Sensors Expo, Chicago, IL, 6-9 June 2005

Sensors for Manufacturing Efficiency Workshop

DOE Sensors & Automation
2005 Annual Portfolio Review

PHASED*: Development of a μGC-on-a-Chip with Interface to NeSSI**–

* **P**hased **H**eater **A**rray **S**tructure for **E**nhanced **D**etection
** **N**ew **S**ampling and **S**ensor **I**nitiative by CPAC
Part of "Wireless and Sensing Solutions Advancing Industrial Efficiency" project

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Sensors Expo, Chicago, IL, 6-9 June 2005
6 June '05 Session on "2005 ITP Sensors & Automation Annual Portfolio Review," Chair: Gideon Varga

PHASED*: Development of a μGC-on-a-Chip with Interface to NeSSI

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Rob Synovec, Vanessa Reid, Bryan Prazen, Gwen Gross, and Dave Veltkamp, Chemistry Department/CPAC, University of Washington, Seattle, WA;
Cyrus Herring, Kirsten Kunze and David Kellner, Caviton, Inc., Champaign, IL

Abstract

As part of the DOE-OIT project on "Wireless and Sensing Solutions Advancing Industrial Efficiency", this sensor and sampling system's development goal is field testing of PHASED* and other microanalytics on NeSSI-II** in the plants of collaborating members of the processing industries.
The presentation of progress on this project will cover: 1) Molecular modeling of analyte-GC film interactions, which guides us in the selection of stationary phase film materials and has quantified the advantageous properties of carbon-like and fluorinated materials; 2) Experimental evaluation of such materials with diverse analytes (C1–C10); 3) Micro-machining and performance evaluation (preconcentration and separation) of PHASED chips and associated electronics; 4) Detector development, for which we have demonstrated the equivalent of >1000 hours of service life; 5) Micropumping via electrostatic actuation and system packaging; and 6) Design and development of NeSSI standards and hardware, component-network evaluation, and pilot-plant tests, all of which help to realize this cross-industry microanalytical platform of the future, which will save capital, installation, maintenance, and plant operation costs.

Acknowledgments: This project is made possible with cost-shared funding by DOE-OIT, Honeywell, and technical collaborators: Michelle Cohn, UOP; Rob DuBois, Dow Chemical; Jeff Gunnell, ExxonMobil; Frank Schweighardt, Air Products; Joe Andrisani, DuPont; Mel Koch, CPAC; Steve Doe, Parker-Hannifin; and David Simko, Swagelock, under the project entitled "Wireless and Sensing Solutions Advancing Industrial Efficiency," and the technical support of NIST-IEEE 1451, Profibus Trade Organization, Fieldbus Foundation, CiA, SAIT, and Jerry Evans, EVCO Consulting.

* PHASED = Phased Heater Array Structure for Enhanced Detection; **NeSSI = New Sampling Sensor Initiative

Presenter Bio: Ulrich Bonne, Sr. Research Fellow, joined the Honeywell Labs at Plymouth, MN, in 1965, and received his MS and PhD in Chemical Physics from the University of Göttingen, Germany. His present R&D interests are focused on microsensors for environmental, industrial, and medical applications.

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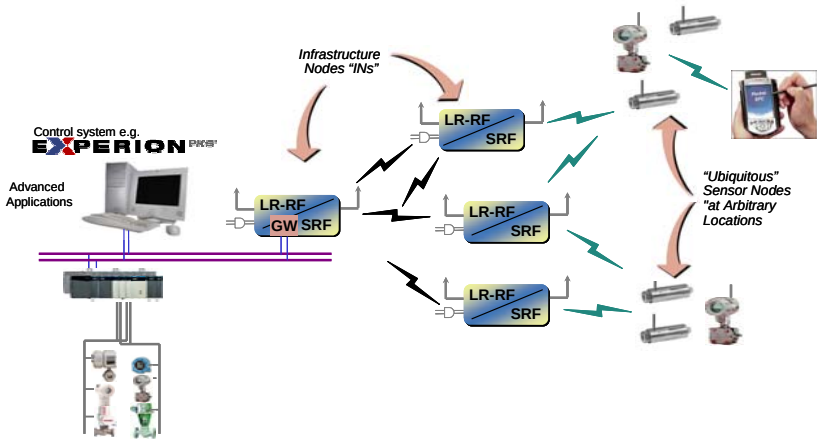
Wireless Sensing Solutions

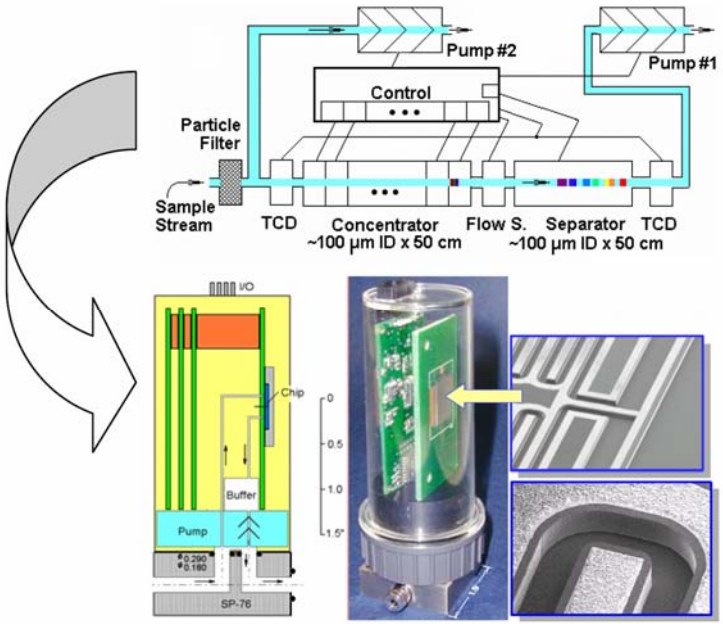


Task A: Wireless Network for Industrial Applications

- Robust industrial wireless infrastructure
- High data security
- Lowest total cost of ownership
- Low power requirements and extended battery life
- Enhanced availability and coexisting with other RF systems

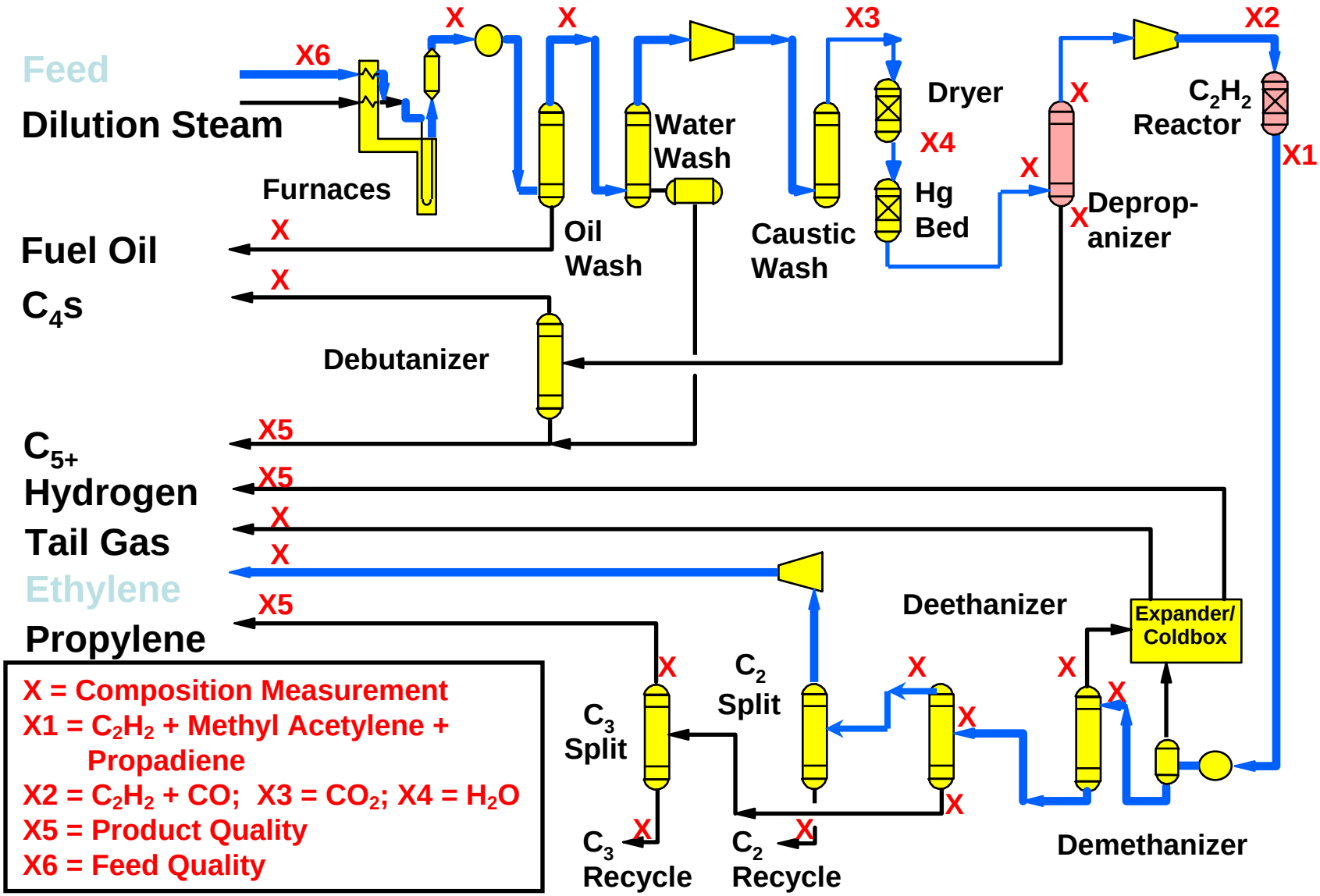
Task B: PHASED Gas Composition MicroAnalyzer

- MEMS based micro gas chromatograph
- Real-Time, on-/by-line measurement of process ccstreams
- High-Speed, sub-second analysis time
- 20-50-Stage, sub-second pre-concentration
- NeSSI-Compatible Microanalytics
- Low-Power requirements
- Affordable



Energy and Emissions Savings via PHASED on NeSSI

Naphtha Cracker – Ethylene Production



X = Composition Measurement
X1 = C_2H_2 + Methyl Acetylene + Propadiene
X2 = C_2H_2 + CO; X3 = CO_2; X4 = H_2O
X5 = Product Quality
X6 = Feed Quality

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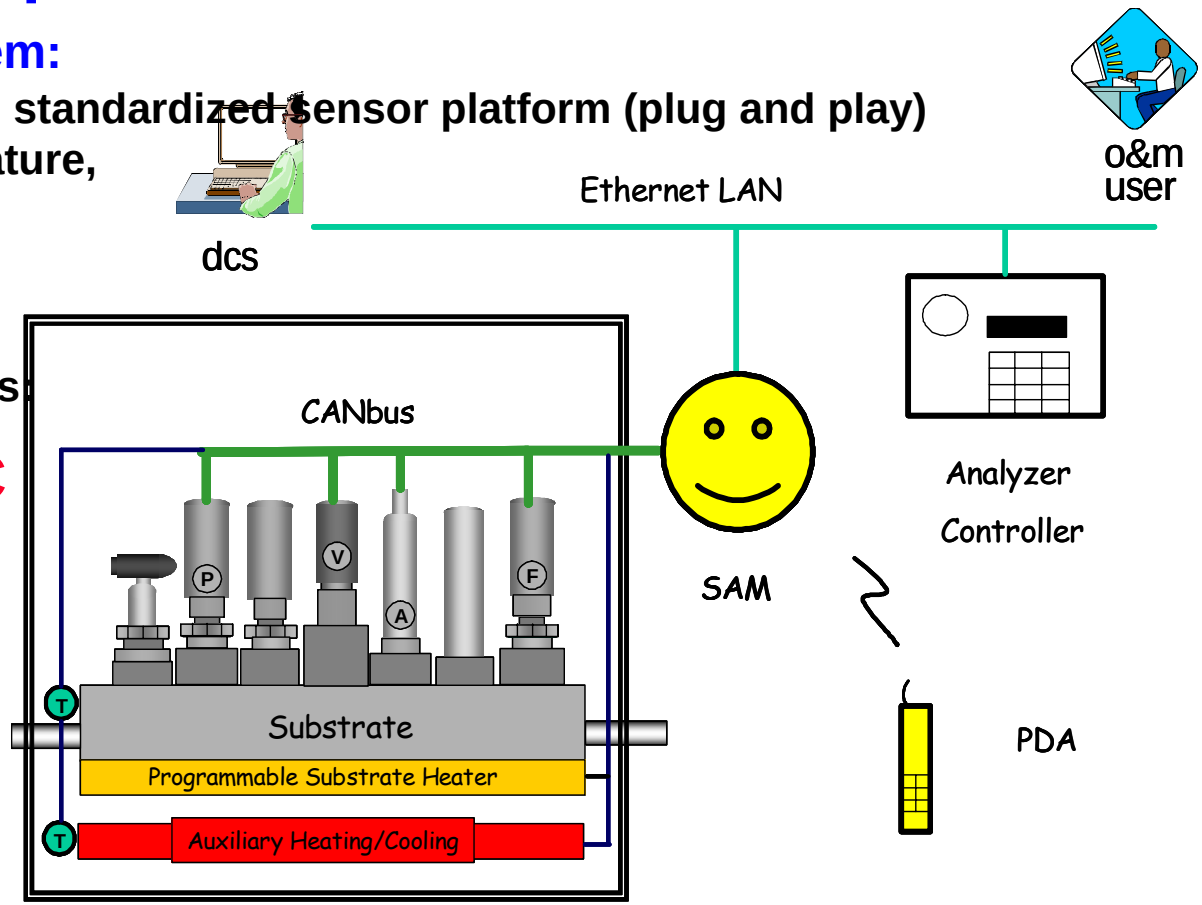
Microanalytics for Process Control Solutions
Technical Concept – NeSSI-II

- **NeSSI-III Sampling System:**
  - Modular, IS, networked, standardized sensor platform (plug and play)
  - Pressure, flow, temperature, and composition
  - Micro-components with lower-cost life cycle
  - Supports microanalytics:

PHASED μGC



Applications:
- In-situ process stream monitoring
- Ind. process control and automation
- Petroleum refineries, chemical processing plants, metals & food processing

Process monitoring with lower-cost of life-cycle and improved safety

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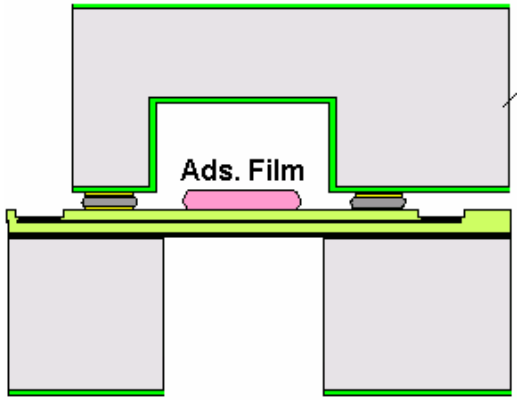
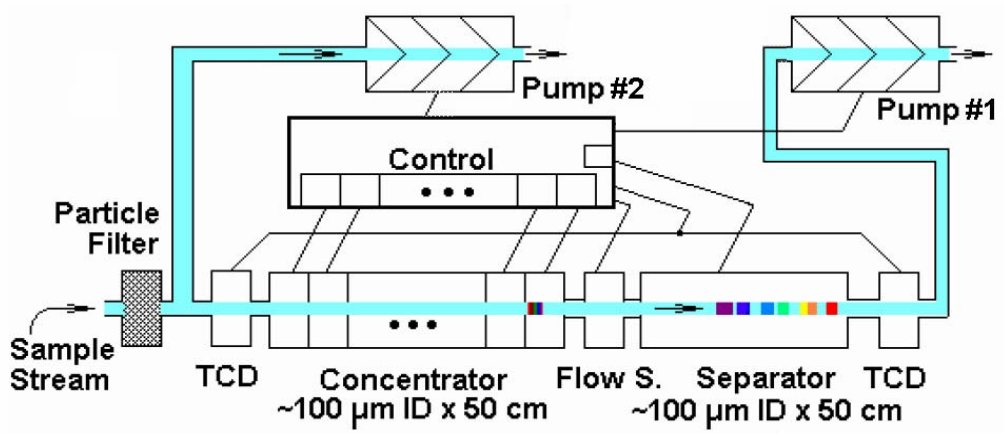
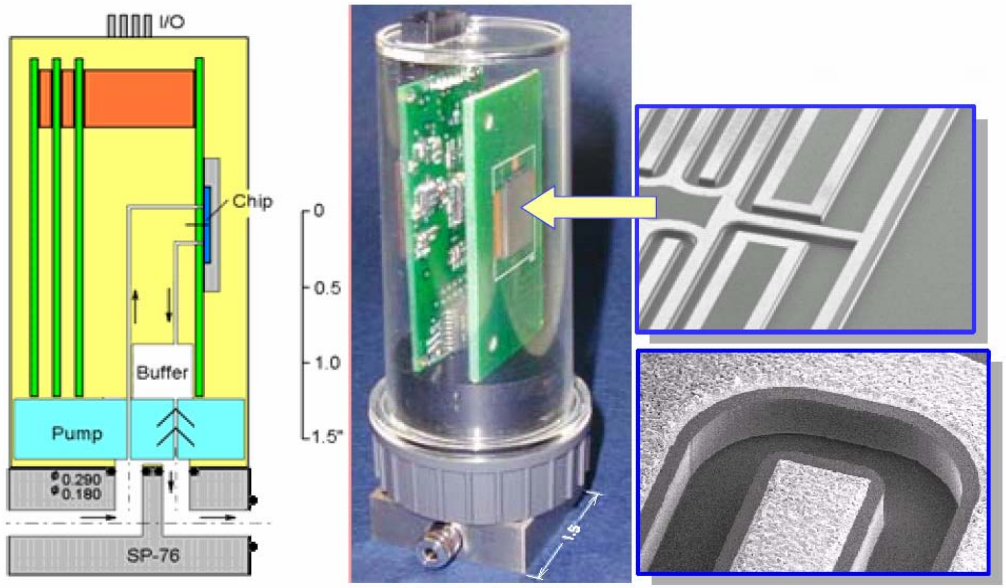
PHASED Analyzer Block Diagrams and Device Packaging



PHASED Cross Section





NeSSI

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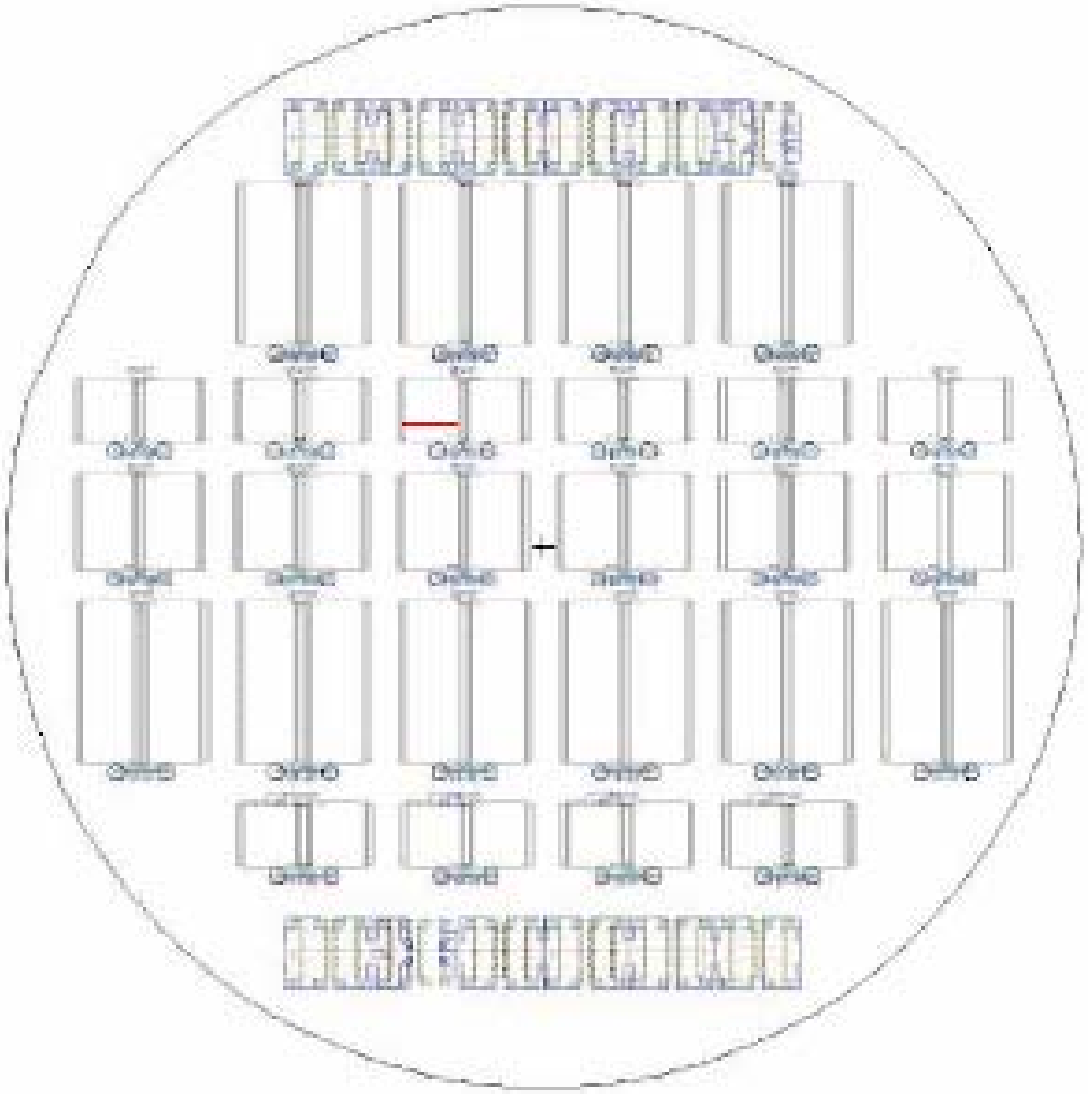

Overall Layout of the PHASED Chips on a 4" Wafer

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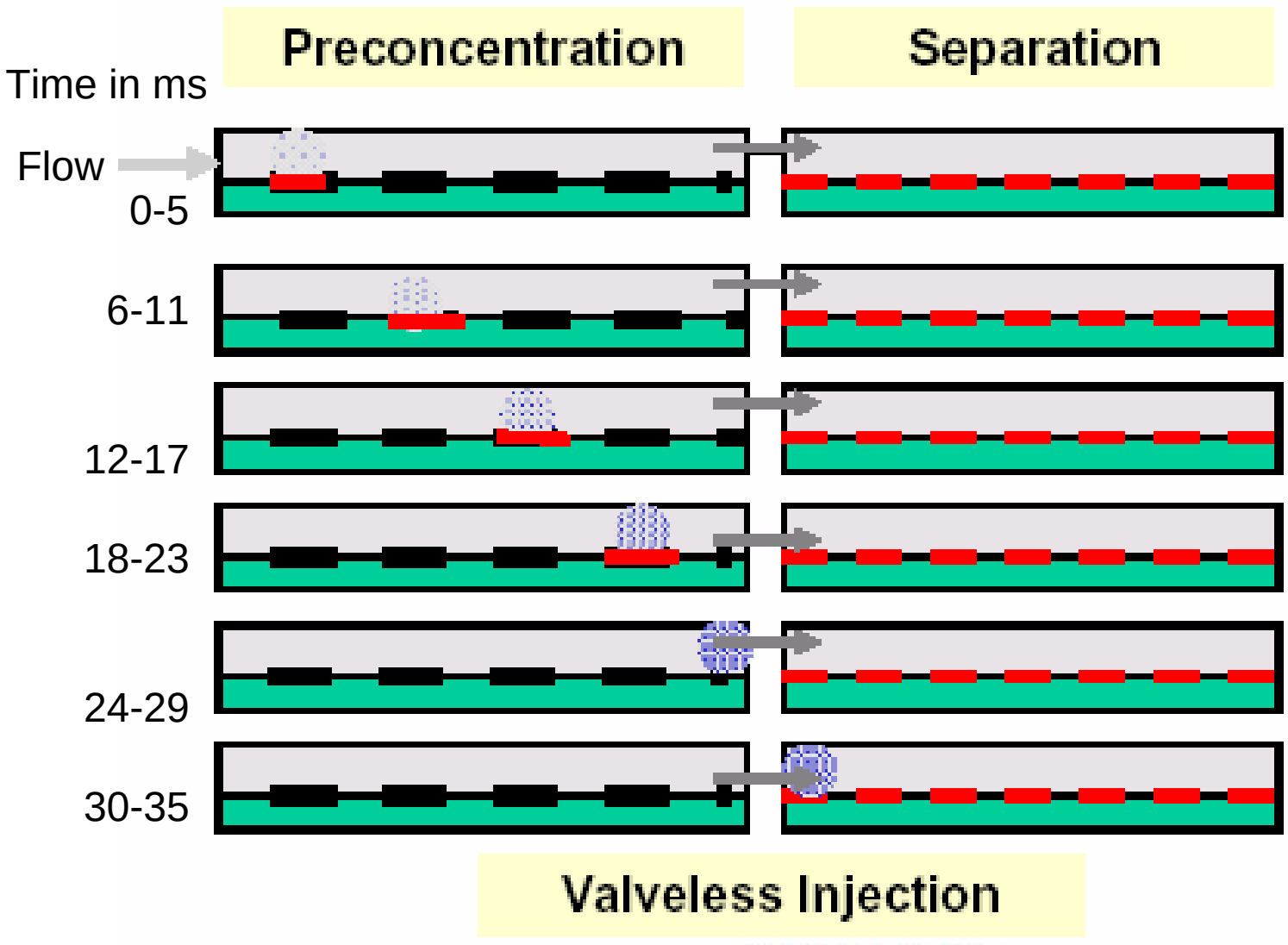
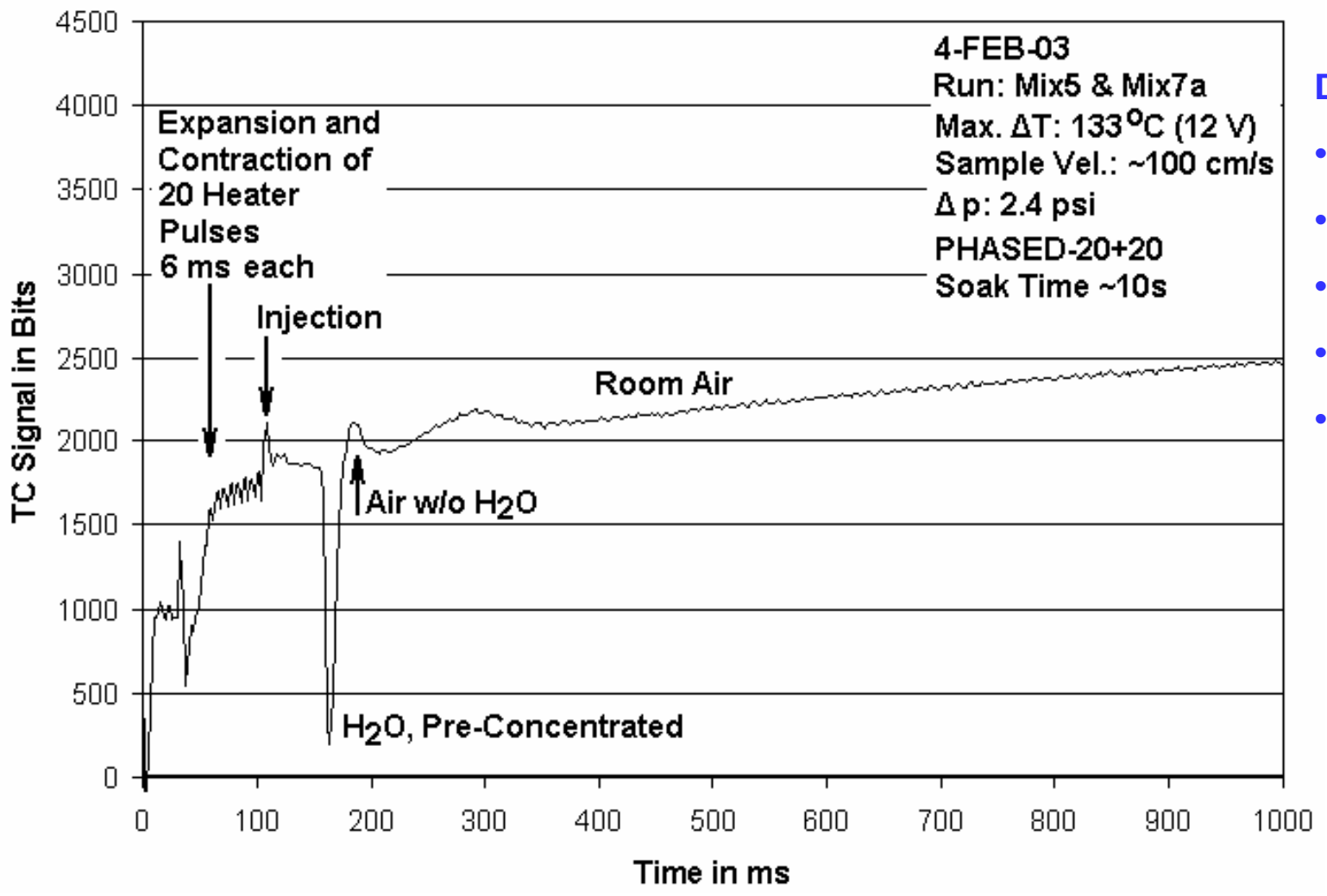
PHASED Pre-Concentration Approach



PHASED: Corrections for N2 & Air Samples



Determine:

- **Peak ID**
- **Leakage**
- **Opt. Synch**
- **Sens.Limit**
- **Pre-Concen.**

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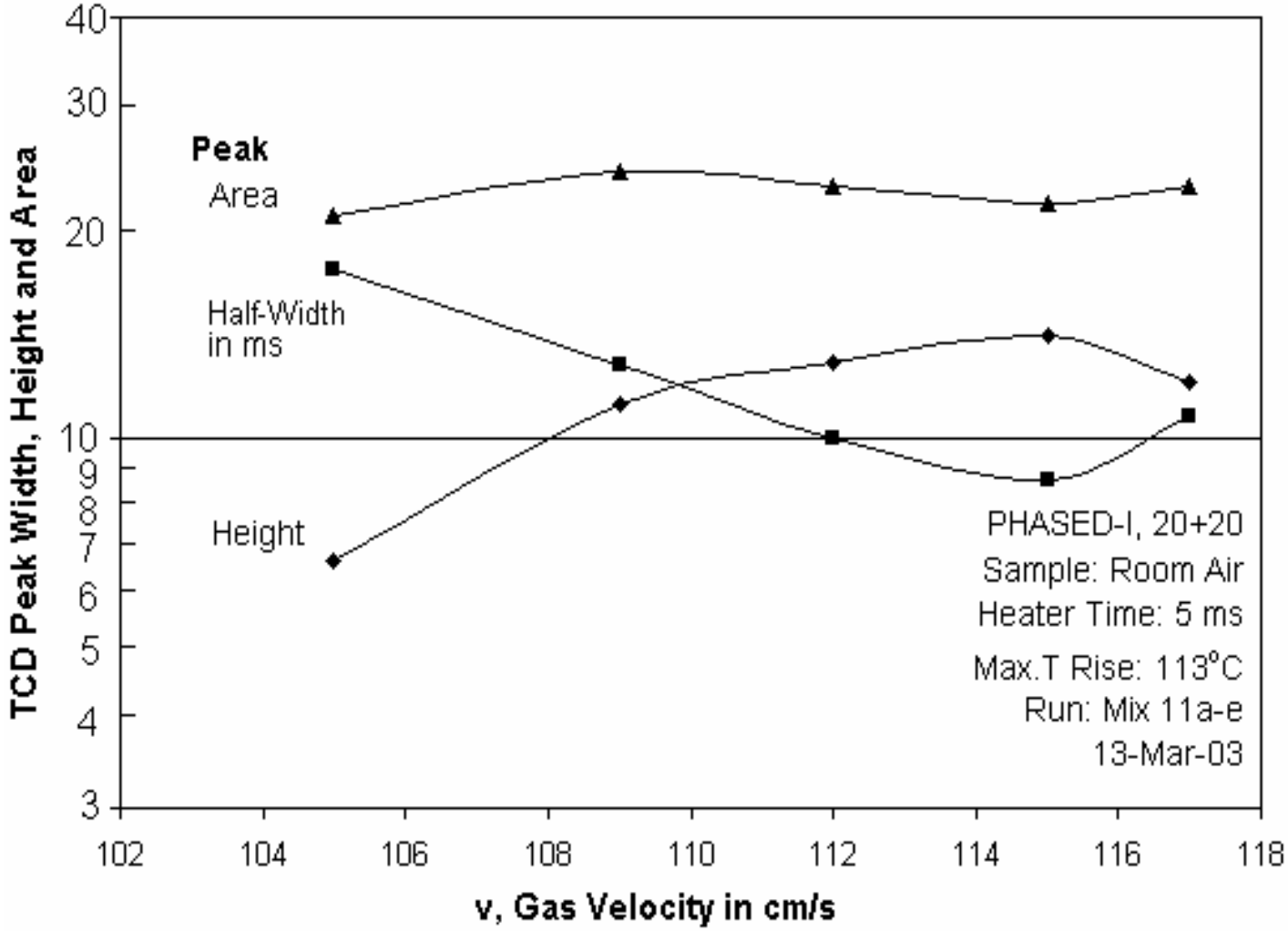

Fig. 2. Synchronization of Sample Gas and Heater Array Velocities.

Sensitivity of PHASED Output to Proper Synchronization between Rate of Gas Velocity and Rate of Heater Array Progression. Minimum Half-Width is Near 8 ms, i.e. Excellent Compared to 5 ms Heater Pulses x 20-fold Stacking+Sep+Det. PHASED Run # 1.

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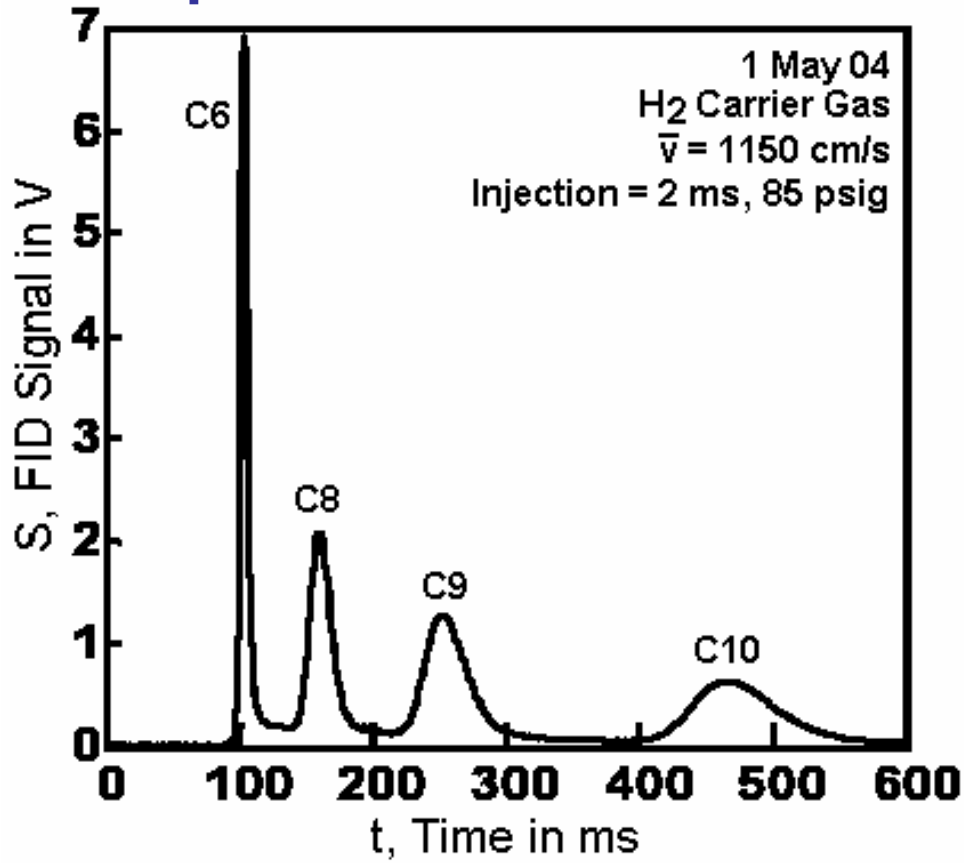
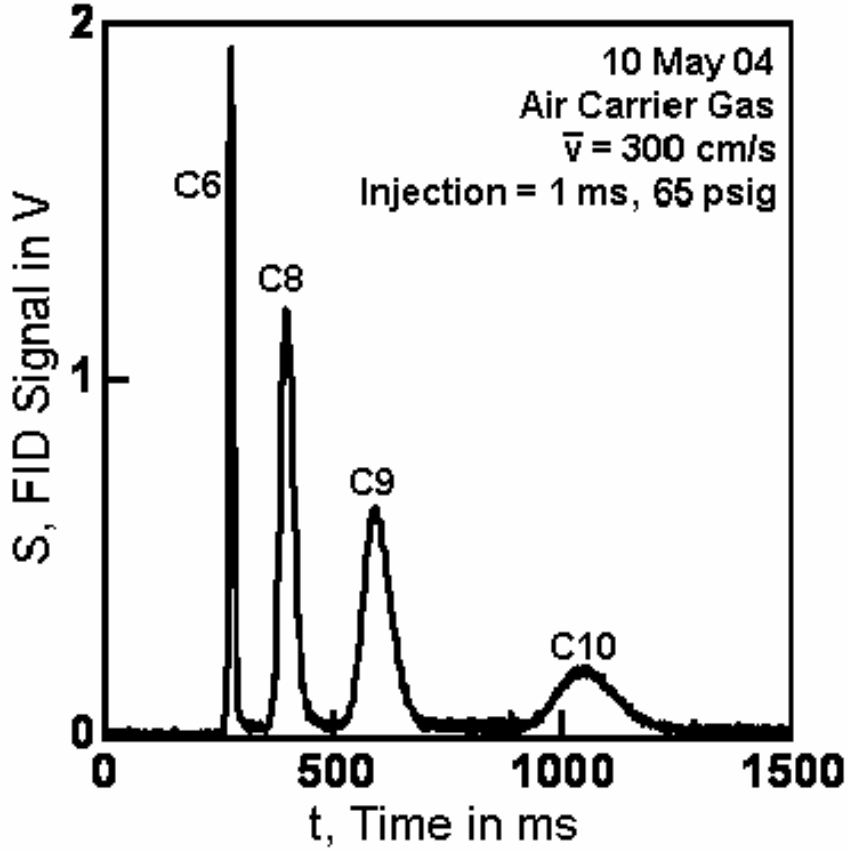
2004 Results on 0.6 μm Nanoglass

•Separation Performance: H2 vs. Air Carrier Gas





Separation of Hexane, Octane, Nonane and Decane.
Capillary #3: 1-m in length,100 μm ID, 3 μm film, 100°C
FID at 250°C, Data Rate: 20 kHz.
*Evaluation Data Courtesy G.Gross and R.Synovec, CPAC

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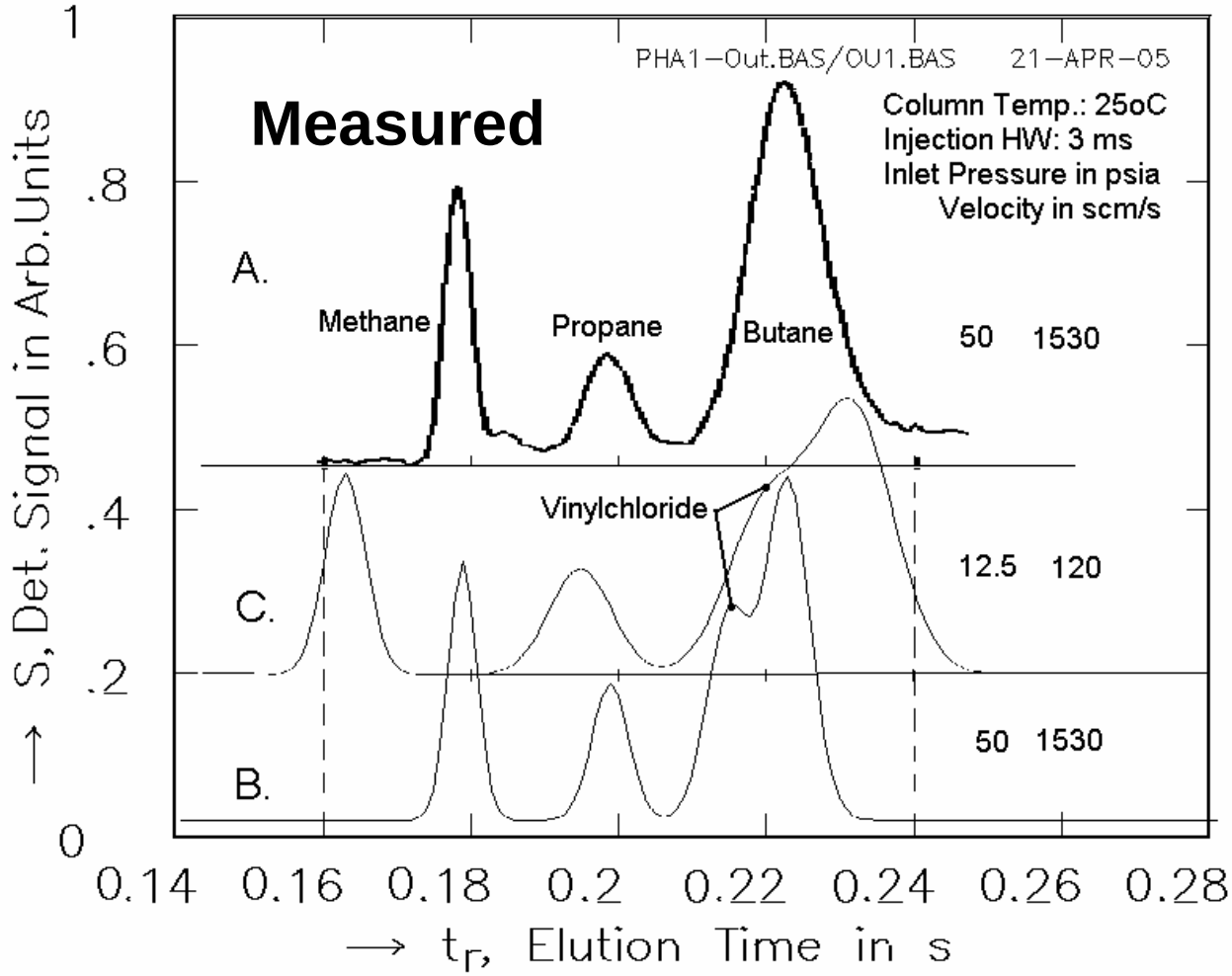

Comparison of measured and simulated high speed separations of low molecular weight gases with standard capillary and PHASED micro-GC columns.

A) Measured via 100cm/100μm/0.4μm DB-5 capillary in H2 at CPAC,

B) Simulation of (A) with addition of vinyl chloride,

C) Simulation of PHASED 25cm/100μm/1.2μm DB-5 in air..

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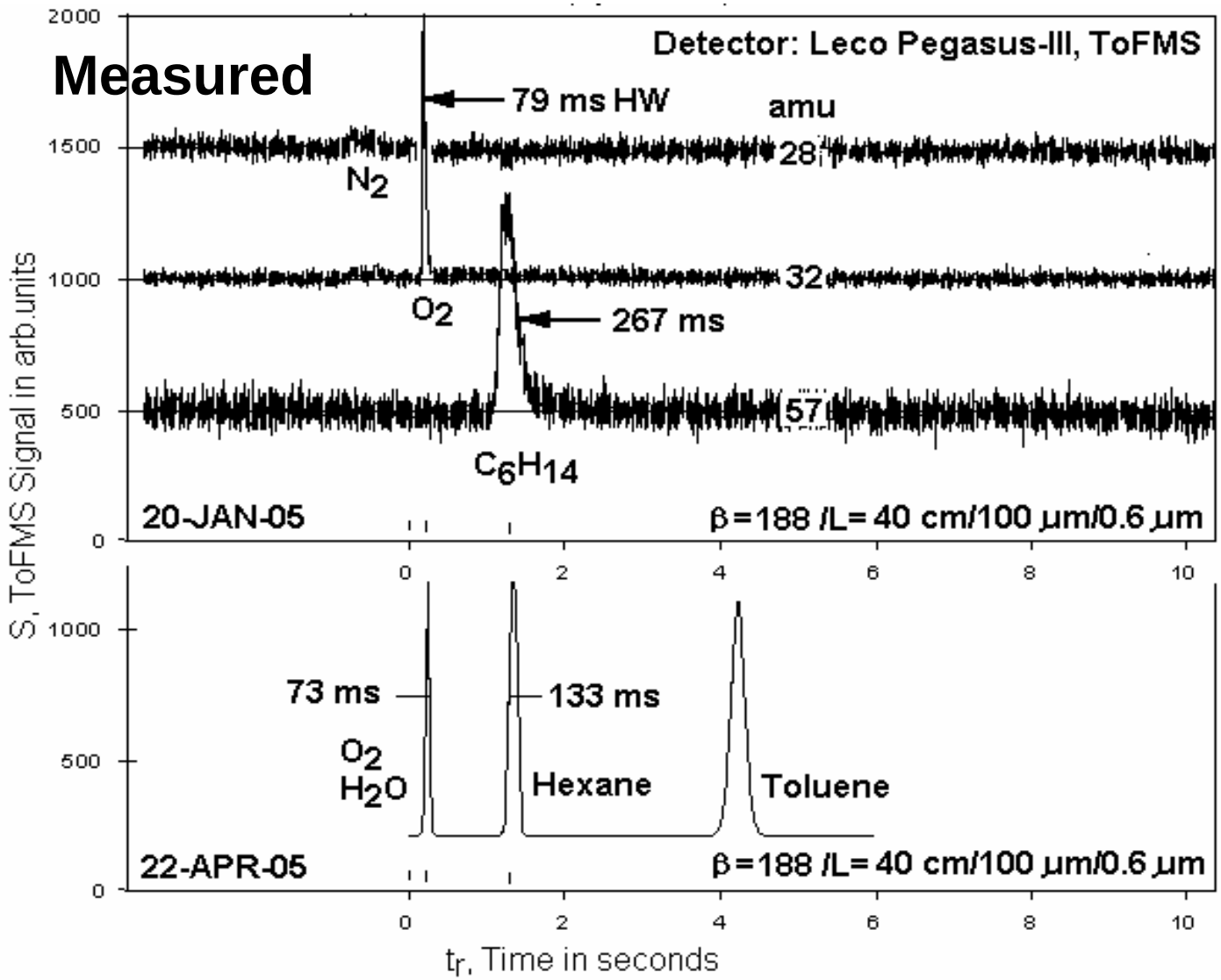

40-cm channel PHASED Analysis of sample gas of 720 ppm hexane in air; carrier gas = N2 at ~90 cm/s

Top: **Gas chromatogram of a 50nL sample injected into N2 within ~70ms at 58°C.**

Bottom: **Simulation of top analysis, po = 19 psia, Δp = 6.5psid, to = 0.18 s, T=58°C, vo = 200 scm/s in air.**

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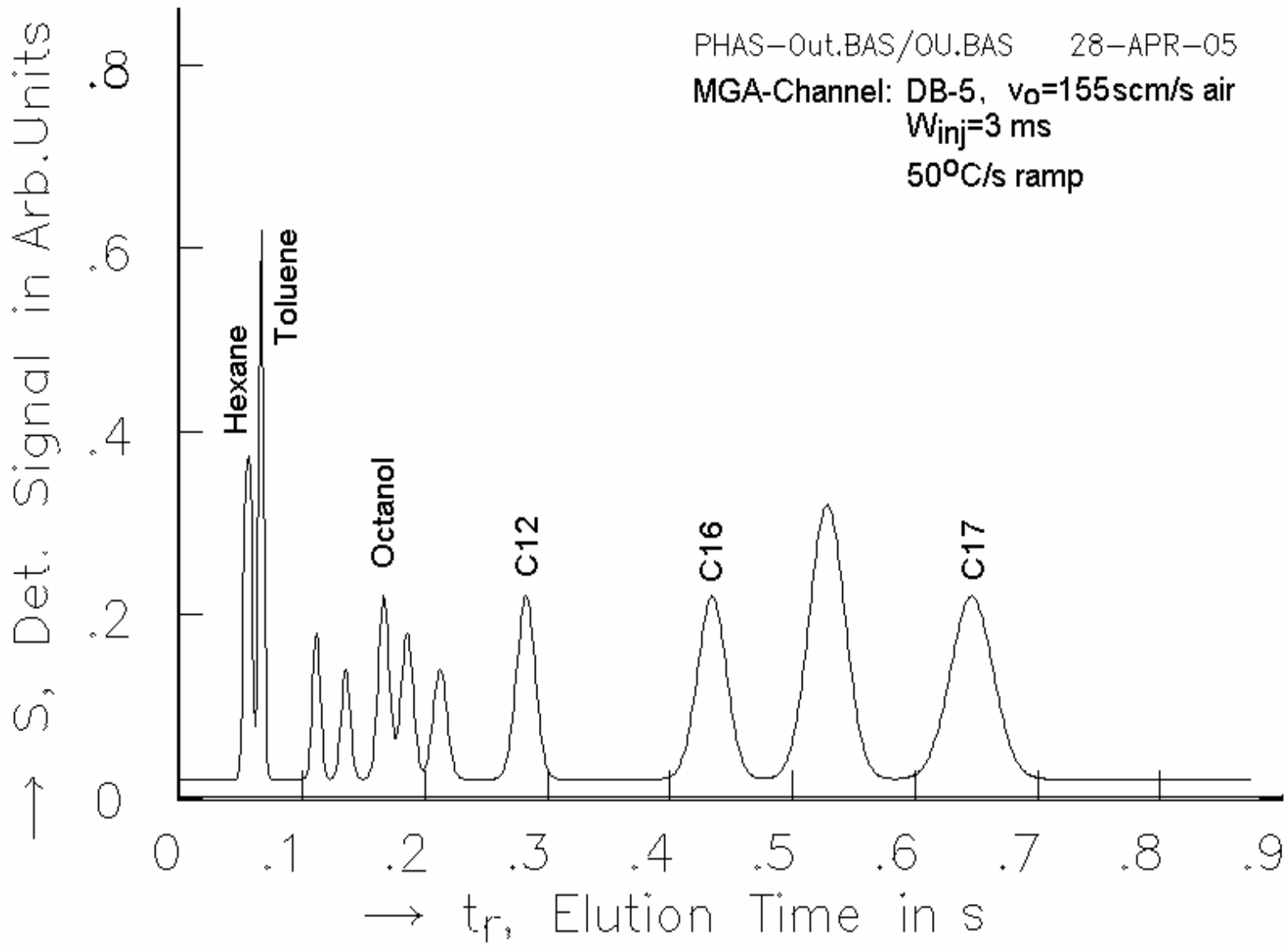

Simulation of a PHASED µGC Run

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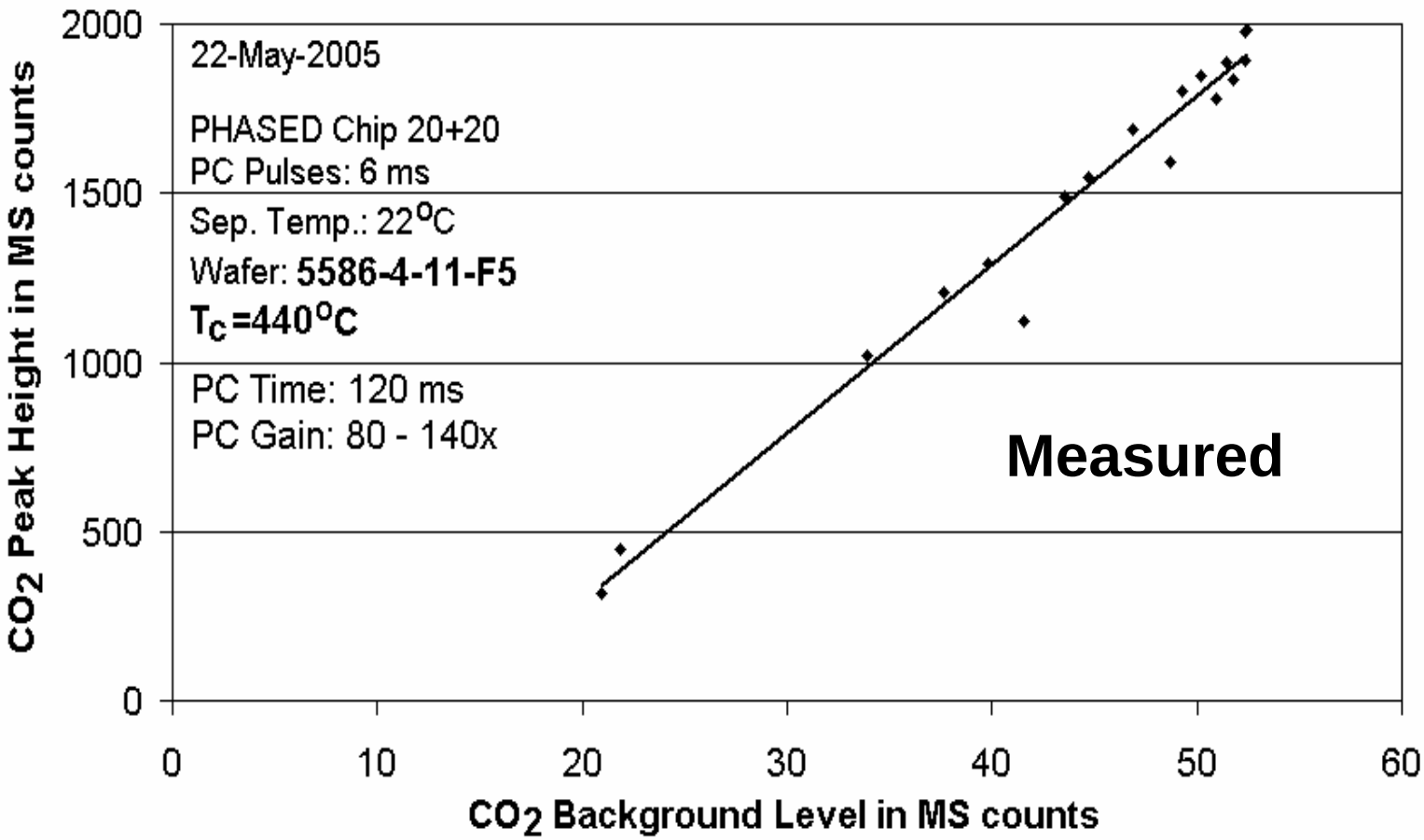

Fig. 33. PreConcentration of CO_2 in N_2 Carrier Gas, Purging Prior Air Flow. The Shown Peak Height Would be ~4x Higher after Correction for Peak Broadening Due to Transport to MS (Leeco ToF).

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Molecular Modeling of Adsorption Enthalpies: Hydration

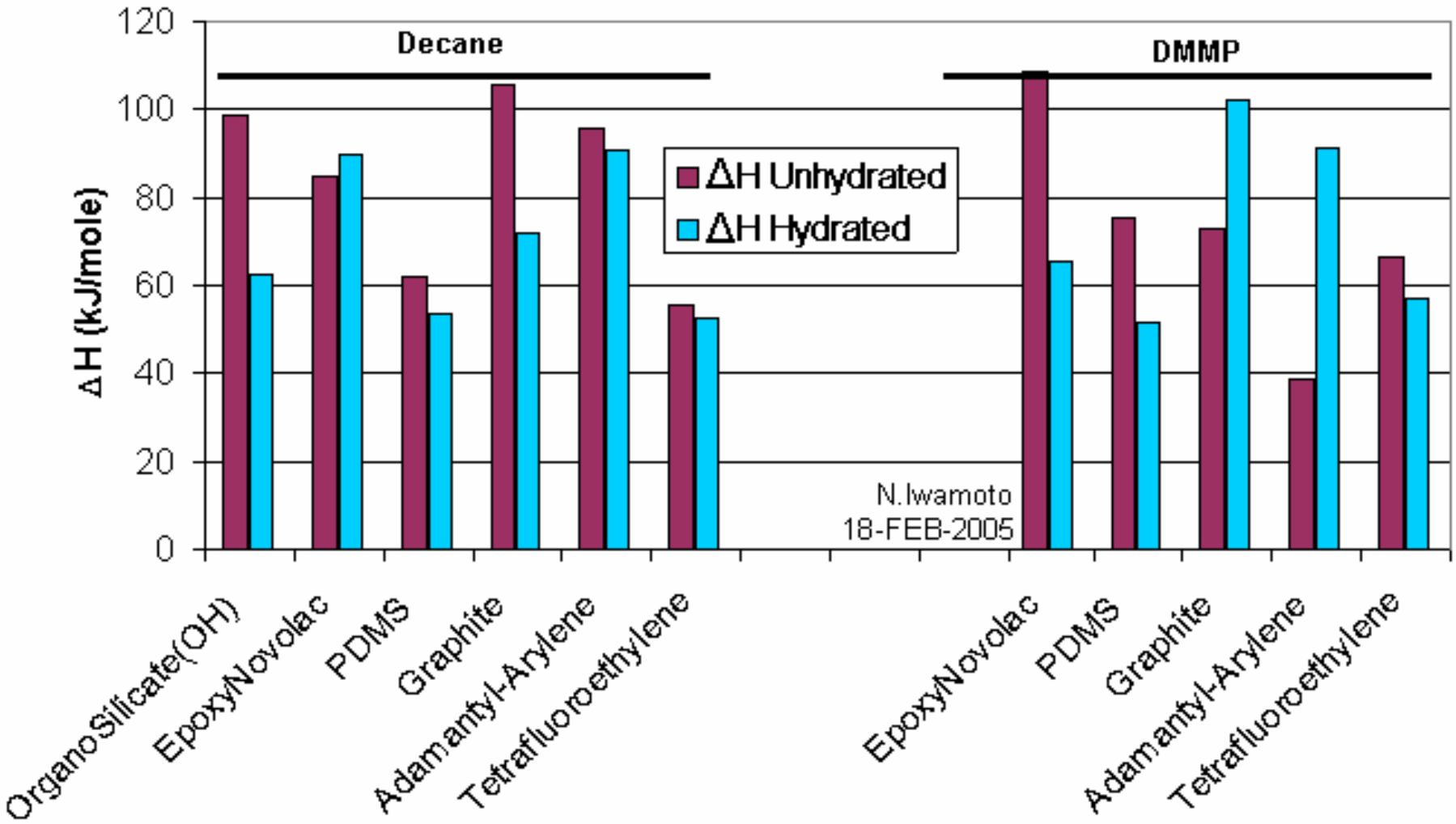

Fig. 2a. Comparison of Interaction Enthalpies, ΔH, before and after Hydration of Several Stationary Phase Films, for Dodecane and PMMD

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PHASED TCD Capabilities

Table 1. TCD Calibration of PHASED Detectors with Argon:

Signal: 128 mV for 100% Ar vs. 100% N2; G=1; Noise: 3 mV RMS.

Detector mean temperature: 50C above ambient.

which requires a Pt-heater temp. of 140C

Gain Factor, G=200 for MDL data below

S/N increases as ΔT-heater: 1x at 140C and 1.5 at 200C

Gas*	Thermal cond. @ 70C	Min. Det.** Limit, now	Min. Det.*** Limit, future	~Min. Det. Limit, 90C
-	μcal/(cmKs)	ppm	ppm	ppm
H2*	496.1028	-3	-0.3	-0.2
CH4*	99.73078	-39	-3.9	-2.6
C2H2*	72.946	-262	-26.2	-17.5
C2H4*	69.258	-1300	-130.0	-86.7
N2	68.32570	-	-	-
CO*	67.12416	1009	100.9	67.3
C2H6*	65.99266	520	52.0	34.6
H2O	51.52115	72	7.2	4.8
CO2*	49.10356	63	6.3	4.2
Ar	47.63631	**59**	**5.9**	3.9

* Included as 100 ppm in test gas mix; MDL values for S/N=1

** MDL = (10^6/2) (N/S/G) (kN2 - kAr) / (kN2 - kx); ***Future MDL=MDL/10

MBrfc/TL-03-PHASED-LeakTest

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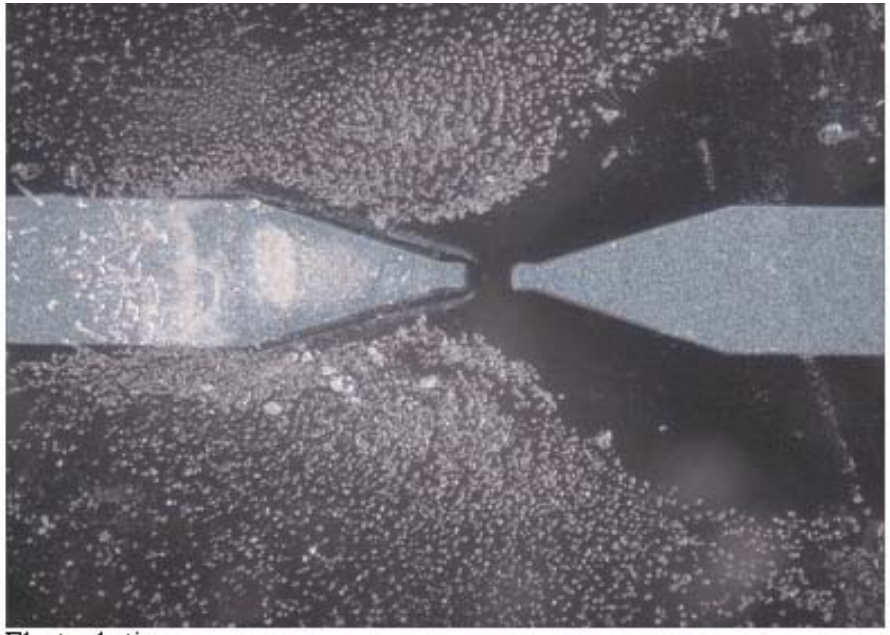
Powered electrode



Electrode tip

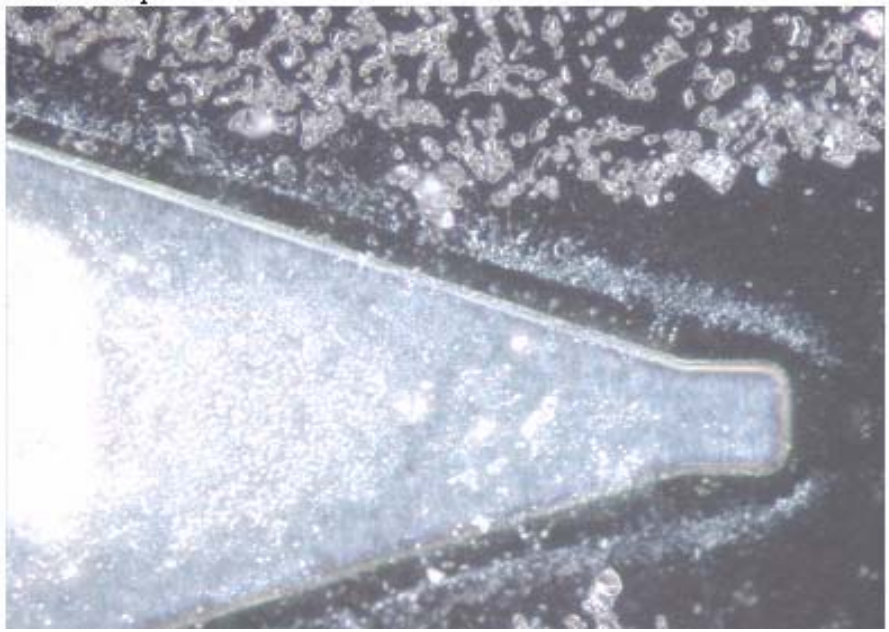


photo by Cy Herring, Caviton, Inc.

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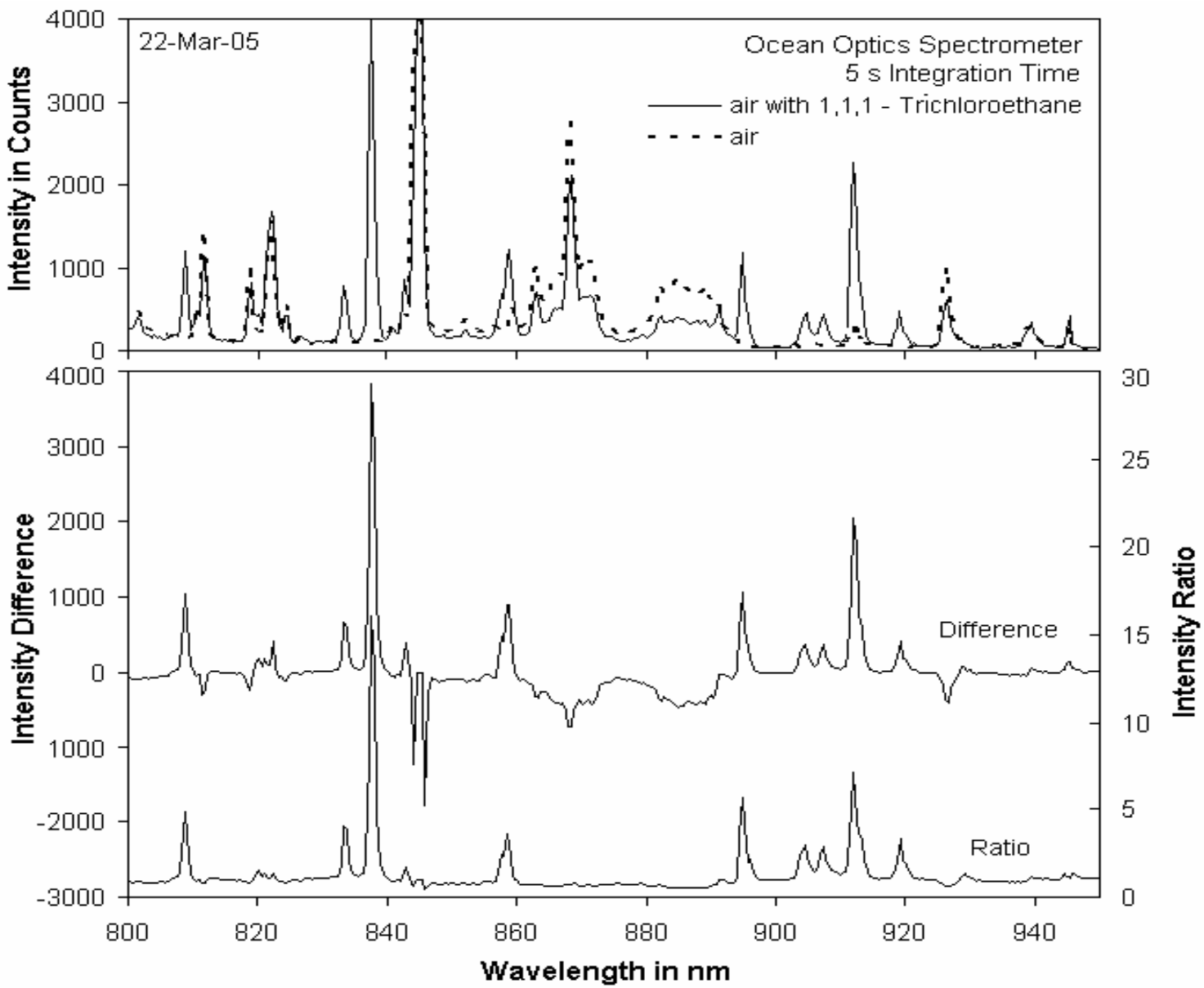

Fig. 3. MDD Trichloroethane Detection In Air. By Caviton, Inc.

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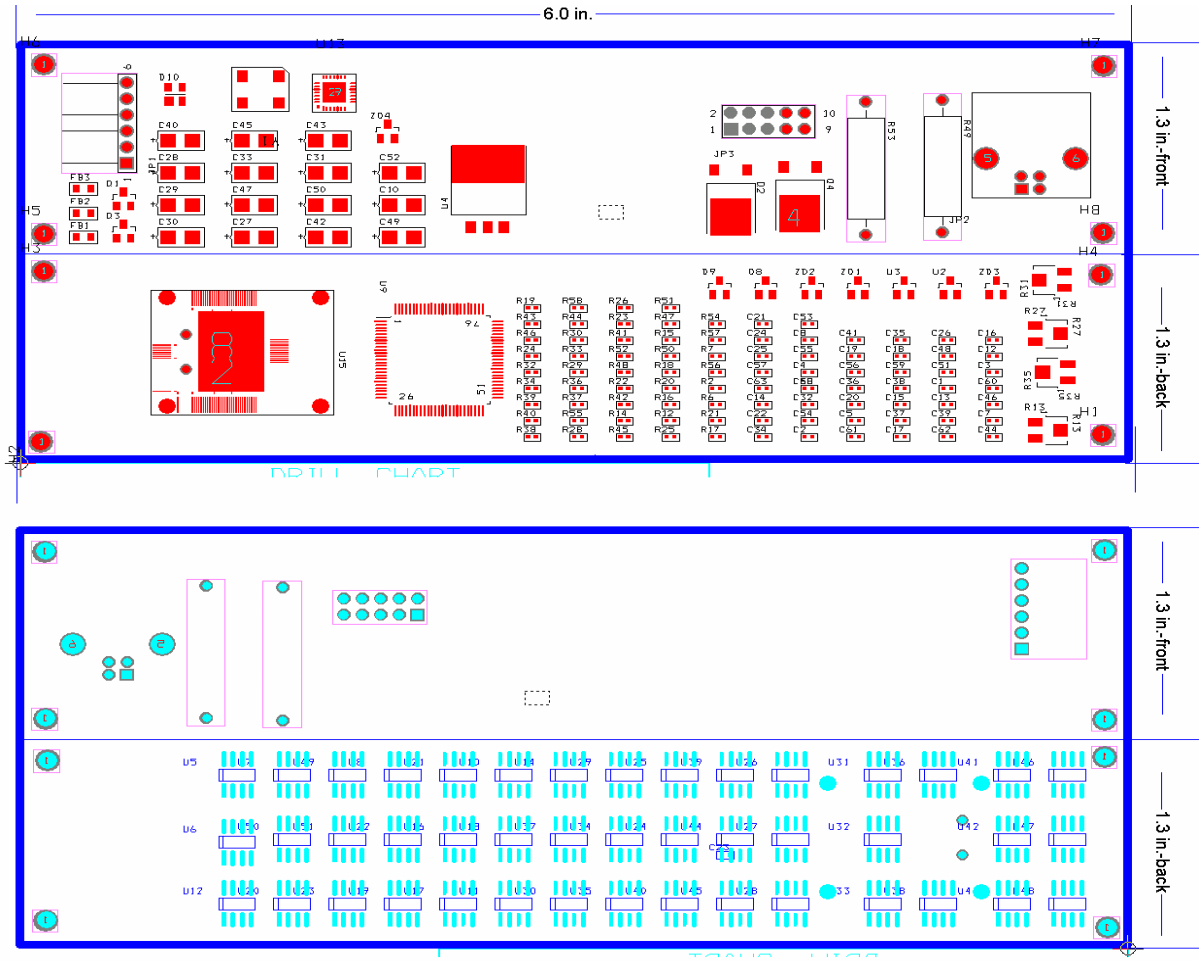
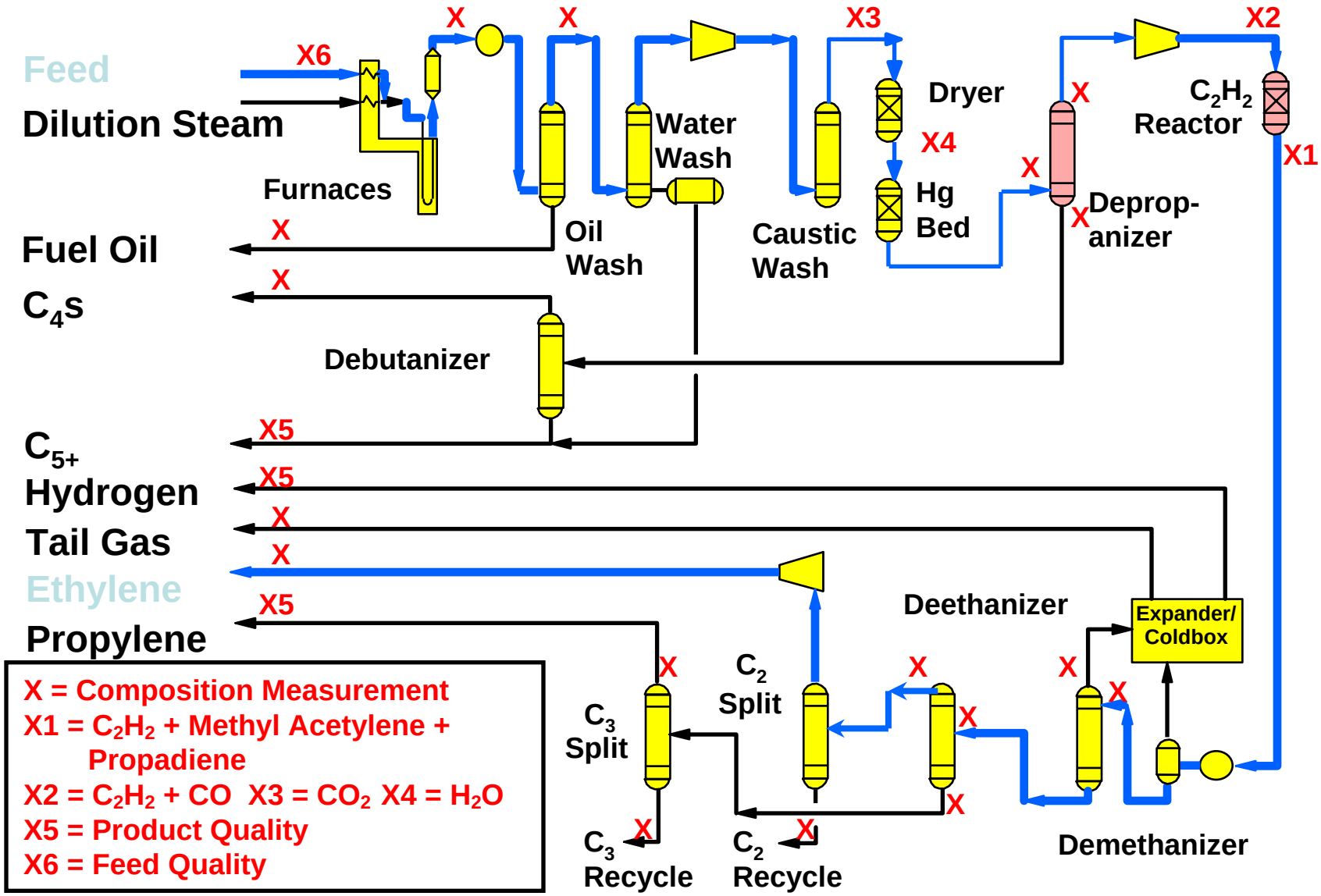
Electronics for PHASED on NeSSI

- **Features:**
  - Individual control for concentrators, up to 50
  - Integrated 12-bit A/D, up to 8 channels
  - TCD, flow, CID, and temperature sensor circuits
  - Dual power supply (+10V up to +30V/ -5V down to -12V)
  - USB/RS232/SPI
  - Ramp up temperature of separators
  - Variable voltage for separators and PCs
  - All package components are standard. except for PHASED chip
- **Removed features (from new Design):**
  - Individual control for separators
  - Variable voltage for concentrators
  - 16bit A/D for TCD, CID, and flow sensor
- **Issues**:
  - Routing might require larger area/more layers
  - Coupling of capillary from PHASED chip to detectors and pump
  - Circuits for MDID and MESO-Pump are not included (would they fit?)

2 (6X1.3 in) boards -1.5 cm apart



Energy and Emissions Savings via PHASED on NeSSI



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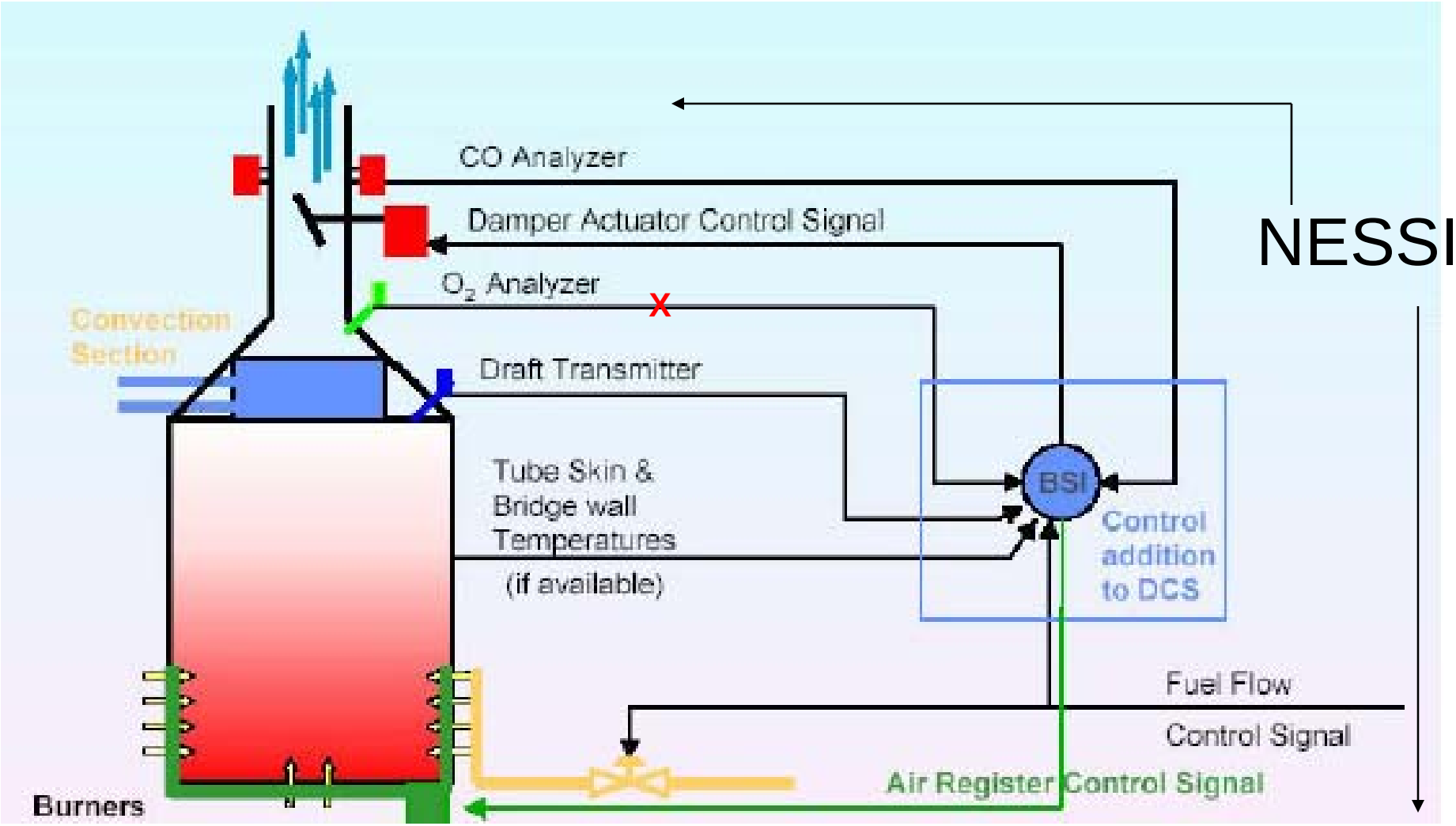
Energy and Emissions Savings via PHASED on NeSSI

- Ethylene Production
  - Savings are derived from two specific areas, control improvements and upset avoidance, accounting for 2.06% of the total energy used in ethylene production in the US, 13.5 TBtu/y saved:
  - Control improvements
    - The ability created by NeSSI and PHASED to incorporate rapid composition analytical devices throughout the process allows fast feed-forward control of the production facility, using the composition data from the feedstock and at various points in the process to more tightly control the operational parameters. This results in a savings of 1.5% of the energy used in the process, or an annual savings of 9.8 Trillion Btu per year.
  - Upset avoidance
    - Industry statistics show that 1% of all feed stocks used for ethylene production end up flared due to various quickly-occurring process upsets. The application of rapid composition analysis to prevent the creation of off-spec material through very early identification of process problems can avoid 75% of the expected upsets per year, resulting in a savings of 3.7 Trillion Btu per year. This represents 674 million pounds of production per year and its associated energy.

Energy and Emissions Savings via PHASED on NeSSI

Fired Heaters

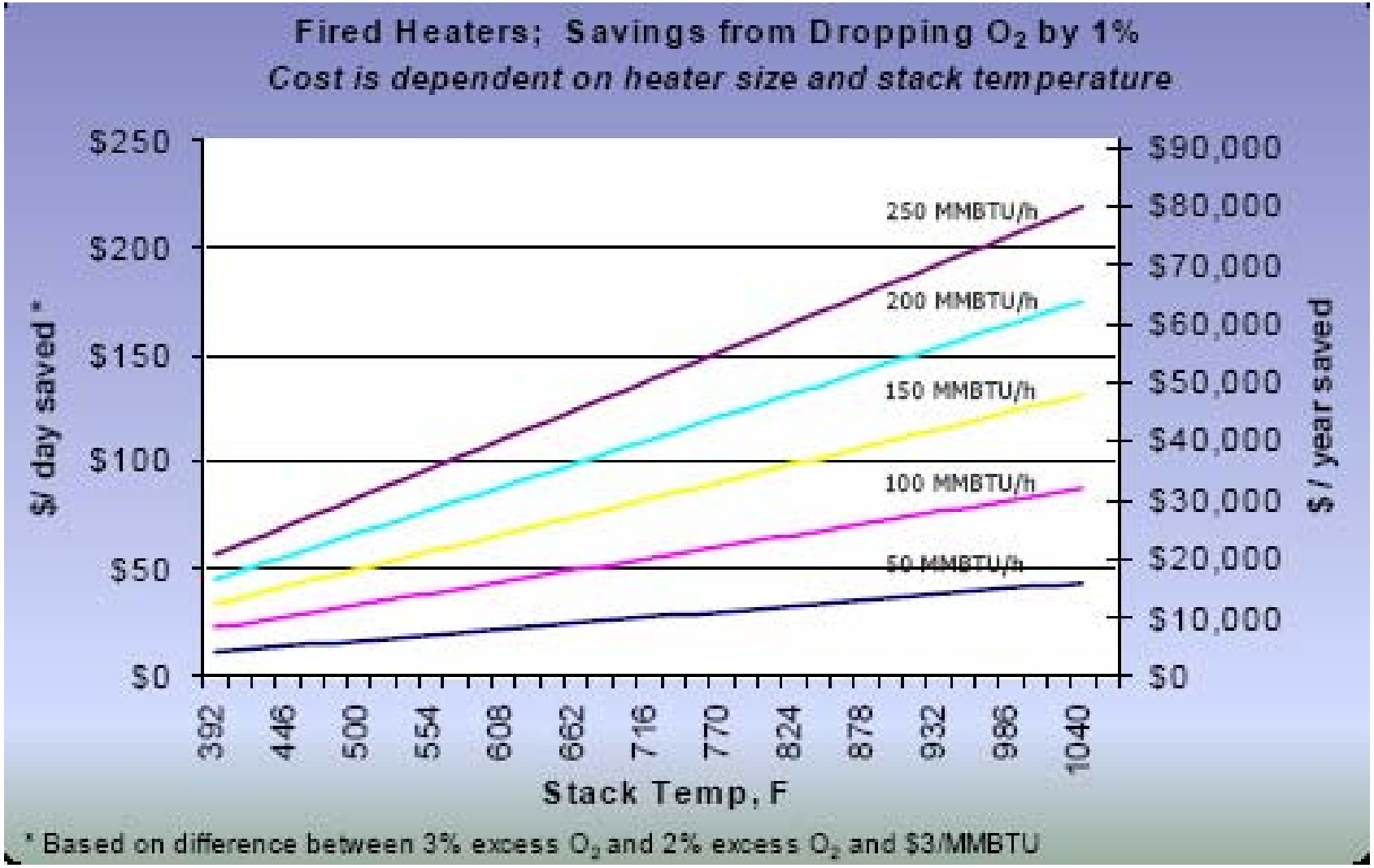


Energy and Emissions Savings via PHASED on NeSSI

- Fired Heaters
  - Savings are derived from continuously sensing and control of both O_2 and CO. Optimal O_2 control results in the highest flame temperature and maximum heat transfer with a minimal heat losses (unburned fuel or unnecessary stack losses)
  - Measuring CO can detect partial burn in the furnace. Controlling CO results in safer operations, improved combustion efficiency, reduced fuel usage, optimized NOx formation, and reduced CO_2 emissions.
  - CO can only be produced when one or more burners are starved of oxygen. By analyzing for CO, maximum heater efficiency can be achieved without unburned fuel waste.
  - Using NESSI technology dynamic process control using multiple sensors(O2, CO, NOx) and continual process optimization of the heater can be achieved. The fuel gas composition in the refinery is in constant flux. Since the burn characteristics are thus changing constant monitoring and control is need to maximize fired heater energy usuage.
  - Savings resulting from control of both O_2 and CO can save 1.3% of the total energy used for fired heaters in the US, which amounts to 19.8 trillion Btu per year. Annual savings for a typical unit are shown on the next slide.

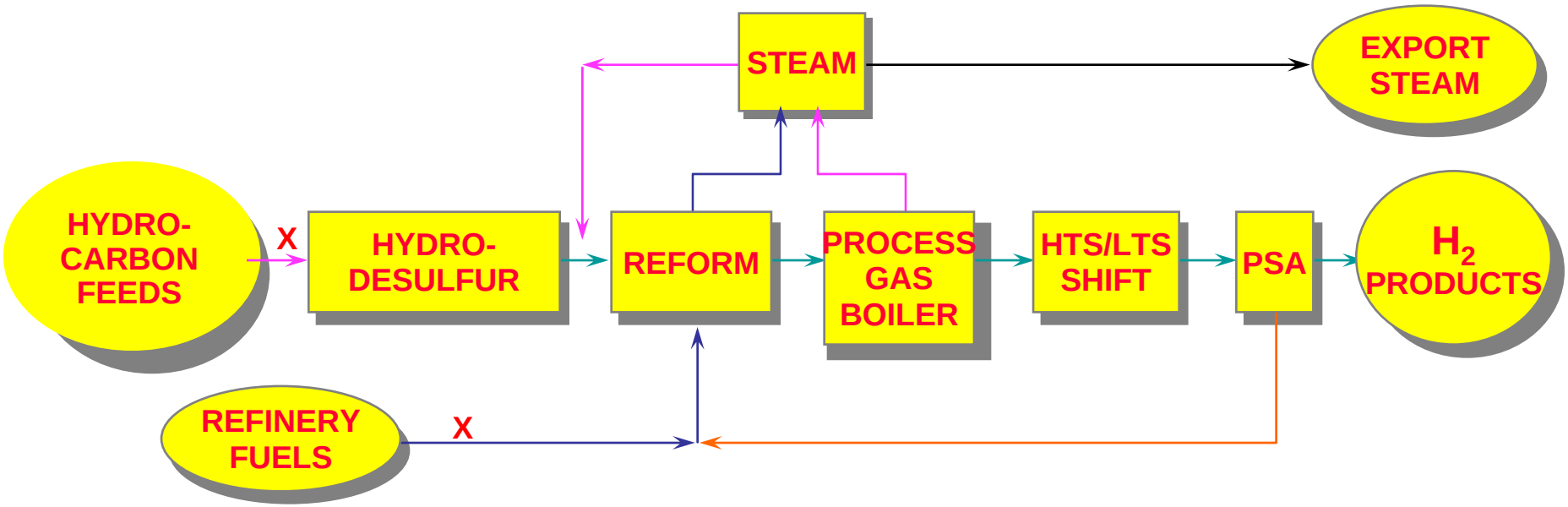
Energy and Emissions Savings via PHASED on NeSSI

Savings from 1% Reduction in O_2



Energy and Emissions Savings via PHASED on NeSSI

X = $C_1 - C_{12}$, Olefins, H_2, CO, O_2, CO_2, N_2, COS, H_2S, SO_X, NO_X



REFORMING

$$CH_4 + H_20 \rightleftharpoons 3H_2 + CO$$

SHIFT

$$CO + H_20 \rightleftharpoons H_2 + CO_2$$

Energy and Emissions Savings via PHASED on NeSSI

Hydrogen Production

Savings can be realized from **two sources** by the application of composition analysis in the process, dynamic reconfiguration and steam-to-carbon ratio control. These together result in savings of 0.83% of the total energy used in hydrogen production in the US.

–**Dynamic reconfiguration**

Refinery fuels, a rapidly changing gas mixture, is the typical feedstock for hydrogen production. It is augmented by hydrocarbon feeds as needed. Energy is applied in the form of steam in the reformer to remove hydrogen from the hydrocarbon gases present. When the refinery fuels contain hydrogen in sufficient quantities that are **measured**, this energy input can be reduced and the addition of hydrocarbons can be curtailed. This results in a savings of **1.75 Trillion Btu per year**.

–**Steam-to-Carbon Ratio Control**

A case study conducted by a major hydrogen producer, comparing two plants of identical capacity, one with such control and one without, show a savings of 6% of the energy used to create steam, or an equivalent of **0.6 Trillion Btu per year**. NeSSI simplifies and reduces the cost of implementing this control mechanism by making the necessary analytical capability readily available.

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Project Description

- **Need:** Modular, standardized, IS and networked sampling system (NeSSI-II) to support composition analyzers of process streams
- **Goal:** Field testing of PHASED and other microanalytics on NeSSI-II in the plants of collaborating members of the processing industries
- **Core Technology:** **Hi-Speed, Multi-Stage Pre-Conc., Affordable μGC**
- **Novel/**Transformational Element**(s):** **PHASED μGC** on SP-76 of **NeSSI-II**
- **Initial Industry for Application:** Ethylene, fired heaters, and hydrogen plants
- **Key Project Deliverable(s):** Report on field test results

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Barriers and Pathways

- **Barrier:** PHASED: Presently available stationary phases were developed for 10- to 60-m long capillary columns and not for 100x shorter and smaller ones of μGCs.

  NeSSI: Communication protocol
- **Pathway:** PHASED: Evaluation of new, nano-porous organo-silicate film shows that it has greater retention than DB-5.

  NeSSI: Wireless or FieldBus

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Energy Savings

- How will energy be saved? Ethylene Plants, Fired Heaters, Hydrogen Plants, etc, benefit from in-situ sampling, more affordable and faster sensing, tighter control, fewer upsets, less product waste

  - Tighter control of operational parameters: E-1.5%, 9.8 TBtu/y; F-1.3% US, 19.8 TBtu/y; H-2.35 TBtu/y

  - Upset avoidance: E-0.75%, 3.7 TBtu/y

- Assumptions used in calc.: 1) Ethylene; 2) Fired Heaters, 3) H2

  - Use feed-forward control based on composition analysis

  - Statistical data on flaring: 1% of all feed-stocks are flared; save 75% of 1%

  - Comparative plant analysis: One with and one w/o control; saved 6%

- How much energy will be saved?

  Extrapolating from the above examples (totaling 15.8 TBtu/y) to across all process industries, we arrived at data in the next VG

PHASED on NeSSI Energy Savings

Table 5. Summary of Energy Savings

4/15/03 8:08 PM

Application	Ind.Group (NAICS Codes)	Type of Savings	Total Energy Consumed (MMBtu/yr)	Energy Savings (MMBtu/yr)	Energy Savings (%)	Total Energy for Industry Group (MMBtu/yr)	Saving for Industry Group (MMBtu/yr)	Energy Savings (%)
Ethylene Prod.	324110	Upset Avoid. & Proc. Improv't.	656,372,200	13,537,675	2.06%	2,146,155,922	44,264,466	2.06%
Metals Process.	331, 332	Waste Avoidan.	352,000,000	35,200,000	10.00%	3,005,000,000	88,260,000	2.94%
H2 Production	325	Proc. Improv't.	283,202,150	2,347,100	0.83%	6,064,000,000	50,256,731	0.83%
TiO_2 Drying	325	Proc. Improv't.	888,462	44,423	5.00%	N/A	N/A	N/A
Fired Heaters	324110	Proc. Improv't.	1,524,240,000	19,815,120	1.30%	4,983,844,078	64,789,973	1.30%
Al Production	3313	Proc. Improv't.	490,000,000	7,350,000	1.50%	N/A	N/A	N/A
Pulp Production	322110	Proc. Improv't.	83,904,000	3,508,713	4.18%	198,000,000	8,280,000	4.18%
TOTAL			3,390,606,812	71,957,449	2.12%	16,397,000,000	255,851,170	1.56%
TOTAL INDUS. CONSUMPTION			23,798,000,000	71,957,449	0.30%		255,851,170	1.08%

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PHASED on NeSSI Energy Savings

Summary of DoE Energy Savings Calculator Results: NeSSI-II

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Application	Industry Group (NAICS Codes)	Type of Savings	2010 Savings (TBtu)	2015 Savings (TBtu)	2020 Savings (TBtu)
Ethylene Production	324110	Upset Avoidance & Process Improvement	2.14	10.26	18.25
Metals Processing	331, 332	Waste Avoidance	2.45	6.96	16.20
Hydrogen Production	325	Process Improvement	0.52	2.73	5.35
TiO_2 Drying	325	Process Improvement	0.01	0.04	0.06
Fired Heaters	324110	Process Improvement	2.14	10.26	18.15
Aluminum Production	3313	Process Improvement	0.39	1.12	2.61
Pulp Production	322110	Process Improvement	0.45	2.06	3.49
TOTAL			8.10	33.42	64.10
Petroleum Refining	324110	Upset Avoidance & Process Improvement	18.59	86.48	149.36
Metals	331, 332	Waste Avoidance	4.41	12.54	29.20
Chemicals	325	Process Improvement	7.95	38.13	67.83
Pulp Mills	322110	Process Improvement	1.06	4.84	8.19
TOTAL			32.01	141.99	254.58
TOTAL SAVINGS @ $\$6/10^6$ Btu, in B$			0.19	0.85	1.53
SAVINGS TO TOTAL IND. CONSUMPTION IN %			0.13	0.60	1.07

Other Important Metrics

of the PHASED μGC:

- Compactness ~ 12 in.3 ~ 250 cm3 to fit on NeSSI
- Speed: Analysis time < 2 s, incl. pre-concentration
- Sensitivity: MDL < 0.1 ppm / PC Gain
- No carrier gas
- No mechanical injection valve
- 10x lower power (2-5 W) than desk-top GC
- 10x lower cost

of the NeSSI systems:

- Standard modules of 1.5 x 1.5” foot-print (SP-76)
- 3 gas streams for: sample, null and span gases
- 4 SP-76 spaces for microanalytics
- Wireless or Field-Bus communication with SAM

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Accomplishments to Date

- Demonstrated high-speed μGC pre-concentr. & separation
- Demonstrated separation of H2O, CH4, C3H8, C4H10, CO2, …., C9, C10
- Modeled feasibility of separation up to C18, w/temp.ramp
- Calculated adsorption enthalpies on dry & hydrated films
- Demonstrated PC gain of 63x for hexane, and ~100x for CO2; modeled PC gains >10,000 for high MW compounds
- Increased PHASED chip fabrication yield to >90%
- Determined that a complete PHASED μGC with electronics will fit into one NeSSI's SP-76 modules
- Agreed with Users to base NeSSI device communication on Wireless or FieldBus

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Next Project Steps

- Agree with field test participants on gases to be pre-concentrated, separated and detected
- Incorporate MDD sensor into PHASED μGC
- Complete the design and fabrication of 2 PHASED μGC packages for NeSSI
- Design, program and debug the PHASED-μGC output software
- Design, program and debug the PHASED-NeSSI-SAM interface software
- Complete design of NeSSI and SAM systems
- Fabricate the NeSSI and SAM

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Completed & Future Milestones

- Preconcentration feasibility 3/31/04
- Separation feasibility 3/31/04
- Demonstrated 90% wafer yield 5/1/05
- NeSSI package design 7/1/05
- PHASED on SP-76 Demonstration 12/01/05
- PHASED on NeSSI lab test 6/30/06
- PHASED on NeSSI field test start 9/30/06
- PHASED on NeSSI field test compl. 4/30/07
- Final Report 6/30/07

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Continuation after ITP-Sponsored Project

The technology developed under this project will be commerialized, providede:

- The NeSSI-II field tests are completed successfully
- The PHASED-on-NeSSI-II field tests are completed successfully
- Agreement(s) with BUs about PHASED and NeSSI manufacturing, and marketing, distribution, sales and service have been reached

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Value Proposition for End User

PHASED μGC on NeSSI-II provides:

- Availability, for the 1st time ever, of a GC **analyzer function in the form and cost of a sensor** (size, speed, simplicity, ruggedness, power, maintenance, environmental protection, cost)

- Greater affordability, speed and sensitivity, which equates to tighter process control, energy savings and **lower product cost**

- Wired communication with its dedicated SAM (Sensor-Actuator Manager, a local computer), which can have a **wireless interface** of low installation cost with the plant control room and with other plant sensors.

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Commercialization Plan

- PHASED represents a new and significant commercial opportunity to Honeywell and it's customers.
- A partnership with Parker-Hannifin is to develop, integrate and commercialize NeSSI hardware and its communication links (wired and wireless)
- Microfabrication of PHASED and its electronics will be transferred to one of three in-house Si-foundries
- Beta-test hardware will continue to be supported by the Honeywell Labs and at least one of several Business Units, which specialize in industrial, environmental, medical and defense applications.
- Key to commercialization of industrial-PHASED is the availability of standardized, networked NeSSI-II.

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Commercial/Technical Risks Remaining

- **Commercial Risks:**

  - Despite past sales of industrial GCs, launching new microanalytics devices requires investment to establish marketing, distribution, sales, and service support
  - The NeSSI infrastructure to support cross-industry microanalytics such as PHASED needs to be established. DOE-OIT funding for the proposed 12 NeSSI field test sites should be re-authorized

- **Technical Risks:**

  - Present versions of PHASED operate at pressures within +/- 10 psi of ambient. Higher-pressure PHASED versions are planned
  - Low-cost, speed, compactness of PHASED is achieved at the price of lower resolution and peak capacity than conventional desk-top GCs. Will that meet User needs? Resolution can be tailored to User's needs.

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Quotes from Users Across Processing Industry

... given the broad industry interest to improve sampling and sensor technology, NeSSI is a revolutionary breakthrough… - Mel Koch, Director, Center for Process Analytical Chemistry (CPAC)

"NeSSI holds great promise....to reduce the cost of process analytics by 30 - 40% as well as energy use, ...but no one company alone can provide sufficient momentum, co-ordination of system design and field tests in a collaborative environment.... therefore securing the full funding from DoE is essential for our success…." - Jeff Gunnell, Lead Specialist, Process Analytics, ExxonMobil Chemical Company

"The NeSSI approach has reduced design time by 25% and improved installation success at start-up per unit by a factor of 2…." - Frank K. Schweighardt, Ph.D., Global Manager- Process Analytical Technology, Air Products & Chemicals, Inc.

"…NeSSI is a breakthrough enabler for technology development…. reducing combined design and construction by more than 30%, while increasing, reliability and flexibility….is a key component for the future of sustainable development…"- Michelle Cohn, Senior Manager, UOP

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