Savannah River National Laboratory

We put science to work.™

Alternatives to Mass Spectrometry and Some Real-time Monitoring Measurements

William A. Spencer
SRNL Science and Technology Directorate, Analytical Research and Development Programs

HEMS 2013
September 15-18, 2013

SRNL-L4110-2013-0027

Savannah River National Laboratory

We put science to work.™

Co-worker Acknowledgement
Laura Tovo,
Ronald Hooper,
Louis Boone,
Jack Zamecnik

SRNL-L4110-2013-0011

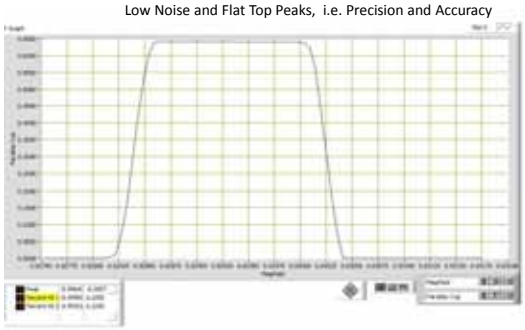
Project Driven Tasks -- Process Gas Measurements

- Search for Alternatives to High Resolution Mass Spectrometry
  - – Facility Consolidation Study
    - *Desire Smaller Footprint than current MAT 271 with Inlet Systems*
    - *Non-radioactive Analysis of Bulk Gases and analysis of H2/D2/He Blends*
- Off-gas Measurements from a Melter System
  - – Defense Waste Project
    - *Change from formic acid based chemistry to glycolate based chemistry*
    - *Objective: Reduce hydrogen generation in Melter headspace*
- Monitoring Trapping-Bed Conditioning Bake-out
  - *Condition new Traps before installing in process*
  - *Bakeout and purge with argon and air under heat profile*
  - *Monitor for impurities, especially chlorides and unknown hydrocarbons*
  - *Evaluate a new transportable mass spectrometer*

Inert Mass Spectrometer

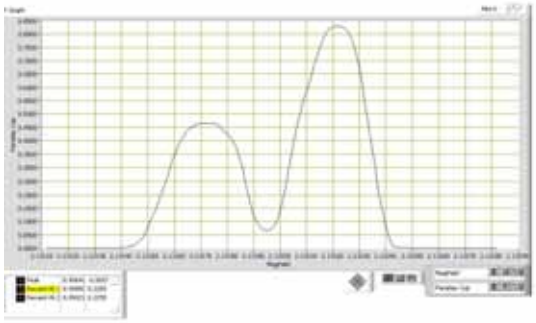
- Mat 271 – VG 3038 Gas Mass Spectrometers
- Non-radioactive Analytical Support
  - Check for Impurities in Bulk Gas – helium, nitrogen, argon, carbon dioxide
  - Isotopic and Co-isotopologue Analysis – e.g.. 4He and D2, 16O and CH4
  - Gas Blending and Atmospheric Gases
    - *– H2, He, D2, Ne, Ar, Kr, Xe, CO2, CO, O2, N2*
  - Detection of C1-C4 Hydrocarbon Gases
- Current System has Double Lab Module with Flexible Two Stage Drop to Molecular Flow Gas Inlet System

Characteristic of High Resolution Systems
Low Noise and Flat Top Peaks, i.e. Precision and Accuracy



High Resolution : CO and N2 on a VG 3038

CO (27.995 AMU)/N2 (28.006 AMU) Axial Faraday Cup Voltage vs. Magnetic Field



Systems are Large –

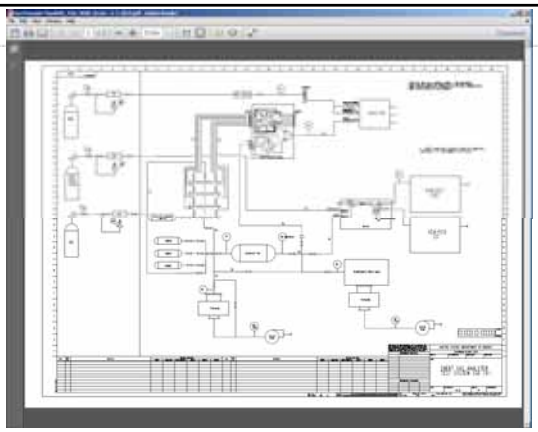
Finnegan MAT 271

Pneumatic Inlet and Stds

Alternatives to High Resolution Mass Spectrometry

Proposed Three Analytical Technologies:

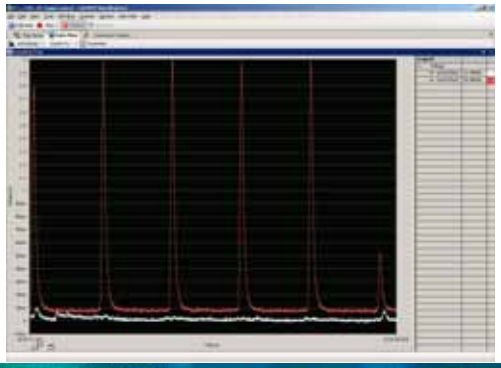
- Gas Chromatography
  - Gas Industry Uses
  - Helium Plasma Detectors
    - Detection from ppb levels thru ppm in helium
  - TCD Detectors
    - Bulk Gas and Helium – alternative carrier gas issues
  - Micro-GC
- IR Measurements
  - Non Dispersive IR (NDIR) – selective filter instruments
  - FTIR – full range
- Low Resolution Quadrupoles with SEM and Faraday Detectors



Horiba ES-510 and VIA-510 NDIR Units for CO2 and CO

- Thermal drift at ppm levels over 24 hours
- Simple Direct Operation
  - Range – Somewhat adjustable ppm to ppt levels
  - Two cell comparison method
- Gas Demand – 1 L/min
- ES Unit
  - Moisture control, 4°C chill
  - Particulate Filter
  - Acidic Gas Removal
- Alternatives available with
  - Much smaller footprints
  - Multi-gas NDIR detector cells –
  - FTIR full system

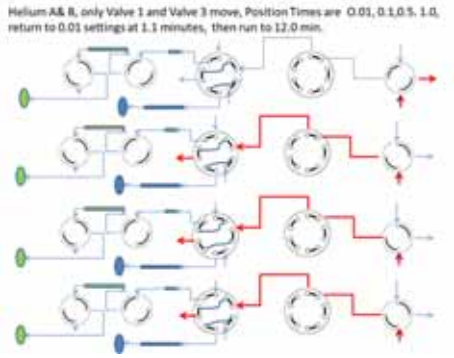
Five Injections of CO – red (20 ppm), CO2- white (< 10 ppm) into Helium Zero Gas
Problem s – first injection low, blank injection after shows carry over in piping



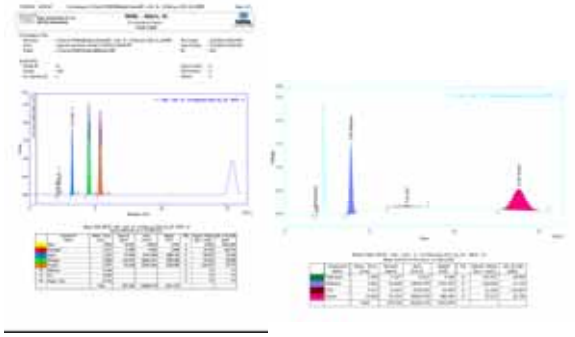
Valco – Trace Gas Analyzer – Model 5722

Dual Micro Column GC
Molecular Sieve 5A
HayeSep D
Isothermal
Dual Helium Plasma Detector
Automated Multiport Sampling and Calibration

Valco Trace Gas Analyzer – TGA 5722 Series



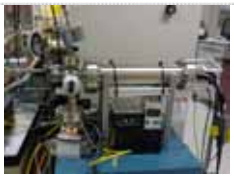
TGA – Think and Do For Valves and Clarity for Chromatography



Valco VICI Trace Gas 5000 Series – Inlet System

- Gas Standard Manifold
  - Mix Automation
- Inlet System
  - 1/8" and 1/16" Valco ZDV Fittings
  - 8 Sample Inlets
  - 4 Cal Gas Inlets

Evaluation of Pfeiffer and Extrel Quadrupoles



Pfeiffer – QMG 700 Controller
Quadera Software
QMA – 400 Lo Res Quad 1-512
QMA- 410 - 1-16 amu Hi Res Quad
SEM and Faraday
Logarithmic Amplifier
Large Turbo

Extrel – Max 60, MAX300-LG
Merlin Software or Questor Software
SEM and Faraday
Manual Amplifier
SAES Getter
Gated Small Turbo

Inert Lab Gas Requirements

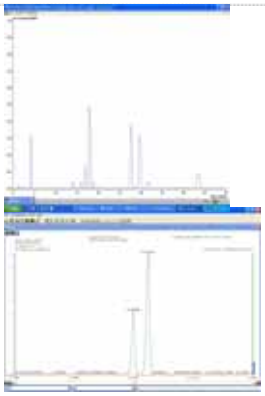
Detect following species with range given:

Component	Range
H_2	0.005-100%
HD	0.005-100%
^4He	0.005-100%
D_2	0.005-100%
H_2O	No Capability*
HDO	No Capability*
D_2O	No Capability*
Ne	0.005-100%
CH_4	0.005-3%
C_2H_6	0.005-3%
C_3H_8	0.005-3%
C_4H_{10}	0.005-3%
N_2	0.005-100%
O_2	0.005-20%
Ar	0.005-100%
CO_2	0.005-100%
CO	0.005-100%

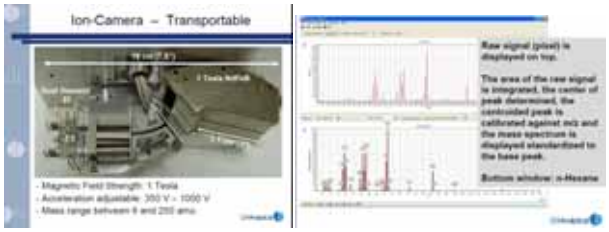
*-Moisture analyzed by alternate instrumentation.
**-The low end of the range represents approximately the LLQ for the method, not the absolute detection limit.

Some Issues - H/D/He Blend Isotopics on Low Resolution Machines

- 4He/D2 – GC separation vs direct
  - Dynamic range vs background
  - Carrier Gas
  - Transfer Lines vs Molecular Leak
- Water/Hydrogen Production
  - Closed cups/Open cups
  - Filaments Rhenium/ Tungsten
  - Passivation
- Ionization Levels
  - Double ions, D+, H3,
  - HD production,
- TGA Column bleed – HayeSep D
- 100% to 0.005% vs ADC converters
  - Log Amps vs Autoranging Linear



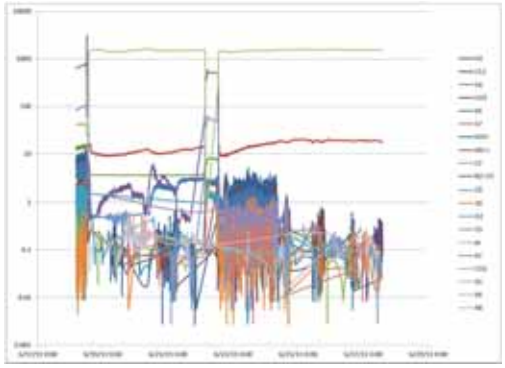
IonCAM is Double Sector With Pixel Faraday Cage Array on Image Plane



Our Unit was modified to cover mass 2 to 70 amu.
Not shown in the image is the 2100 pixel Faraday array detector on the magnet image plane.

Rev. Sci. Instrum. 83, 0641011 (2012)

When All Works Well You Get Something Like This Mess of Useful Data



CEF - Melter

Real-time Monitoring Mass Spectrometers
- Extrel MAX300-LG System – small Quad running Questor Software
- Monitor Instruments - transportable backup cycloidal mass spec

MKS FTIR – liquid nitrogen cooled detector – full IR scan

Agilent/Inficon Micro-GC with dual columns and TCD detectors
- 50 ppm up,
- MS 5A and Porapak Q columns,
- EZ Chrom Software

Melter Monitors: 2 Mass Specs, UPS, FTIR, Micro-GC, Stds, Summertime Cooling Fan,

CEF ran 5 days, 24/7, two man off-gas coverage, 2 man melter operation

Work stations for Mass Spec, IR, and GC- linked directly to the melter controller
- 15 day run is planned for July

CEF – Melter Off-gas Measurements

Summary - Observations

Alternatives to high resolution mass spectrometry are available.

-- *It might be simpler to repackage the MAT 271*
-- *IR and GC often complement MS and provide lower detection*
-- *dynamic range and isotopic resolution is hard to beat MS*

Newer On-line Instruments for Real-time measurements are available

-- and can be made to work
-- software quality varies greatly