Unregulated (and Unwanted) Emissions from Diesel Engine Emissions Control Devices.

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2007 and 2009: How do we get there?

- **NOx: dual strategies emerging**
  - **Urea-SCR**
  - **NOx Adsorbers**
- **PM: Diesel Particulate Filters**
- **Is it possible?**
  - **DVECSE (West, Sluder) 2009 Light-Duty Bin 5 with Mercedes A class, NOx Adsorber, CDPF, syn-gas regen**
  - **Cummins (Stang *et al*.) 2009 Light-duty Bin with Durango, NOx Adsorber, CDPF, in-pipe regen**
  - **SwRI (Khair *et al*.) 2007 HD with Urea-SCR, fuel-borne catalyst, DPF**

SAE 2001-01-1933, 2001-01-2065, 2000-01-1933

What else gets produced?

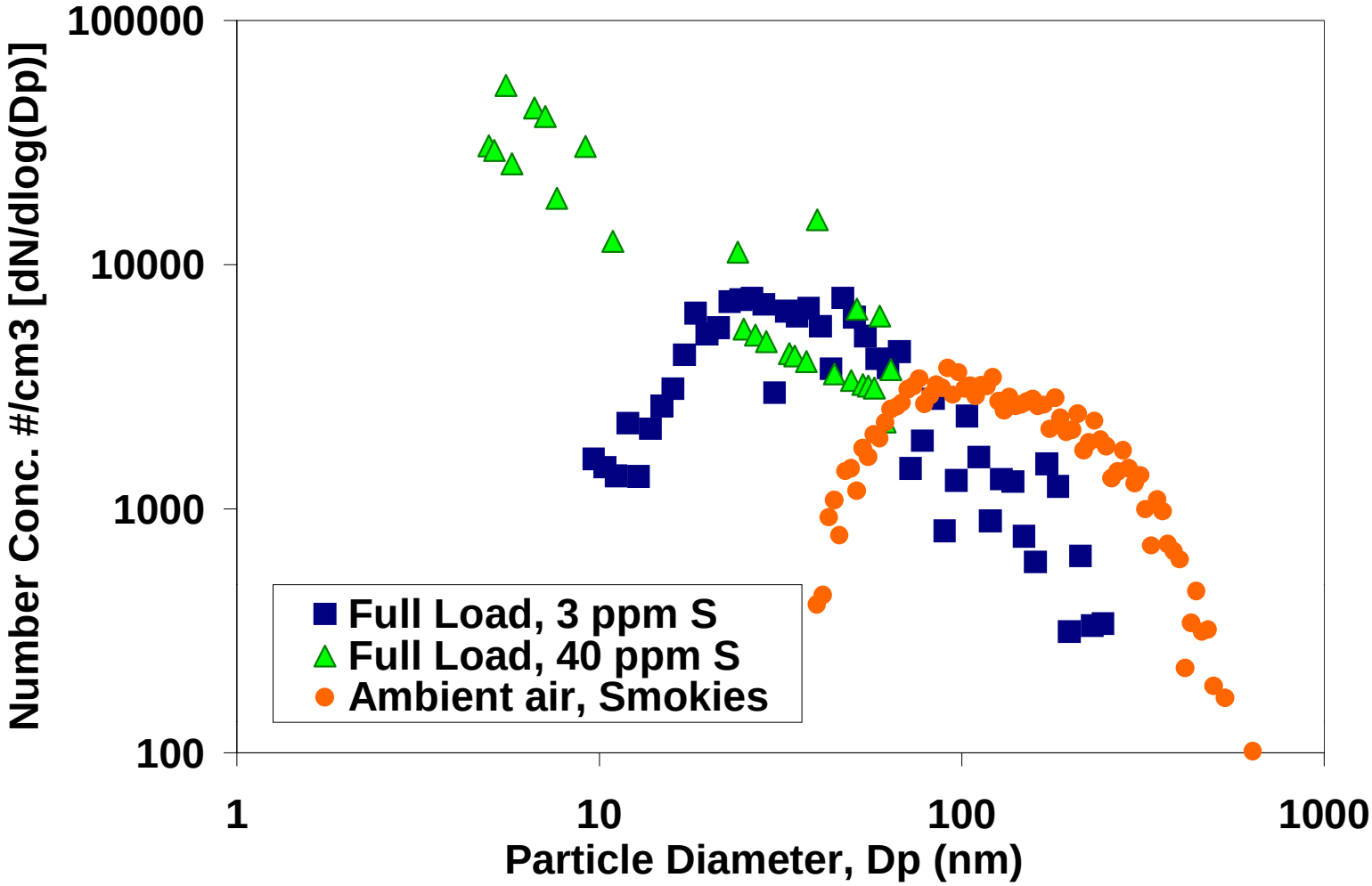
- **DPFs – low temperature oxidation, nitrogenation products**
- **Urea-SCR – Urea decomposition products**

- **NOx adsorbers – NH_3, H_2S, Nitroxy-alkanes (potentially)**

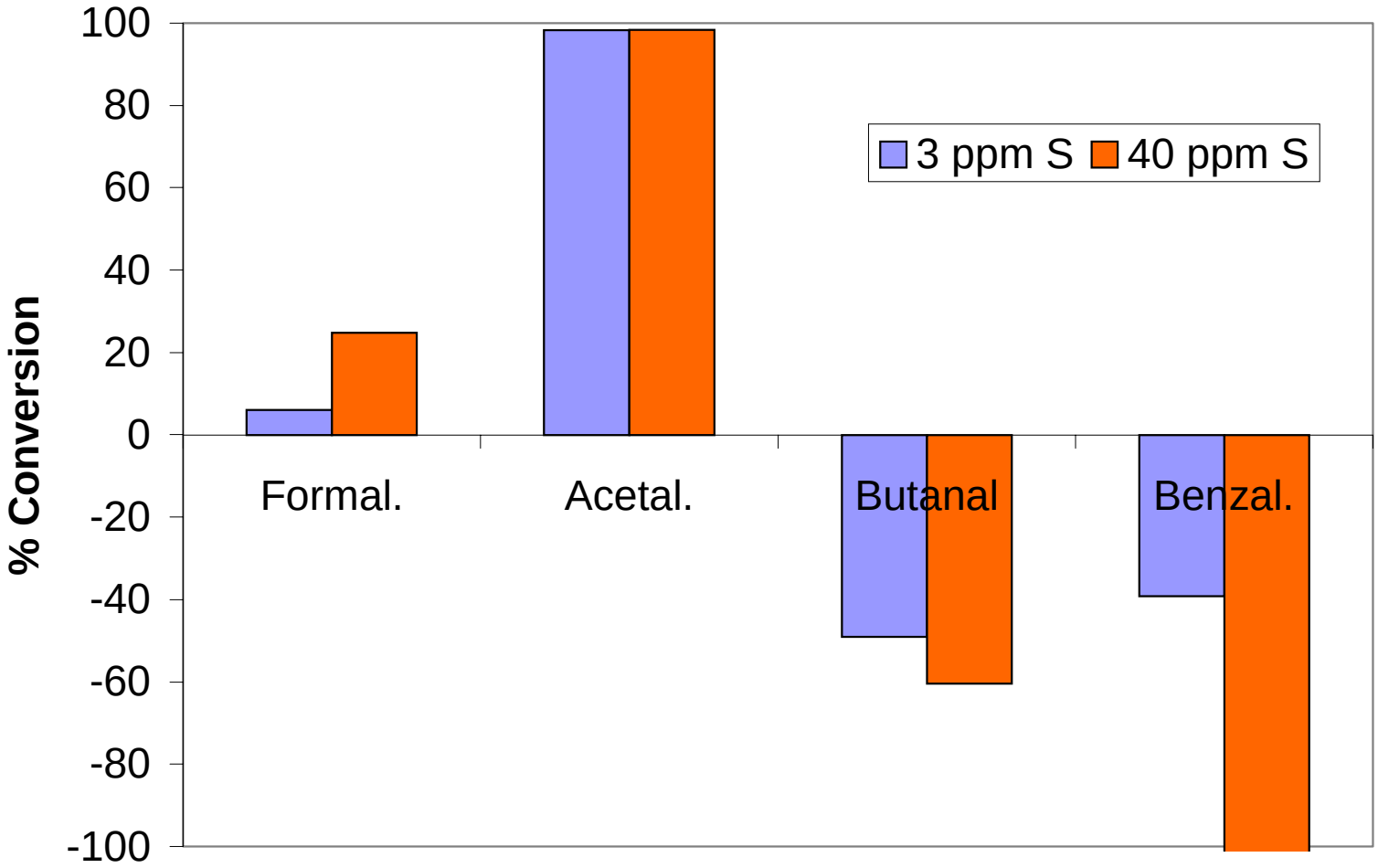
DECSE Complementary Study at ORNL

- **Focus is on fuel sulfur effects on PM size and unregulated emissions**
- **Uses same fuel and Diesel Particulate Filters (DPFs) as DECSE**
- **Results show removal of light HCs, air toxics, PAH by DPFs**
- **PM size affected by S in fuel: 2-3 order of magnitude increase in smallest PM**

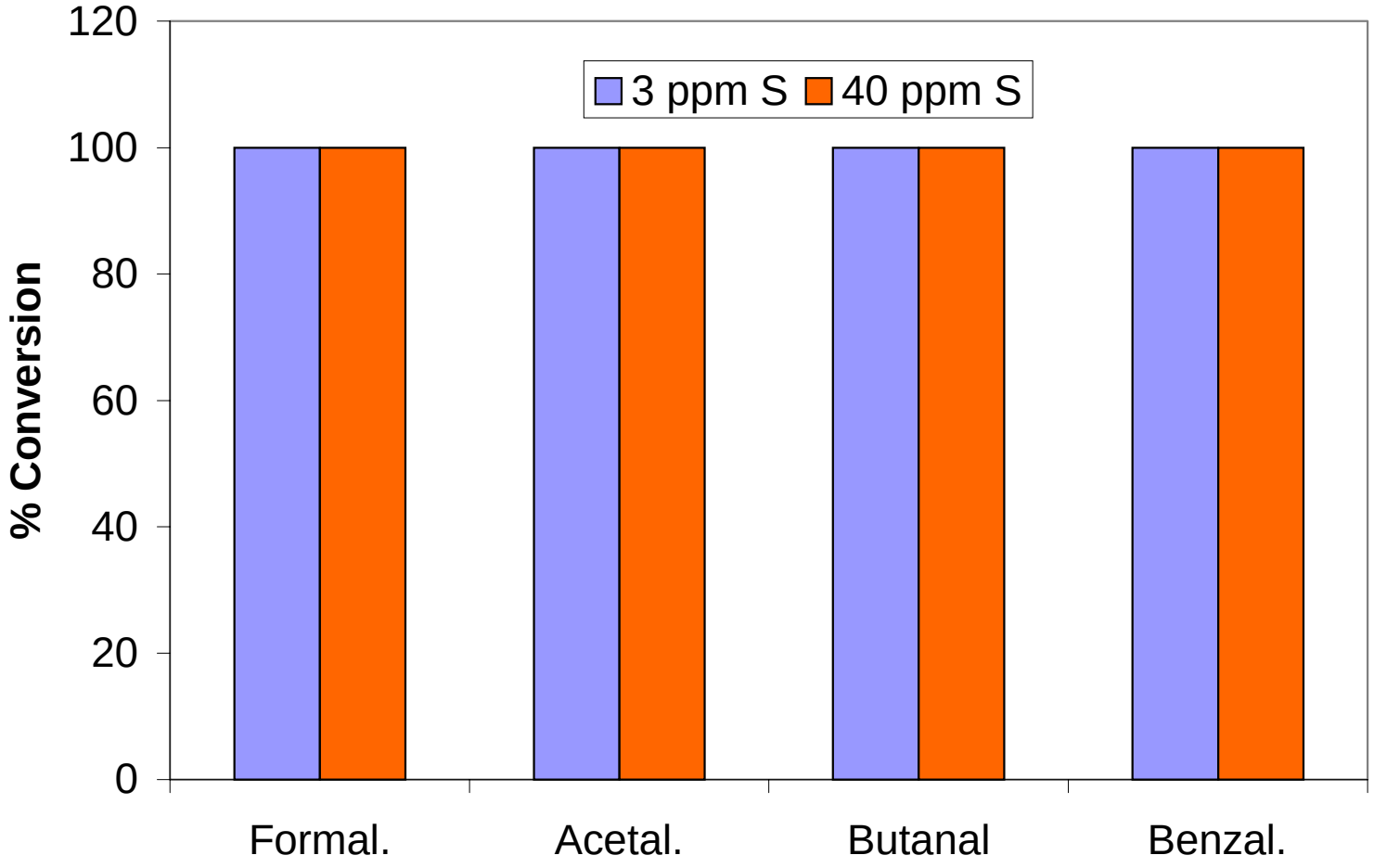
Sulfur in fuel creates nanoparticles after CDPF (Full load, rated speed)



At idle, CR-DPF converts, creates aldehydes



At rated speed, low T, CR-DPF converts all aldehydes



APBF Toxics and Unregulated Emissions

- **Develop methods for "unusual" compounds, potential problem compounds formed in both urea-SCR and NOx adsorber systems**
  - **Impetus was Jim Ball (Ford) report on urea-decomposition products; Karl Kharas *et al.* (Delphi-ASEC) report on NOx adsorbers SAE 982604**

- **Specify measurements and methods for all three teams**
  - **Lubes, Urea-SCR, NOx adsorber**

Methods Development Highlights for Urea Decomposition Products

- Identified dependency on pH for increased solubility of some compounds (ammelide, ammeline)
- Demonstrated that melamine and cyanuric acid precipitate from solution above a pH of 2 due to the formation of a water-insoluble melamine-cyanurate complex
- Identified the melamine-cyanurate complex by Raman Spectroscopy that can form under exhaust conditions
- Designed a separation method capable of isolating the melamine-cyanurate complex for Raman analysis.
- Analyzed real impinger and particulate samples from diesel engine-DPF-urea-SCR catalyst system.

Analytical Method for Impinger and Filter Samples

Impinger Sample Preparation:

-Collect samples in a 10% solution of isopropyl alcohol.

-Adjust the sample pH

-Concentrate and transfer the sample to CE vial

Filter Sample Preparation:

A. Water Soluble Components

-Wash the filter with water

-Collect the wash, and adjust the pH

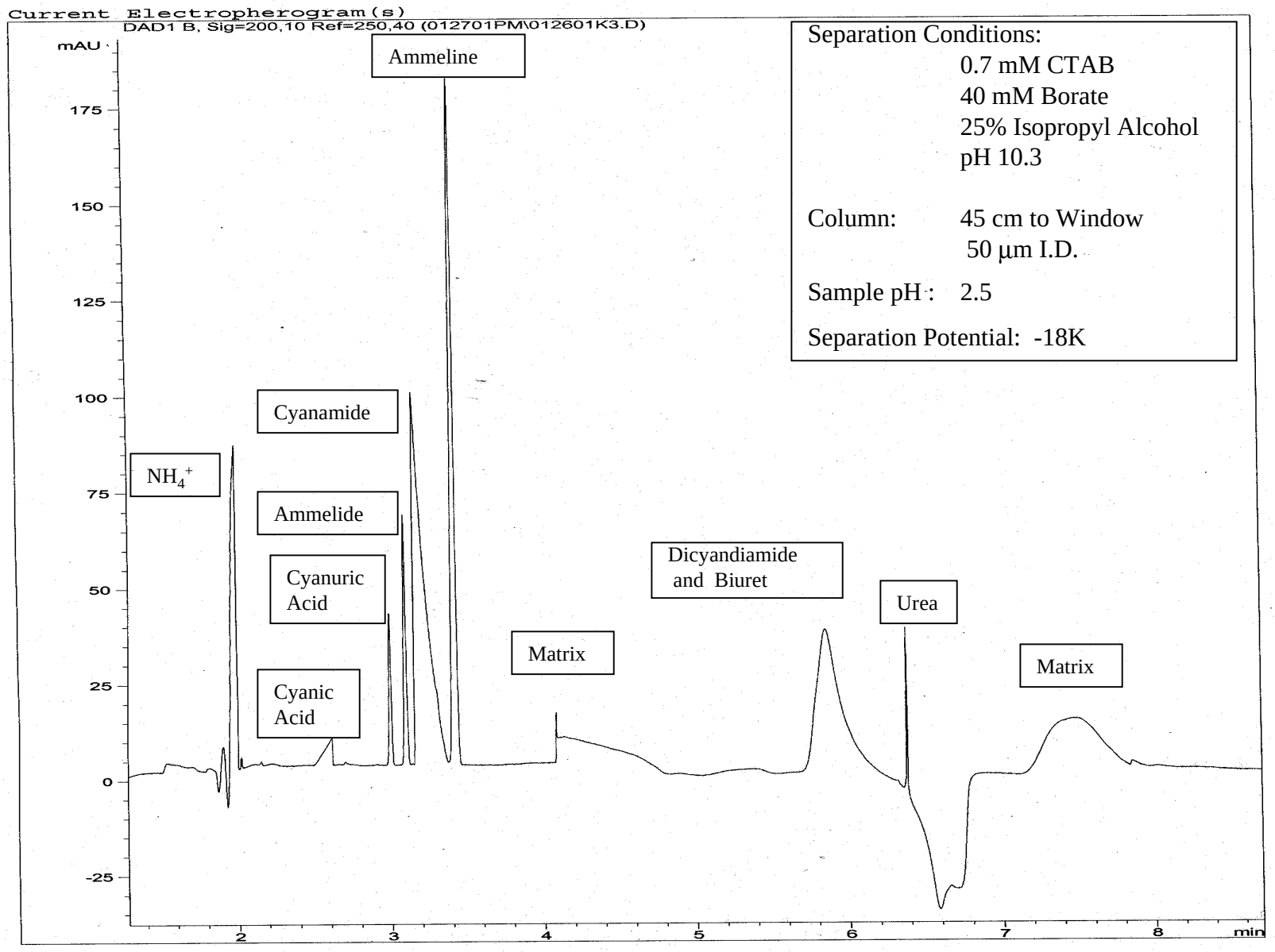
-Concentrate and transfer the sample to CE vial.

B. Melamine Cyanurate Complex

-Wash the filter with warm ammonium hydroxide.

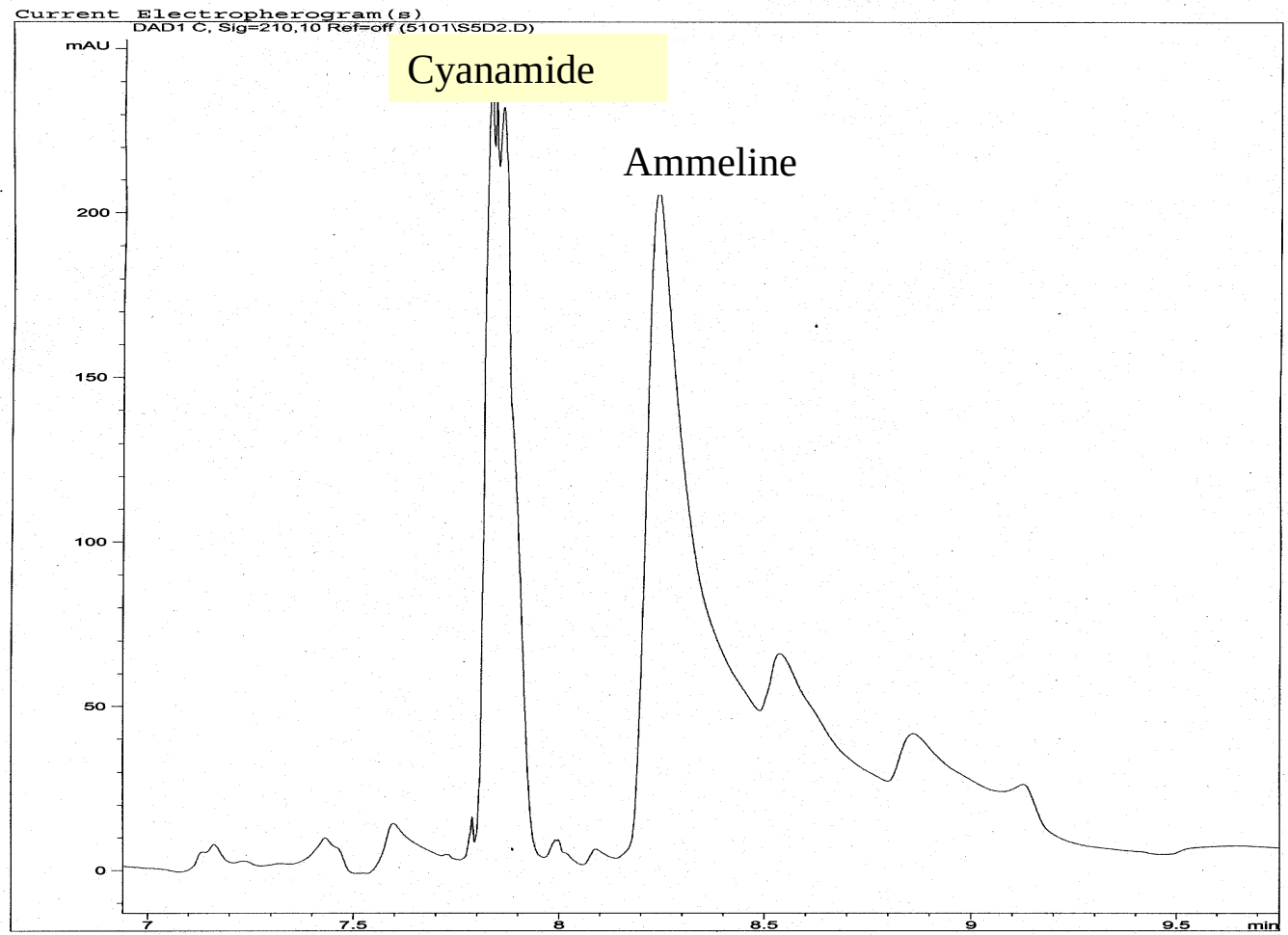
-Collect the wash, and reduce the volume

-Concentrate and transfer the solution to a micro-well slide


Current Electropherogram(s)
DAD1 B, Sig=200,10 Ref=250,40 (012701PM\012601K3.D)
mAU
175
150
125
100
75
50
25
0
-25
2
3
4
5
6
7
8
min
Ammeline
Cyanamide
NH_4^+
Ammelide
Cyanuric Acid
Cyanic Acid
Matrix
Dicyandiamide and Biuret
Urea
Matrix
Separation Conditions:
0.7 mM CTAB
40 mM Borate
25% Isopropyl Alcohol
pH 10.3
Column: 45 cm to Window
50 µm I.D.
Sample pH: 2.5
Separation Potential: -18K

Capillary Electrophoresis Electropherogram of Impinger Sample

Mode 6: Front



HP 3D CE 5/31/2001 10:57:37 AM llewis

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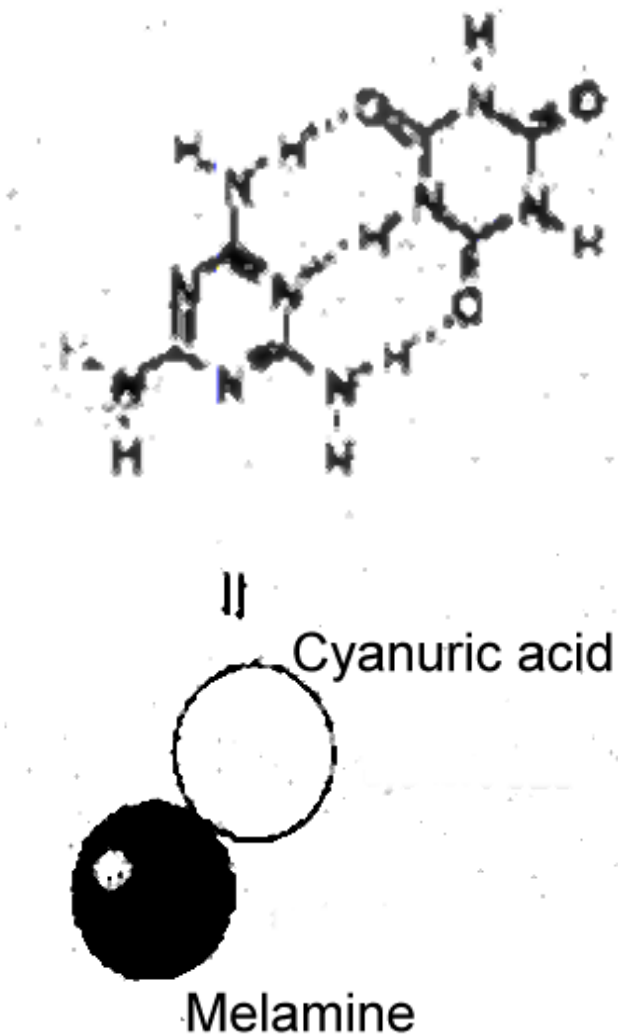
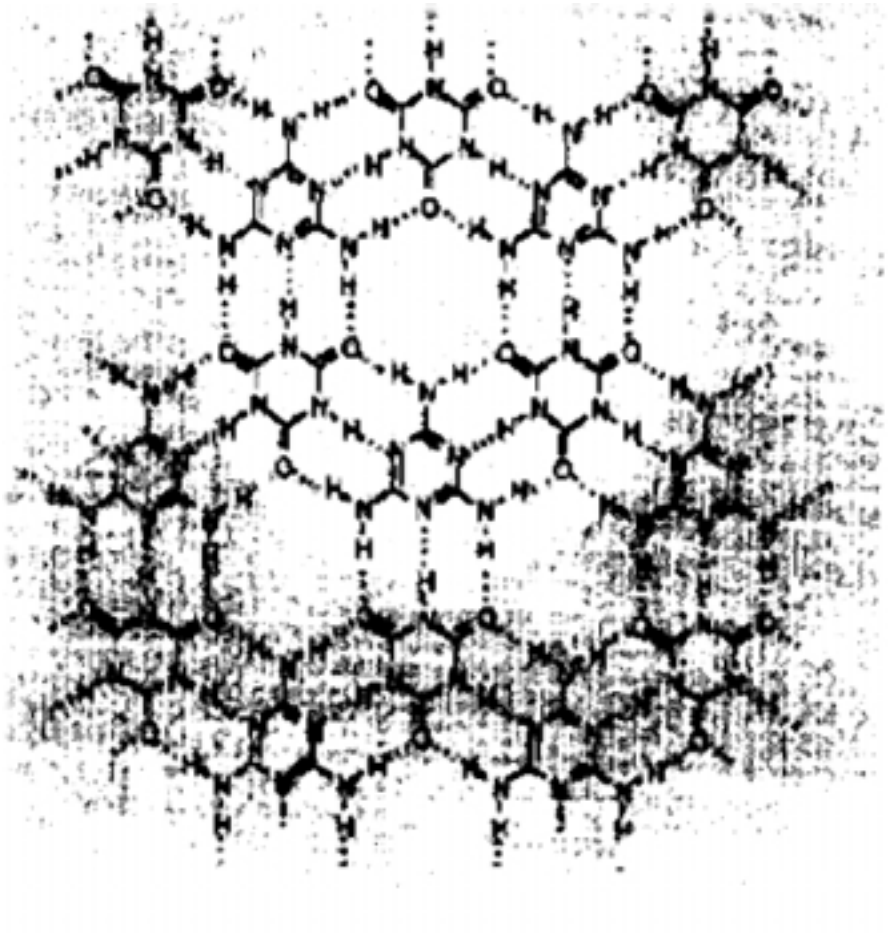
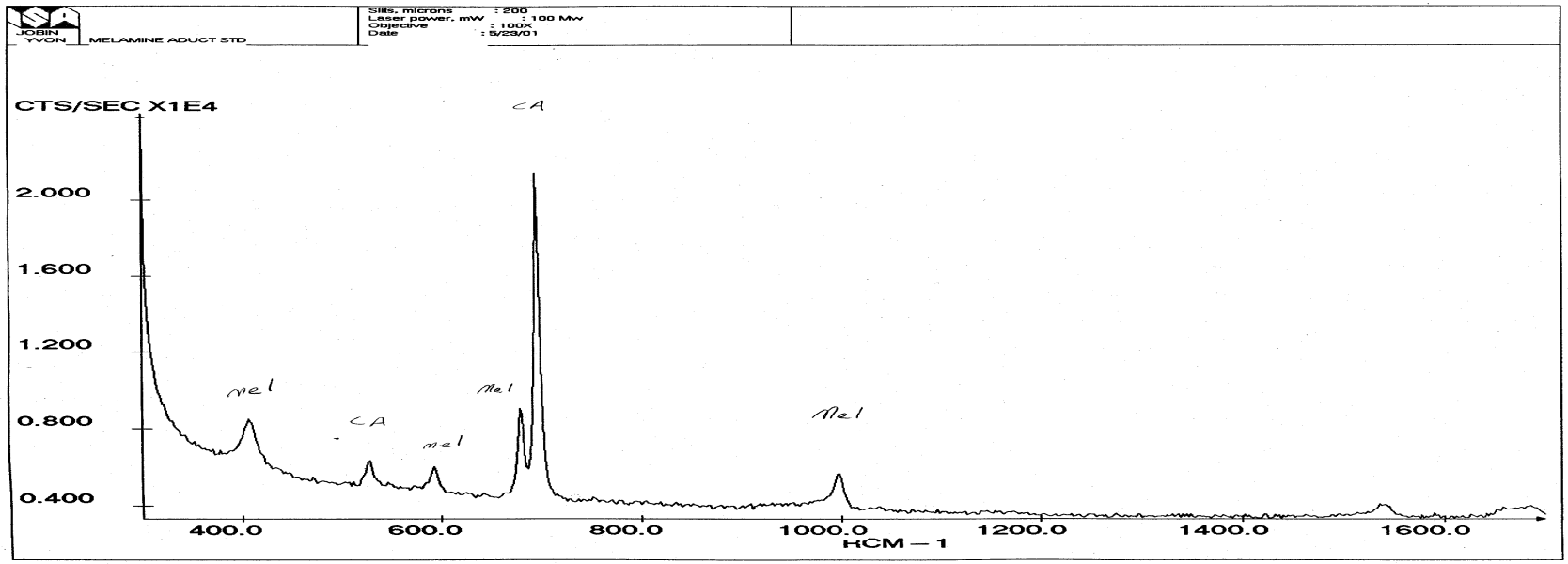




Cyanuric Acid and Melamine Lattice

Published in *Tetrahedron* Vol. 51, No. 2, pp. 607-619, 1995.


JOBIN YVON
MELAMINE ADUCT STD
Slits, microns : 200
Laser power, mW : 100 Mw
Objective : 100X
Date : 5/23/01
CTS/SEC X1E4
2.000
1.600
1.200
0.800
0.400
400.0
600.0
800.0
1000.0
1200.0
1400.0
1600.0
HCM — 1
CA
mel
CA
mel
mel
mel