New Methods of Sampling and Analysis of Formaldehyde

SR-134-04

PO 134 Indoor Environmental Quality I

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Introduction

- Ambient formaldehyde levels: few ppb to ~ 20 ppb
- Outdoor sources
  - Wood/timber
  - Reaction of ozone with unsaturated hydrocarbons
  - Combustion
    - Automobile exhaust, wildfires, tobacco smoke
- Indoor sources
  - Wood and other building products
    - Particle board, engineered wood products, fiberboard, etc.
    - Paints and coatings, wallpaper, insulation
  - Lifestyle/personal care products, including treated fabrics
  - Combustion
    - Appliances, wood stoves/fireplaces, tobacco smoke

Introduction (continued)

- Health concern
  - Reclassified as carcinogenic to humans (June 2004) by International Agency for Research on Cancer (IARC)
  - Irritant to throat, nose, eyes, and skin
- Odor
  - Strong, pungent odor
  - Threshold: 25 to >1000 ug/m^3 (30 to >800 ppb) [1]
- Exposure limits vary widely
  - Workplace
    - 16 ppb (NIOSH TWA REL); 750 ppb (OSHA TWA PEL)
  - Non-workplace
    - Recommended levels also vary (Country, long term vs. short term)
    - ~30-100 ppb (36-120 µg/$m^{3)}$

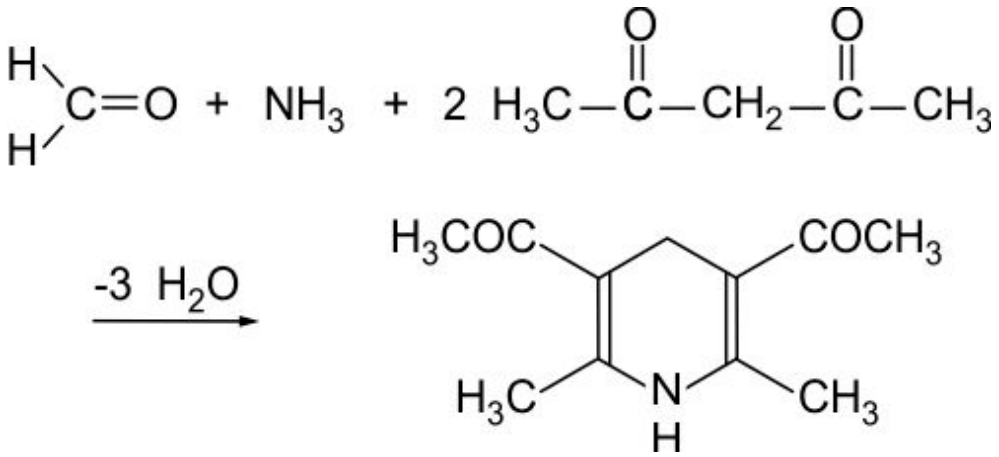
Sample Collection

- Custom thermal desorption tube
  - Molecular Sieve 13x
  - Tenax GR
- Low flow pump (0.2 L/min)
- 20-30 minute sample collection time
  - Concentrate sample
  - Reduce water competition in high humidity environment

Sample Analysis

- Thermal desorption
  - 250 °C for 25 minutes using dry Nitrogen
- Aero-Laser GmbH AL4021
  - Continuous Formaldehyde in Air & Water Monitor[2]
  - Fluorescence detection at 510 nm
  - Selective using acetyl-acetone or Hantzsch method

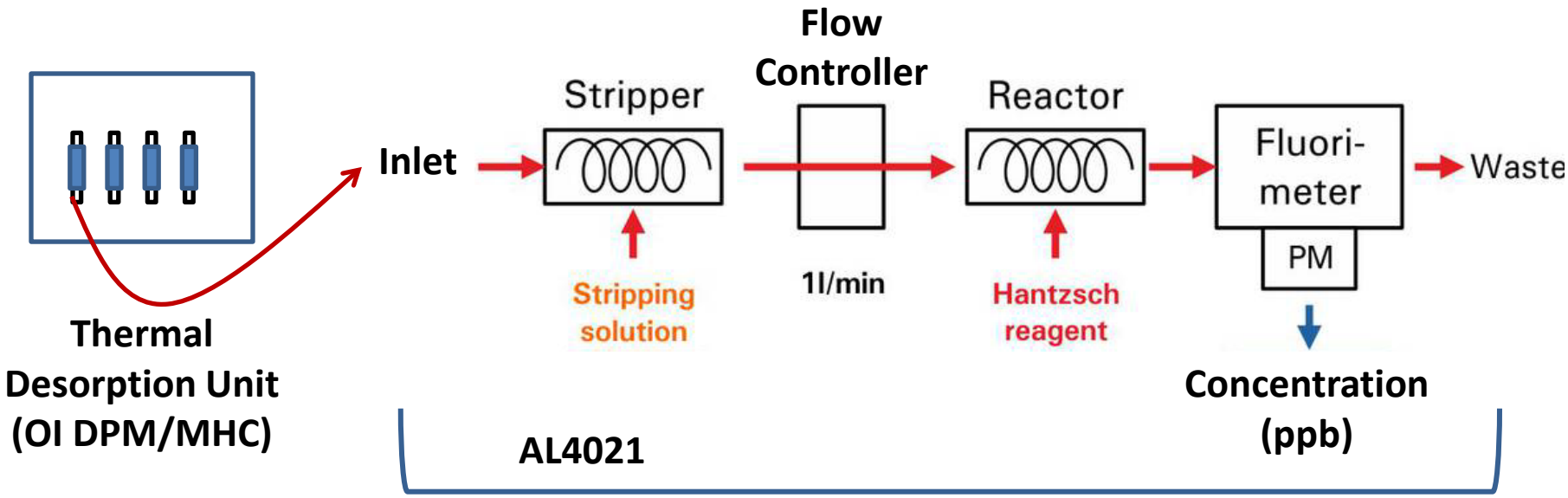
Hantzsch (acetyl-acetone) Reaction



- Liquid phase reaction of formaldehyde with acetyl-acetone (2,4-pentadione) and ammonia → produces 3,5-diacetyl-1,4-dihydrolutidine (DDL)

Reaction scheme from Aero-Laser GmbH

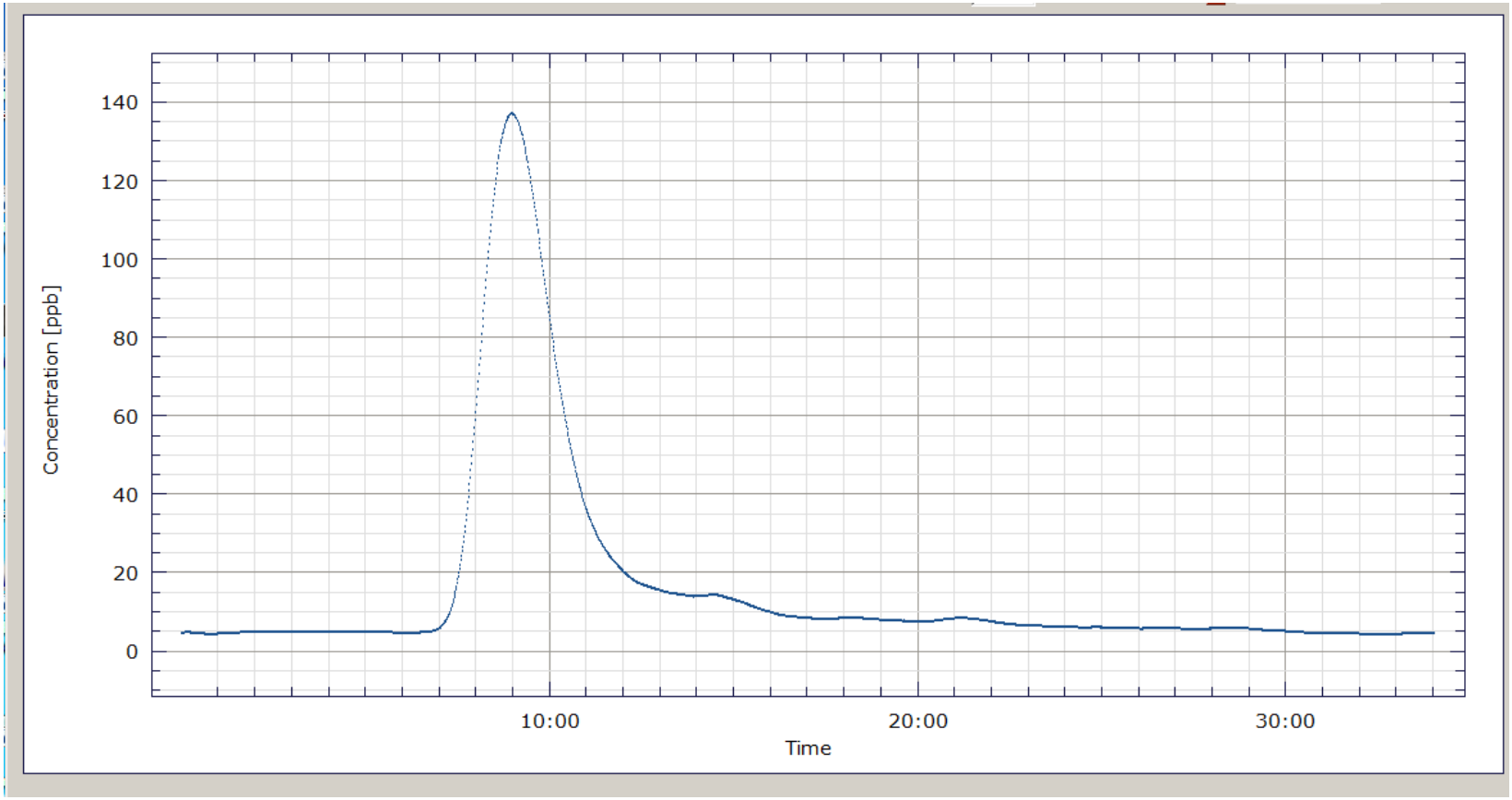
Analysis Process



- Thermal desorption: drives Formaldehyde off sample media
- Stripper: dissolves Formaldehyde in aqueous solution
- Reactor: introduction of acetyl-acetone and ammonia
- Fluorimeter: detection at 510 nm

Sample Data

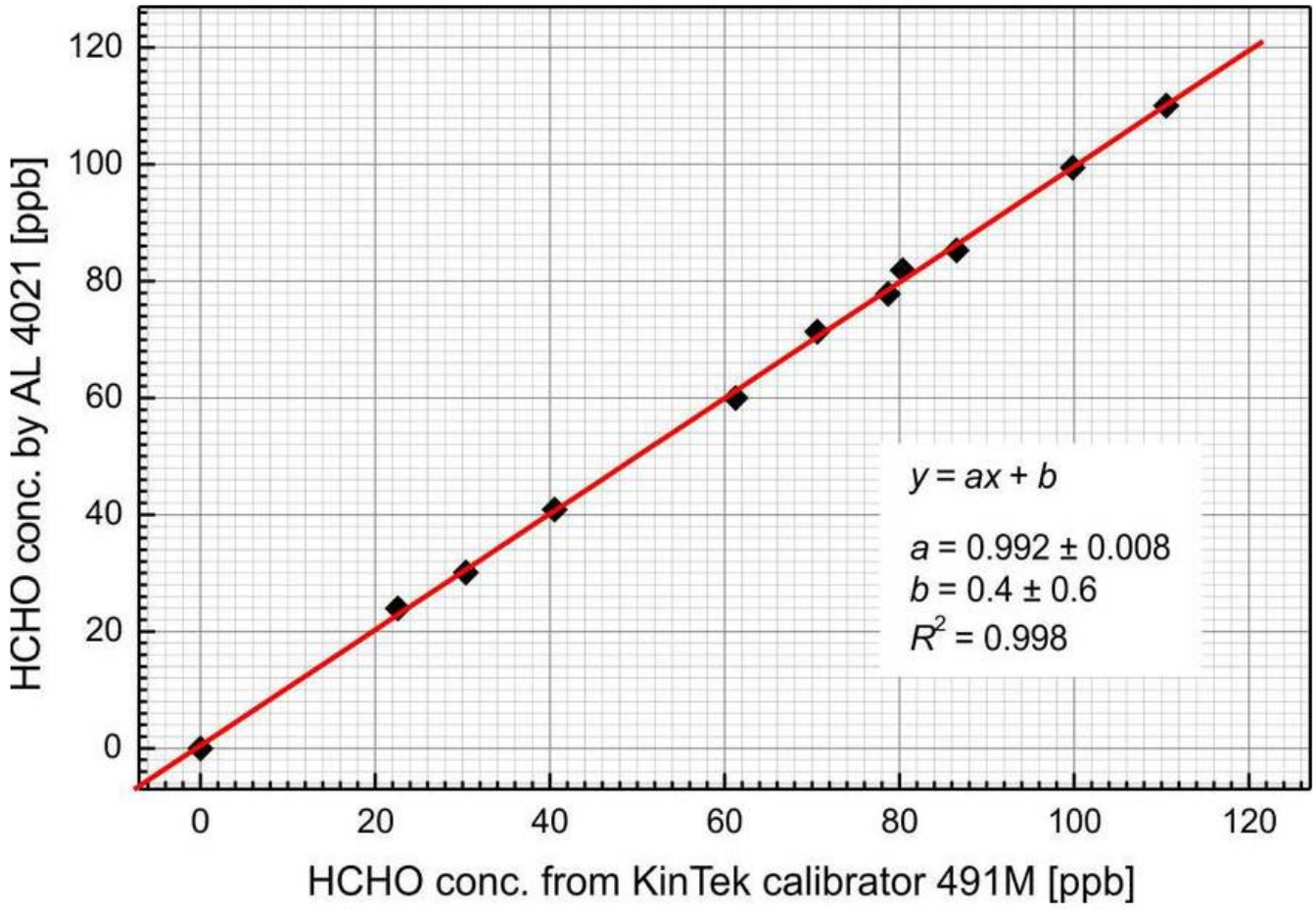
Integration over peak



Instrument Specifications

- Fast, continuous measurement
  - Time resolution: 1 data point/second
- Integrated chemical processing
- Sensitive
  - Detection limit: 0.1 ppb (100 ppt)
  - Linear range: 0.1 ppb – 2 ppm
    - Can be extended to 50 ppm

Instrument Accuracy



From AeroLaser GmbH

Interference Ratios

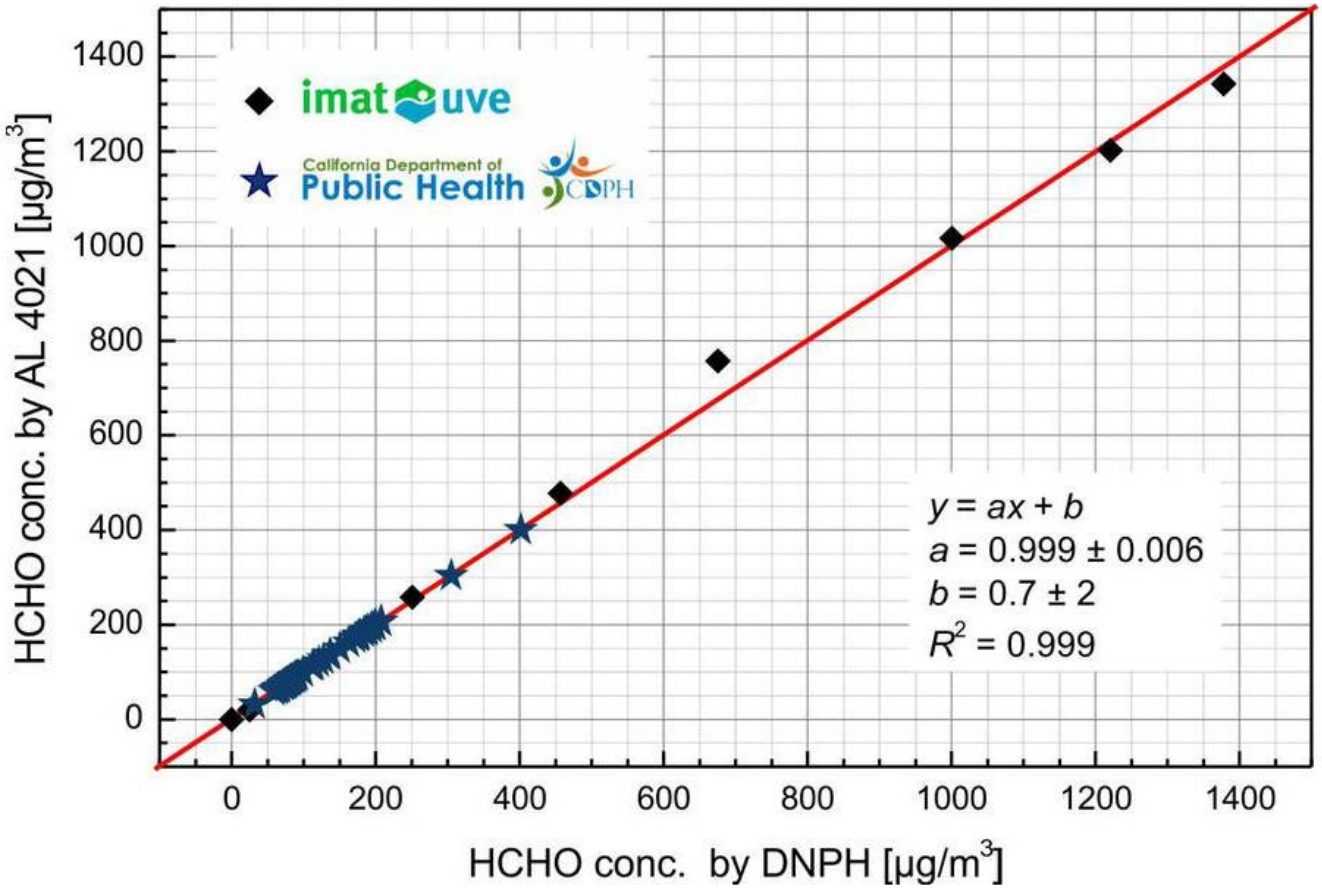
- Minimal sensitivity to other aldehydes & ketones
  - Short reaction time

Benzaldehyde	< 1 : 20000	Glyoxal	< 1 : 123
Butanol	< 1 : 900	NO	< 1 : 300000
Acetaldehyde	< 1 : 10000	Methanol	< 1 : 50000
HNO_3	< 1 : 1000	NO_2	< 1 : 500000
Acrolein	< 1 : 10000	H_2O_2	< 1 : 100
Acetone	< 1 : 300000	SO_2	< 1 : 300000
Propanal	< 1 : 20000	O_3	< 1 : 800
Isobutane	< 1 : 300000		

Method Validation

- Accuracy: ± 15%
  - Verified with liquid standard and independent gas cylinder
- Precision: RSD 4.3%
  - 400 ng check standard (87 values)
- Measured Detection Limit: 4 ppb (5 µg/m^3)

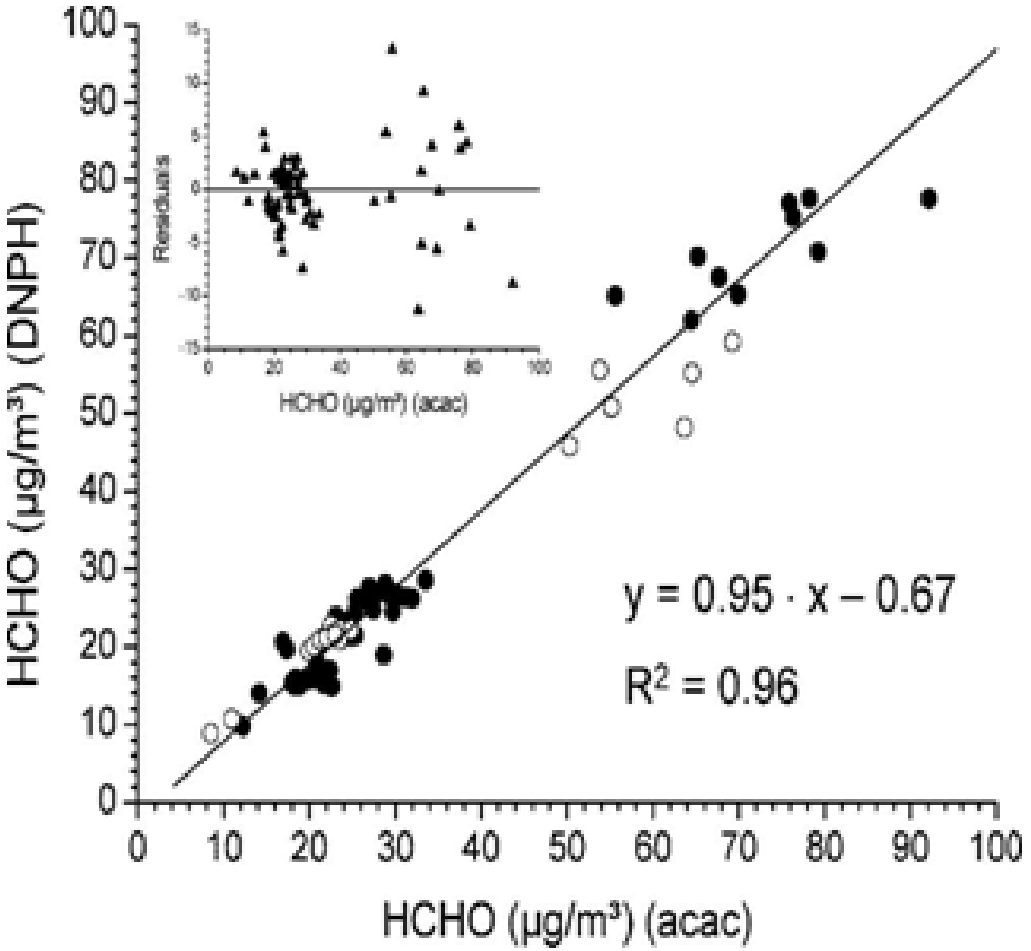
Results Comparison with DNPH



From AeroLaser GmbH. Data produced by IMAT/UVE and California Dept. of Public Health.

Results Comparison with DNPH

- Linear relationship between DNPH and acetyl-acetone methods
  - Salthammer et al. [1] (Chemosphere 2008, 73, 1351)



Method Feature Comparison

TDT/AL-4021 method

- Specific to formaldehyde
- Minimal interferences
- Applicable in dry and humid environments
- Reusable media, no chemical treatment
- Low detection limit
- Short sample collection time

DNPH method

- Other aldehydes/ketones
- Interferences
  - e.g., ozone, some isomeric aldehydes and ketones
- Under estimation in dry environments
  - Wisthaler et al. [3]
- Single use treated media
- Low detection limit
- Variable sample collection time

Case Study 1: Homes

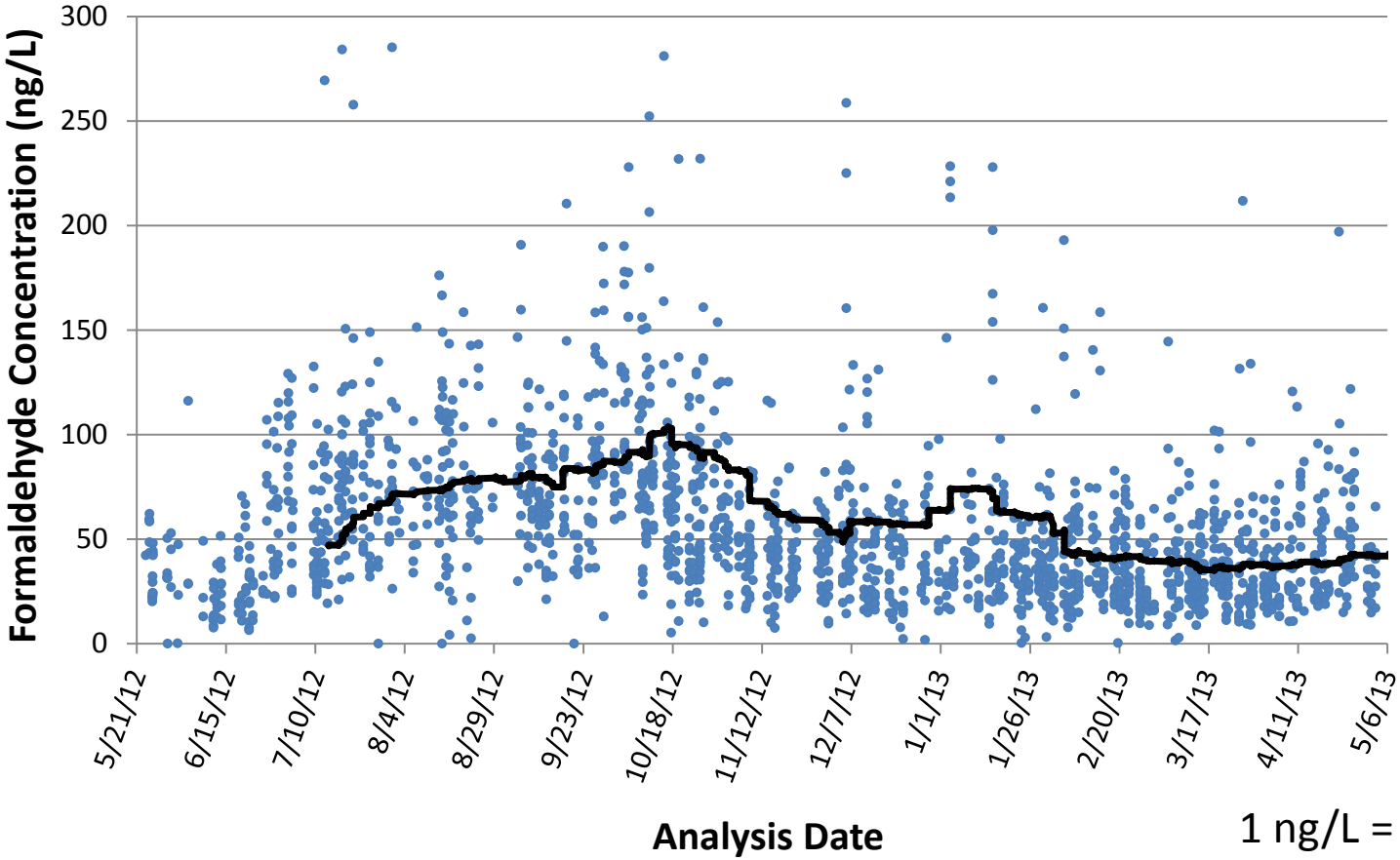
- Literature
  - Average ~15-20 ppb (18-24 µg/m^3)
    - CA Air Resources Board offices/homes/classrooms [4]
  - Average 24-32 ppb (30-40 µg/m^3)
    - Health Canada Residential Indoor Air Quality Guideline 2006 [5]
  - Averages in new homes [6]
    - 50-80 ppb (60-96 µg/m^3) in southern California
    - 79-130 ppb (95-160 µg/m^3) in Florida (AC off)
    - 40-400 ppb (48-480 µg/m^3) in Louisiana (AC off)

Case Study 1: Homes (continued)

- TDT/AL4021 method
  - ~2,000 samples (May 2012 – May 2013)
  - Concentrations
    - < 5 to 1,400 µg/m^3 (< 4 to 1,100 ppb)
    - Mean: 59 µg/m^3 (47 ppb)
    - Median: 46 µg/m^3 (37 ppb)
  - Seasonal variability
    - Temperature
    - Humidity

Case Study 1: Homes (continued)

Seasonal variation in ambient concentrations observed



1 ng/L = µg/m^3

Case Study 2: Emissions from Cadavers

- University study of cadaver emissions
  - 48 samples
  - Testing new removal system
- Results
  - Min: 330 µg/m^3 (260 ppb)
  - Max: 1,400 µg/m^3 (1,100 ppb)
  - Median: 640 µg/m^3 (510 ppb)

Conclusion

- Developed reliable method for formaldehyde
  - Active sample collection on dry sorbent tube
  - Analysis by thermal desorption
  - followed by self-contained derivatization and fluorescence detection
- Features
  - Detection limit below 5 µg/m^3 (4 ppb)
  - Very few interferences
  - Sample collection time of ~ 30 minutes
  - Reusable media
  - Ability to perform off gas analysis of bulk materials
- Tested in several environments

References

- (1) Salthammer, T., et al., Formaldehyde in the Indoor Environment, Chem. Rev. 2010, 110, 2536-2572.
- (2) Aero-Laser GmbH AL4021 Continuous Formaldehyde in Air and Water Monitor
  http://www.aero-laser.de/gas_analyzers/hcho_al4021.html
- (3) Wisthaler, A., et al., Technical Note: Intercomparison of formaldehyde measurements at the atmosphere simulation chamber SAPHIR, Atmos. Chem. Phys. 2008, 8, 2189-2200.
- (4) CARB, Indoor Air Quality Guideline-Formaldehyde in the Home, 2004.
- (5) Health Canada, Residential Indoor Air Quality Guide-Formaldehyde, 2006.
- (6) Offerman, F J, Ventilation and Indoor Air Quality in New Homes, CA Air Resources Board and CA Energy Commission, 2009, PIER Energy Related Environmental Research Program, Collaborative Report CEC-500-2009-085.