Thermal desorption tube analytical method development for alpha-diketones and benzene

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- Associate Service Fellow, NIOSH
- Education
  - MS in Industrial Hygiene Engineering, West Virginia University, 2016
  - BA in Chemistry, West Virginia University, 2008
- Current research focused on VOC sampling and analytical method development

Agenda

- Volatile organic compounds
- Comparison of sampling methods
- Materials and equipment
- Experimental design
- Results
- Discussion and Conclusions

Volatile Organic Compounds (VOCs)

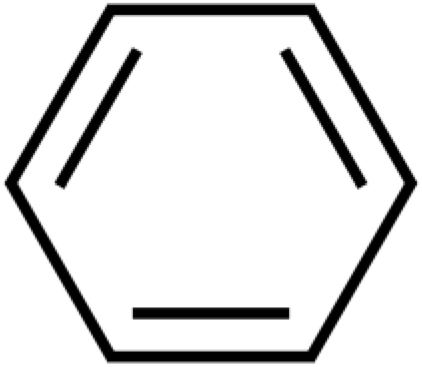
- Vapor Pressure > 0.1 mmHg at 25˚C
- Exposure can produce adverse health effects
- Ubiquitous pollutants
- Specific VOCs targeted for compliance

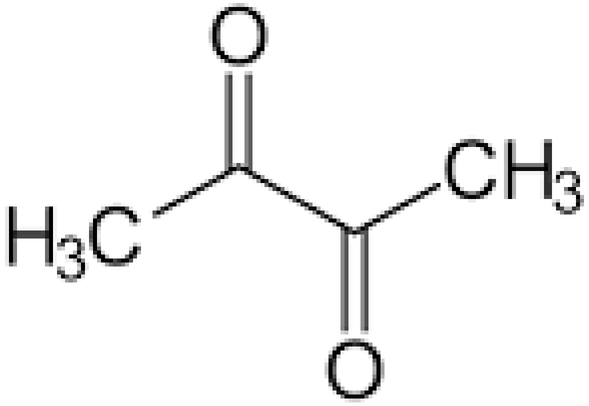
Suite of 20 VOCs

Acetaldehyde	Ethanol	Acetonitrile	Acetone	Isopropyl Alcohol
Methylene Chloride	**2,3-Butanedione**	*n*-Hexane	Chloroform	**Benzene**
2,3-Pentanedione	Methyl Methacrylate	Toluene	**2,3-Hexanedione**	Ethylbenzene
m,*p*-Xylene*	Styrene	*o*-Xylene	alpha-Pinene	*d*-Limonene

Benzene and alpha-Diketones

- Benzene
  - IARC Group 1 – carcinogenic to humans
    - Leukemia, multiple myeloma, non-Hodgkin lymphoma
  - Many manufacturing industries
  - 100ppb recommended exposure limit (REL)
- alpha-Diketones
  - Obliterative bronchiolitis
    - Fibrosis and obstruction of airways
  - Flavorings and coffee manufacturing industries
  - RELs
    - 2,3-Butanedione – 5ppb
    - 2,3-Pentanedione – 9.3ppb





Thermal Desorption Tubes

- Advantages
  - Affinity for wide range of VOCs
  - No toxic desorption solvents
  - Reduced shipping concerns
  - Reusable
  - Small size
  - Reduced humidity effects
  - Enhanced sensitivity and detection limits
- Disadvantages
  - Unreliable sampling pumps
  - No backup section to detect breakthrough
    - Must sample with multiple tubes in series

Materials and equipment

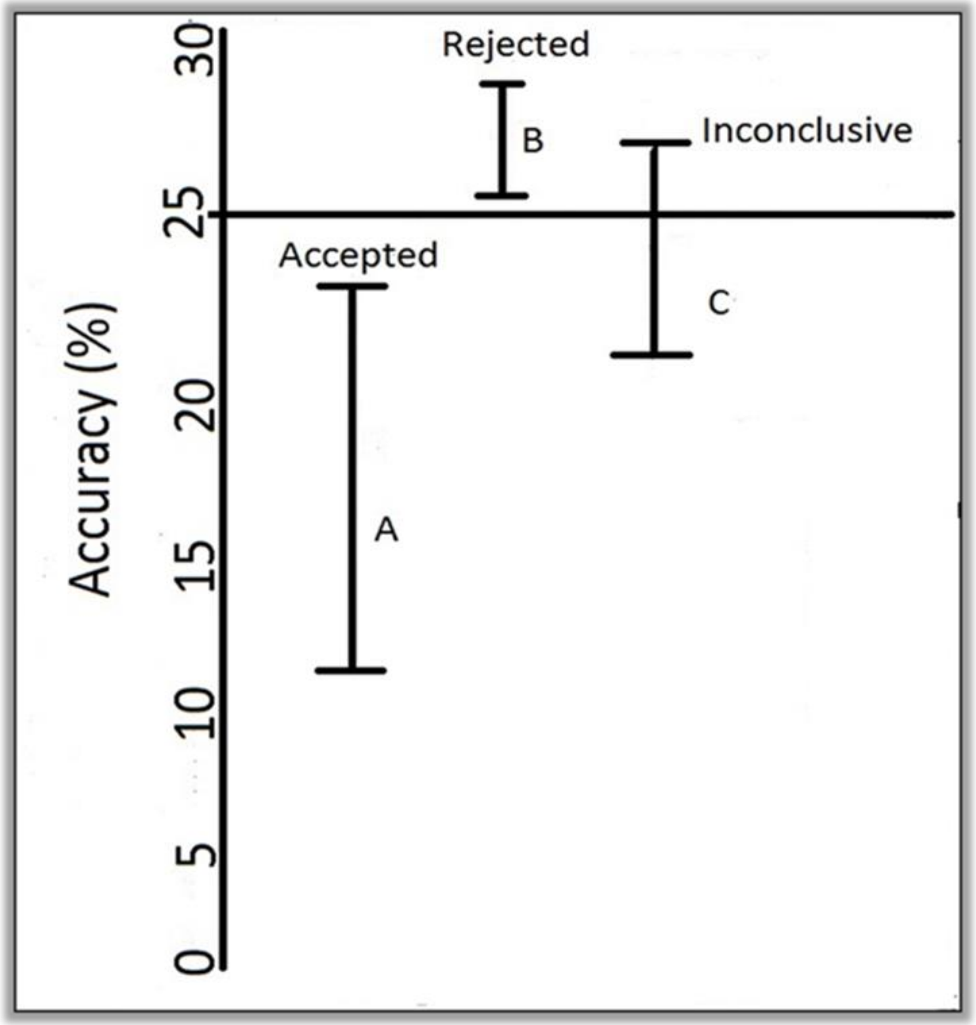
- Markes® Universal inert-coated thermal desorption (TD) tubes
  - Markes International, Inc.
  - Fused-silica inert-coated multibed sorbent tubes
    - Tenax TA
    - Carbograph 1TD
    - Carboxen 1003
- ISO 17025 certified gas standard
  - Linde® PLC
- Markes® Calibration Solution Loading Rig (CSLR)
- Markes® UNITY–ULTRA-xr™
- Agilent® 5977B gas chromatograph and 7890B mass spectrometer (GC-MS)

Experimental Design

- Sample sets:
  - Calibration curve dynamic range assessment
    - n=10
  - Limits of detection and quantification (LOD/LOQ)
    - n=6
  - Recovery assessment
    - Four loading levels ranging from 0.1*REL (~0.5ppb) to 2.0*REL (~10ppb)
    - n=6 per loading level
  - Storage stability
    - One loading level equivalent to 0.5*REL or ~2.5ppb
    - n=30

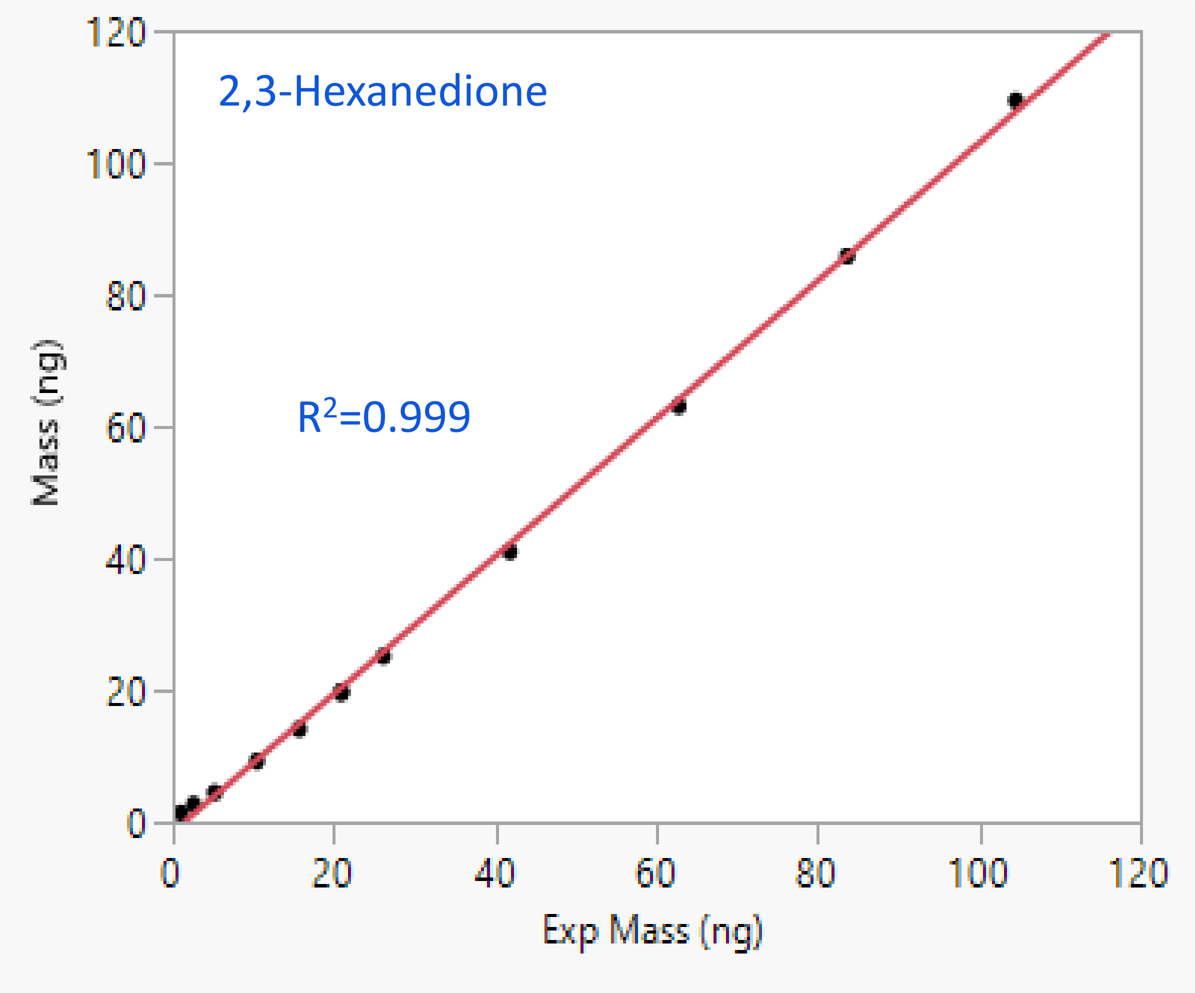
Method Development and Evaluation

- NIOSH criterion
  - +/- 25% error
  - Bias and precision
  - 95% confidence interval on accuracy
- Storage stability assessment
  - Relative percent difference
  - Refrigerated storage
    - 4°C



Calibration Curve Dynamic Range

- Curves for most compounds linear across two orders of magnitude
  - 0.1 to >100ng
- R^2 coefficient of linearity
  - Mean = 0.996
  - Maximum = 0.999
  - Minimum = 0.958

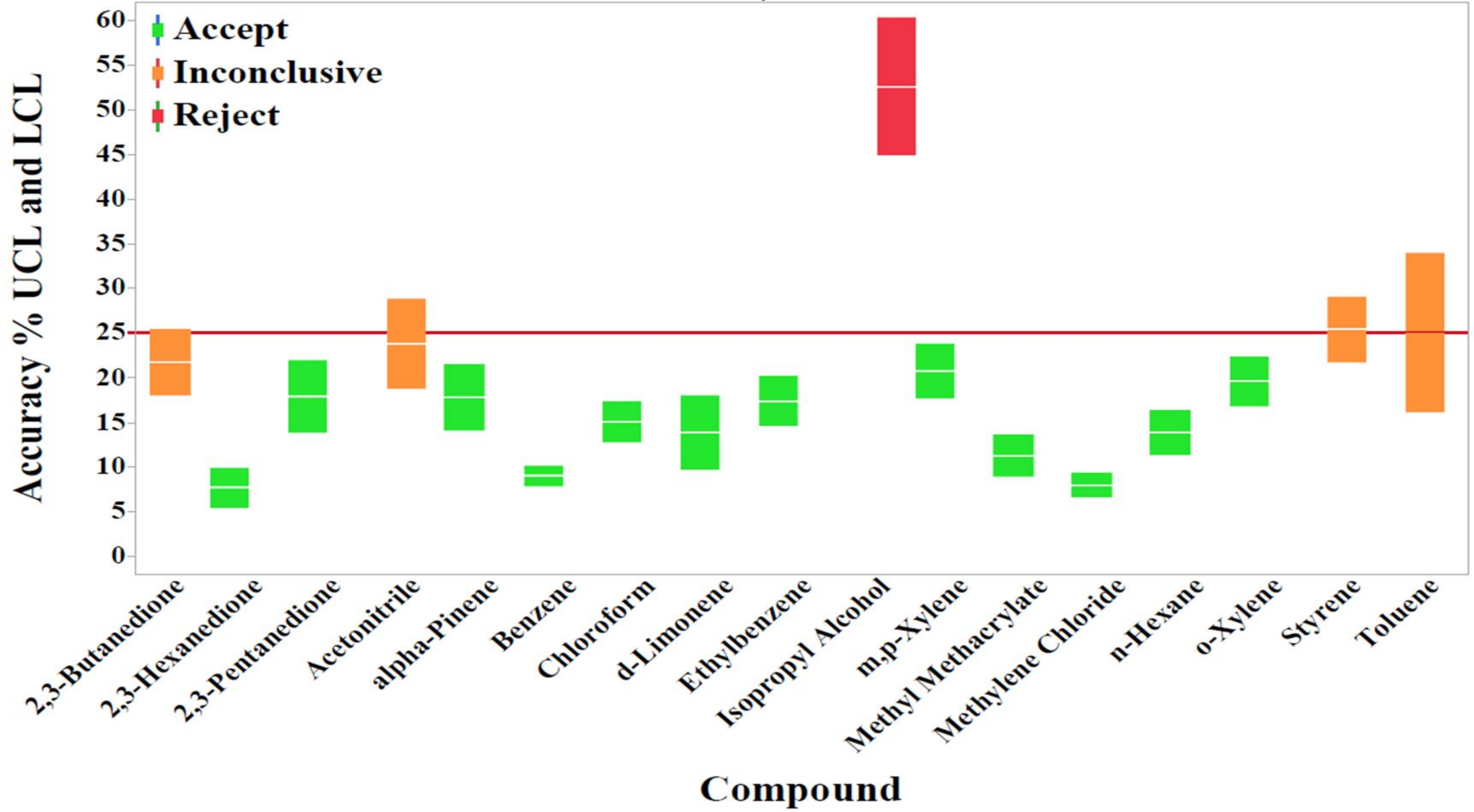


Limits of Detection and Quantification

Compound	LOD (ng , ppb)	LOQ (ng , ppb)
2,3-Butanedione	0.46 , 0.13	1.53 , 0.43
2,3-Hexanedione	1.96 , 0.42	6.53 , 1.40
2,3-Pentanedione	0.22 , 0.05	0.73 , 0.18
Benzene	0.27 , 0.08	0.89 , 0.28

- Other compounds
  - LODs range from 0.19 to 6.47 ng (0.05 ppb to 3.59 ppb)
  - LOQs range from 0.64 to 21.55 ng (0.14 ppb to 10.78 ppb)

Upper and Lower 95% Confidence Intervals (UCL & LCL) on Point Estimates of Analytical Method Accuracy


Accept
Inconclusive
Reject
Accuracy % UCL and LCL
60
55
50
45
40
35
30
25
20
15
10
5
0
2,3-Butanedione
2,3-Hexanedione
2,3-Pentanedione
Acetonitrile
alpha-Pinene
Benzene
Chloroform
d-Limonene
Ethylbenzene
Isopropyl Alcohol
m,p-Xylene
Methyl Methacrylate
Methylene Chloride
n-Hexane
o-Xylene
Styrene
Toluene
Compound

Storage stability

- Percent difference detected mass from Day 0
  - +/-10% change
- Refrigerated storage
  - 4ºC
- Day 7 data questionable
- Many compounds stable beyond 14 days
  - Some stable at 30 days

Compound	Day 7	Day 10	Day 14	Day 21	Day 30
2,3-Butanedione	18.0	6.3	5.1	19.7	25.0
2,3-Hexanedione	6.1	9.8	9.9	1.4	5.5
2,3-Pentanedione	4.5	0.5	1.6	24.8	17.6
Acetonitrile	4.8	22.6	28.6	12.3	11.8
alpha-Pinene	11.6	3.7	5.6	0.1	5.3
Benzene	15.5	3.0	2.0	4.4	4.9
Chloroform	1.2	7.8	1.9	3.1	4.3
d-Limonene	4.6	4.3	0.5	3.7	2.4
Ethylbenzene	7.2	6.4	5.1	2.4	1.6
Isopropyl Alcohol	12.3	49.6	46.9	20.6	10.5
m,p-Xylene	8.3	7.0	4.8	1.4	2.0
Methyl Methacrylate	11.8	15.3	15.3	6.5	7.6
Methylene Chloride	6.8	9.4	8.4	2.9	1.1
n-Hexane	5.3	5.1	3.0	0.1	0.1
o-Xylene	8.4	7.8	6.2	3.1	3.3
Styrene	6.6	6.9	4.7	1.1	1.7
Toluene	11.4	11.0	12.5	6.6	10.4

Discussion and Conclusions

- Analytical method passes NIOSH accuracy criterion for 12 compounds including two of the alpha-diketones and benzene
  - 2,3-pentanedione and 2,3-hexanedione pass
  - 2,3-butanedione result is inconclusive
    - Repeat assessment
- Day 7 sample storage stability data appears to disagree with Days 0, 10, 14, 21, and 30 data
  - Repeat assessment at refrigerated and ambient storage conditions
- Analytical method evaluation only
  - Full evaluation of NIOSH accuracy criterion applied to sampling AND analytical error

Takeaway

- NIOSH RHD/FSB are working on TD tube sampling and analytical method development for alpha-diketones, benzene, and a selection of other VOCs
  - Current method not yet ready for field sampling use
  - Other groups within NIOSH are working on a passive TD tube method for alpha-diketones

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    - West Virginia University

Thank you

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For more information, contact CDC
1-800-CDC-INFO (232-4636)
TTY: 1-888-232-6348 www.cdc.gov

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Selected References

- Images:
  - Sorbent Tubes | Markes International
  - Calibration solution loading rig (CSLR) | Markes International
  - Sorbent Tube Sampling With UNITY–ULTRA-xr | Markes International