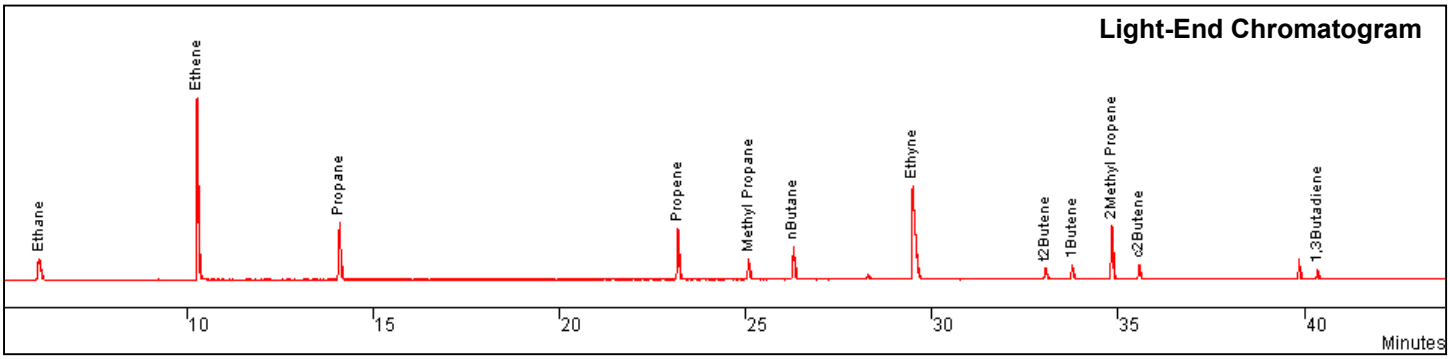
Ultra Trace Hydrocarbon System (UTHS)

The Ultra Trace Hydrocarbon System from Lotus Consulting provides impressive separations of trace hydrocarbons in ambient air samples. The system features the Varian 3800 Gas Chromatograph with built-in high performance sample concentrator and dual column narrow-bore column chromatography. This system handles both pressurized canisters and Tedlar bags without hardware changes. And the system meets the exacting requirements for the US EPA PAMS implementation for speciation of ozone precursors and the California Air Resources Board SOP No. MLD032 for determination of non-methane hydrocarbon compounds in ambient air.

The fully automated system is designed to fully resolve nearly all hydrocarbons from ethane to tridecane to levels below 0.2 ppbC (300 ml injection). Samples are loaded through a 16-position (optional 31-position) automated sampler and trapped onto a low-volume cold trap with a mass flow controller (MFC) setting the sample size. All major hydrocarbons from Ethane to Methyl Butane are fully resolved to baseline on a narrow-bore PLOT column; water and heavy hydrocarbons are kept from the PLOT with a stripper column. Hydrocarbons after Methyl Butane are then separated via a column switching valve by directing the chromatographic stream to a non-polar narrow-bore column. Quantitation is performed with dual flame ionization detectors; peak identity of most olefins and aromatics can be confirmed with optional in-series photo-ionization detectors.

Full speciation of hydrocarbons 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 hydrocarbons (>300) must be “fully” resolved to avoid improperly assigning concentrations from overlapping peaks. And the full gamut of peaks must be identified and quantitated with limited standards (Propane and Benzene). The system involves a cold trap, at least 4 automated valves, 16- or 31-position automated sampler, three capillary columns, usually two detectors and one workstation. All of these operations utilize nearly all of the powerful and comprehensive capabilities of the Varian 3800 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.

Ambient air sample from Chongqing, China, October 22, 1999. 300 ml sample loading. Column temperature program: 0 °C, 9 min. hold, 3 °C/minute to 90 °C, 1 min hold, 5 °C/minute to 200 °C. Trap temperature program: -172°C, 9 min. hold , 300 °C/minute to 200 °C. Detector range - 12.



SOLUTIONS TO DIFFICULT ANALYTICAL PROBLEMS…

Clean System Blanks

- Empty tubing or glass beads for trap
  - No thermal breakdown products
  - Maximum temperature limit of 450 °C
- All valves are heated; limited to 350 °C max, except column switching valve (225 °C limit)
- 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
- Efficient trapping of Ethane on empty tubing or glass beads at –172°C

Full Recovery of "Heavy" Hydrocarbons

- 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 heating rate – 300 °C/min

Elimination of Interfering Artifacts

- Empty tubing or glass bead 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 450 °C

Huge Dynamic Range for Hydrocarbon Detection

- Floating point math with signal conversion
- Effective range from 100 microvolts to 1000 volts – **10^7 without range change!**
- Both major and minor peaks detectable within single run without range change

Sharp Chromatographic Peaks

- Minimum distance from trap to column (~15 cm)
- Trap isolation during trap heating
- Columns attached directly to column switching valve in column oven
  - minimum effect of extra-column volumes at critical chromatographic point
- No refocusing required
- Trap volume:
  - Empty tubing - ~120 microliters
  - Glass bead trap – ~600 microliters
- Ethane peakwidth$_{½\ height}$: < 4 sec

Accurate Measure of Sample Volume

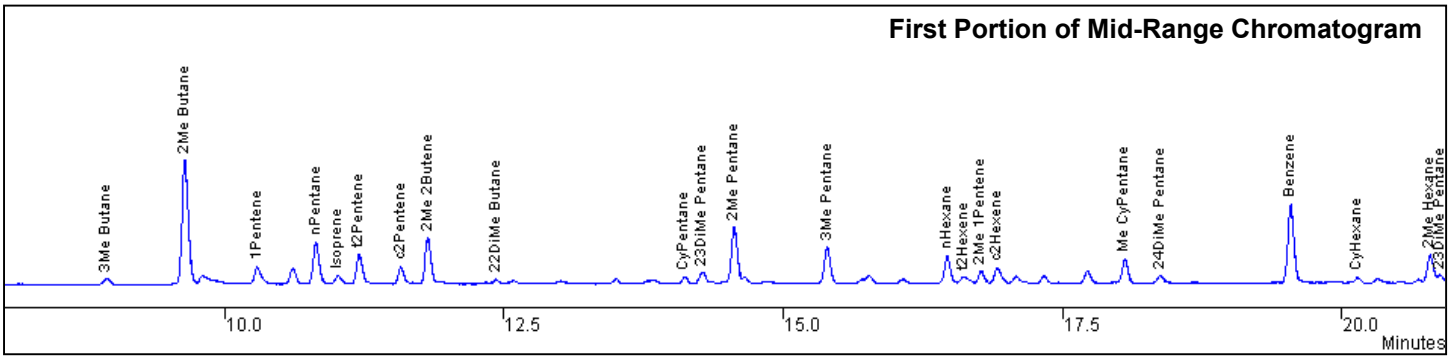
- Sample flow to vent just before trapping
  - Stabilizes MFC
  - Sweeps sample lines with new sample
- Volume-measuring flow path swept with nitrogen prior to trap heating
- Accurate volumes from 25 ml to 2400 ml
- Sample pressure can be below atmospheric and still maintain proper loading
- Sample loading independent of canister pressure

High Concentrations of CO2

- 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 100 ml
  - Multiple loadings to trap for larger volumes
  - Full recovery of all hydrocarbons
  - Accurate measure of sample volume - even mixtures

Water Treatment

- Nafion dryer effective for all hydrocarbons on PAMS list
  - Allows full recovery of both light-ends and heavies
- Bypass of dryer
  - Restricts large sample volumes (<100 ml)
  - Allows full recovery, including very polar compounds



…AND MORE SOLUTIONS

Minimal Carry-over

- Nafion dryer, sample pressure regulator and trap continuously purged with nitrogen when sample not loading
- Sample lines swept to vent with new sample just before trapping
- Carry-over « 0.1 %

Maximizing Detection Sensitivity

- Nitrogen make-up for FID
- 0.01" flame tip
- Sharp chromatographic peaks
- FID sensitivity - < 2 pgC/sec

Lowering Detection Limits

- Maximized sensitivity – larger peaks
- Low detector noise (< 2 X 10^{-14} amperes)

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
- Sample lines purged to vent prior to loading
- Measuring flow path swept with nitrogen prior to trap heating
- Typical area reproducibility - < 3 %

Effective Column Switching

- Pre-column performs retention of residual water and light-end column protection from mid-range compounds
- Suggested column/valve configuration minimizes flow/pressure disruptions at switch
- No pressure/flow "tuning" required around switch

Proper Introduction of Surrogate/ Internal Standard

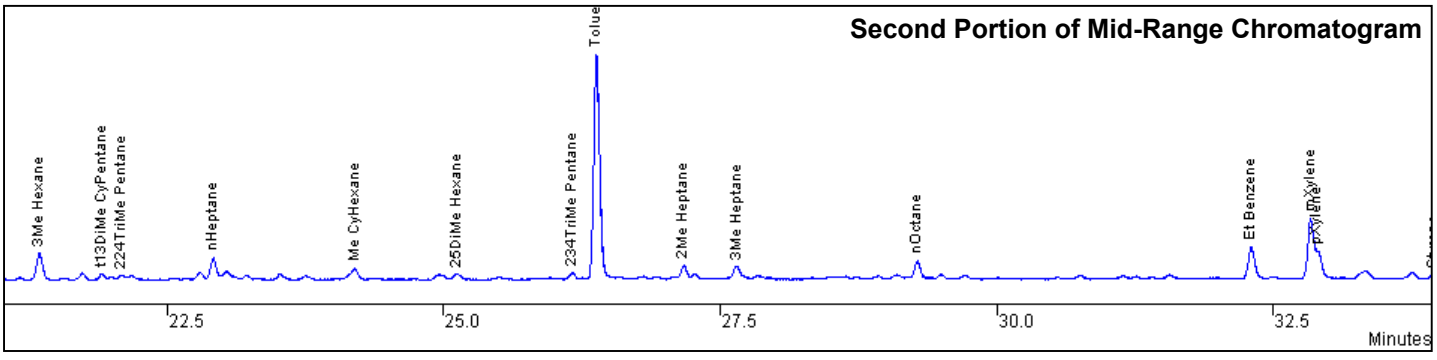
- Fixed volume sample loop
- Loop comes to atmosphere before injection
- Loaded onto trap as trap is purged

Monitoring of Operations

- True electronic **flow** control for columns – not pressure control
  - Generated backpressure becomes a diagnostic
  - Flow remains constant without computations/fudging, even with column switching
- Both analog gauges and digital displays for column pressure
- Flows/pressures documented in results report
- Optional recording of MFC flows and reporting of sample volume
- Sample line leak test documentation
- Visual indication of sample loading
- Complete system status with developing chromatograms on one screen
- User-specified temperature limits for all thermal zones

Data Processing

- Single stored data file contains raw chromatographic data for both detectors, both final reports, run method including trap parameters, stream position, run log and error messages
- Data collection, report generation, system control, custom report and StarFinder operate in Windows 95, 98, NT and 2000.
- Maximum data collection rate: 40 Hz for each channel
- 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
- File names can be labeled with sample id, injection date/time and module source as variables



Specifications

Concentrator Trap

- 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 internal volume: ~120 microliters – empty tubing
  ~600 microliters – glass beads
- 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; Optional: 31-position
- Micro-electric actuation, self-aligning
- Independently controlled valve oven, mounted in canister tree (optional); heated transfer line to GC
- Maximum temperature limit: 350 °C
- Position documented in final report and archived with data

Valving

- Fully automated under time-programmable control of GC
- Valves mounted in heated enclosures
- Micro-electric actuation, easy realignment
- Most valves - Valco Series CWT;
  maximum temperature: 350 °C
- Column switching valve - Valco Series NWE; mounted in column oven; maximum temperature: 225 °C
- Valves can be turned on/off 21 separate event times within single method
- Automatic addition of surrogate/internal standard

Recommended Column Configuration

- Stripper: J&W DB-1, 0.32mm ID, 15 m (or equivalent)
- Light-end: Varian Chrompak Alumina-SO_4, 0.32mm ID, 50 m
- Mid-range: J&W DB-1, 0.32mm ID, 60 m (or equivalent)
- All columns operating under identical temperature programming
- Column switch occurs at Methyl Butane

System Performance

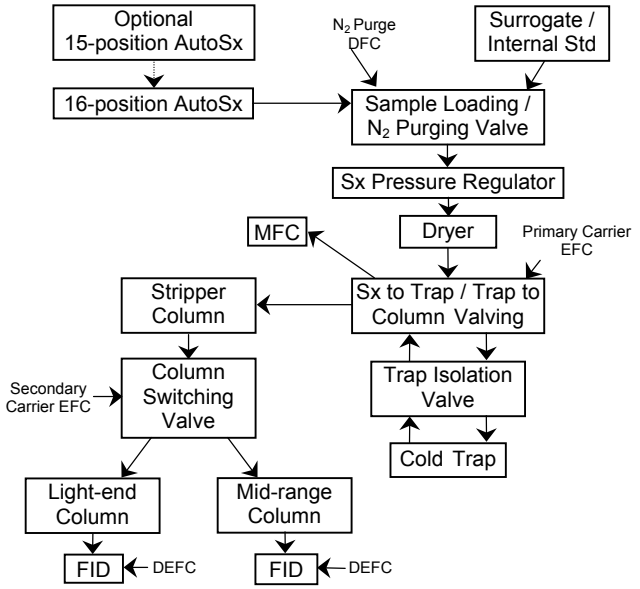
- Detection limit: < 0.2 ppbC for all hydrocarbons
- Typical linearity: R^2 > 0.99995 from 1.4 to 250 ppbC
- Concentration reproducibility: < 3% at 10X detection limit
- Sample carry-over: < 0.1%
- Retention time reproducibility: < 0.03 minutes

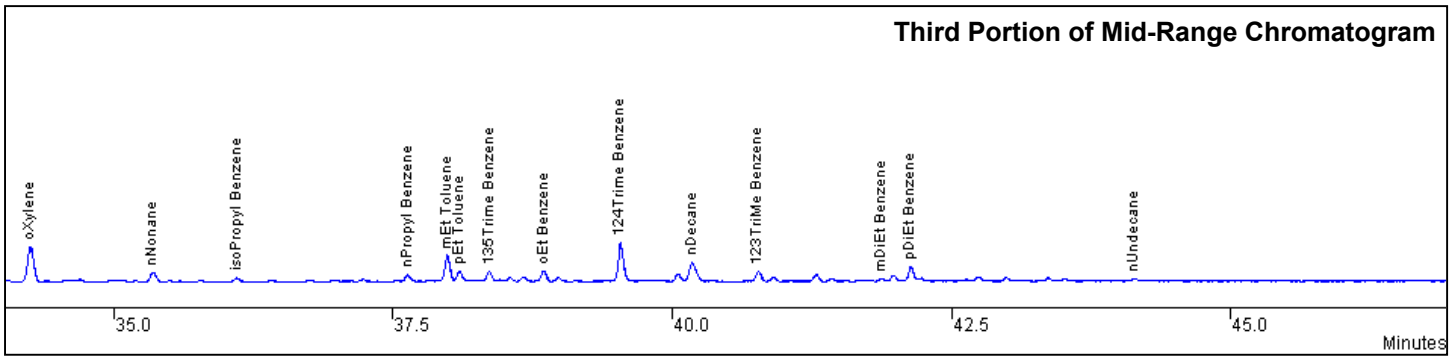
Pneumatics

- All column flows use Electronic Flow Controllers (EFC)
- Detector flows for H2, make-up and air controlled with Detector Electronic Flow Controllers (DEFC)
- Temperature-sensitive flow elements maintained at 45 °C
- Flows automatically adjusted for atmospheric pressure

Detectors

- FID Noise: <2 X 10^{-14} amperes
- FID sensitivity: <2 pgC/sec
- Typical response factor: 2700 µV·sec/ppbC for 300 ml sample
- Electrometer time constant: 50 msec
- FIDs mounted in independently controlled oven
- Maximum temperature: 450 °C





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