Offgas from Radiolysis

Difficult analysis needing High Resolution Mass Spectrometry

SRNL™

SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

William A. Spencer, Charles L. Crawford, Thomas L. White,
Stephen L. Crump, Robert J. Lascola, Chris Beam, and Laura L. Tovo,

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Operated for Department of Energy by
Westinghouse Savannah River Company, Aiken, SC

Basic Radiolysis

- **High doses of radiation [gamma and alpha] can generate reactive and flammable gas mixtures. The gases limit plant processes because of the requirements to meet the lower flammability limits [LFL/LEL].** The analytical chemist must determine the rates of gas generation and often determine the LFL.

- ***Interaction with Water – production of hydrogen***

  $H_2O \rightarrow e^-, H, H_2, OH, H_2O_2, HO_2, H^+$

- ***Interaction with Air***

  Air $(N_2+O_2) \rightarrow NO, NO_2, N_2O_4, N_2O$

  Air + water vapor, $H_2 \rightarrow NH_3, NH_4OH, NH_4^+$

  [good online ref – www.nap.edu/openbook/N1000156/html/125.html
  [Radiochemistry in Nuclear Power Reactors (1966), National Academy of Sciences]

- ***Interaction with Organic compounds***

  Tributylphosphate [extractant for U/Pu]

  - **TBP → DBP + t- butanol**
  - **DBP → MBP + t-butanol**
  - **Butanol → isobutane, isopentanol, butanal, methane, → ethylene, hydrogen, peroxides**

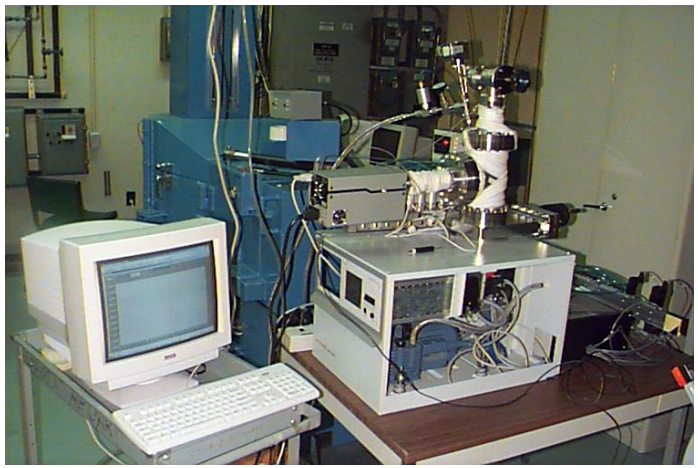
  Tetraphenylborate (extractant for Cs)

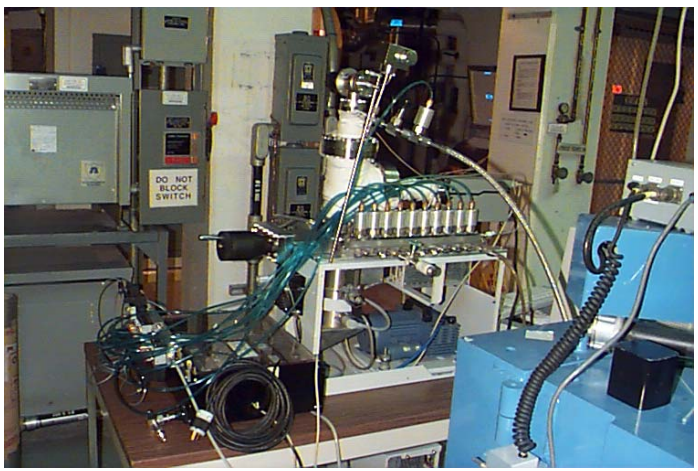
  - **TPB → phenols, benzene, hydrogen, methane, →cyclohexenes, cyclohexanol, phenylates, PAHs**

Gamma Radiolysis Studies

- Radiation – Cobalt 60*
  - Chamber 6”x8” or 1O” cube
- Sample Size - up to liter
- Exposures
  - minutes to weeks
  - Rad dose is adjustable
    - 1 R/hr to 2 E6 R/hr
    - distance from source
- Web – www.srs.gov/general/scitech/srtc/srtchtm/gamma.htm
- * note – yellow light is fake

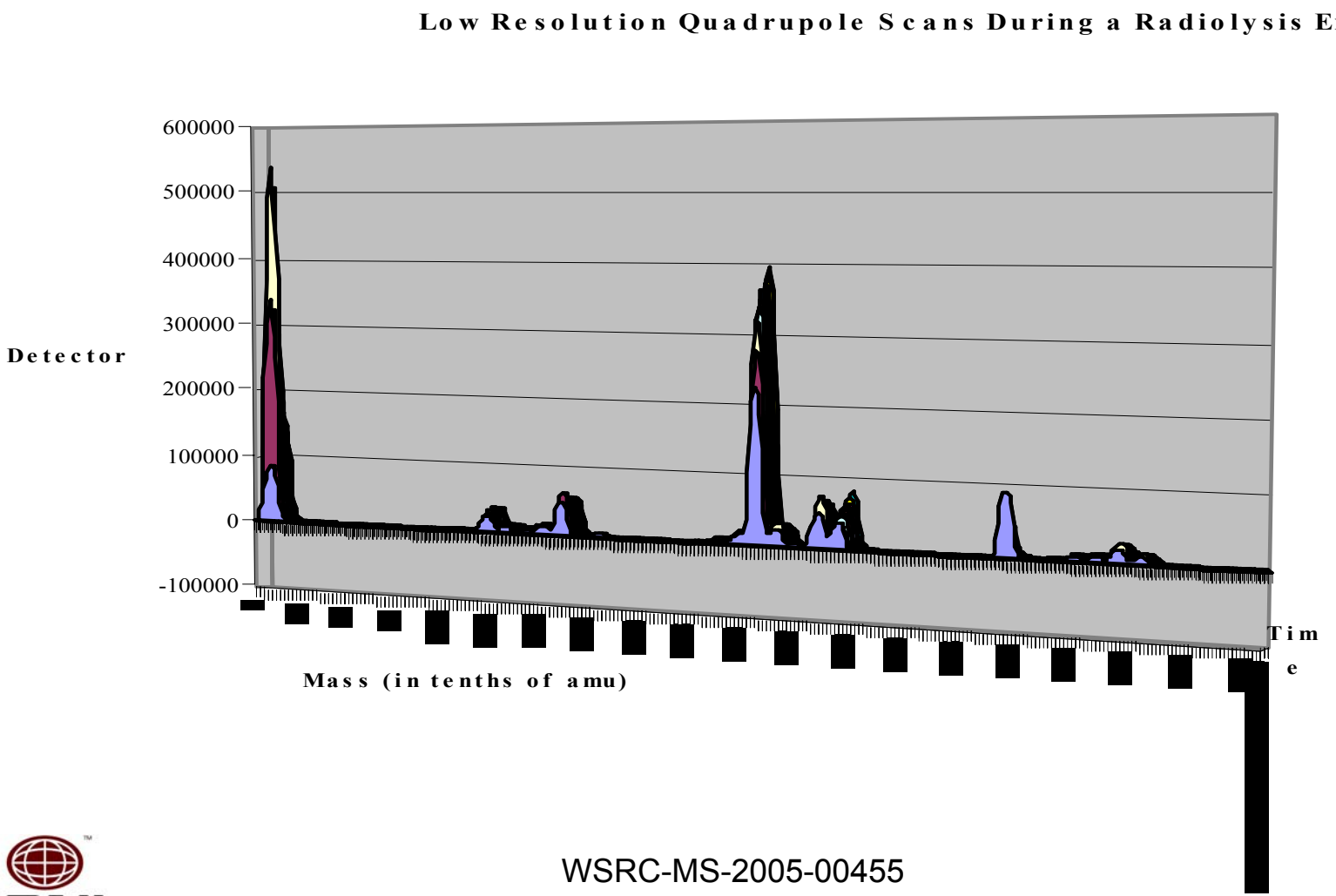
Gamma Radiolysis Studies





- **Material/Offgas analyzed**
  - **Pressure Measured real-time**
  - **Temperature Watched real-time**
  - **Mass Scan – in-situ**
  - **GC Scan – in-situ**
  - **Microscopy**
  - **Hardness/Tensile Testing**
  - **DMA/TMA/IR/TGA**

Most Measurements are made with GC or Quadrupoles Mass Spectrometers



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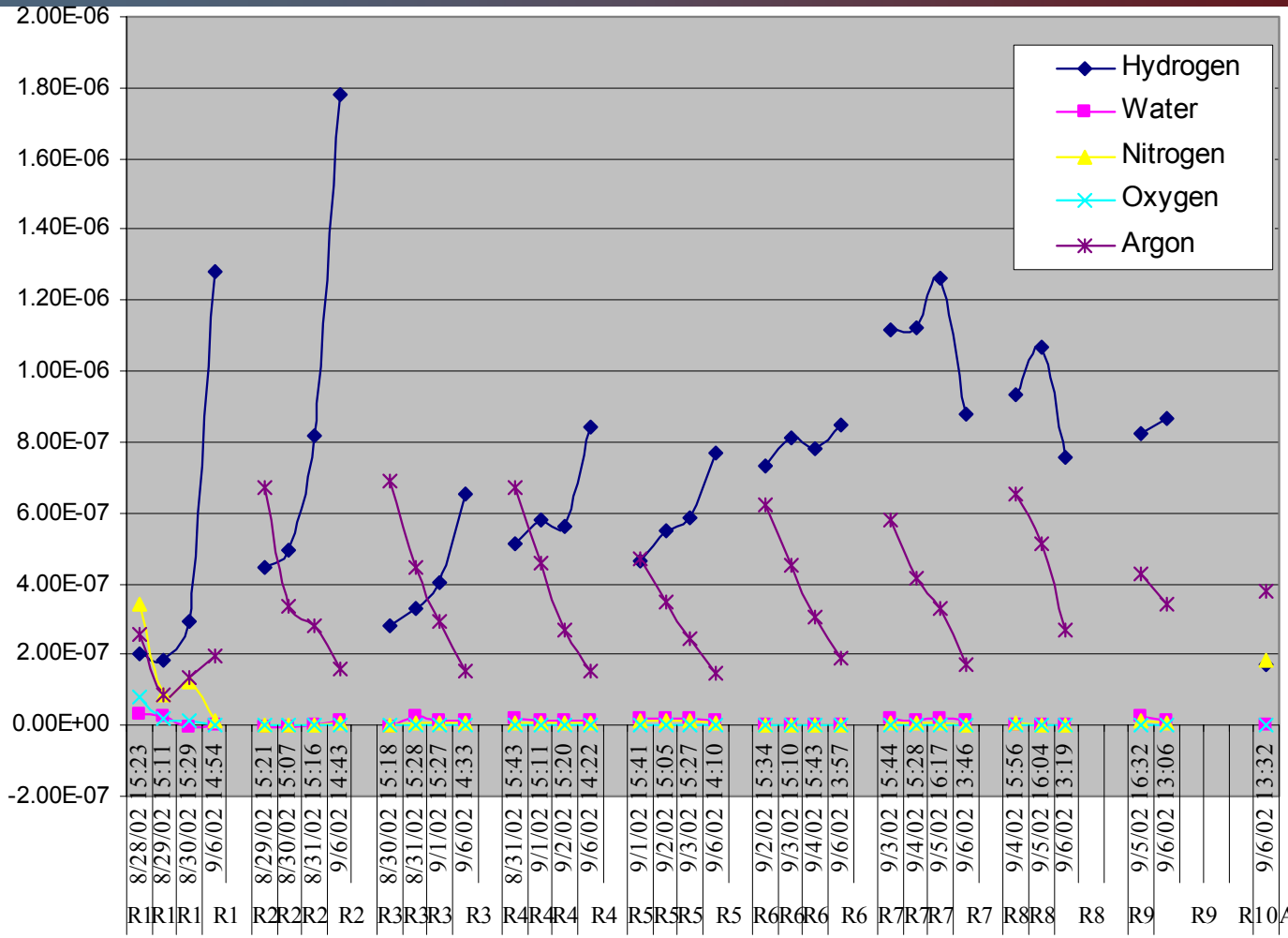
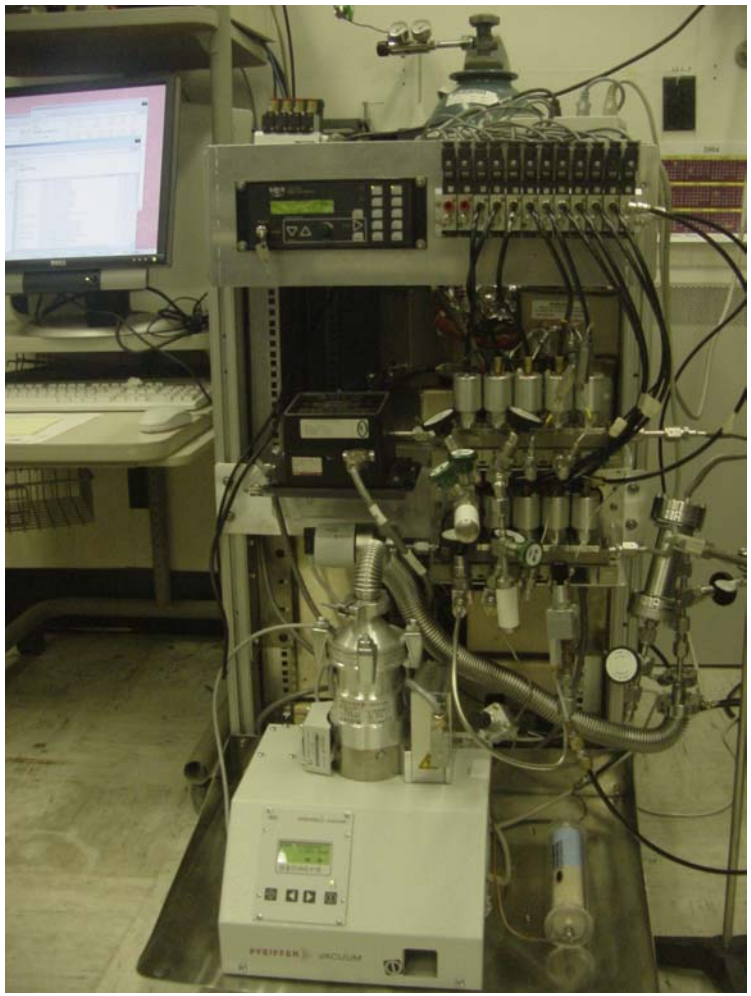


Common Mass Problem
Is it CH4 or O, CO or N2, CO2 or N2O?

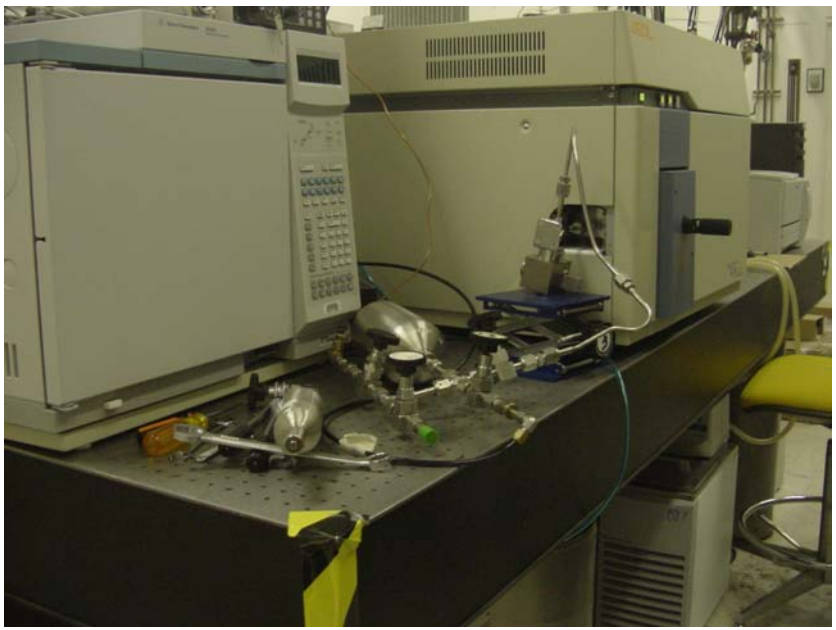
Species	M/z	Possible Source
O	15.9949	oxygen
NH2	16.0186	ammonia fragment
CH4	16.0312	methane
OH	17.0027	hydroxide -water fragment, alcohols
NH3	17.0265	ammonia
H2O	18.0100	water
NH4	18.0350	ammonium ion
Ar++	19.9811	argon
Ne	19.9924	neon
D2O	20.0229	heavy water
Si	27.9769	from silanization or Si oxides, [sand is in all our samples from airborne dust - we work on top of sand hills inside concrete structures]
CO	27.9949	carbon monoxide
N2	28.0061	nitrogen
C2H4	28.0313	ethylene
N2H	29.0118	protonated nitrogen - [common in traps]
C2H5	29.0390	ethane organic fragment
NO	29.9979	nitrogen monoxide
C2H6	30.0468	ethane
CH2O		aldehyde or alcohol fragment
Ar	39.9623	argon
C3H4		propane fragment
CO2	43.9898	carbon dioxide
N20	44.0010	nitrous oxide
C2H4O	44.0260	acetal aldehyde –or ethanol fragment [we see from HEDTA extractants]
C3H8	44.062	Propane

Siemens Quantra FTICR



- Extremely High Resolution - >30K at M28
- Ion Trap
  - Limits on mixtures
  - Ion interactions
- Ion Pump – no Turbo
  - Pico-liter injection valve
  - Flow Across inlet
- Mass Range 6- 1000

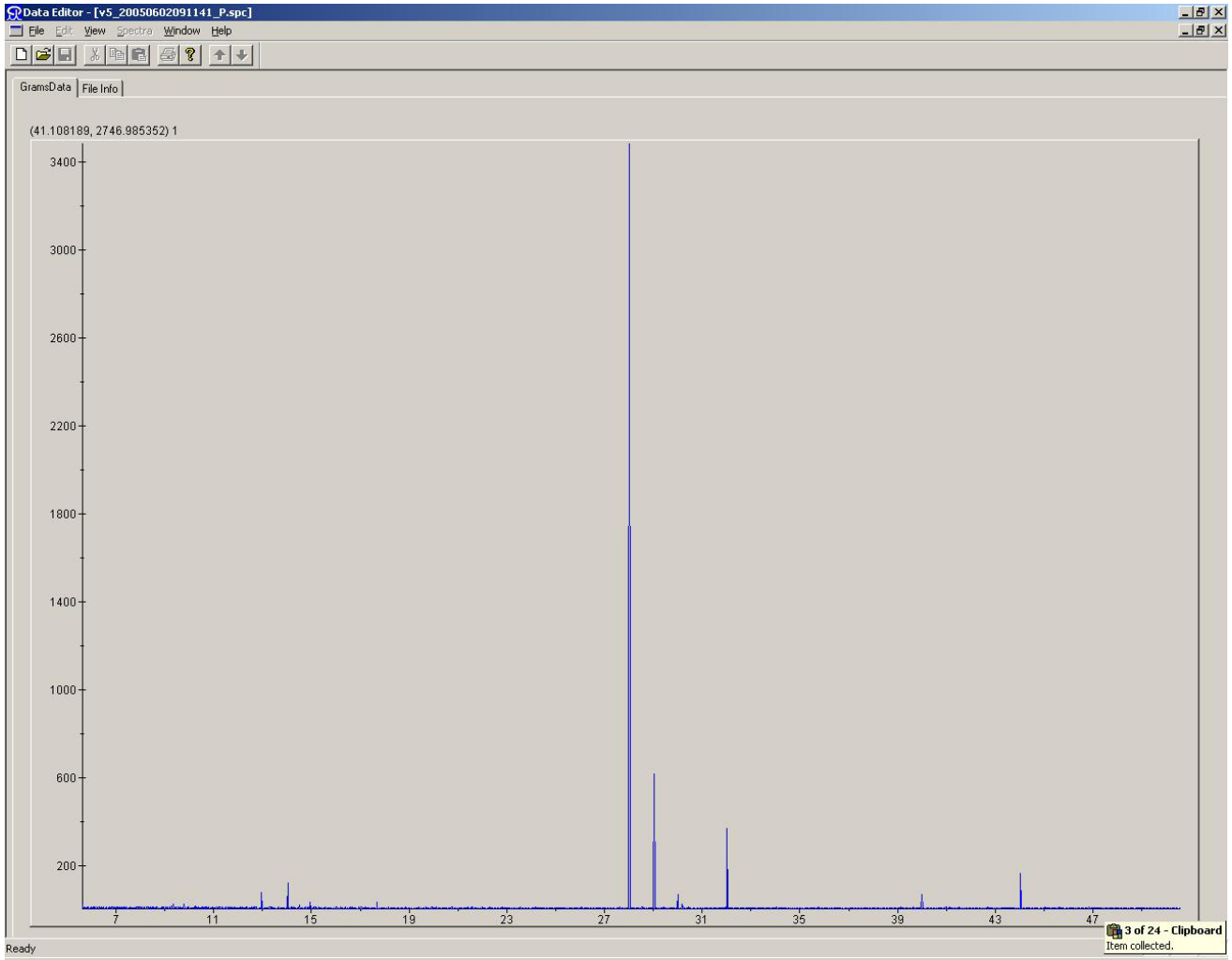
JEOL GCMATE II



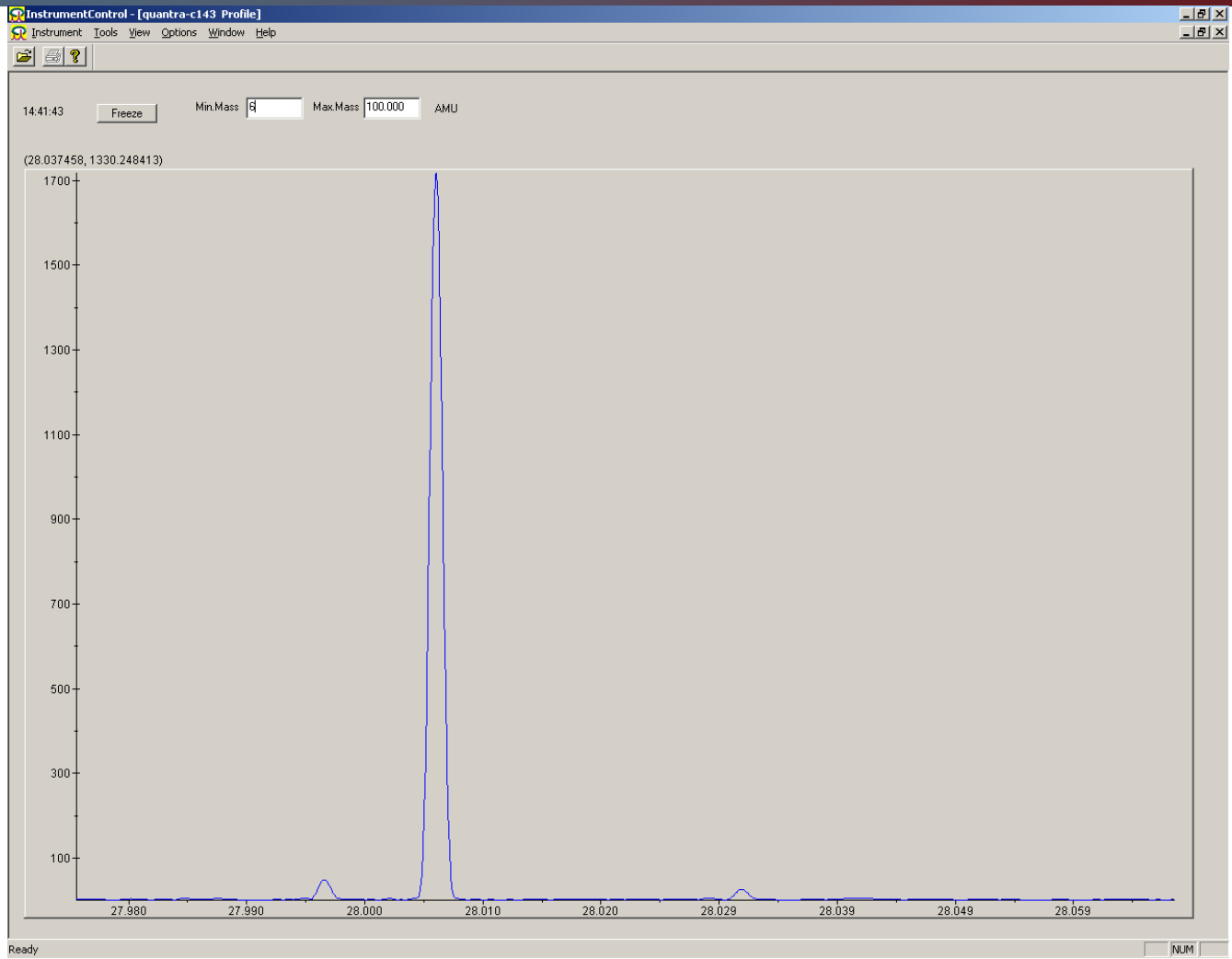
- GC/MS
  - Resolution >5000
  - Mass Spectral Library
- Mass Range 1- 1000
- Dual Pumping
- Multi-Sector
  - Magnetic Electron Source
  - Tunable Plates
    - Easy Acceleration Adjustments
    - Adjustable Beam Focus
  - Electrostatic or Magnet Sweep
- Low (<20) vs High Mass (>20)
  - Separate tuning

High Resolution – Siemens Quantra Spectra

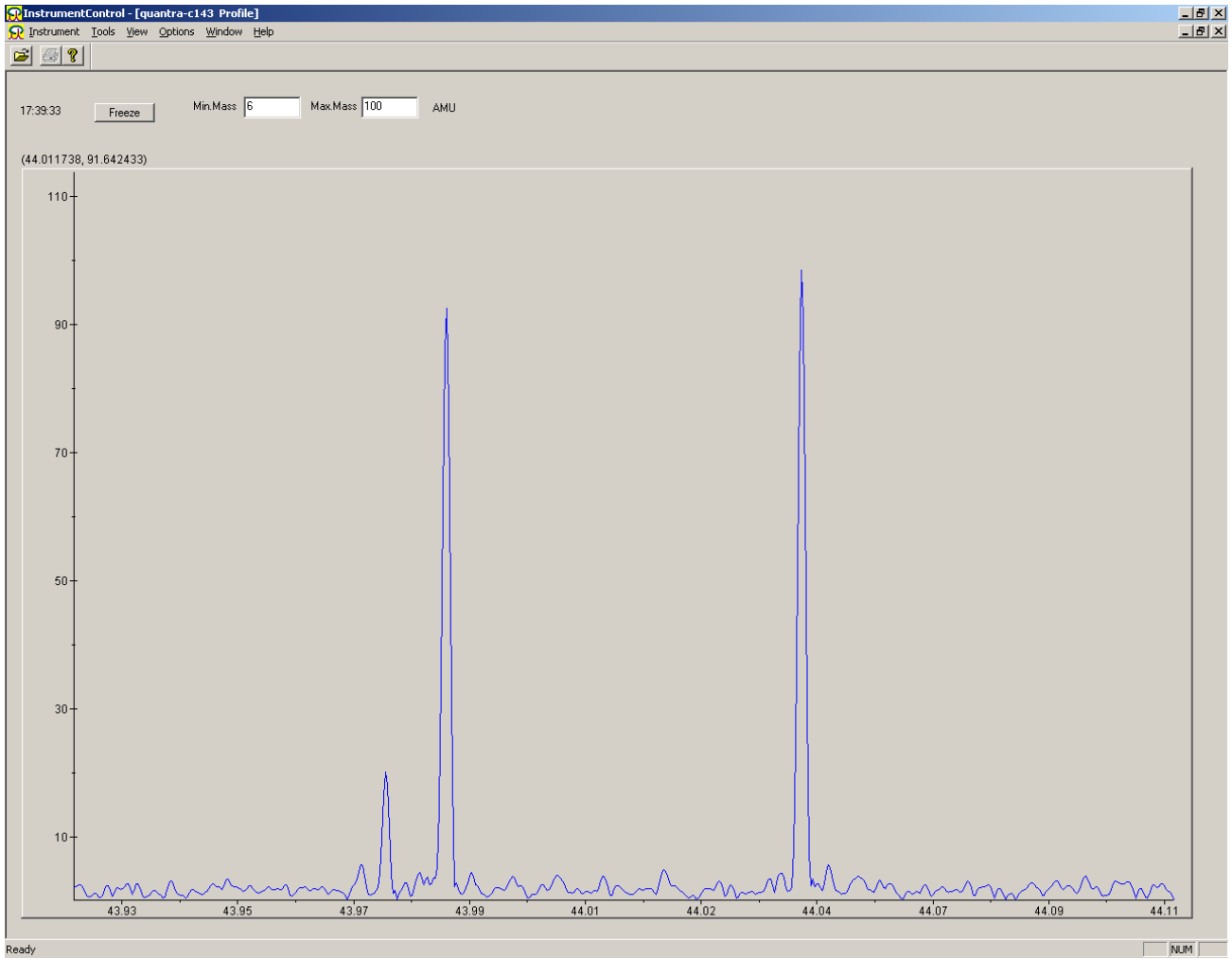
note: Chemical Ionization of H2 and N2 forming N2H at mass 29



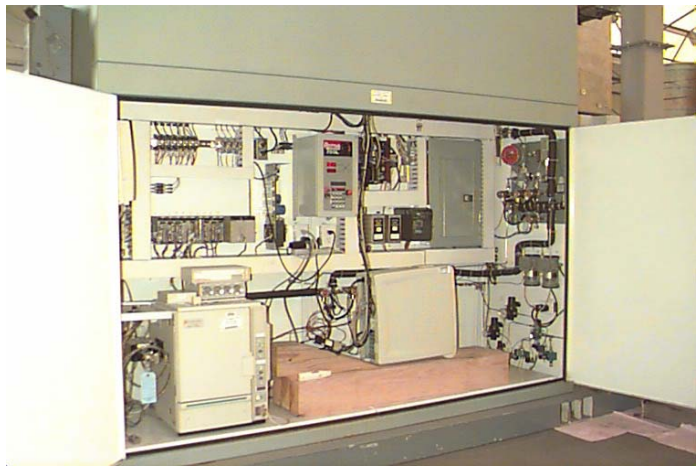
Mass 28
Carbon Monoxide, Nitrogen Gas, Ethylene

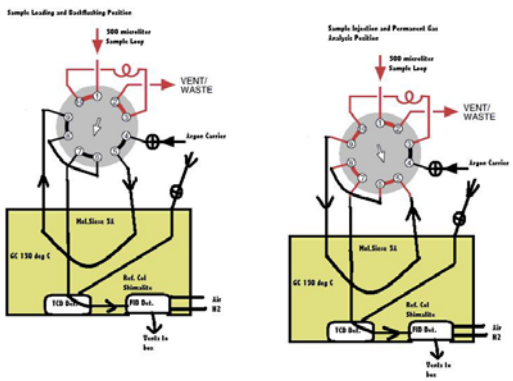


Mass 44 – Carbon Dioxide, Nitrous Oxide, Propane
Resolution > 8900



TRU Waste Drums
Initial Movements from Pad Burial





- **Issue**
  - Thousands of Drums
    - To Ship to Carlsbad, NM
  - For initial movement,
    - need below LFL
    - Hydrogen – Up to 50%
    - Methane – Up to 44%
    - Total Non-Methane VOCs -
    - O2 + N2
- **Vent and Purge - Monitor**
- **Full Characterization**
  - GC/MS after vent safe
  - Verify Radiological Data
  - X-Ray – no liquids, etc.

TRU Drums Have Complex VOC Mixtures

Restek Silco Canisters are used to collect samples from waste drums and the gases are verified in our laboratory. Full GC/MS scans can take several hours. The spectra were too complex for direct high resolution mass spectral analysis. Several total VOC sensors were evaluated as an alternative field screen and compared to the current column GC w/FID and TCD detection method but they did not provide enough information to determine a reasonable LFL without using a large flash point correction factor to allow for the different types of possible organics that the sensors would detect.

hsgbdr		Number above Trigger	Trigger	Maximum
Acetone		13132	9	879.700
Butanol		11206	9	232.600
Methanol		10143	9	670.300
Methane		9544	0.01	0.440
1,1,1-Trichloroethane		3779	9	1017.600
2-methyl 2-propanol	75-65-0	2448	0	494.330
Ethyl Ether		1712	9	9.220
Toluene		1214	9	523.400
Hydrogen		1166	0.01	0.493
Methylene Chloride		638	9	480.000
cyclohexanone	108-94-1	373	0	279.680
Trichloroethylene		363	9	904.200
Isopropyl Alcohol	67-63-0	298	0	498.480
M,P-Xylene		293	9	574.600
Benzene		164	9	318.800
(s) 2-hydroxypropanoic acid	79-33-4	163	0	3422.010
1,1-Dichloroethane		136	9	215.600
Methyl Ethyl Ketone		120	36	854.900
Ethyl Benzene		93	9	164.900
3-Butyn-2-ol, 2-methyl	115-19-5	93	0	67.340
Chloroform		67	9	204.800
Acetic acid, 1-methylethyl ester	108-21-4	63	0	428.730
O-Xylene		54	9	96.600
Tetrachloroethylene		49	9	371.300
acetic acid, methyl ester	79-20-9	42	0	245.430
Ethanol, 2-butoxy-	111-76-2	41	0	311.940
1,1,2-Trichloro-1,2,2-Trifluoroethane		36	9	470.800
1-Propene, 2-methyl	115-11-7	36	0	275.120
TETRAHYDRO-3-FURANOL	453-20-3	34	0	135.800
methyl-cyclohexane	108-87-2	32	0	259.800
Propane, 2-methyl-1-nitro	625-74-1	28	0	213.530
2,4-Dimethyl-1-heptene	19549-87-2	22	0	98.500
Butanal	123-72-8	19	0	102.240
Hexane, 3-methyl-	589-34-4	17	0	156.970
1,3,6-Trioxocane	1779-19-7	16	0	97.000
Ethyl Acetate	141-78-6	16	0	146.330
1,2-Dichloroethane		15	9	108.800
Methyl Isobutyl Ketone		15	36	629.800
cyclopentanol	96-41-3	14	0	151.970

Savannah River National Laboratory
Future Hydrogen Technology Studies

- SRTC Became SRNL
- SRP Nuclear Processes
  - Shutdown separation facilities
  - D&D cleanup completed in many areas
  - Reduction in Force
    - up to 50% from historic high
    - ~12% this year
- New Missions Allowed
  - Hydrogen Technology
    - Hydride- bed storage
    - Hydrogen Sensors
    - Material Science
  - R&D Opportunities
- New Lab – 66,000 sq ft
  - Built - Owned by Aiken County
  - Half Rented by DOE for 5 years
  - Outside the Fence
    - uncleared okay!
  - Other Half – University and Industry
    - Several auto industries

New Hydrogen Technology Research Laboratory
8 modules for Analytical Sensor Development

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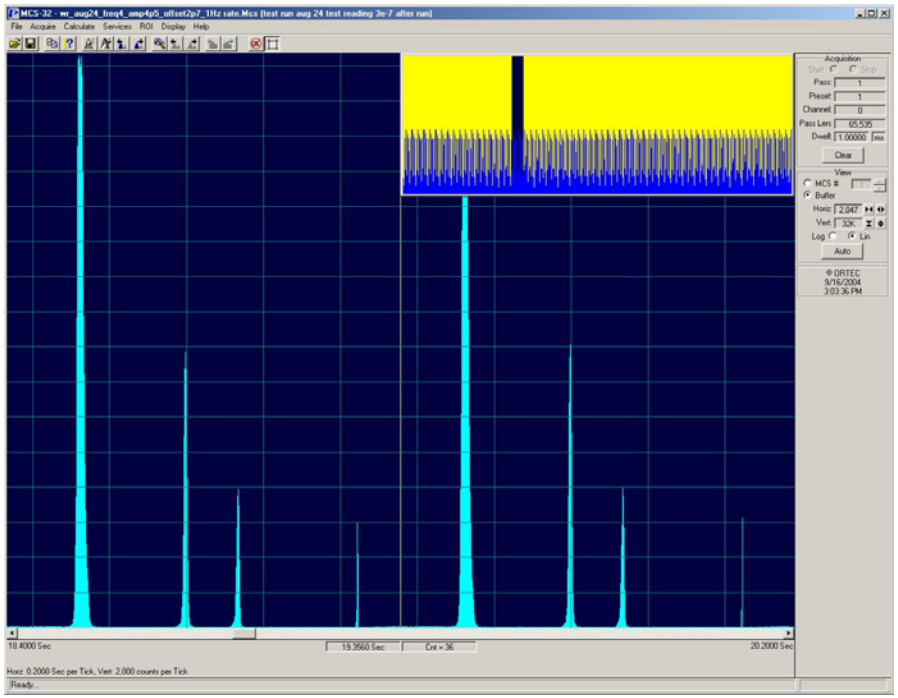
MiniMass Spectroscopy On Hold for FY05



- Fast Hydrogen Analysis
  - Mass Sensors, Inc R8
  - Fast Electrostatic Voltage Sweep
    - Acceleration
    - Fixed Magnetic Field
  - Data Collected
    - Pulse counts
    - Amtek/ORTEC MCS
      - Sweeps in 20 ms
      - Bins 0.1 ms
  - SERMACS, Nov 2004
  - Some New Funding for FY06

SERMACS 2006

- Savannah River Section of the American Chemical Society will host the South Eastern Regional Meeting of the American Society [SERMACS]
  - Augusta, Georgia
  - November 1-4, 2006

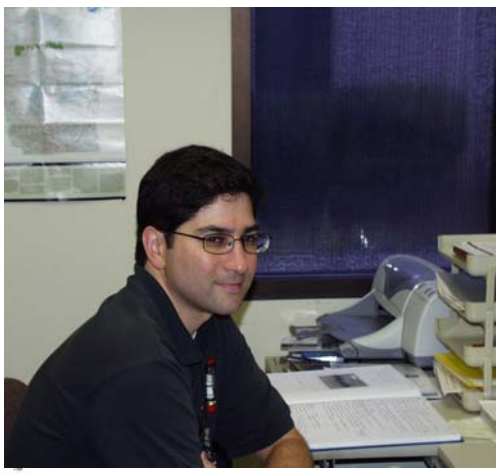
- Hope some of you will attend and send your students to give talks and posters.

Acknowledgements

Charles Crawford

Tom White

Chris Beam



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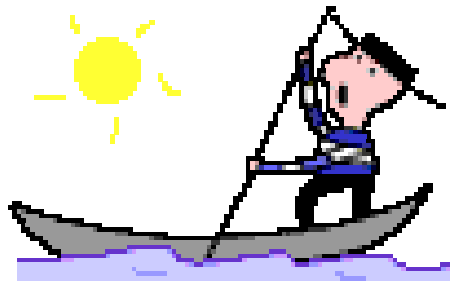

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