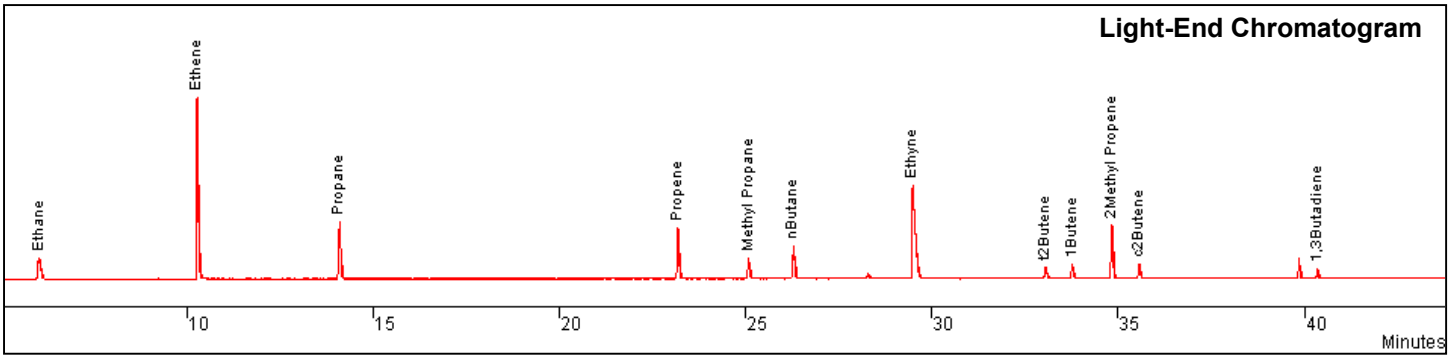
Micro Trace Hydrocarbon System (MTHS)

The Micro Trace Hydrocarbon System from Lotus Consulting provides impressive separations of trace hydrocarbons in vehicle exhaust samples. The system features two Varian 3800 Gas Chromatographs with built-in high performance sample concentrators and dual 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 California Air Resources Board SOP No. MLD 1002 and 1003 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 (400 ml injection). Samples are loaded through a 16-position automated sampler and trapped onto two separate low-volume cold traps, with a fixed volume sample loop setting the sample size. All major hydrocarbons from Ethane to n-Heptane are fully resolved to baseline on a narrow-bore PLOT column; water and heavy hydrocarbons are kept from the PLOT with a stripper column. The heavy hydrocarbons are separated via a non-polar narrow-bore column in the second column oven. Quantitation is performed with two flame ionization detectors; peak identity of most olefins and aromatics can be confirmed with optional in-series photo-ionization detectors; all peaks can be identified with on-line mass spectrometer for simultaneous detection with FIDs and MS without sample splitting.

Full speciation of hydrocarbons in vehicle exhaust 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 four cold traps, at least 9 automated valves, 16-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 and glass beads for traps
  - No thermal breakdown products
  - Maximum temperature limit of 450 °C
- All valves are heated; limited to 350 °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 temperatures (< ±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 switching valve
  - 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
  - Sweeps sample lines with new sample
- Volume-measuring flow path swept with nitrogen prior to trap heating
- Excess sample pressure is always released to achieve atmospheric pressure in loop
- Sample loading independent of canister pressure or Tedlar bag use

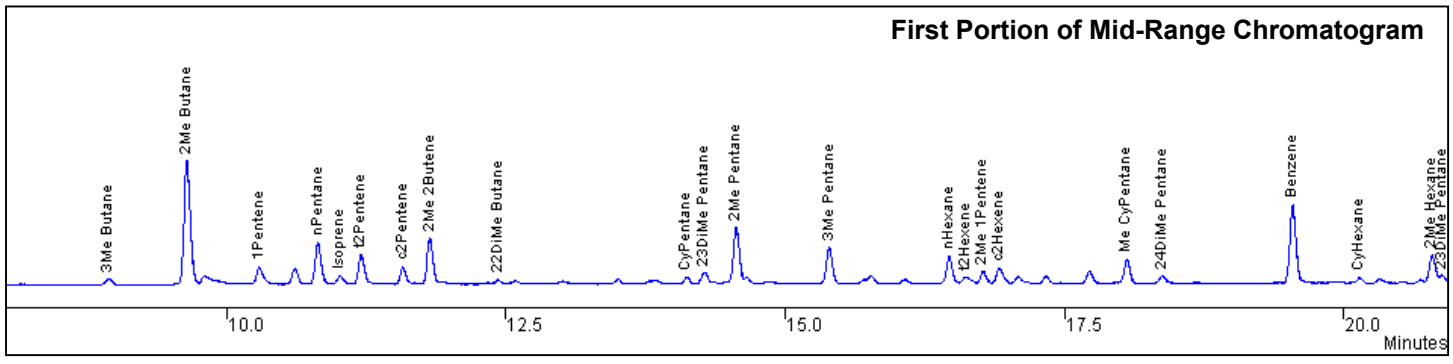
High Concentrations of CO2

- Fixed volume sample loop to 400 ml
  - Volume not altered by CO_2 concentration
  - Multiple loadings to trap for larger volumes
  - Full recovery of all hydrocarbons
  - Accurate measure of sample volume - even mixtures of bulk gas mixtures

[Note: Mass Flow Controllers (MFC) not accurate with major portions of CO_2
- MFC usually calibrated for air; cannot handle gas mixtures properly
- 50% CO_2 sample yields **double** the sample volume!!]

Water Treatment

- Water is kept off of PLOT column with a megabore stripper column mounted in separately controlled oven
- Nafion dryer is installed in mid-range measurement to prevent water blocks at column



…AND MORE SOLUTIONS

Minimal Carry-over

- Nafion dryer and traps continuously purged with nitrogen when sample not loading
- 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 with computed flow
- Reproducible + accurate control of column oven temperature
  - proportional control (PID)
  - platinum probe (RTD)
- Typical RT reproducibility - < 0.03 minutes

Quantitation Reproducibility

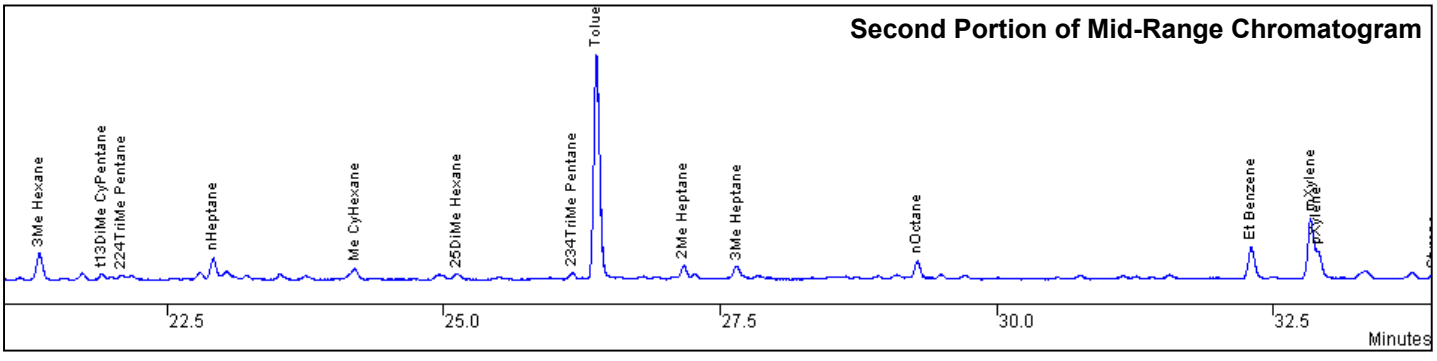
- Column leaks detected with pressure monitoring
- Sample lines purged to vent prior to loading
- Measuring flow path swept with nitrogen prior to trap heating
- Typical area reproducibility - < 3 %

Monitoring of Operations

- True electronic **flow** control for columns – not pressure control
  - Generated backpressure becomes a diagnostic
  - Flow remains constant without computations/fudging
- Both analog gauges and digital displays for column pressure
- Flows/pressures documented in results report
- Visual indication of sample loading
- Complete system status displayed 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

- 16-position with sample lines heated
- 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 CWE;
  maximum temperature: 225 °C
- Valves can be turned on/off 21 separate event times within single method

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

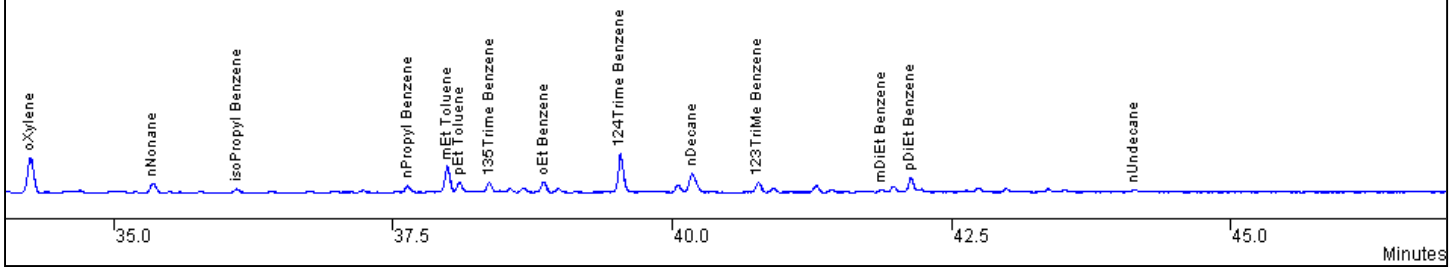
Pneumatics

- All analytical 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: 3500 μV·sec/ppbC for 400 ml sample
- Electrometer time constant: 50 msec
- FIDs mounted in independently controlled oven
- Maximum temperature: 450 °C

Third Portion of Mid-Range Chromatogram



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