

Concerns Regarding 24-hr Sampling for Formaldehyde, Acetaldehyde, and Acrolein with 2,4-dinitrophenylhydrazine (DNPH)-coated Solid Sorbents

Jason Herrington, Ph.D.
Air Innovations Chemist

The Five Ws

- Who
- What
- When
- Where
- Why



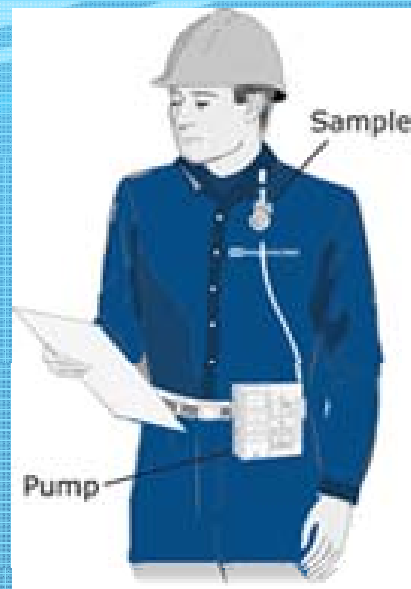
WHAT... are DNPH-coated solid sorbents?

- Silica-Gel packed cartridge coated with acidified 2,4-dinitrophenylhydrazine (DNPH)
- Air is drawn over the cartridge actively or passively
 - Carbonyls (aldehydes and ketones) are collected by derivatizing with DNPH on cartridge
- Sample is extracted with ACN and analyzed with HPLC-UV technique



WHERE... are the used?

- The list goes on ad infinitum...



WHO... wrote this method?

- Several national and international standardized methods
 - U.S. EPA Method TO-11A
 - CARB 1004
 - ASTM 5197
 - Deutsche Forschungsgemeinschaft Methoden Nr.2



- “Gold Standard”

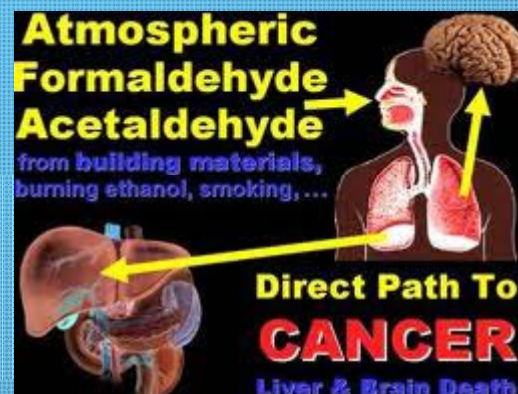
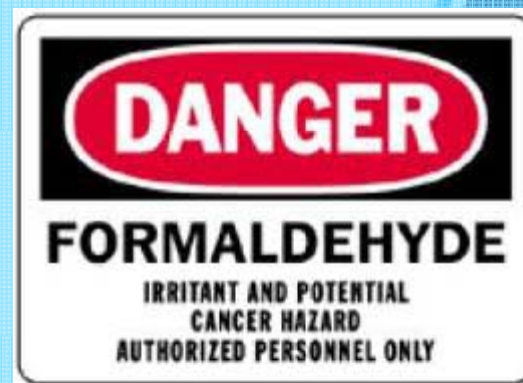
WHAT... concerns?

- Method has been around for 30 years
- Extensively developed and evaluated
- What concerns... what could have been missed?
 - **Wrong question!**
- What has not been accurately reflected in the standardized methods?



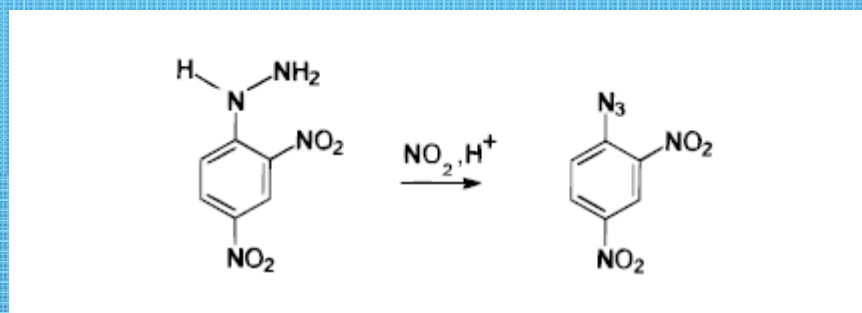
WHAT... compounds?

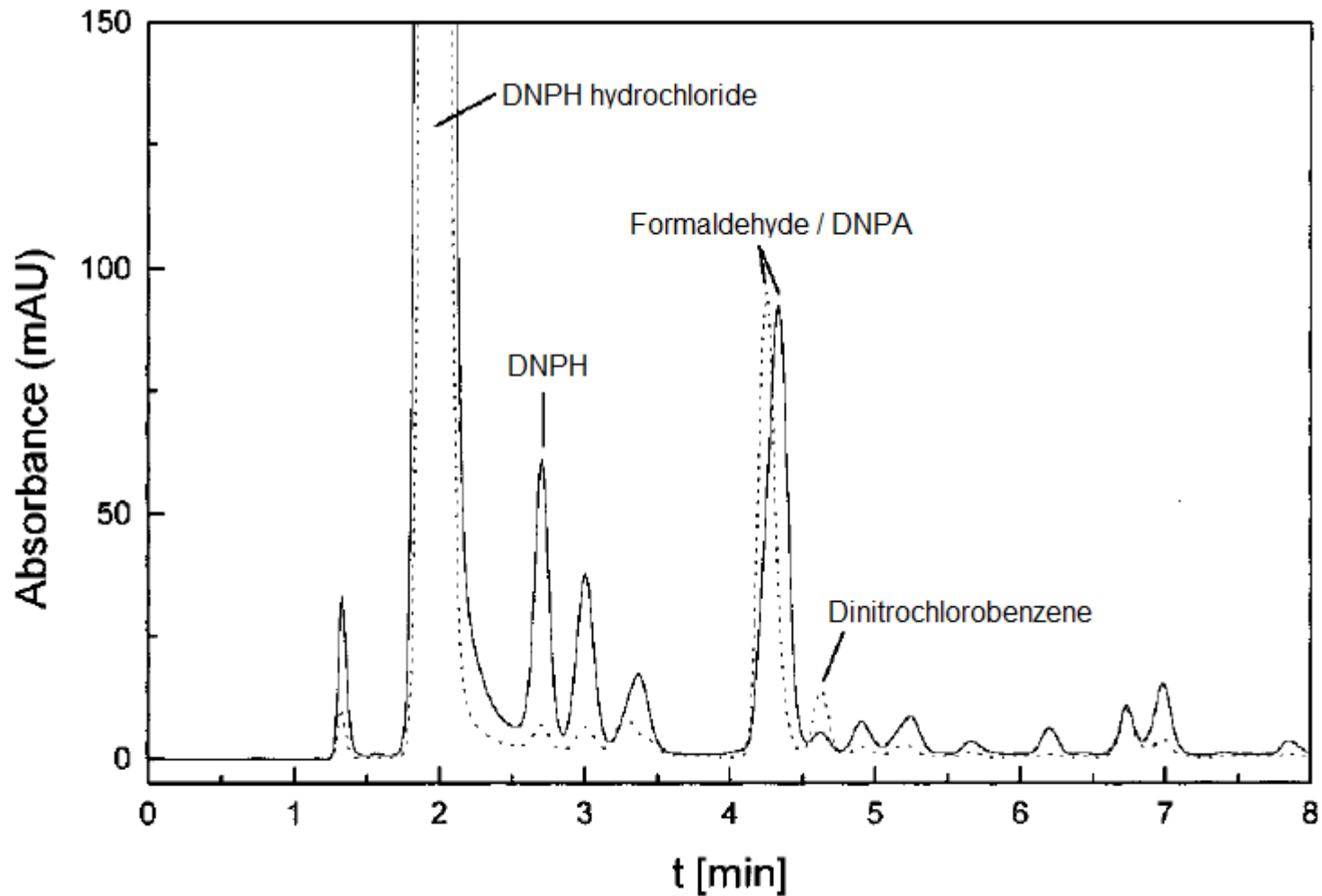
- DNPA interference with Formaldehyde
 - **Known human carcinogen**
- Low collection efficiencies for 24-hour sampling Acetaldehyde
 - **Probable human carcinogen**
- Plagued by several issues for Acrolein
 - **Highly actuely toxic**



WHAT... is DNPA?

- DNPH reacts with NO_2 to form 2,4-Dinitrophenylazide (DNPA)
- DNPA coelutes with the formaldehyde-DNPH derivative





Adopted from Potter and Karst, 1996

WHAT... is the solution for DNPA?

- Altering/optimizing the HPLC gradient can overcome the DNPA interference.
 - Several studies have capitalized on the formation of DNPA for the sampling of NO_2 , by altering/optimizing their HPLC gradient
- Diode array detector set at 300 nm for DNPA can be utilized

WHY... am I talking about DNPA then?

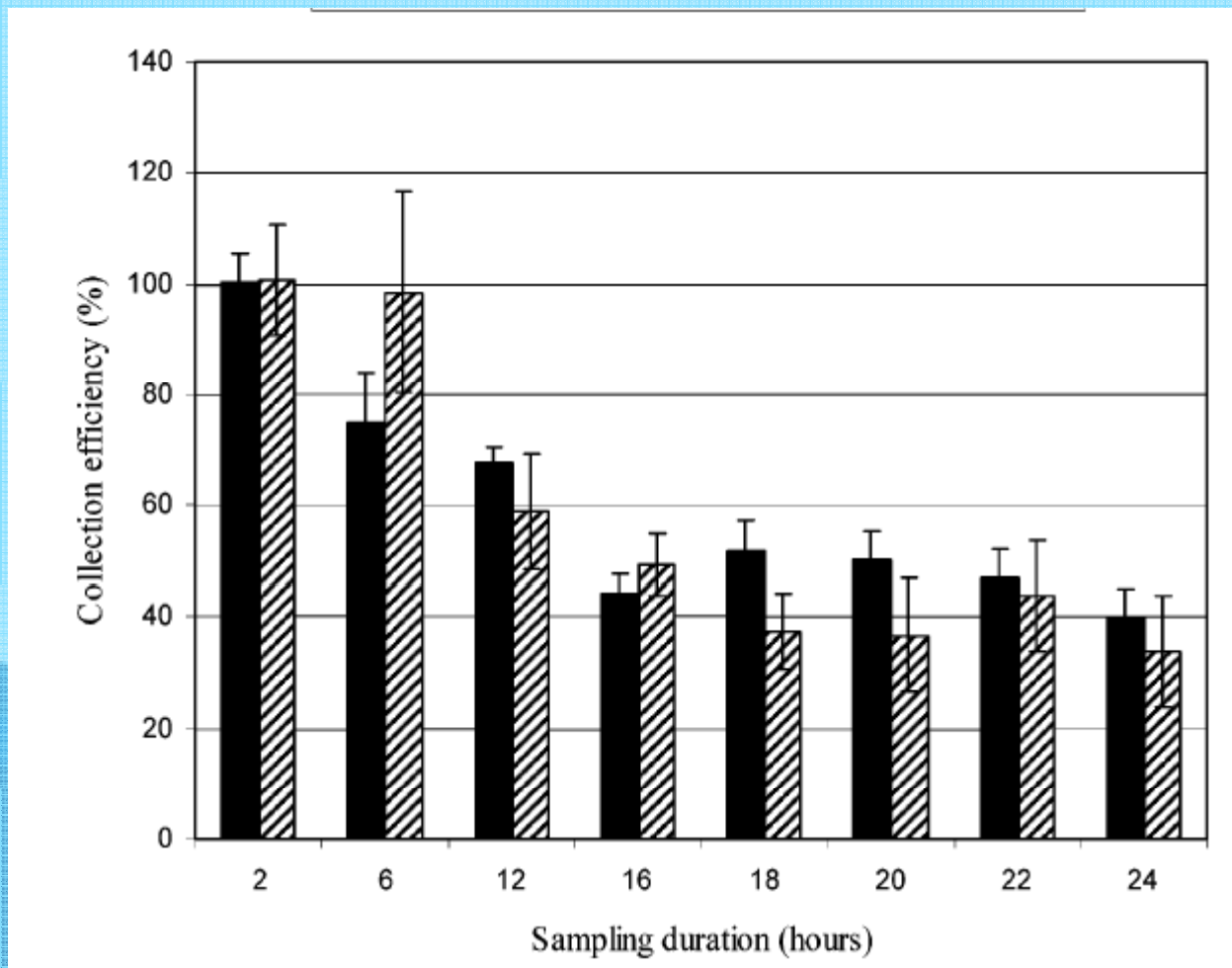
- Remember OZONE???
- The use of KI scrubbers (as recommended in the methods) to limit O₃ interferences promotes NO₂ by the oxidation of NO.
- The standardized methods do not reflect any of the aforementioned information
 - TO-11A 1999 revision overlooked this issue

WHAT... is up with acetaldehyde

- Through an extensive literature search, we were only able to find three studies during which carbonyls other than formaldehyde were evaluated on DNPH-coated solid sorbents for long-term sampling (i.e., **24 hour or greater**).
- Lazarus (1999) reported low acetaldehyde collection efficiencies (CE); and Grosjean (1991), and Grosjean and Grosjean (1995) evaluated breakthrough of the collection media, which does not necessarily reflect CE.

Experimental condition	Carbonyl	SUPELCO	WATERS	XPOSURE	HOUSE
3 hours at 30% RH	Formaldehyde	89 ± 10 ^c (3)			
	Acetaldehyde	93 ± 8 ^c (3)			
24 hours at 30% RH	Formaldehyde	83 ± 4 (3)	87 ± 11 (3)	111 ± 4 (3)	104 ± 25 (3)
	Acetaldehyde	39 ± 7 (3)	43 ± 3 (3)	62 ± 7 (3)	1 ± 2 (3)
48 hours at 30% RH	Formaldehyde	89 ± 8 (3)	93 ± 4 (3)	105 ± 19 (3)	14 ± 8 (3)
	Acetaldehyde	51 ± 22 (3)	43 ± 2 (3)	40 ± 11 (3)	0 (3)
24 hours at 60% RH	Formaldehyde	101 ± 8 (3)	101 ± 13 (3)	121 ± 32 (3)	133 ± 27 (3)
	Acetaldehyde	27 ± 4 (3)	29 ± 2 (3)	30 ± 2 (3)	9 ± 2 (3)

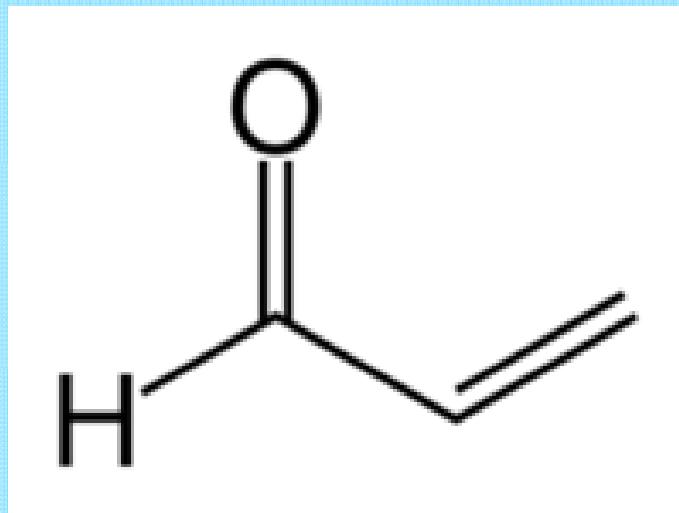
Herrington, J.; Fan, Z.; Liou, P. J.; Zhang, J. Low acetaldehyde collection efficiencies for 24-hour sampling with 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents. *Environ. Sci. Technol.* **2007**, *41*, 580-585.



Herrington, J.; Fan, Z.; Liyo, P. J.; Zhang, J. Low acetaldehyde collection efficiencies for 24-hour sampling with 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents. *Environ. Sci. Technol.* **2007**, *41*, 580-585.

WHAT... is the solution for acetaldehyde?

- To date... there is none for DNPH-based methods
- Again... the standardized methods do not reflect any of the aforementioned information



- L. Benning and A. Wahner, *J. Atmos. Chem.*, 1998, 31, 105–117.
- E. Goelen, M. Lamrechts and F. Geyskens, *Analyst*, 1997, 122, 411–419.
- S. B. Tejada, *J. Environ. Anal. Chem.*, 1986, 26, 167–185.
- K. Olson and S. J. Swarin, *J. Chromatogr.*, 1985, 333, 337–347.
- M. Possanzini and V. DiPalo, *Chromatographia.*, 1995, 40, 134–138.
- C. H. Risner and P. Martin, *J. Chromatogr. Sci.*, 1994, 32, 76–82.
- C. H. Risner and P. Martin, *J. Chromatogr. Sci.*, 1994, 32, 76–82.
- A. Sakuragawa, T. Yoneno, K. Inoue and T. Okutani, *J. Chromatogr.*, 1999, 844A, 403–408.
- R. Schulte-Ladbeck, R. Lindahl, J. O. Levin and U. Karst, *J. Environ. Monit.*, 2001, 3, 306–310.

WHAT... is the solution

- In 2010 acrolein was finally removed from the list of TO-11A target analytes
- I hear rumors of DNPH methods, but yet to see any methods published in the peer reviewed literature.
- Other derivatizing agents:
 - DNSH
 - PFBHA

WHY... am I talking about old news?

- Current methods do not reflect the aforementioned information
- Therefore, end users are completely un-aware of the aforementioned
- To date... no single DNPH-based method has addressed all of the issues outlined here

WHEN... did all this take place?

- **First discovered:**
- Acrolein - 1985
- Formaldehyde – 1996
- Acetaldehyde – 2007
- **Reflected in methods:**
- **2010 (25 years later)**
- **???? (16 years so far)**
- **???? (5 years so far)**

WHERE... do we go from here?

- U.S. EPA (and other standardizing entities) need to publish appropriate **amendments** to the methods **NOW**
 - End users need to be made aware
- Laboratories need to develop methods for formaldehyde, acetaldehyde, and acrolein... at a minimum
 - **No more narrow-sightedness on just acrolein**
- Need to rigorously test methods
 - Use a dynamic gas generation system
 - Evaluate temperature, relative humidity, time, etc... **“Real World” variables**
 - No more assumptions!

WHAT... more questions?

- ChromaBLOGraphy
– <http://blog.restek.com/>
- Herrington and Hays, 2012. Concerns regarding 24-h sampling for formaldehyde, acetaldehyde, and acrolein using 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents. *Atmospheric Environment*, 55, 179-18.