

- MDLs = 101 pptv on average
- Precision = 13.3 %RSD on average
- Accuracy = 7.6% on average
- Just follow the outlined analytical parameters

Blog

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NJDEP-SRP Low Level TO-15 Series: Part 3 – How to calibrate your system Joisey style… but first I shall digress on ISTDs

December 3rd, 2015 by Jason S. Herrington

Last time, I showed you how well the Markes CIA Advantage™ and the Rtx®-VMS concentrate and separate the volatile organic compounds (VOCs) of interest for NJ LL TO-15. Next on the agenda would be calibrating our system (i.e., preconcentrator-GC-MS). NJ tells us to calibrate our systems with a minimum of 5 points (more allowed) and that the range must be from 0.2 to 40 ppbv for the majority of compounds (exceptions to be discussed in the next blog).

So… the single biggest complaint I have heard from laboratories running (or attempting to run) NJ LL TO-15 is the 0.2 to 40 ppbv calibration criterion. In fact, I have had laboratories (who will remain anonymous) admit to running two different curves to span the required range. I do not think this is legit, but bottom line I can now attest to the fact that achieving linear calibration across this range can be challenging, especially for all components. It is a fine balancing act between injection volume, breakthrough volume, detection limits, saturation limits, etc… However, now I am writing this blog to hopefully save you some of the headaches I have acquired. The other stipulation NJ puts out there is that we must use internal standards (ISTDs) and that their concentration needs to be 10 ppbv. So here comes the digression…

Photo courtesy of nj.com

Since we are required to use ISTDs and our calibration is based on RRF, we obviously need to have some tight RSDs on our ISTD injections. Now I will spare you the details on how many different iterations I ran on the "Pre Sampling" ISTD loop fill parameters to optimize my system (or any of the other parameters for that matter), but those are the parameters I found to work best on my system. It is important to note that no two preconcentration systems are identical… they all have slightly

Application Note

- Literally as I speak today…

Thank You!

- Co-authors
- Markes International