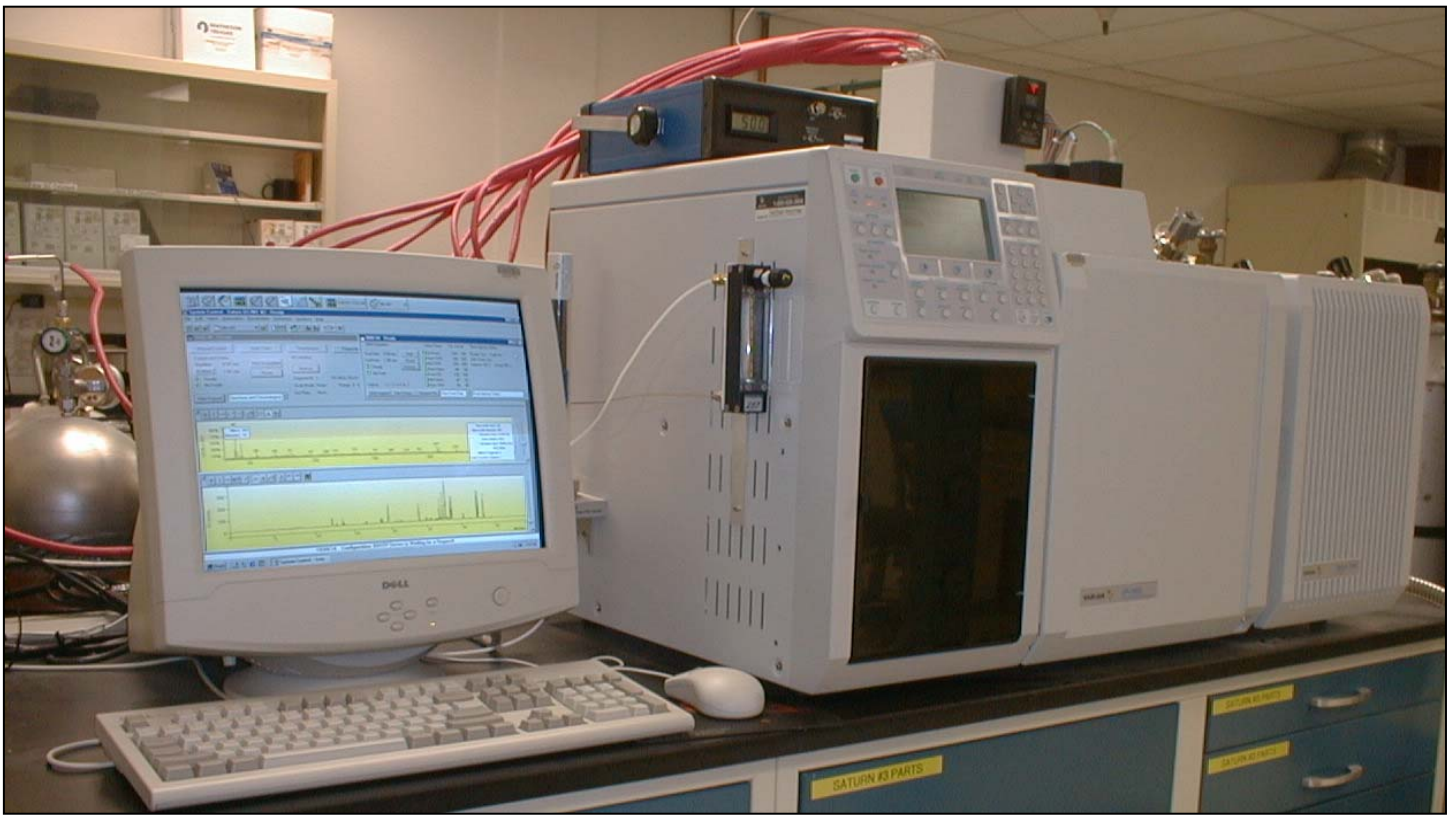
Lotus Consulting presents:

Ultra Trace Toxics System - MS -TO15 (UTTS - MS - TO15)

The Ultra Trace Toxics System - MS – TO15 from Lotus Consulting provides impressive separations of trace volatile organics in ambient air samples. The system features the Varian 3800 Gas Chromatograph with built-in high performance sample concentrator and the Varian Saturn 2200 Ion Trap Mass Spectrometer. This system handles both pressurized canisters and Tedlar bags without hardware changes. And the system meets the exacting requirements for the US EPA TO-15 implementation for speciation of toxic compounds and the California Air Resources Board SOP No. MLD052 for determination of toxic organic compounds in ambient air.

The fully automated system is designed to fully resolve nearly all volatile organics from Freons to DiChloroBenzenes to levels below 0.07 ppb V/V (150 ml injection). Samples are loaded through a 16-position automated sampler and trapped onto a low-volume adsorbent trap, with a mass flow controller (MFC) setting the sample size.

Detection of toxic organic compounds in ambient air is undoubtedly one of the most difficult analyses in gas chromatography. Samples must be concentrated into a small volume to enhance detection. A very large number of possible organics (>300) must be “fully” resolved to avoid improperly assigning concentrations from overlapping peaks. Identification and detection is facilitated with the extremely sensitive Saturn 2200 MS. The system involves a cold trap, at least 4 automated valves, 16- or 31-position automated sampler, and one workstation. All of these operations utilize nearly all of the powerful and comprehensive capabilities of the Varian 3800, Saturn 2200 and Star Workstation. Such a complex analyzer requires assurances that the data is valid, that the system is fully functional and easy to use, and that the ultimate performance is achievable.



SOLUTIONS TO DIFFICULT ANALYTICAL PROBLEMS…

Clean System Blanks

- Empty tubing or carbon adsorbents for trap
  - No thermal breakdown products
  - Maximum temperature limit of 400 °C
- All valves are heated; limited to 225 °C max
- Cryogenic cleansing of purge gas – vented after each cycle

Efficient Recovery of Light-End Components

- Area reproducibility for Ethane - < 2 %
- Accurate control of trap temperature (< ±2 °C) over complete temperature range
  - Self-calibrating platinum probe (RTD)
- Stable control of trap temperature (< ±2 °C)
  - Proportional controller
  - Close contact between heater, cryogen and trap
  - Silver-soldered connection of trap to mandrill
- Efficient trapping of Ethane on empty tubing and glass beads at –172°C

Full Recovery of "Heavy" Compounds

- All sample lines heated – no cold spots
- Smooth and inert sample lines – electroformed nickel
- Trap desorbing temperatures to 450 °C
- Effective release (>90 % of C_{12}; >80 % of C_{13}) from empty tubing or glass beads at 200 °C
- Maximum trap heating rate – 300 °C/min

Elimination of Interfering Artifacts

- Empty tubing or carbon adsobent traps standard
- No thermal breakdown that would yield interfering hydrocarbons (i.e. Benzene with Tenax)
- No reaction with NO_x that would yield interfering hydrocarbons (Ethene)
- Trap temperature limit to 400 °C

Sharp Chromatographic Peaks

- Minimum distance from cryofocus trap to column (~15 cm)
- Cryofocus trap isolation during trap heating
- Columns attached directly to final valve
  - minimum effect of extra-column volumes at critical chromatographic point
- Trap volume:
  - Empty tubing - ~120 microliters
  - Adsorbent trap – ~600 microliters
- diCl diF Methane peakwidth$_{½\ height}$: < 6 sec

Accurate Measure of Sample Volume

- Sample flow to vent just before trapping
  - Stabilizes MFC
  - Sweeps sample lines with new sample
- Volume-measuring flow path swept with nitrogen prior to trap heating
- Accurate volumes from 5 ml to 2400 ml
- Sample pressure can be below atmospheric and still maintain proper loading
- Sample loading independent of canister pressure

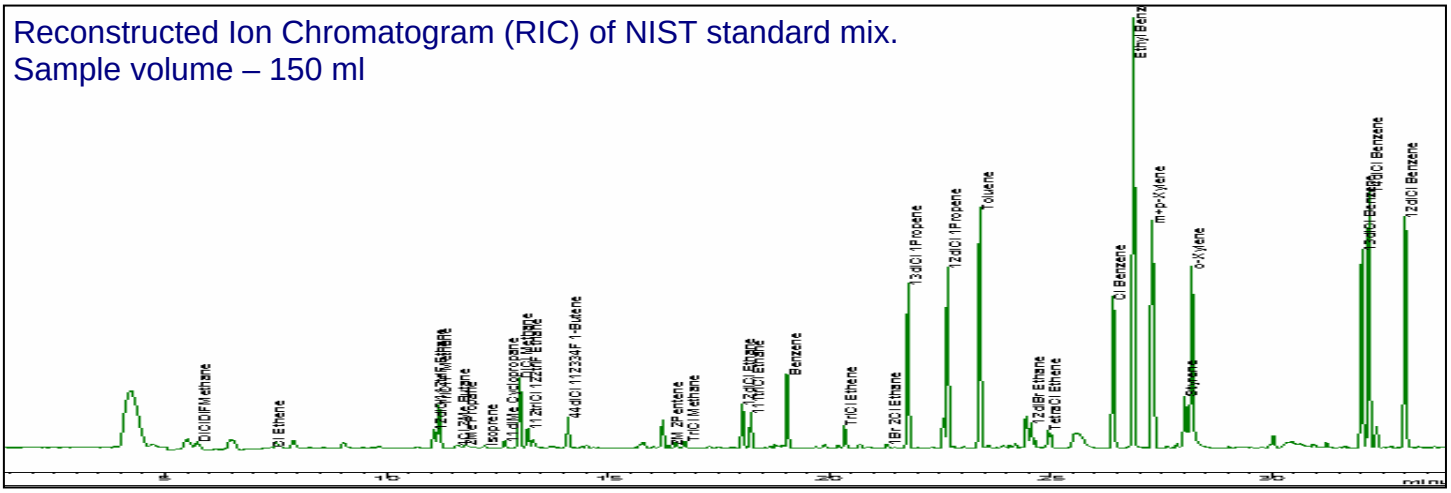
High Concentrations of CO_2?

- Mass Flow Controller (MFC) not accurate with major portions of CO_2
  - MFC usually calibrated for air; cannot handle gas mixtures properly
  - 50% CO_2 yields **double** the sample volume!!
- Optional fixed volume sample loop to 400 ml
  - Multiple loadings to trap for larger volumes
  - Full recovery of all hydrocarbons
  - Accurate measure of sample volume - even mixtures
- CO2 normally elutes prior to first toxic and not interfere spectrally

Water Treatment

- Carbon absorbents are hydrophobic and do not trap water at ambient temperatures and are effective traps for all components on TO15 list
  - Allows full recovery of both light-ends and heavies
  - Effectively handles water-saturated samples

Reconstructed Ion Chromatogram (RIC) of NIST standard mix.
Sample volume – 150 ml



…AND MORE SOLUTIONS

Minimal Carry-over

- Traps continuously purged with nitrogen when sample not loading
- Sample lines swept to vent with new sample just before trapping
- Carry-over « 0.1 %

Retention Time Reproducibility

- True electronic **flow** control - not pressure control
- Reproducible + accurate control of column oven temperature
  - proportional control (PID)
  - platinum probe (RTD)
- Typical RT reproducibility - < 0.03 minutes

Quantitation Reproducibility

- Column leaks detected with pressure monitoring
- Measuring flow path swept with nitrogen prior to trap heating
- Typical area reproducibility - < 3 %

Proper Introduction of Surrogate/ Internal Standard

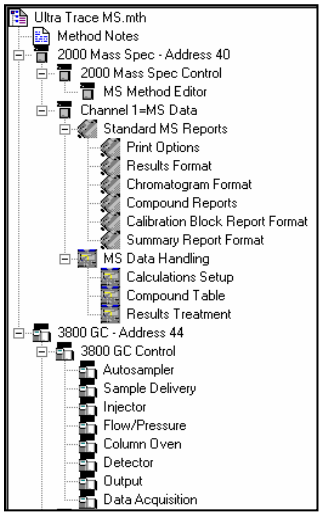
- Fixed volume sample loop
- Loop comes to atmosphere before injection
- Loaded onto trap as trap is purged

Monitoring of Operations

- True electronic **flow** control for columns – not pressure control
  - Generated backpressure becomes a diagnostic
  - Flow remains constant throughout run without computations/fudging
- Both analog gauges and digital displays for column pressure
- Flows/pressures documented in results report
- User-specified temperature limits for all thermal zones
- Visual indication of sample loading
- Complete system status with developing chromatograms on one screen

Simplified Method Execution

- Single run method contains **all** operating parameters for both GC and MS, including cold traps ("Injector"), valve actuations ("Sample Delivery"), compound table, computation entries and report formatting. Simply activating this single method sets up the complete system, to minimize operator errors.



Data Processing

- User can easily view both the developing chromatogram and MS spectra in real time
- Workstation can perform library searches on peaks in developing chromatogram for immediate confirmation of peak ID
- Single stored data file contains raw chromatographic data, final report, complete run method (including GC, MS, trap parameters), stream position, run log and error messages
- MFC flows recorded and sample volume reported
- Data collection, report generation, system control, custom report and StarFinder operate in Windows 95, 98, NT, or 2000.
- No overprinting of retention times on chromatogram
- Edit/lock calibration coefficients
- View/edit calibration curves
- Batching printing of reports from Windows Explorer
- Multi-level security with passwords
- Peak names to 39 characters; first 12 printed in reports

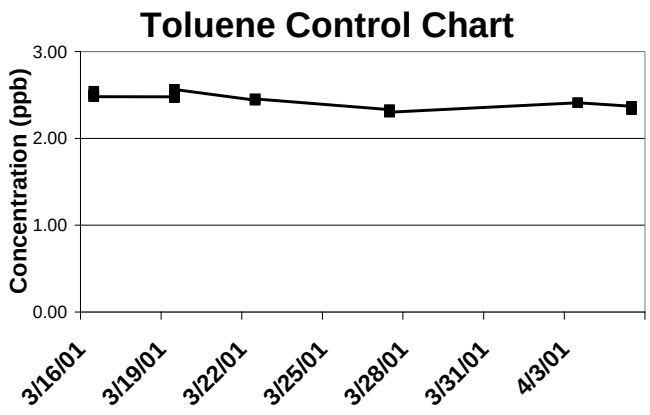
Data Integrity

- No overwriting of data files
- Operator cannot change Sample ID after collection
- Operator cannot change Date/Time of injection
- Cannot alter log files after collection
- Cannot change sample notes after collection
- All calibration data is archived with every raw data file
- Message log contains compete listing of system operations
- Instrument run log documents operating conditions
- File names can be labeled with sample ID, injection date/time and module source as variables
- File names can be 255 characters long

Options

- Fixed volume sample loop for proper handling of high CO_2 samples
- Addition of other detectors, such as Flame Ionization Detectors (for quantitation of hydrocarbons, especially the very light ones, including ethane, ethene, ethyne, propane, propene and propyne) and Pulsed Flame Photometric Detector (for sulfur compounds)
- LeakChek to provide full documentation of integrity of sample lines and sample connections
- Pressure station to bring canisters above atmospheric pressure to proper loadings
- Automatic insertion into SampleList of pressure station readings before and after pressurization for dilution corrections
- Canister cleaner with single high capacity, non-oil pump

Performance

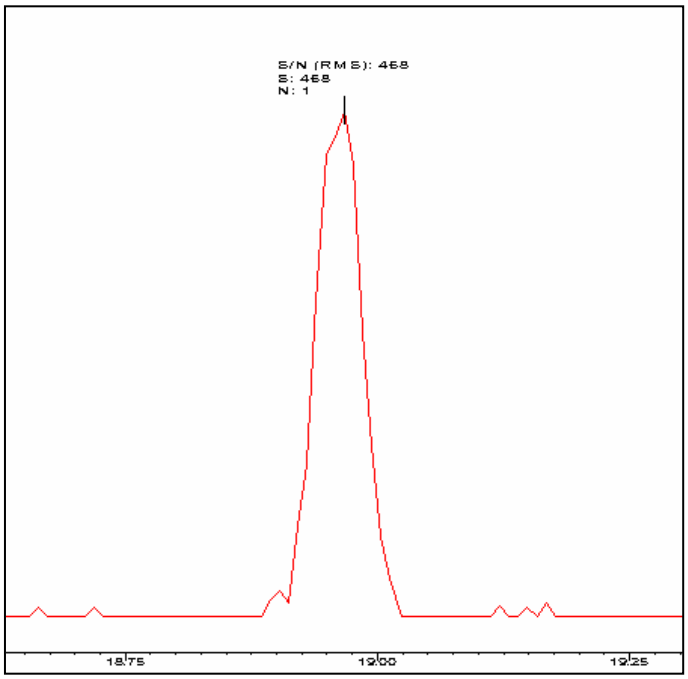


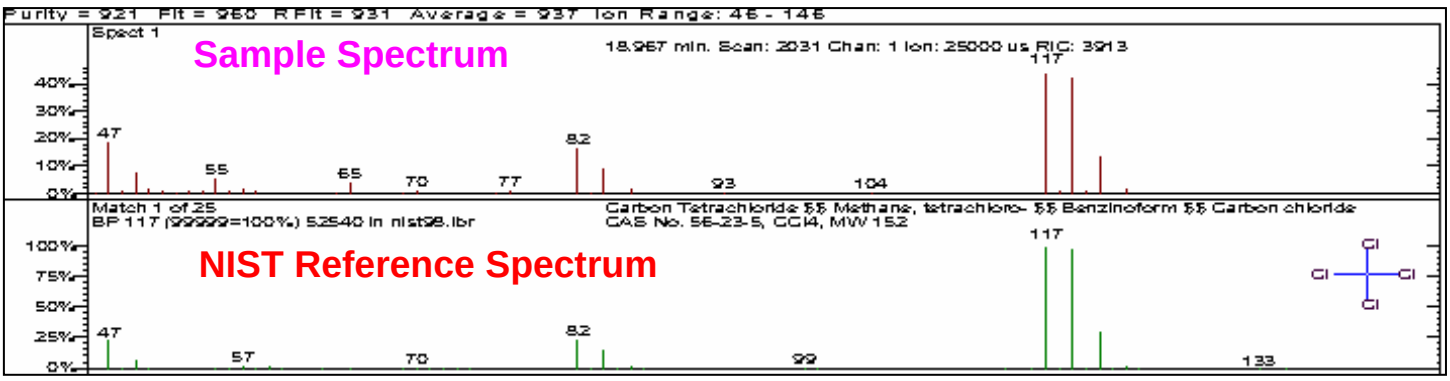
PROFOUND STABILITY

The efficiency of the concentrator and the stability of the Saturn Mass Spectrometer are illustrated with a typical control chart of 2.50 ppb Toluene over a month of monitoring. These results were generated *without* the use of internal standard. The %RSD over the month was < 6%.

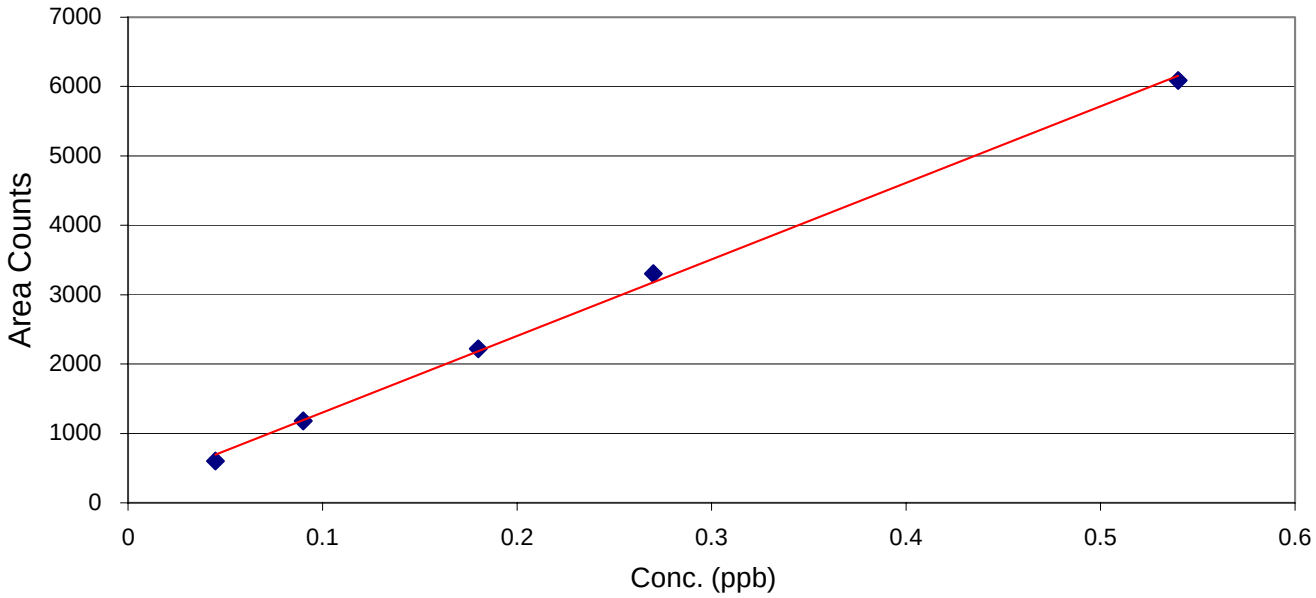
EXTREME SENSITIVITY

Sensitivity is demonstrated with this chromatogram of Carbon Tetrachloride (right). This NIST component concentration is 70 ppt V/V (0.07 ppb)! Loaded sample volume is just 150 ml. Displayed is the quantitation ion 77 m/z only for the region at the elution of carbon tetrachloride. Despite the very low concentration, its mass spectrum (below) matches very well with the NIST library.





…and More Performance

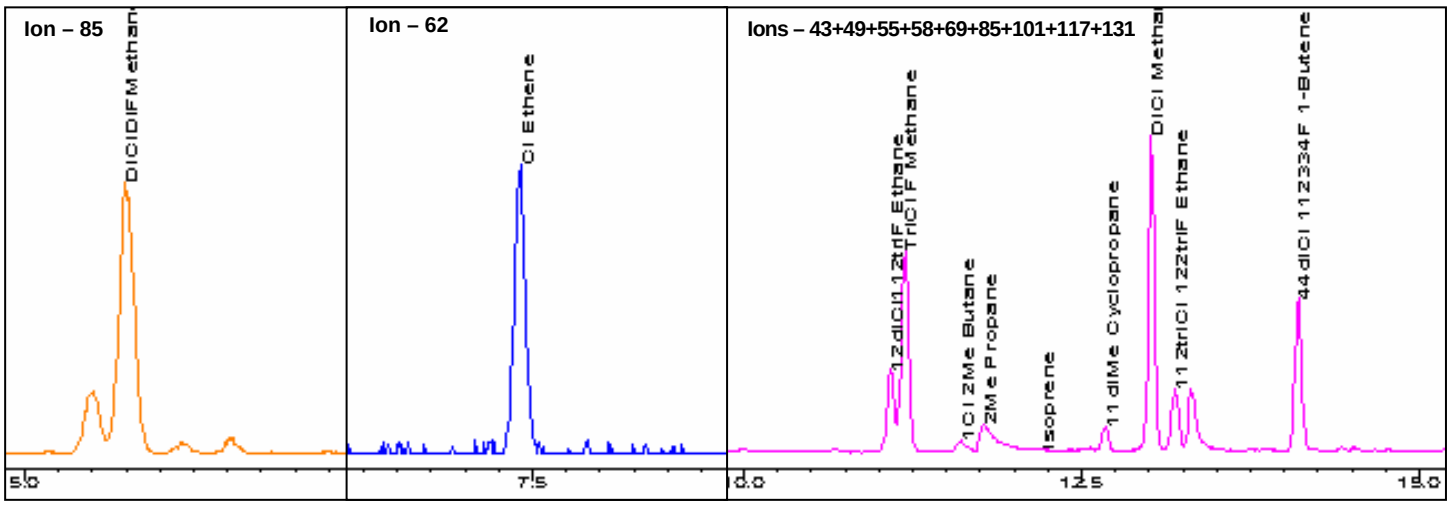


GREAT LINEARITY

A nice advantage of Mass Flow Controllers is that we can use them to generate multiple level calibrations, all based on a single standard. As the sample flow to the cold trap remains constant, the sampling time is varied to yield the different concentrations.

The graph above illustrates the linearity from 0.05 ppb to 1.08 ppb by setting the MFC to 50 ml/min and varying the sampling time from 0.5 minutes to 12 minutes.

The chromatograms below are displayed with the quantitation ions for the shown compounds. The ordinate scale varies.



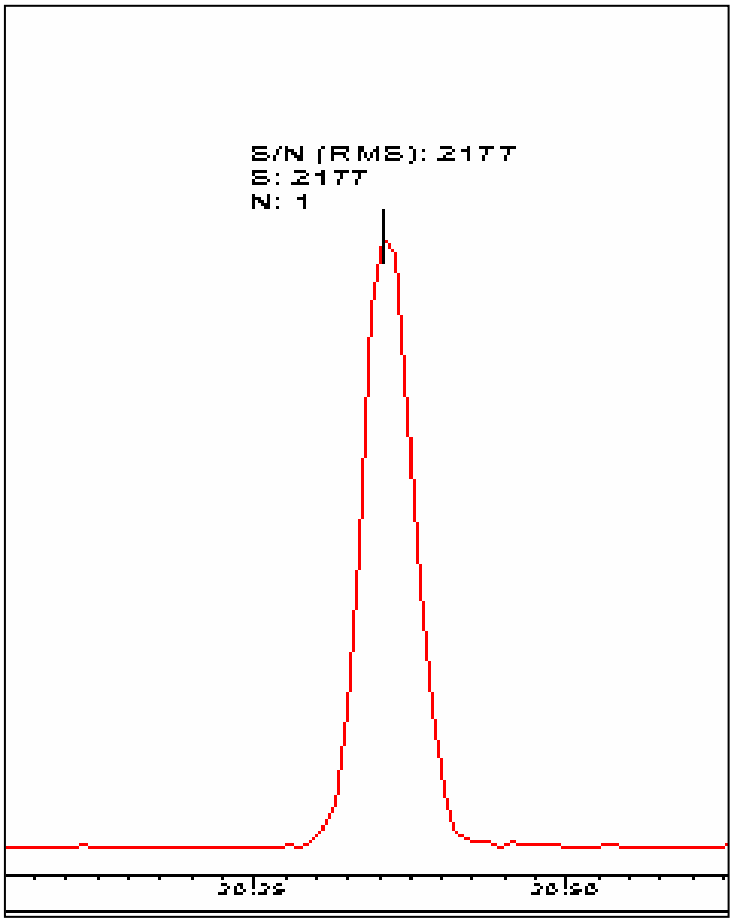
…and Even More Performance

TYPICAL DETECTION LIMITS

for Selected Compounds (150 ml sample)

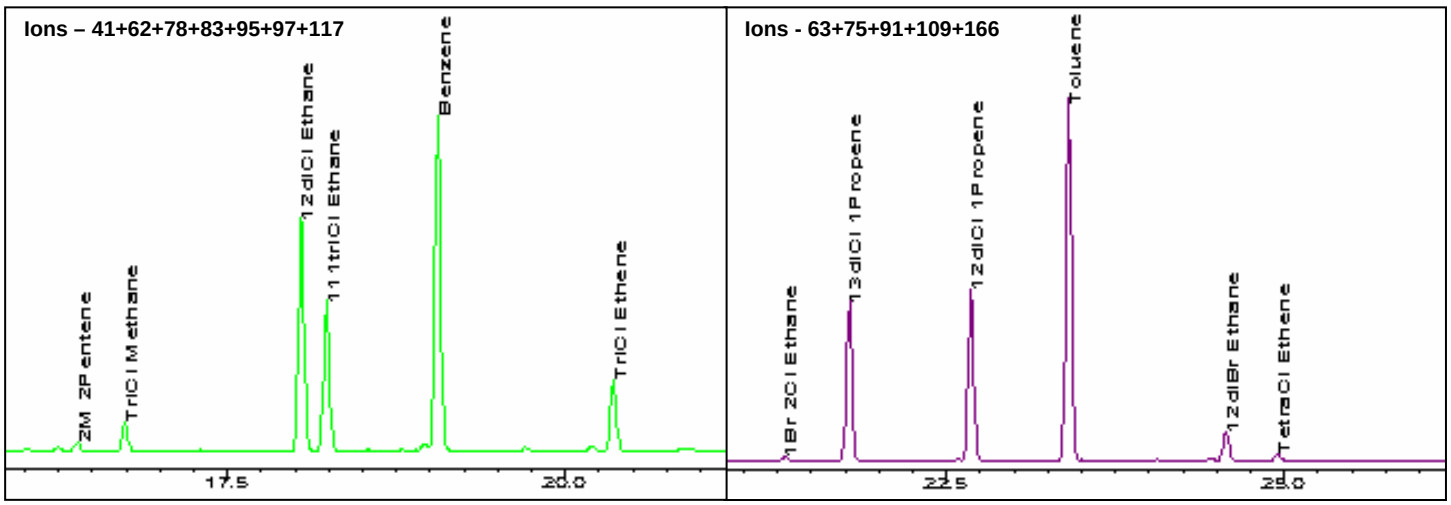
Compound	Detection Limit[1]	NIST Standard Label Concentration[2]
diCl diF Methane	**0.03** ppb V/V	0.75 ppb V/V
Vinyl Cl (Cl Ethene)	**0.03** ppb V/V	0.27 ppb V/V
CCl3F	**0.06** ppb V/V	2.00 ppb V/V
2Me13Butadiene (Isoprene)	**0.02** ppb V/V	0.73 ppb V/V
diCl Methane	**0.05** ppb V/V	2.80 ppb V/V
12diCl Ethane	**0.04** ppb V/V	1.94 ppb V/V
CHCl3	**0.002** ppb V/V	0.24 ppb V/V
111triCl Ethane	**0.03** ppb V/V	0.91 ppb V/V
Carbon tetraCl	**0.002** ppb V/V	0.08 ppb V/V
Benzene	**0.05** ppb V/V	2.02 ppb V/V
triCl Ethene	**0.01** ppb V/V	0.56 ppb V/V
13diCl Propene	**0.02** ppb V/V	4.73 ppb V/V
Toluene	**0.07** ppb V/V	4.82 ppb V/V
12diBr Ethane	**0.02** ppb V/V	0.99 ppb V/V
TetraCl Ethene	**0.005** ppb V/V	0.34 ppb V/V
ClBenzene	**0.05** ppb V/V	2.97 ppb V/V
EtBenzene	**0.02** ppb V/V	4.72 ppb V/V
m/pXylene	**0.01** ppb V/V	6.46 ppb V/V
Styrene	**0.02** ppb V/V	4.10 ppb V/V
oXylene	**0.06** ppb V/V	2.81 ppb V/V
13diCl Benzene	**0.03** ppb V/V	3.77 ppb V/V
14diCl Benzene	**0.03** ppb V/V	5.16 ppb V/V
12diCl Benzene	**0.03** ppb V/V	4.41 ppb V/V

[1] Detection Limit is 3X Std Dev at or near this level.
[2] Standard employed to generate detection limits.

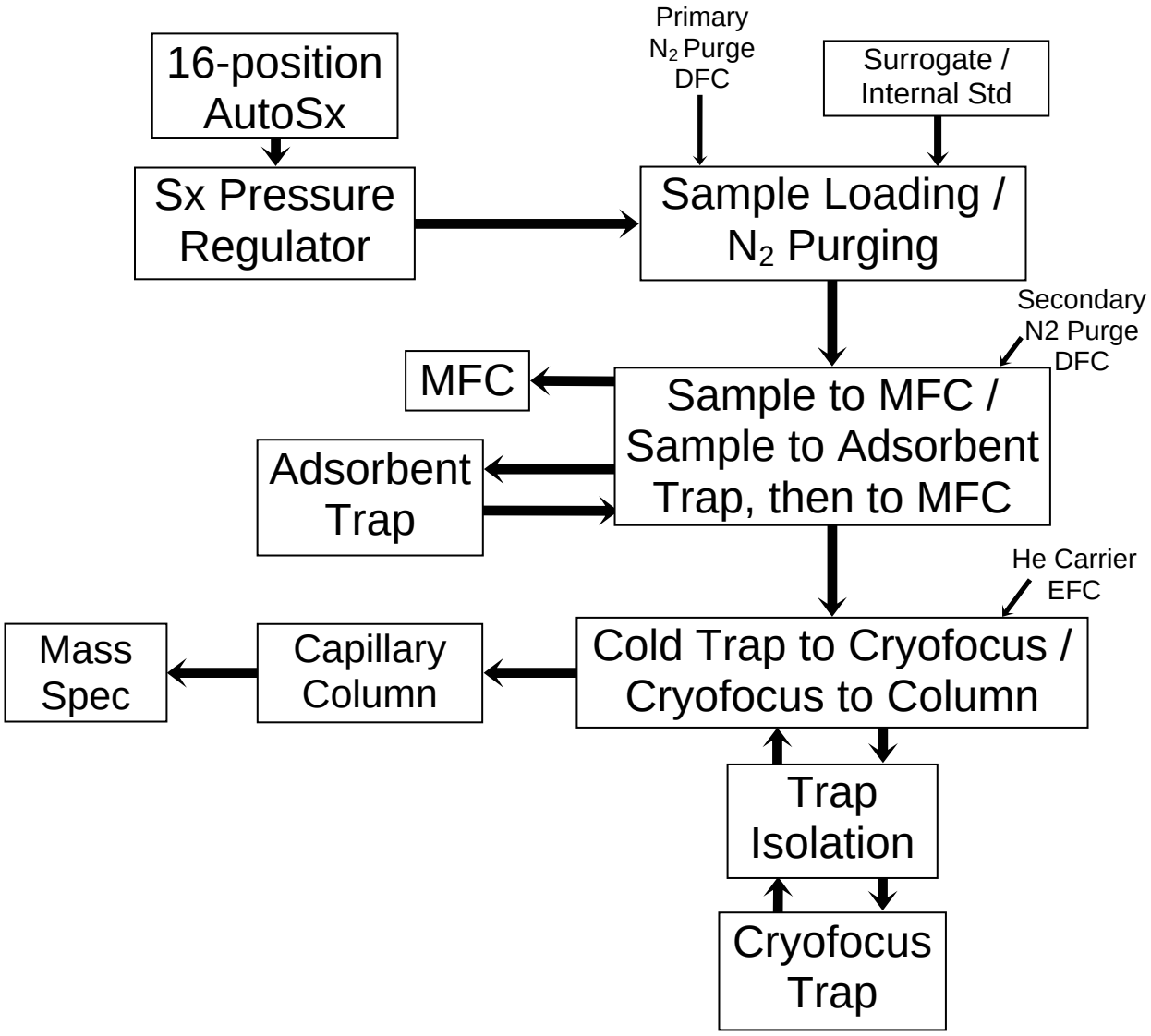


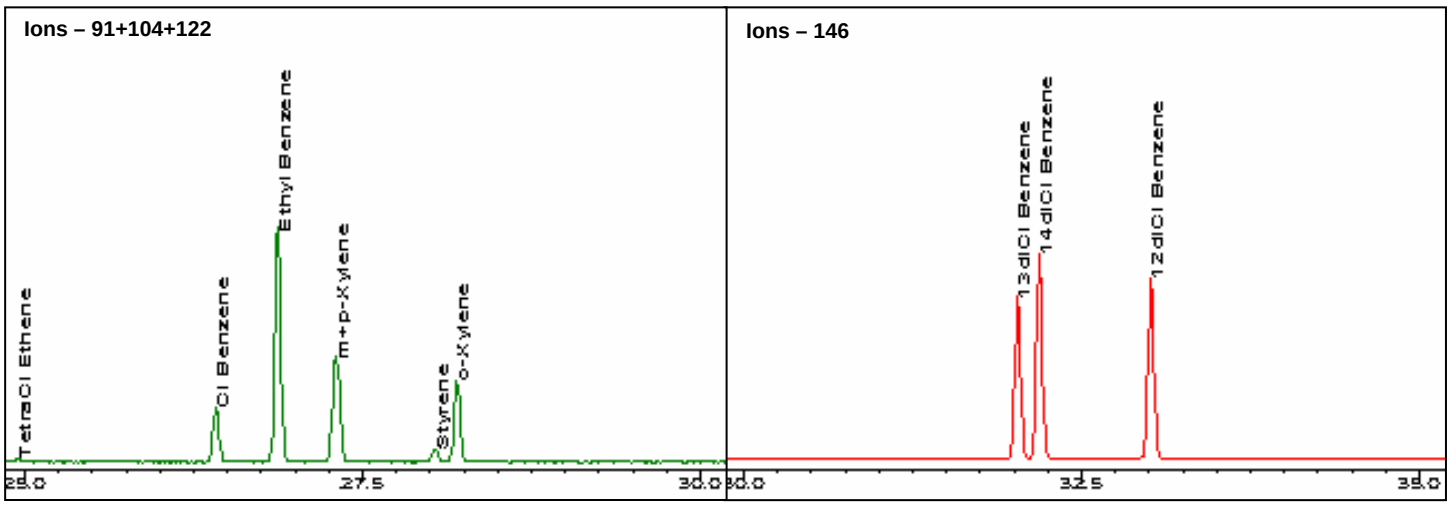
RADICAL SIGNAL-TO-NOISE

Just 150 ml sample loading of 0.56 ppb V/V TriChloroEthene (TCE) yields a superb signal-to-noise ratio (shown above). The effective trapping and remarkable performance of the Varian Saturn 2200 team together to provide this achievement.



System Diagram





System Specifications

Concentrator Traps

- Temperature range: -196 °C to 400 °C
- Maximum heating rate: >300 °C/minute
- Maximum cooling rate: typically >400 °C/minute
- Temperature stability: < 2 °C after 1 minute stabilization
- Temperature overshoot: max. <10 °C, typically <5 °C
- Trap Cryogen usage: < 4 liters per sample
- Trap internal volume: ~120 microliters – cryofocus
  ~600 microliters – adsorbent trap
- All trap settings controlled/monitored through GC with platinum probe (RTD) and proportional controller (PID)
- Programmable in 5 temperature steps with holds

Automated Sampler

- Standard: 16-position
- Micro-electric actuation, self-aligning
- Independently controlled valve oven
- Maximum temperature limit: 225 °C
- Sample position selected through workstation's sample list
- Position documented in final report and archived with data
- Sample lines heated through control of system

Valving

- Fully automated under time-programmable control of GC
- Valves mounted in heated enclosures
- Micro-electric actuation, easy realignment
- Most valves - Valco Series CWE;
  maximum temperature: 225 °C
- Valves can be turned on/off 21 separate event times within single method
- Automatic addition of surrogate/internal standard

Sampling

- Sample loading volume user-seletcable through workstation from 5 ml to 1600 ml
- Samples in canisters or Tedlar bags can be handled without hardware changes
- Loaded sample volume independent of canister pressure
- Optional fixed loop sampling for high CO_2 samples

System Performance

- Detection limit: < 0.002 ppb V/V to < 0.07 ppb V/V (compound dependent) with 150 ml sample volume
- Area reproducibility for Ethane - < 2 %
- Carry-over « 0.1 %
- Typical RT reproducibility - < 0.03 minutes

Pneumatics

- Column flow employs true Electronic Flow Controller (EFC), not pressure control with computed flow
- Temperature-sensitive flow elements maintained at 45 °C
- Flows automatically adjusted for atmospheric pressure

Column Oven

- Temperature range: -99 °C to 450 °C
- Temperature program rate: 0.1 °C/min to 100 °C/min
- Oven cool-down: 400 °C to 50 °C in 4.5 minutes without cryogen
- Programmable in 7 temperature steps with holds
- Coolant timeout to preserve cryogen when system idle
- Negative temperature programming to save coolant during sample loading

Mass Spectrometer

- Quadruple Ion Trap Design
- Mass range: 10 to 650 u, programmable throughout the analysis
- Scan rate: 5600 u/second
- Resolution: better than unit mass (with 10% valley)
- Ionization modes: Electron impact and Selected Ion Storage with programmable control from one mode to another within single analysis
- Internal ionization for superior low mass detection
- Ion gauge included
- Independent manifold heater of ion trap to 250 °C
- Turbomolecular pumping rate: 70 L/sec
- Sensitivity: 1 pg Octafluornapthalene produces a peak with S/N (RMS) 50:1 or greater

General

- GC keyboard 11 lines and 35 characters/line for ease of programming and monitoring
- Ethernet communications between GC and Workstation
- Line voltage for GC: 120 V, 20 amperes;
  for MS: 120V, 15 amperes

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