Lotus Consulting presents:

Vapor Intrusion Analyzer (VIA)

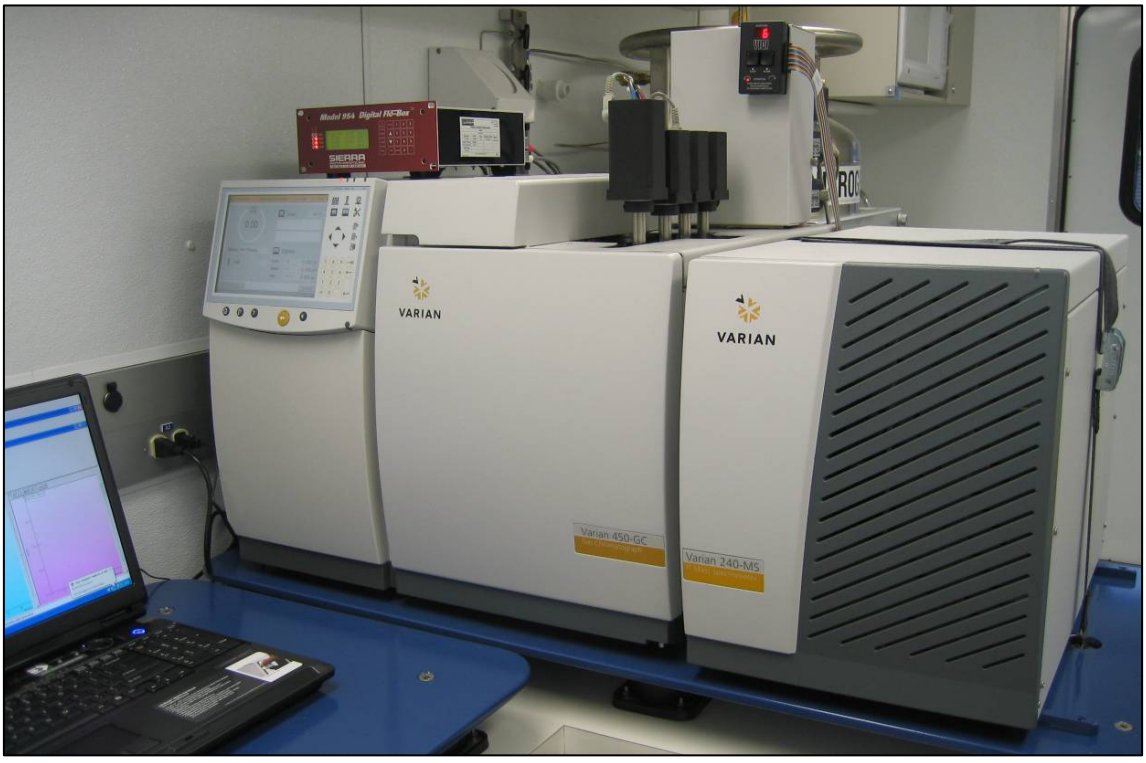
Measurement of toxic chemicals involved in vapor intrusion into residential and commercial buildings presents a very daunting task. Target objectives can vary from low-pptV for some analytes, and way up in the high ppmV for others – all in the same sample. And since these are mandatory screening levels, the analyzer needs to be well below the low levels to ensure that the reporting concentration is accurate. A dynamic range needed for this measurement approaches 30,000,000, typically well beyond the capabilities of most GCMS systems.

The Vapor Intrusion Analyzer by Lotus Consulting is designed to first assess the level of organics in the sample by a rapid prescreen run with a flame ionization detector. Based on user-selectable judgments, one of two GCMS instrument methods is automatically set up. One method is set up measure concentrations from under 10 pptV levels to 100 ppbV, and the other can handle levels from 30 ppbV to 300 ppmV. This process helps avoid the time-consuming and costly process of reruns to get the sample within range of the instrument.

The system can completely resolve nearly all volatile organics from Freons to Hexachloro-butadiene and Naphthalene, with a total analysis time of under 60 minutes, including sample loading and trapping. 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.

The low level method loads a typical volume of 300 ml, and uses a secondary cryofocus trap to reduce the sample components into a smaller volume for injection into the column.

The high-concentration method loads a smaller volume, usually 5 ml, and employs a separate low-volume adsorbent trap to ensnare the analytes away from water and carbon dioxide. A splitter is used to effectively reduce the volume injected onto the column by another factor of 100 or more. Switch between modes requires no hardware or sample modifications.



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 Varian 240 MS. The system involves dual adsorbent traps, a cold trap, at least 9 automated valves, a flame ionization detector for prescreening, 16-position automated sampler, and one workstation for full control of all operations with a single method and single sample list. All of these operations utilize nearly all of the powerful and comprehensive capabilities of the Varian 450, Varian 240 MS and Varian 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.

The selectivity and sensitivity gains achieved with MS-MS significantly enhance the performance for measuring naphthalene in ambient air, especially at very low levels. An extremely wide linear calibration range offers high sensitivity with a method detection limit for naphthalene at 8.5 pptV, while being capable of analyzing compound concentrations up to 100 ppbV without diluting samples or changing instrument operating conditions. Sample throughput is improved by the ability to avoid reruns due to samples being outside a narrower operating range. And since this method is "whole air" sample processing direct into the Ultra Trace Toxics System, sample preparation for analysis is minimal. Full rejection of ions, other than naphthalene, that coelute with this target ensures that proper quantitation is achieved without inclusion of these interferences that could yield a wrong, elevated result.

California Human Health Screening Levels (CHHSL) for Vapor Intrusion

Chemical	Indoor – Residential (ppbV)	Indoor – Commercial (ppbV)	Soil Gas – Residential (ppbV)	Soil Gas – Commercial (ppbV)
Benzene	0.026	0.044	11.4	38.5
Carbon Tetrachloride	0.0095	0.016	4	13.5
1,2-Dichloroethane	0.030	0.050	12.3	41.5
cis-1,3-Dichloroethene	9.2	13	4,000	11,200
trans-1,3-Dichloroethene	18	26	8,000	22,500
MTBE (Methyl *tert*-butyl ether)	2.6	4.4	1,100	3,800
Naphthalene	0.014	0.023	6.1	20.2
Tetrachloroethene (PCE)	0.060	0.10	28	89
Toluene	83	116	36,000	100,000
1,1,1-Trichloroethane	420	588	182,000	511,000
Trichloroethene (TCE)	0.230	0.380	222	745
Vinyl chloride	0.012	0.020	5.2	17.5
Xylenes (m&p)	168	235	73,000	200,000
Xylene (o)	168	235	73,000	200,000

Source: Use of California Human Health Screening Levels (CHHSLs) in Evaluation of Contaminated Properties, www.calepa.ca.gov/brownfields/documents/2005/CHHSLsGuide.pdf, January 2005.

Notes: Mercury and Tetraethyl Lead are not included here as certified calibration standards are not readily available at the listed levels. Concentrations are converted to ppbV from the listed $\mu g/m^3$.

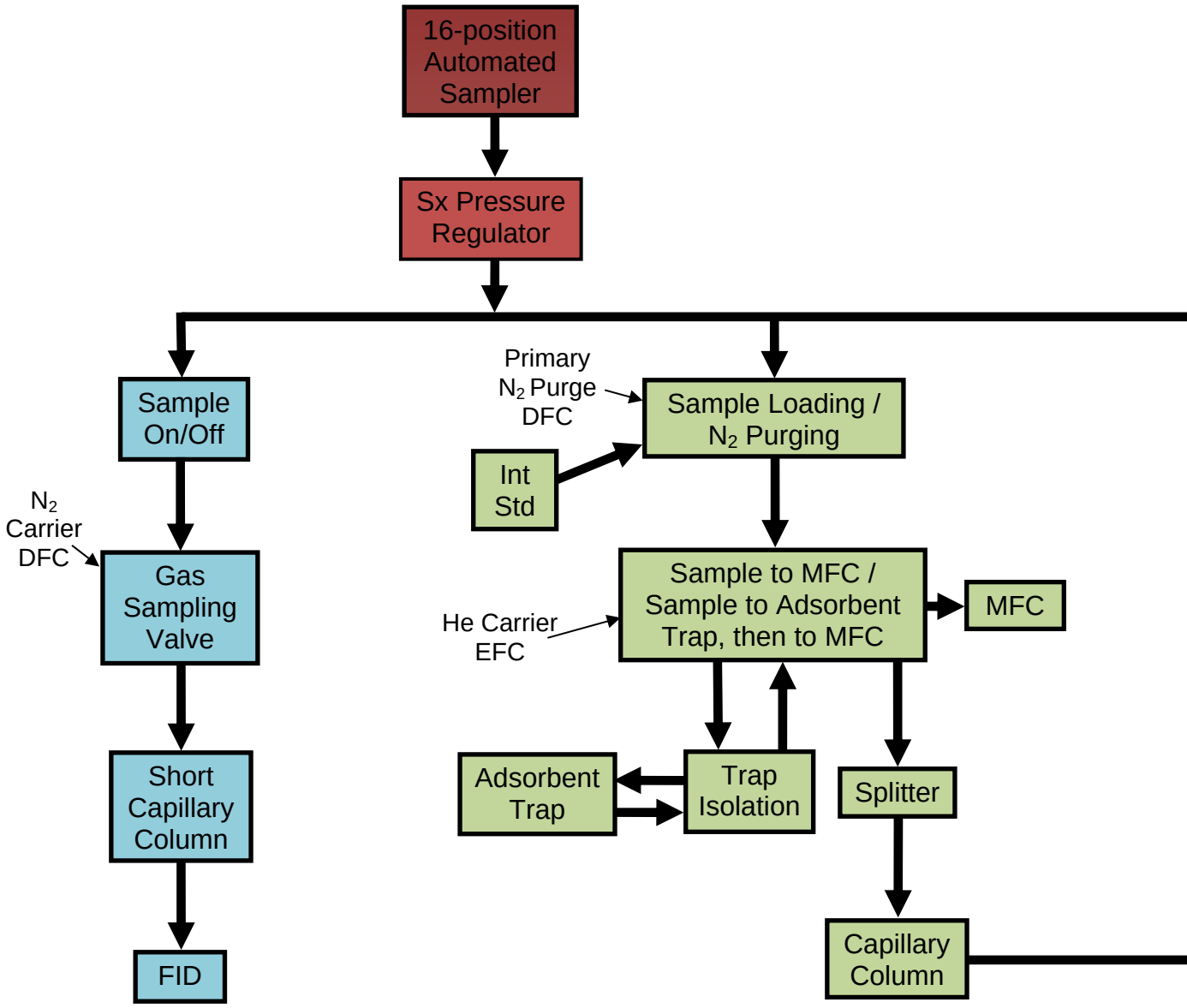
Illinois Tiered Approach to Corrective Action Objectives (TACO) for Vapor Intrusion

Chemical	Soil Gas – Residential (ppbV)	Soil Gas – Commercial (ppbV)
Acetone	316,000	316,000
Benzene	13	94
Bromodichloromethane	67,100	67,100
Bromoform	174	1,290
2-Butanone	149,000	915,000
Carbon Disulfide	26,000	161,000
Carbon Tetrachloride	3.8	28.6
Chlorobenzene	1,800	11,000
Chloroform	2.5	18
Dibromochloromethane	6,700	6,700
1,2-Dibromoethane	0.2	1.6
1,2-Dichlorobenzene	1,830	1,830
1,4-Dichlorobenzene	53	45
Dichlorodifluoromethane	6,500	39,000
1,1-Dichloroethane	20,000	124,000
1,2-Dichloroethane	2.5	19
1,1-Dichloroethene	61	404
1,2-Dichloropropane	1.6	11.5
cis-1,3-Dichloroethene	6,800	28,000
trans-1,3-Dichloroethene	2,500	16,000
cis-1,3-Dichloropropene	24	183
trans-1,3-Dichloropropene	24	183
Ethylbenzene	13,600	13,600
Methylene chloride	170	1,300
MTBE (Methyl *tert*-butyl ether)	97,100	333,000
Naphthalene	116	118
Styrene	8,000	8,000
Tetrachloroethene	9.8	72
Toluene	37,100	37,100
1,2,4-Trichlorobenzene	215	579
1,1,1-Trichloroethane	141,000	159,000
1,1,2-Trichloroethane	31,000	31,000
Trichloroethene (TCE)	33	242
Trichlorofluoromethane (Freon 11)	17,000	106,000
Vinyl chloride	12	172
m&p-Xylenes	3,700	12,000
o-Xylene	3,900	12,000

Source: Illinois Pollution Control Board Regulations, Title 35, Subtitle G, Chapter I, Subcharter f, Part 742. www.ipcb.state.il.us/SLR/IPCBandIEPAEnvironmentalRegulations-Title35.asp, September 2008.

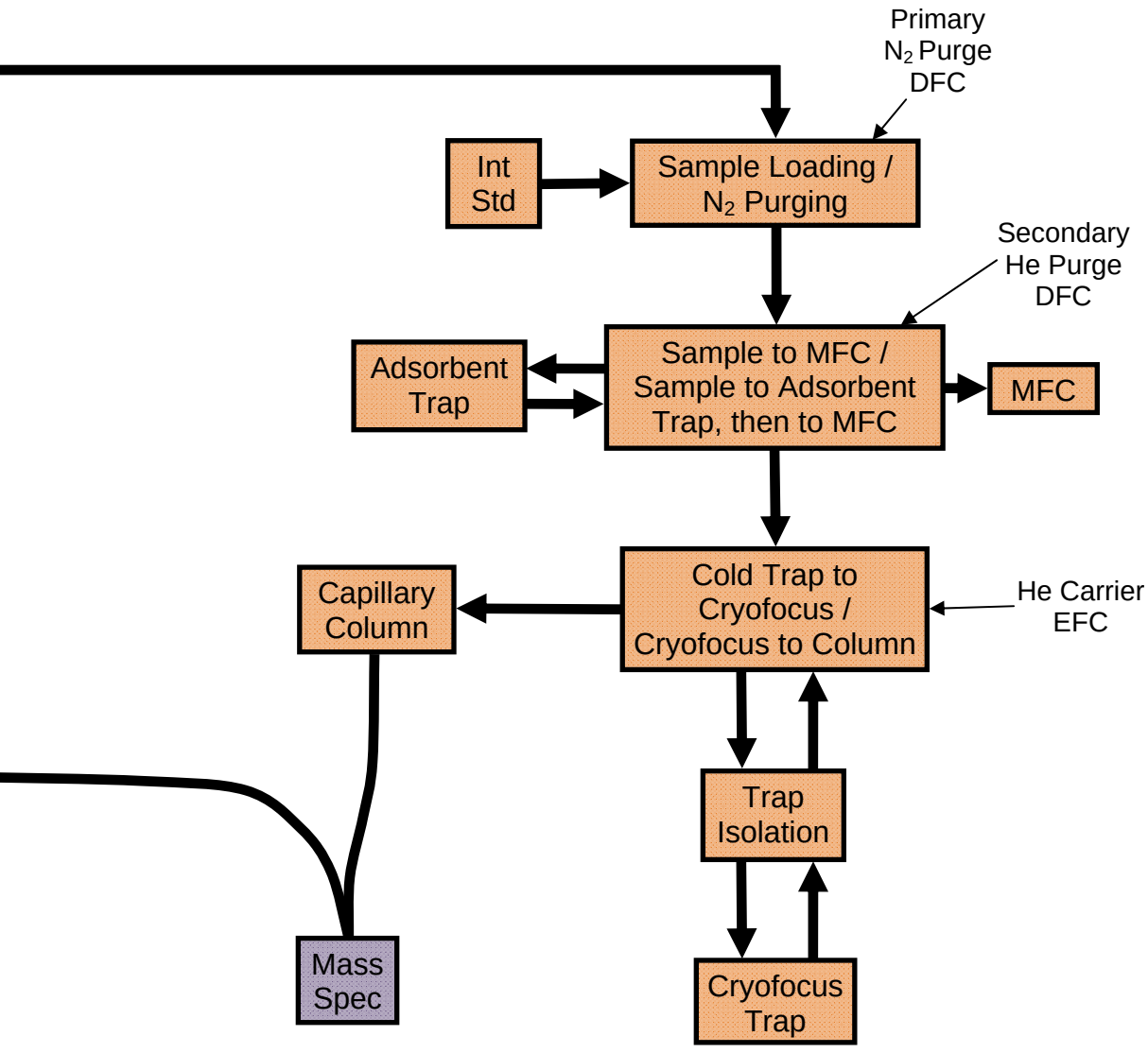
Notes: Some listed chemicals in TACO are not included here, as certified calibration standards are not readily available at the listed levels. Concentrations are converted to ppbV from the listed $\mu g/m^3$.

System Diagram



Prescreen

High Concentrations



Low Concentrations

Solutions for Difficult Analytical Problems…

Clean System Blanks

- Empty tubing or carbon adsorbents for traps
  - No thermal breakdown products
  - Maximum temperature limit of 250 °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 cryotrap to mandrill
- Efficient trapping of Ethane on adsorbent trap

Full Recovery of "Heavy" Compounds

- All sample lines heated – no cold spots
- Smooth and inert sample lines – electroformed nickel
- Trap desorbing temperatures to 250 °C
- Effective release (>90 % of C_{12}; >80 % of C_{13}) from adsorbent and cryotraps at 200 °C
- Maximum trap heating rate: 300 °C/min

Elimination of Interfering Artifacts

- Dual multi-bed carbon adsorbent traps and cryofocus trap standard
- No thermal breakdown of trap adsorbents that would yield interfering hydrocarbons (i.e. Benzene and Toluene with Tenax)
- No reaction with NO_x that would yield interfering hydrocarbons (Ethene)
- Trap temperature limit to 250 °C

Sharp Chromatographic Peaks

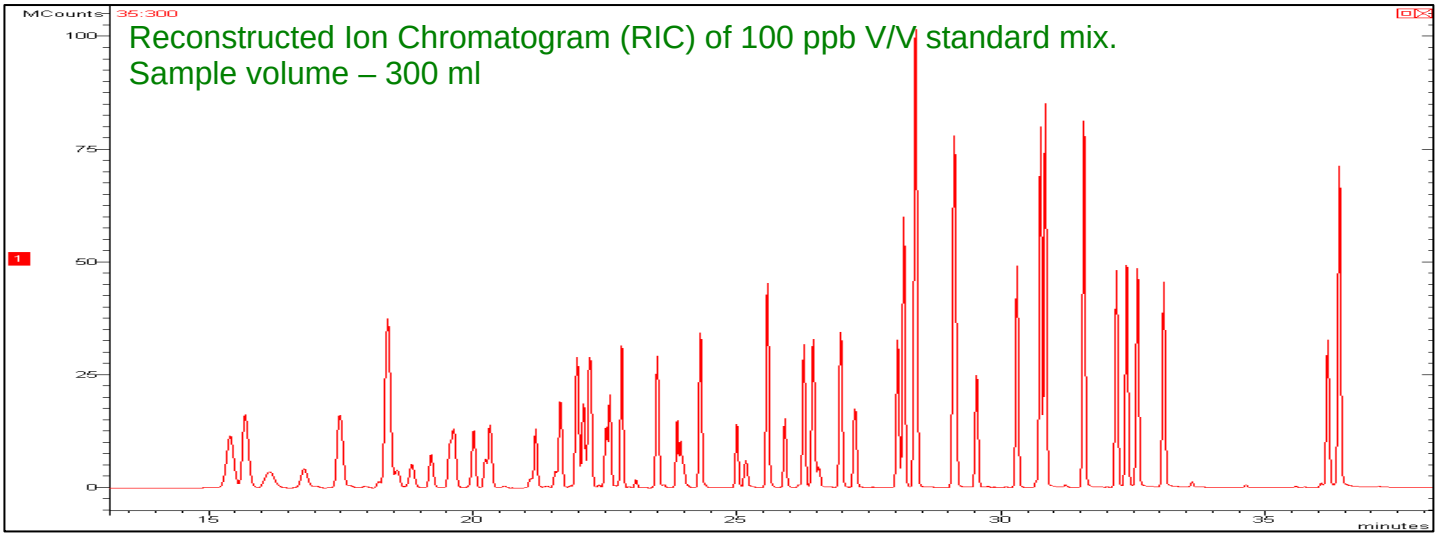
- Minimum distance from cryofocus trap to column (~15 cm)
- Cryofocus trap isolation during trap heating
- Columns attached directly to final valve
  - minimum effect of extra-column volumes at critical chromatographic point
- Trap volume:
  - Adsorbent trap – ~600 microliters
  - Empty tubing - ~90 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 1 ml to 2400 ml
- Sample pressure can be below atmospheric and still maintain proper loading
- Sample loading independent of canister pressure

Water Treatment

- Multi-bed 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
  - Dry purge step time-programmable



…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

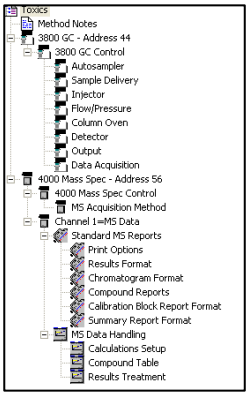
- Fixed volume sample loop
- Loop comes to atmosphere before injection
- Loaded onto trap as trap is purged with nitrogen

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 pressures
- 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 GC, FID 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
- Data collection, report generation, system control, custom report and StarFinder operate in Window XP
- View/edit calibration curves
- Batching printing of reports from Windows Explorer
- Multi-level security with passwords
- Peak names to 40 characters

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, method used and module source as variables
- File names can be up to 255 characters long

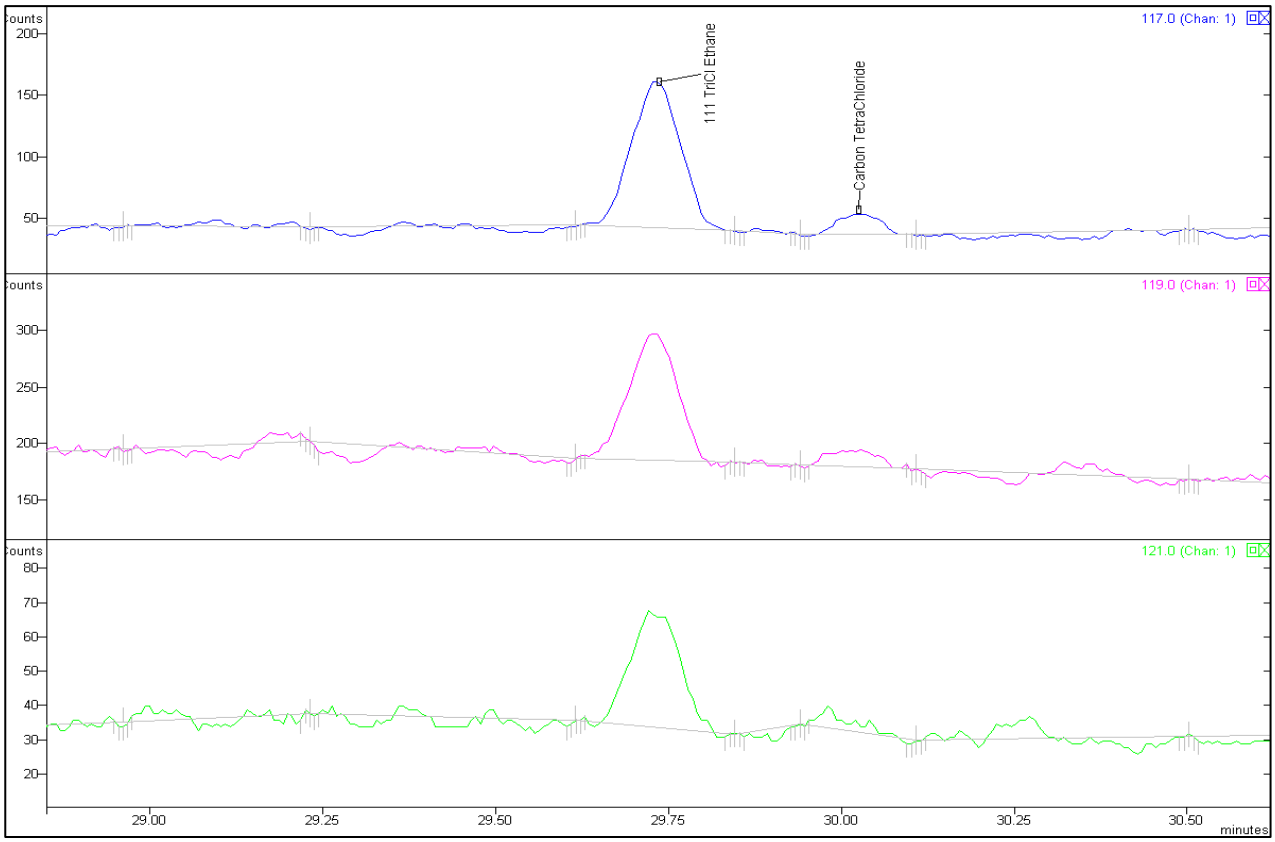
Options

- 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), Pulsed Flame Photometric Detector (for sulfur compounds), and Thermal-Ionic Specific Detector for acrylonitrile.
- 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
- 10 position Canister cleaner with single high capacity, oil-less pump

Performance

EXTREME SENSITIVITY

Sensitivity is demonstrated with this chromatogram of Carbon Tetrachloride (below). This NIST component concentration is 930 ppQ V/V (0.0009 ppb)! Loaded sample volume is equivalent to just 150 ml. Displayed is the quantitation ion 117, 119 and 121 m/z only for the region at the elution of Carbon Tetrachloride and 111 TriChloroEthane.



The Varian Ion Trap is inherently more sensitive than conventional linear quadrupole mass spectrometers because nearly all of the sample ions are held within the ion trap until ejected out by the varying RF field when the proper mass is selected. For a classical quadrupole MS, only ions of a particular mass are allowed to pass through the quad for just a few microseconds as the RF field ramps through the mass range, often with only 0.1% of the original ions reaching the detector. More importantly, higher mass ions have lower transfer efficiencies with quadrupole MSs.

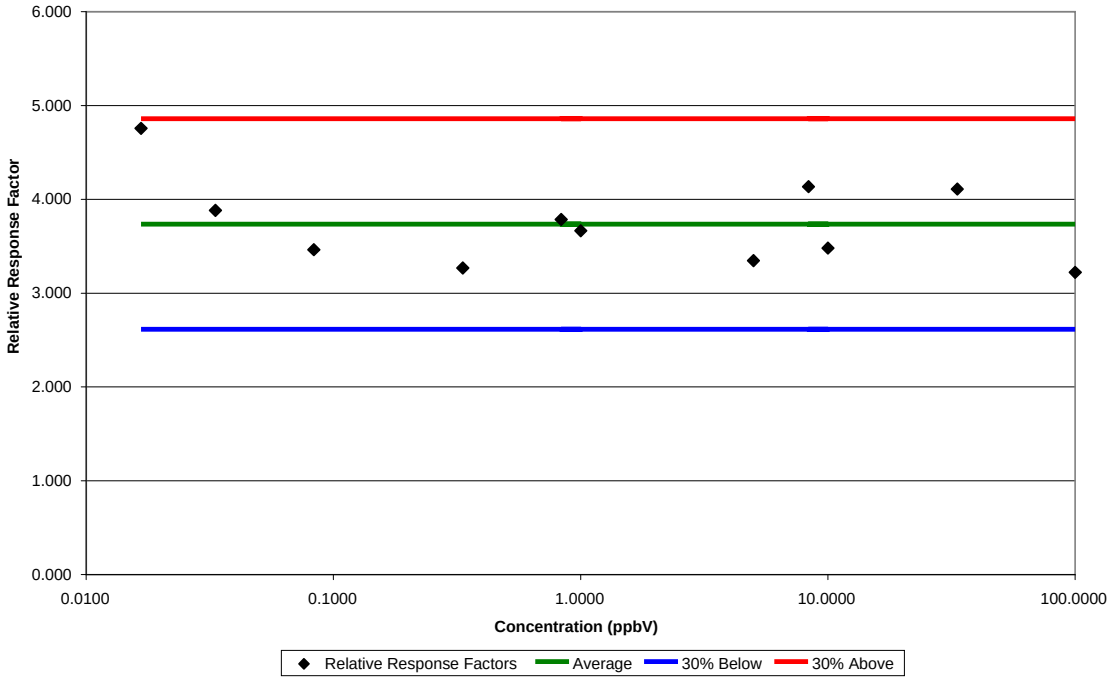
The Varian 240 Ion Trap takes the next step in achieving enhanced performance by transferring more ions to the detector through a physical change in the electrode design and a new, patented ejecting waveform. Its detector is mounted 90^{o} to the exit of the trap so that neutrals, photons and stray electrical charges end up going straight and miss the bend, while the ions of interest make the curve, resulting in more desirable signal and less noise. The linear range is also extended with these improvements.

Single Ion Monitoring (SIM) is frequently used to make quadrupoles perform closer to ion traps in sensitivity. By monitoring only one mass, losing the full spectrum and identification with NIST library is no longer possible. With ion traps, since all ions are held up anyway, Selected Ion Storage (SIS) offers no great enhancement and we can still use library searches with the full scan, even at extremely low levels.

…and More Performance

GREAT LINEAR RANGE
> 6,600

Bromodichloromethane
from 0.016 ppbV/V to 100 ppbV/V



A nice advantage of Mass Flow Controllers for sample loading is that they can be used them to generate multiple level calibrations, all based on a single standard or just a few standards. 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 0.016 ppb to 100 ppb by setting the MFC to 50 ml/min and varying the sampling time from 0.1 minutes to 6 minutes for three standards of 100 ppb V, 10 ppbV and 1 ppbV.

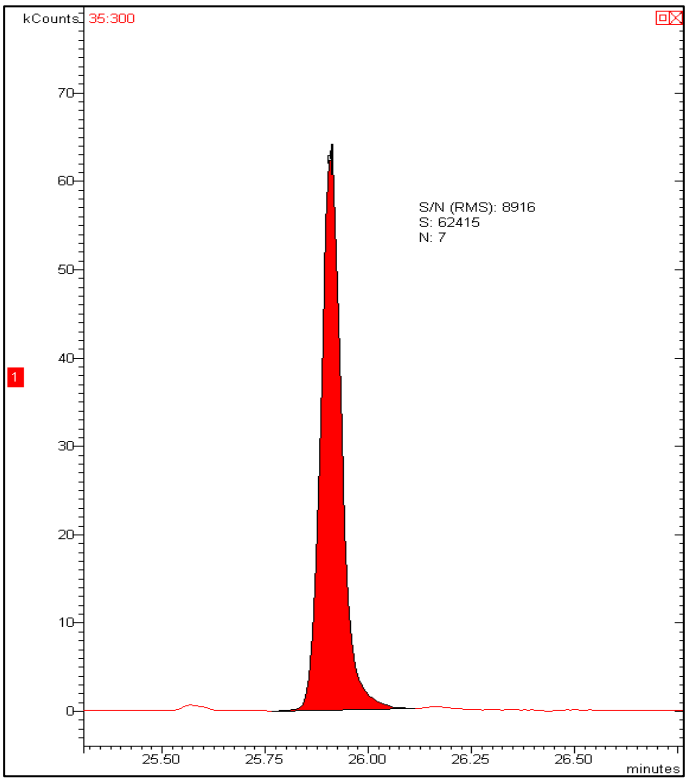
...and Even More Performance

TYPICAL DETECTION LIMITS
for Selected Compounds
(300 ml sample, full scan)

Compound	Quant Ion	Detection Limit[1]	Standard Concentration
diCl diF Methane	85	0.008 ppb V/V	0.028 ppb V/V
Vinyl Cl (Cl Ethene)	62	0.012 ppb V/V	0.030 ppb V/V
CCl3F	101	0.008 ppb V/V	0.030 ppb V/V
13Butadiene	54	0.006 ppb V/V	0.024 ppb V/V
Bromomethane	94	0.006 ppb V/V	0.031 ppb V/V
diCl Methane	49	0.008 ppb V/V	0.064 ppb V/V
12diCl Ethane	62	0.007 ppb V/V	0.024 ppb V/V
Chloroform	83	0.006 ppb V/V	0.025 ppb V/V
111triCl Ethane	97	0.006 ppb V/V	0.024 ppb V/V
Benzene	78	0.003 ppb V/V	0.026 ppb V/V
12diCl Propane	76	0.004 ppb V/V	0.014 ppb V/V
c13diCl Propene	75	0.009 ppb V/V	0.028 ppb V/V
Toluene	91	0.001 ppb V/V	0.032 ppb V/V
t13diCl Propene	75	0.004 ppb V/V	0.030 ppb V/V
TetraCl Ethene	166	0.005 ppb V/V	0.031 ppb V/V
ClBenzene	112	0.010 ppb V/V	0.031 ppb V/V
EtBenzene	106	0.009 ppb V/V	0.035 ppb V/V
m/pXylene	106	0.013 ppb V/V	0.069 ppb V/V
Styrene	104	0.008 ppb V/V	0.022 ppb V/V
oXylene	106	0.008 ppb V/V	0.040 ppb V/V
13diCl Benzene	146	0.006 ppb V/V	0.029 ppb V/V
14diCl Benzene	146	0.006 ppb V/V	0.029 ppb V/V
12diCl Benzene	146	0.007 ppb V/V	0.031 ppb V/V
HexaChloro Butadiene	225	0.009 ppb V/V	0.041 ppb V/V
Naphthalene (MSMS)	MSMS 128→ 106	0.009 ppb V/V	0.004 ppb V/V

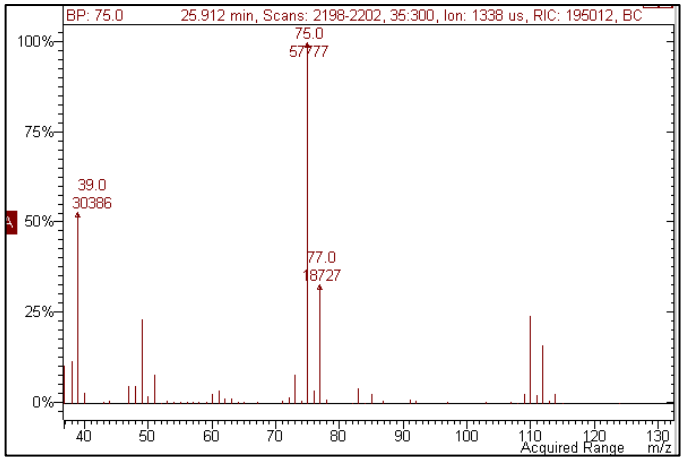
[1] Detection Limit is 3X Std Dev at or near this level.
Standard employed to generate detection limits;
Sample flow rate – 50 ml/min
.Sampling time – 0.05 min
Sample Volume Injected – 5 milliliter

RADICAL SIGNAL-TO-NOISE

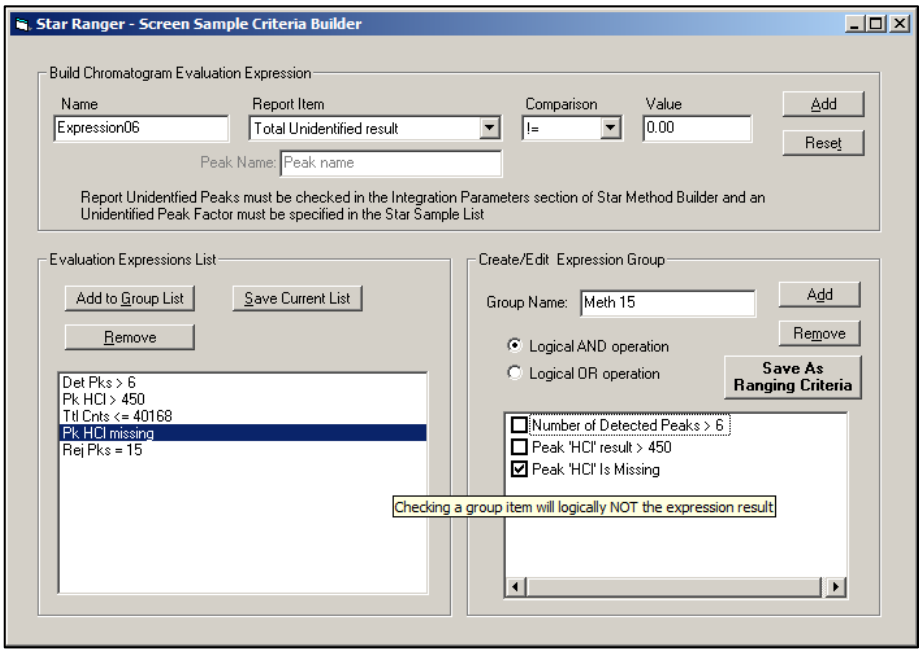


Just 300 ml sample loading of 0.030 ppb V/V trans-1,3 Dichloropropene yields a superb signal-to-noise ratio and still with full scan. Effective trapping and remarkable performance of the Varian 240 team together to provide this achievement.

Spectrum of 0.030 ppbV/V trans-1,3 Dichloropropene

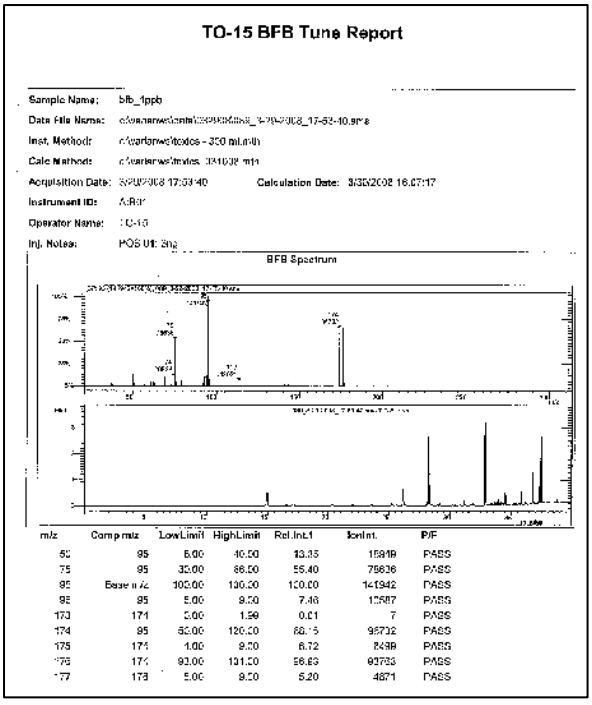


Selection of Method Based on FID Prescreen



The dynamic range mandated for this measurement requires a prescreen assessment of the expected concentration range of the sample to opt for a suitable method to accurately report results. The operator can set up a judgment based on results from a quick run with an flame ionization detector. Once the sample is run with this prescreen, the Varian MS Workstation is then automatically set up to use the appropriate method. The criteria is preselected by the operator based on virtually any result in the prescreen report, using Boolean logic expressions for the decision.

BFB Tune Compliance



Ion traps are inherently very gentle and effective at ionizating target analytes, and they generate spectra that emphasize the heavier ions, often the ones that uniquely characterize the compound. Without modifications to the mass responses, these native spectra may not fully match NIST libraries from other MS instrument types. To allow a perfect tune to p-Bromofluoro-benzene (BFB) criteria, specific mass regions can be scaled down (or up) through adjustments to Ion Time Factors as a function of mass, as shown to the right.

Tune

Type: BFB

	Low Mass (m/z)	High Mass (m/z)	RF Storage Level (m/z)	Ion Time Factor (%)
1	10	60	27	130
2	61	77	35	80
3	78	149	35	100
4	150	1000	35	70
5				
6				

System Specifications

Concentrator Traps

- Temperature range: -196 °C to 450 °C, to 250 °C for adsorbent traps
- 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: ~90 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
- Coolant timeout to preserve cryogen when system idle
- Negative temperature programming to save coolant during sample loading

Automated Sampler

- Standard: 16-position, optional 31-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
- 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-selectable 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

Sample Prescreen by FID

- Performed without hardware changes and without moving sample container
- 3 minute run time for each sample
- User-selectable judgments for assessment for automatic selection of GCMS method by Boolean Logic

System Performance

- Detection limit: 0.001 ppb V/V to < 0.013 ppb V/V (compound dependent) with 300 ml sample volume under full scan
- Area reproducibility typically < 2 %
- Carry-over « 0.1 %
- Typical RT reproducibility - < 0.03 minutes
- Linear range for low-level method: <10 pptV to 100 ppbV with only 300 ml sample loading and MS full scan
- Linear range for high-level method: < 30 ppbV to >300 ppmV with only 5 ml sample loading, 1:100 split and MS full scan

Pneumatics for Low-level Method

- 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 or vacuum

Pneumatics for High-level Method

- Split flow 1-10,000 (column dependent)
- Temperature-sensitive flow elements maintained at 45 °C
- Flows automatically adjusted for atmospheric pressure or vacuum

Column Oven

- Temperature range: -99 °C to 450 °C with LN_2 cryogen
- Temperature program rate: 0.1 °C/min to 120 °C/min
- Oven cool-down: 400 °C to 50 °C in 4.5 minutes without cryogen
- Programmable in 24 temperature steps with 25 holds
- Coolant timeout to preserve cryogen when system idle
- Negative temperature programming to save coolant during sample loading

Mass Spectrometer

- Quadrupole Ion Trap Design
- Mass range: 10 to 1000 u, in 0.1 u increments programmable throughout the analysis
- Scan rate: 10,000 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
- Manifold ion gauge and foreline gauge included
- Independent manifold heater of ion trap to 250 °C
- Turbomolecular pumping rate: 280 L/sec
- Oil-less Dry Scroll foreline pump
- Sensitivity: 200 fg Octafluornaphthalene produces a peak with S/N (RMS) 20:1 or greater, internal mode
- MSMS time-programmable and activated through method operations
- Silcochrom electrodes standard for maximum inertness

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