AIR FORCE RESEARCH LABORATORY

ATMOSPHERIC CHEMISTRY OF OXYGENATED ORGANIC COMPOUNDS

Ray Wells, Steve Baxley, Stewart Markgraf, Sheryl Wyatt

AFRL/MLQR
Air Team
(850)283-6087
ray.wells@ccmail.aleq.tyndall.af.mil

AIR TEAM

Lt. Leon Perkowski

Dr. Ray Wells

Darrell Winner

Stewart Markgraf

Steve Baxley

Sheryl Wyatt

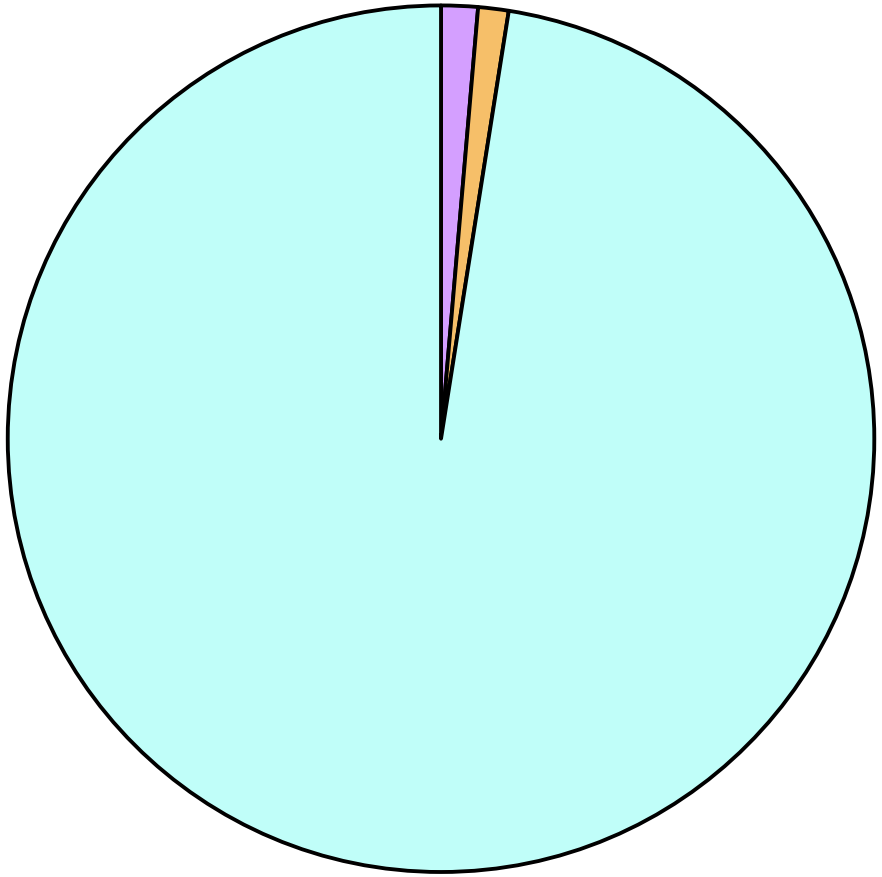
Bill Bradley

We determine impact on air quality.

DoD Releases by Media, 1994

Land **1.31%**

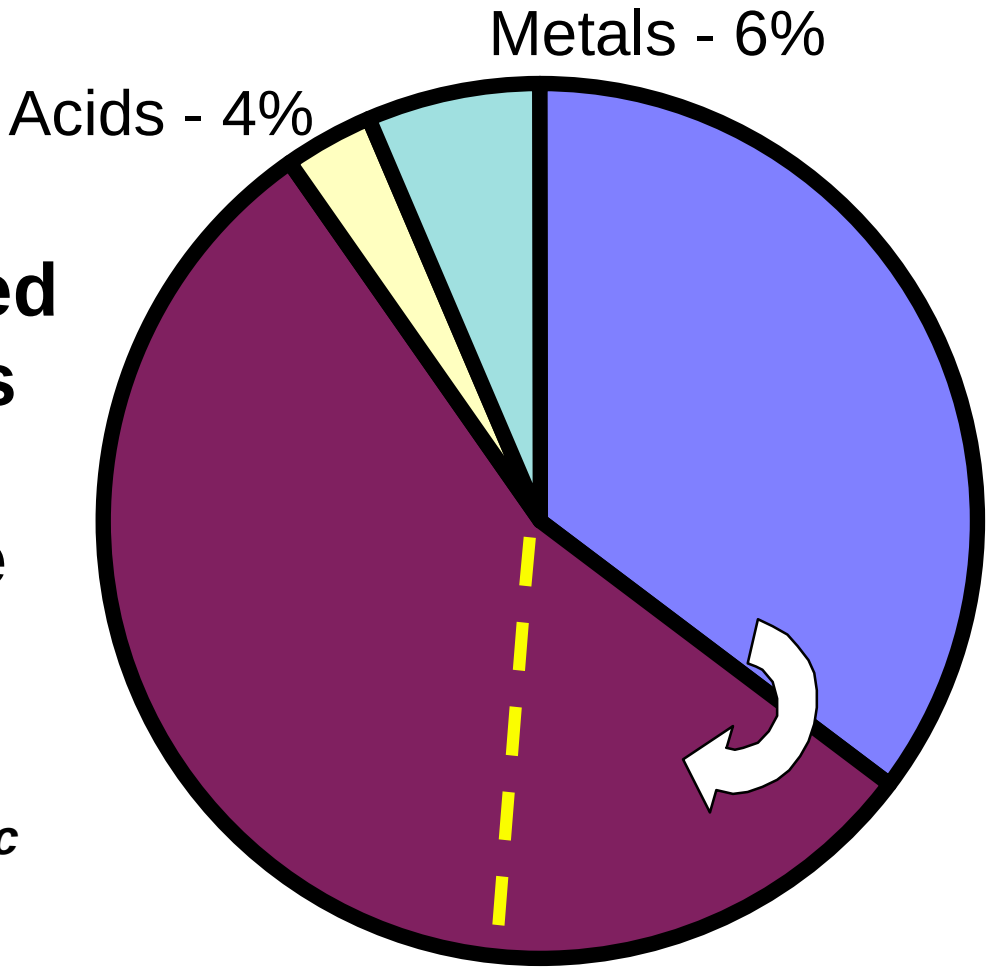
Water **1.25%**



Air 97.44%

From: 1994 Toxics Release Inventory for the DoD Public Data Report, March 7, 1996

Of That 97%...



Chlorinated organics and chlorine 55%

Impacts Stratospheric ozone

Volatile Organic Compounds 35%

Impacts Ground level ozone

*Compromise ozone formation **and** depletion*

URGENCY

- 1990 Clean Air Act -

<u>200</u> new regulations
and guidance documents

They impact our missions!

Sources of Pollution

Paints

Thinners

Solvents

Combustion

Exhausts

Emissions

New replacements affect these sources

Purpose

GOAL: *Prevent pollution intelligently while maintaining performance*

Achieved by addressing:

1. What is being emitted?

2. What happens to emitted chemicals?

Tech Need: 1940 - Replacement of chlorinated cleaners for engines (High)

Pertinent Radical Formation Reactions

OH Radical

$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \longrightarrow 2\ OH\ (0.04\ ppt!)$$

$$RH + OH \longrightarrow R + H_2O$$

NO_3 Radical

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_2 + NO_3 \rightleftharpoons N_2O_5$$

$$RH + NO_3 \longrightarrow R + HNO_3$$

Atmospheric Transformation Processes

$$RH + OH^{\cdot} \longrightarrow R^{\cdot} + H_2O$$
$$R^{\cdot} + O_2 \longrightarrow RO_2$$
$$RO_2 + NO \longrightarrow NO_2 + RO$$
$$NO_2 + h\nu \longrightarrow NO + O$$
$$O + O_2 + M \longrightarrow O_3 + M$$

$$RH + OH^{\cdot} + 2O_2 \longrightarrow RO + H_2O + O_3$$

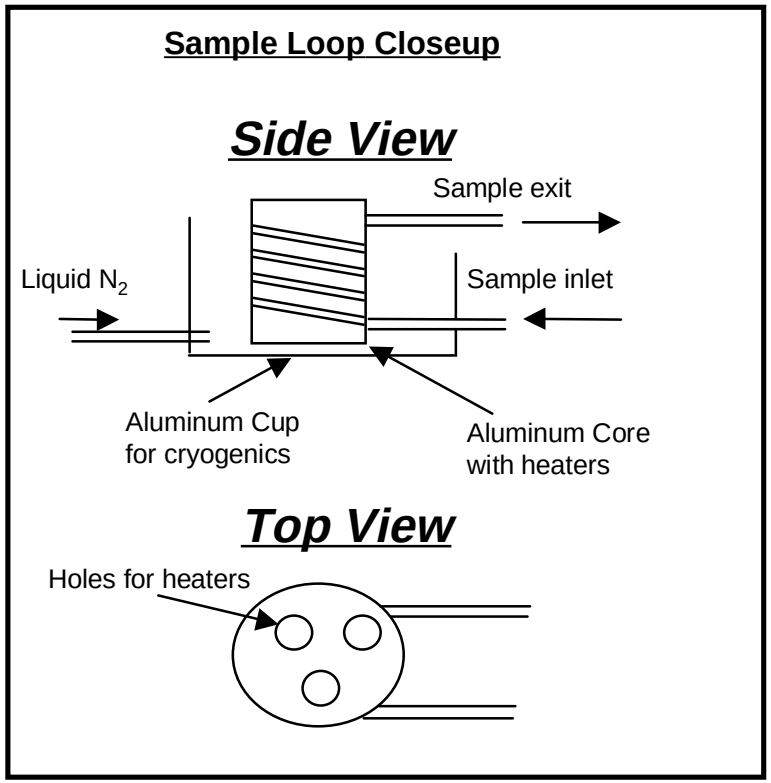
Experimental Apparatus

Gas Chromatograph

Infrared Spectometer

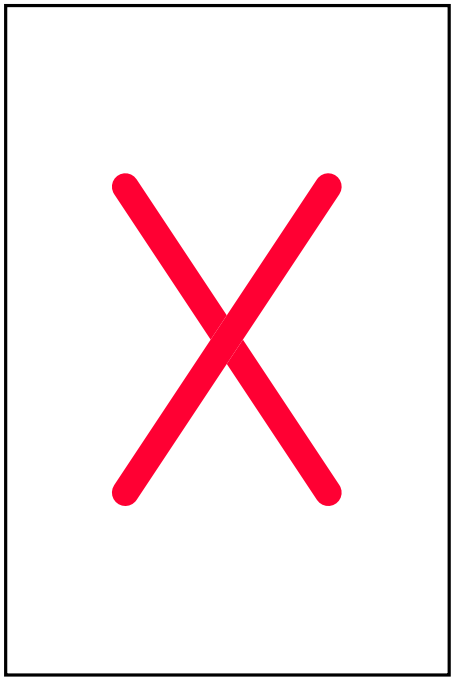
Mass Spectometer

Flame Ionization Detector



Experimental Apparatus

Reaction Chamber ⟶ Sample Loop ⟶ Analysis System



Experimental Methods

I. Relative Rate Technique:

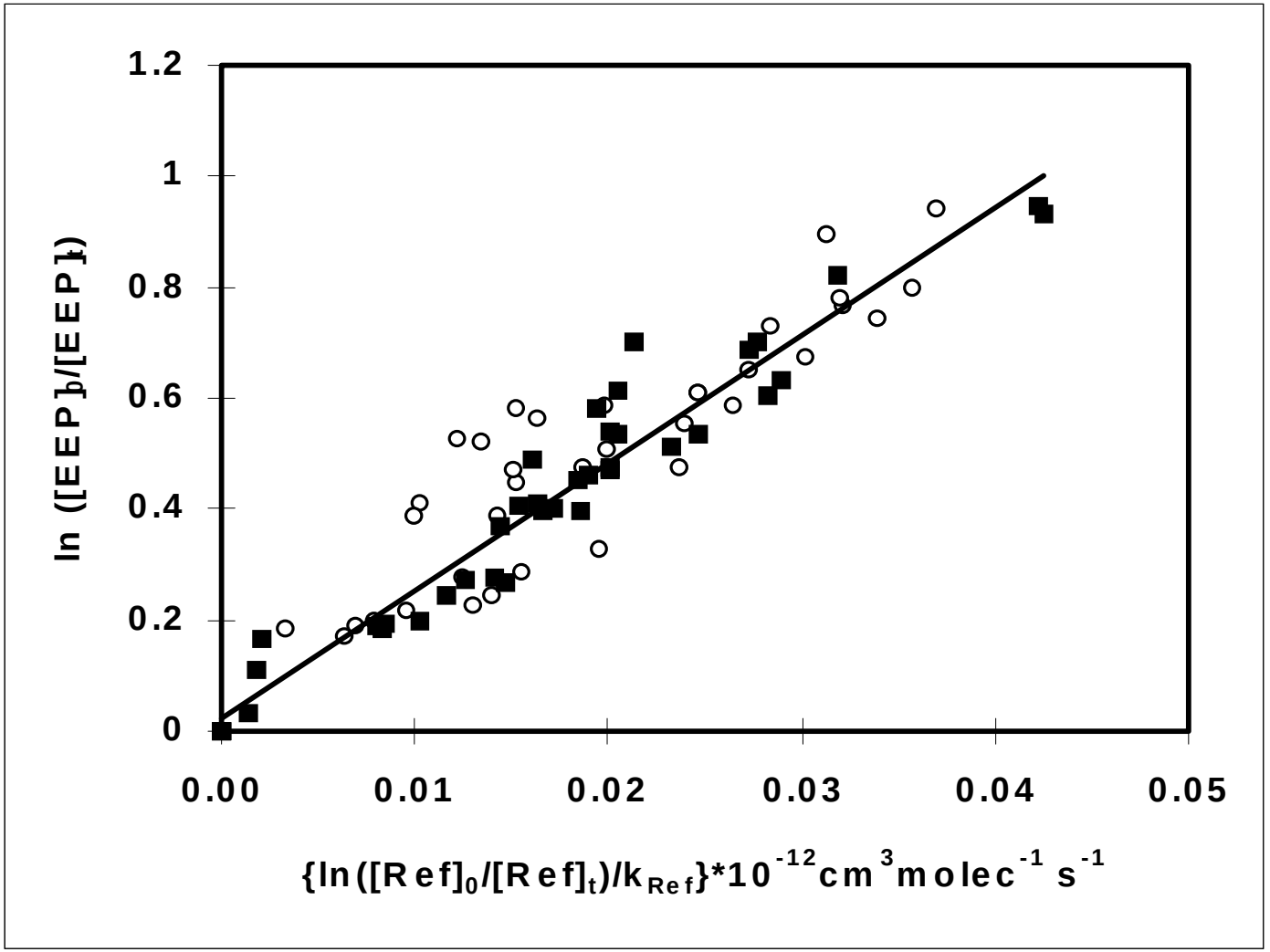
Compare unknown hydroxyl reaction rate to one that is known:

1) Reference + OH $\longrightarrow$ Products
2) Unknown + OH $\longrightarrow$ Products

Dividing differential equations to remove OH concentration and time and integrating yields:

$$\frac{\ln[\text{Unknown}]_0}{\ln[\text{Unknown}]_t} = \frac{k_{\text{Unknown}}}{k_{\text{Reference}}} \frac{\ln[\text{Reference}]_0}{\ln[\text{Reference}]_t}$$

Hydroxyl Radical Rate Constant for EEP
$CH_3CH_2OCH_2CH_2C(=O)OCH_2CH_3$



Hydroxyl Radical Rate Constants

Rate constants and chemical structures are variable

Compound/Structure	$k_{OH}(10^{-12}cm^3molecule^{-1}s^{-1})$/lifetime (hr)
Ethyl 3-ethoxypropionate $CH_3CH_2OCH_2CH_2C(=O)OCH_2CH_3$	23/12
Hexyl Acetate $CH_3(CH_2)_5OC(=O)CH_3$	9.3/30
2-Butoxyethanol $CH_3(CH_2)_3OCH_2CH_2(OH)$	22.5/12
2-Butanol $CH_3CH_2CH(OH)CH_3$	8.1/34

Experimental Methods

II. Product Identification and Yields:

$$\text{Unknown} + \text{OH} \longrightarrow \text{Products}$$

Must correct for transformation product/OH reaction to determine yield:

$$F = \frac{k_{Unknown} - k_{Product}}{k_{Unknown}} \; x \; \frac{1 - \frac{[Unknown]_t}{[Unknown]_0}}{\left(\frac{[Unknown]_t}{[Unknown]_0}\right)^{\frac{k_{Product}}{k_{Unknown}}} - \frac{[Unknown]_t}{[Unknown]_0}}$$

CH_3-CH_2-O-CH_2-CH_2-C(=O)O-CH_2-CH_3 + OH

CH_3-*CH*-O-CH_2-CH_2-C(=O)O-CH_2-CH_3

O_2, NO → ***NO_2*** decompose

HC(=O)-O-CH_2-CH_2-C(=O)O-CH_2-CH_3

Ethyl (3-formyloxy) propionate (EFP)

CH_3-CH_2-O-*CH*-CH_2-C(=O)O-CH_2-CH_3

O_2, NO → ***NO_2*** decompose

HC(=O)-CH_2-C(=O)O-CH_2-CH_3

Ethyl (2-formyl) acetate (EFA)

+

CH_3-C(=O)H

Acetaldehyde

CH_3-CH_2-O-C(=O)-CH_2-C(=O)O-CH_2-CH_3

Diethyl Malonate (DM)

CH_3-CH_2-O-CH_2-*CH*-C(=O)O-CH_2-CH_3

O_2, NO → ***NO_2*** decompose

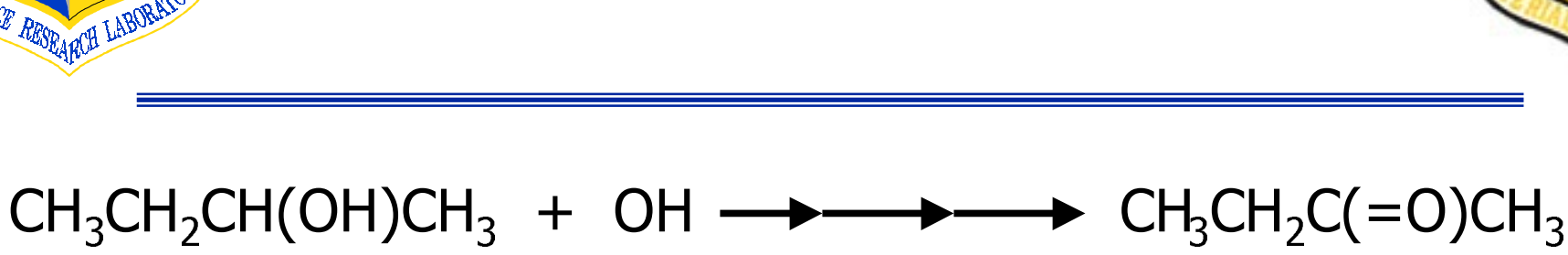
CH(=O)-C(=O)O-CH_2-CH_3

Ethyl Glyoxate (EG)

CH_3-CH_2-O-C(=O)H

Ethyl Formate (EF)

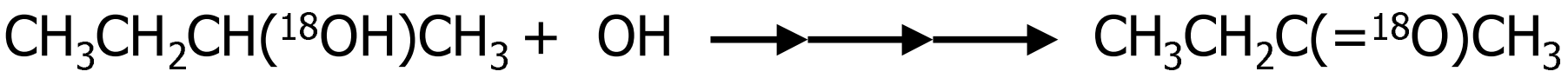
2-Butanol



? Where did oxygen come from in methyl ethyl ketone product?

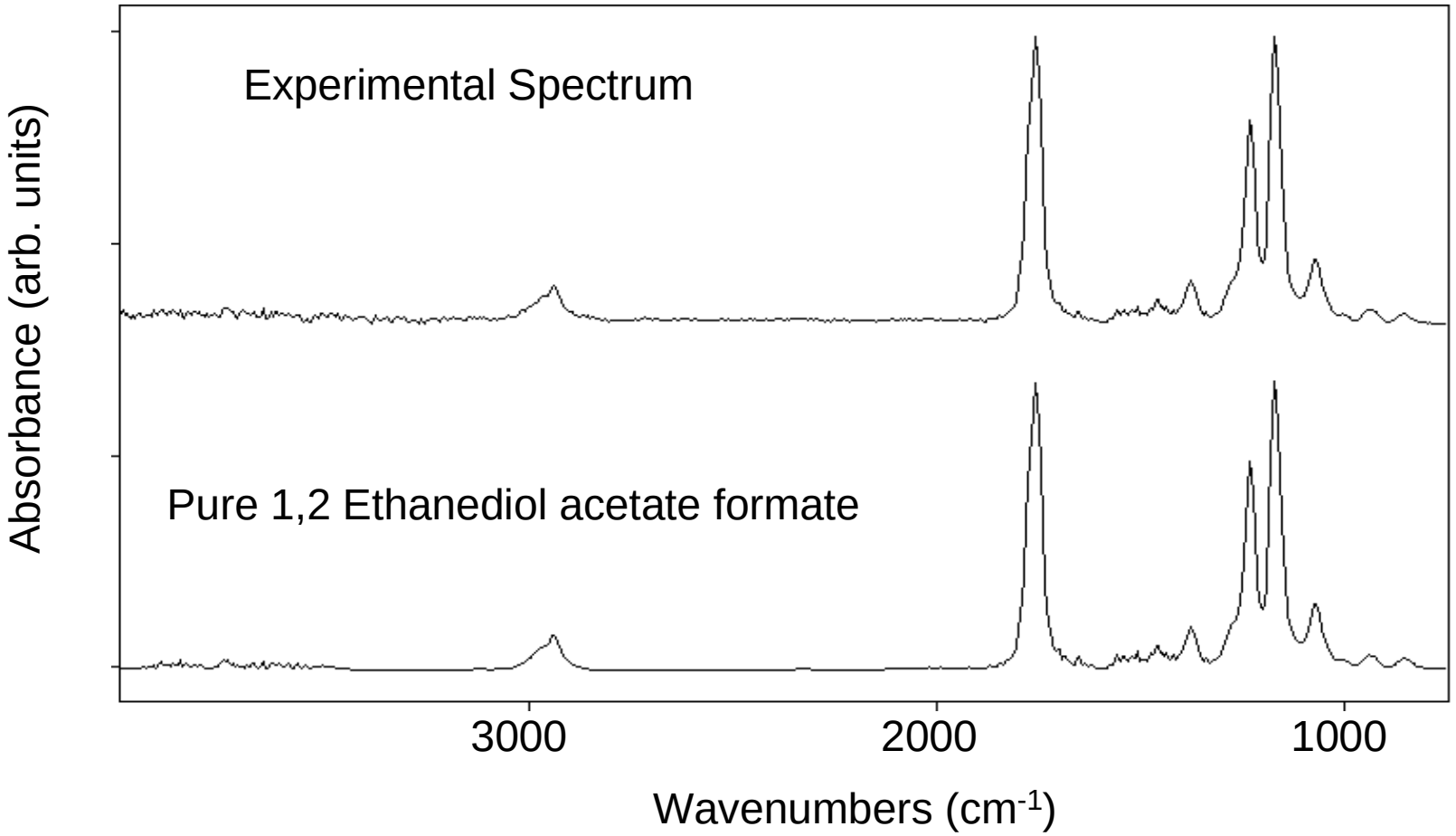
? Is this major transformation pathway a source of ozone?

Experiment to reveal mechanism:

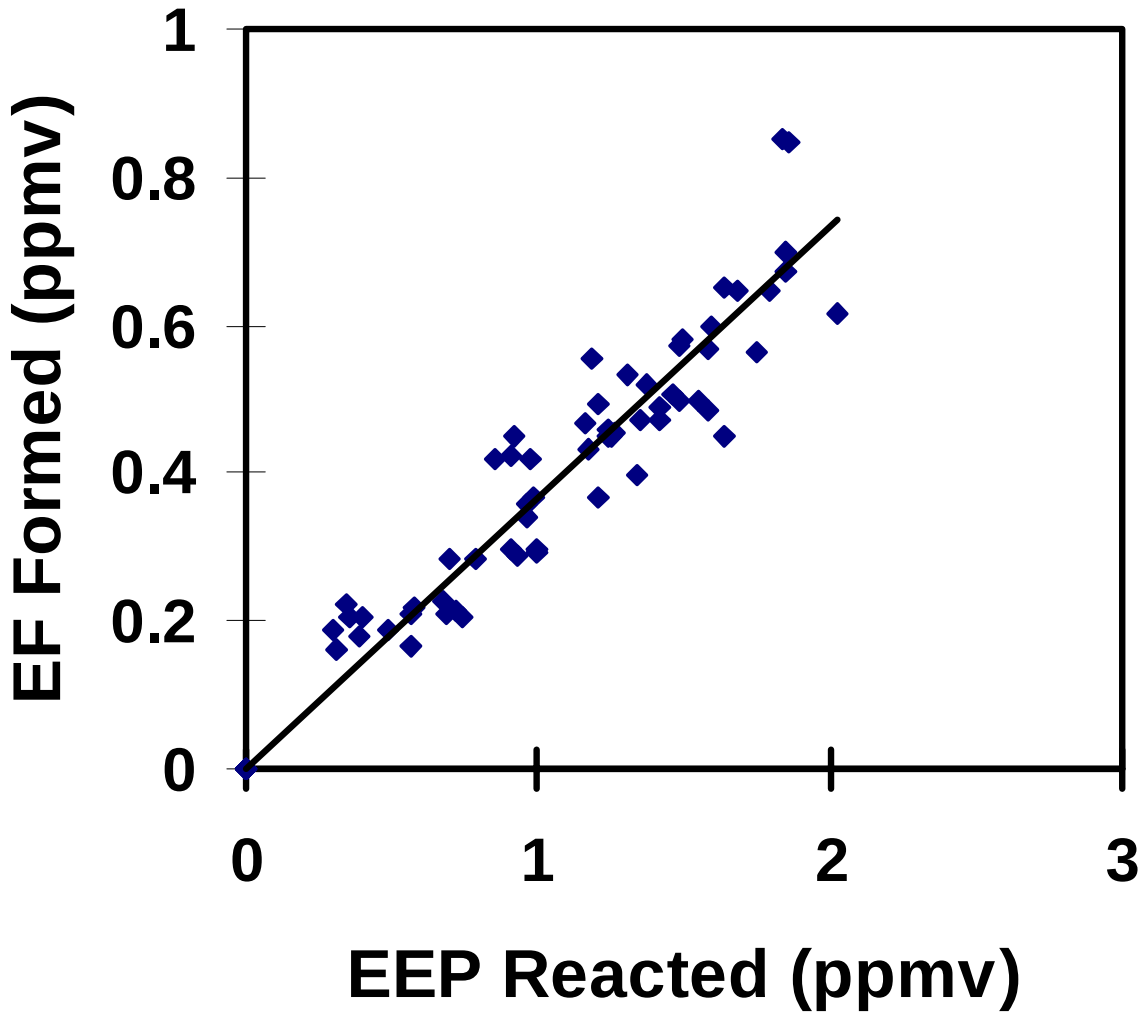


Experiment reveals that major transformation pathway is not a source of ozone.

Reaction Product Identification



Corrected Ethyl Formate Product Yield



Reactivity of Emissions

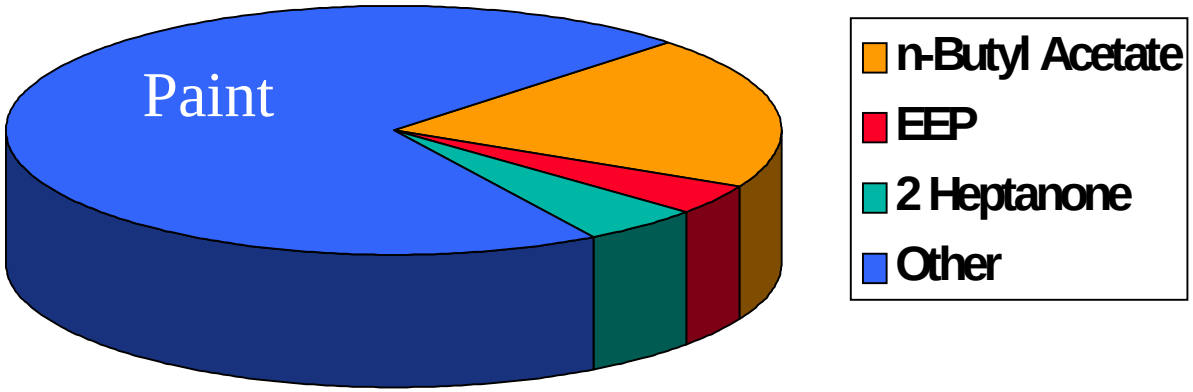
- Reactivity(ozone forming potential) of individual chemicals requires knowledge of atmospheric kinetics and mechanisms.

- Reactivity of emissions is based on summation of reactivity of individual chemicals.

- Reactivity values for each formulation are used to assess impact on air quality and minimize regulatory impact.

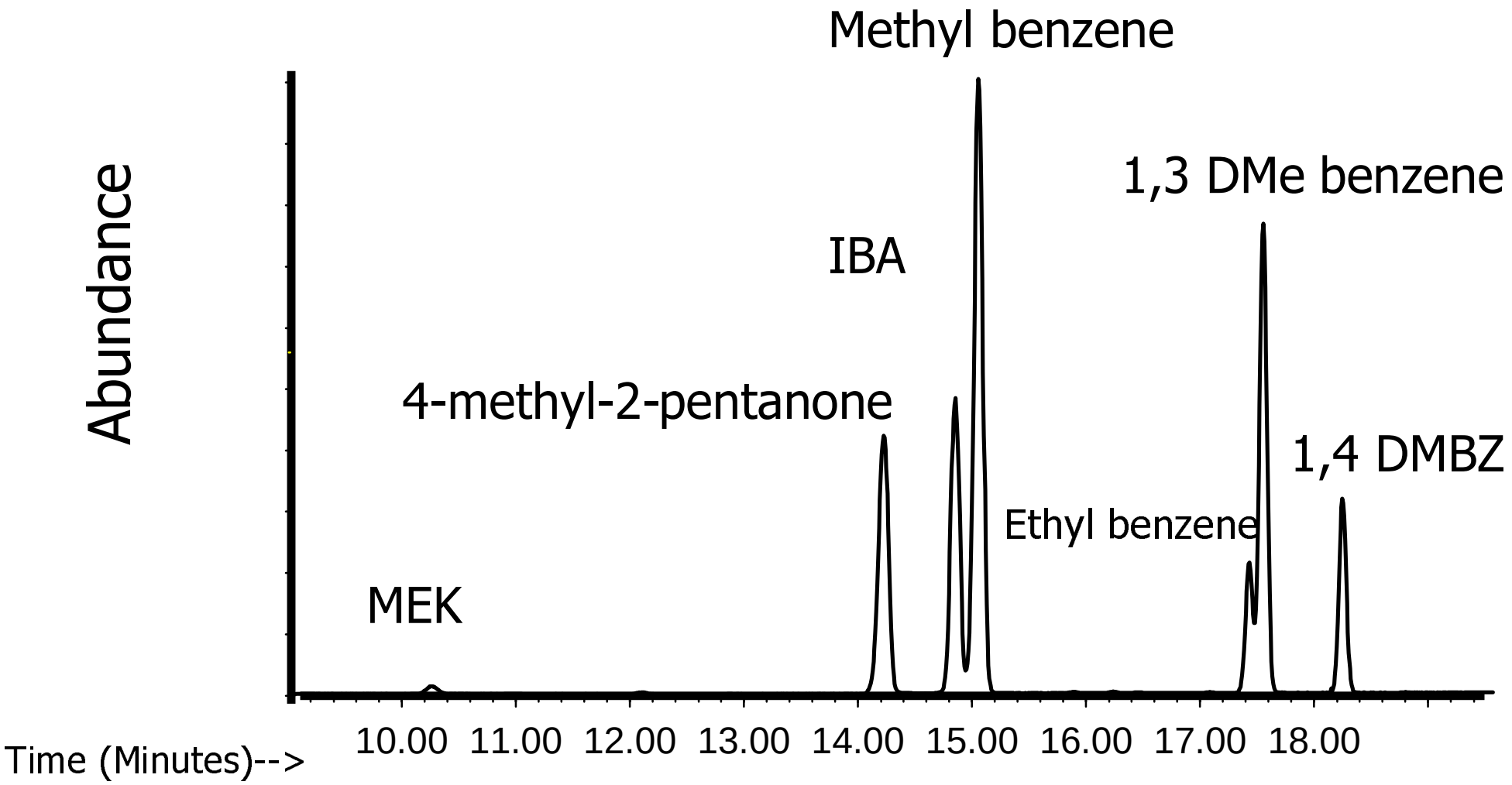
EMISSIONS - The Real Problem

Evaporation!



Emissions **NOT** ***content*** **!**

TIC for MIL-P-23377F



Air Quality Impact

Coating A = 0.27 g O_3/g paint

Coating B = 0.27 g O_3/g paint

MIL-P-23377F = 0.75 g O_3/g paint

gram O_3/gram paint **= Σ (gram emitted VOC/gram paint)* $Factor_{VOC}$**

Materials Benefits

- Reduce regulatory burden.
- Green chemistry.