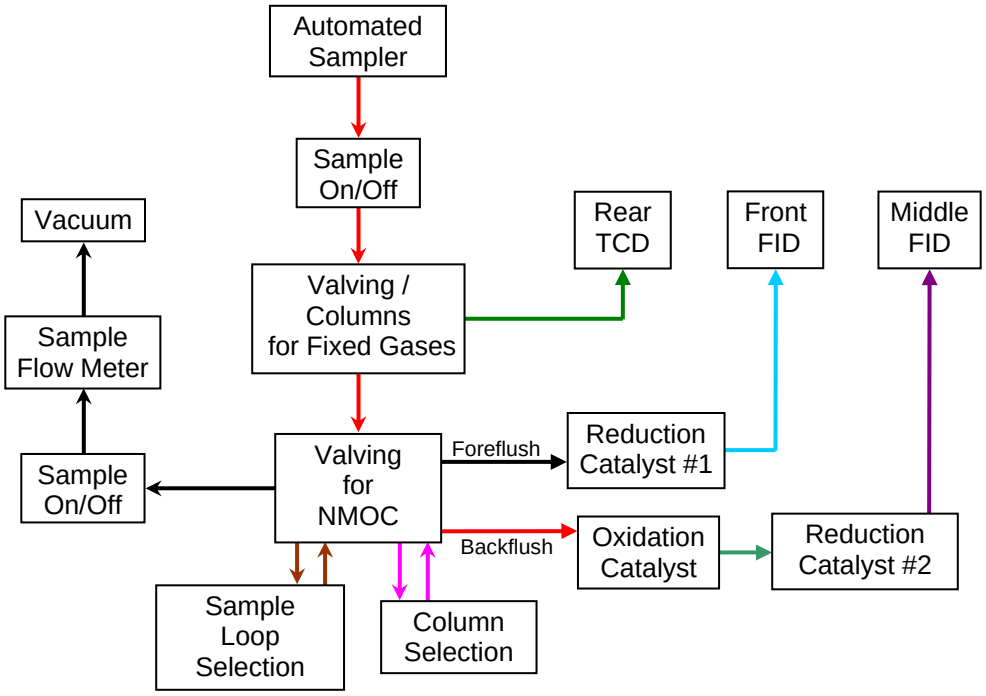
NON-METHANE ORGANIC CARBON ANALYZER (NMOC – Method 25)

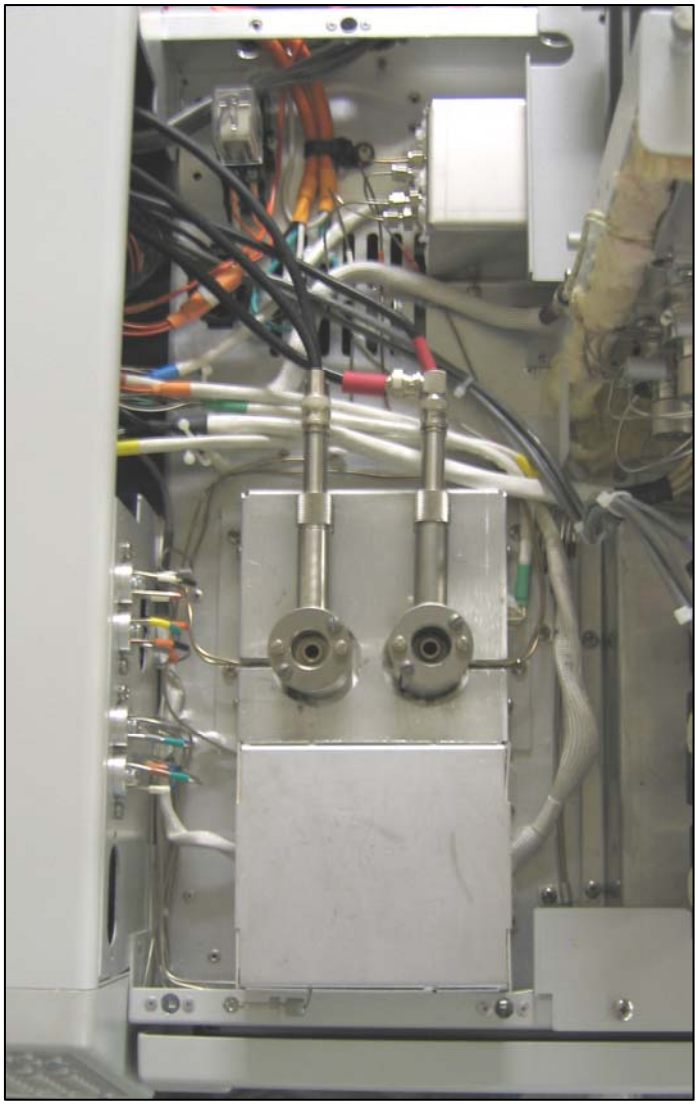
The Non-Methane Organic Compounds (NMOC) Analyzer is a gas chromatograph configured for analyzing gaseous samples for total organic carbon content, detected as Methane. The system is designed to determine concentrations of Methane, Carbon Dioxide, Carbon Monoxide, Ethane/Ethane, and all organics from Propane and heavier as a single peak. Additional hardware is configured to measure Fixed Gases (including Oxygen, Nitrogen, Hydrogen, Carbon Monoxide, and Methane). The methodology employed in this analyzer meets the requirements of both EPA Method 25 and South Coast Air Quality Management District Method 25.3.

The system is based on the Scion 456 Gas Chromatograph and takes advantage of virtual every feature available on the instrument. Three detectors are installed and fully operational at all times. Valves are mounted in two heated valve ovens controlled through the instrument.

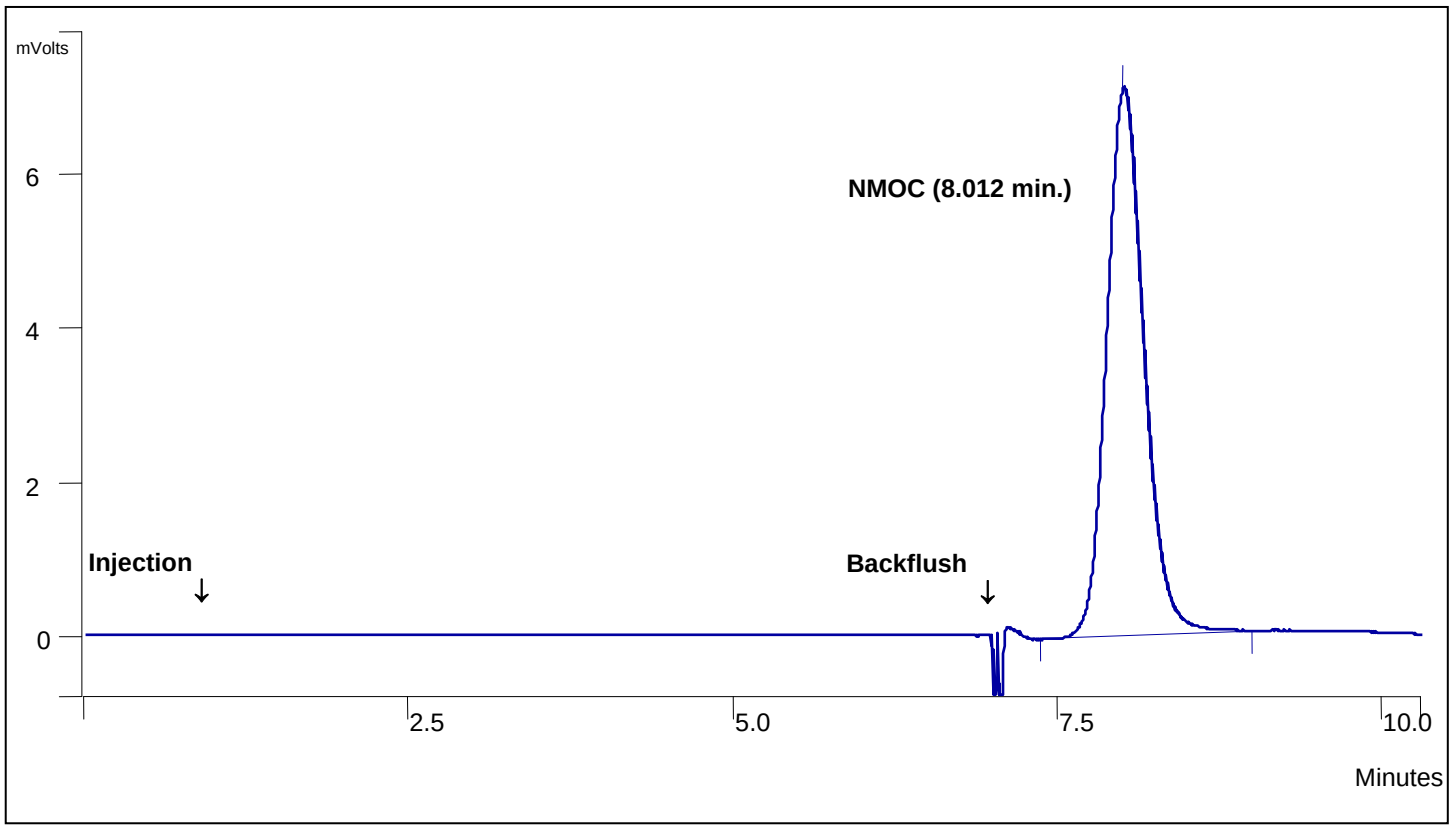
An automated sampler is controlled through special software with Scion Workstation. The sample position is user-specified in the Star SampleList with each sample line. The order is not mandated; samples can be examined in any order and even repeated later in the sequence. The sampling position is documented in the MessageLog and can be listed through a Final Report along with the final results.



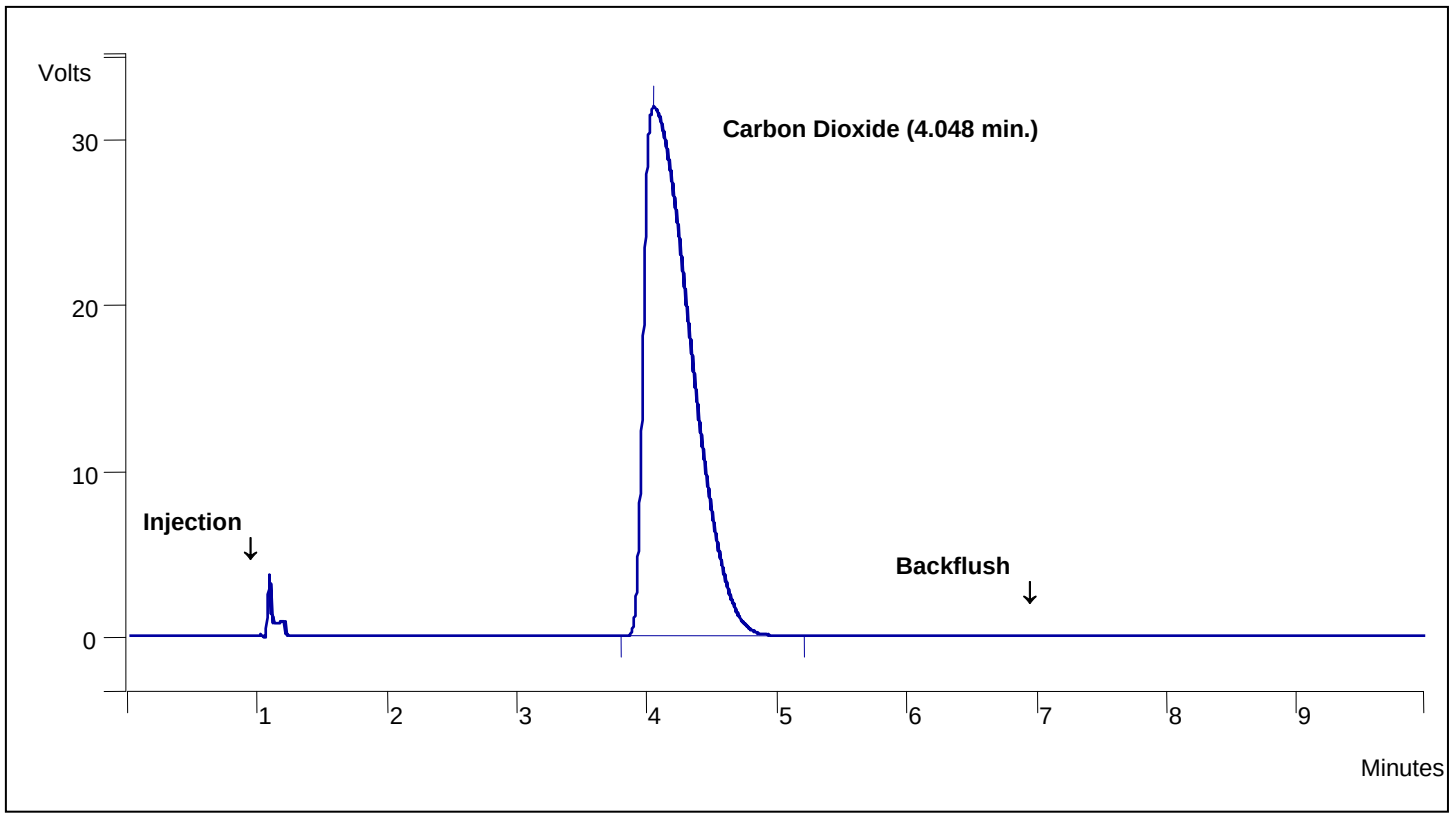
Principles of operation for NMOC are quite straightforward. The sample is introduced into a fixed volume sample loop. This sample aliquot is then directed to a column set designed to retain all components from Propane and heavier (C_3+). The "light" components (Methane, Carbon Dioxide, Carbon Monoxide, and Ethanes) are allowed to pass through the column set in the forward direction. These light-end components are then passed to a reduction catalyst to convert Carbon Monoxide and Carbon Dioxide to Methane and then on to the Front Flame Ionization Detector for detection and quantitation of all these components. The heavy components (C_3+) are backflushed off of the holding column, passed through an oxidation catalyst to convert all organic compounds to Carbon Dioxide, through a second reduction catalyst to create Methane, and on to the Middle Flame Ionization Detector for detection and quantitation of C_3+ as a single total concentration.



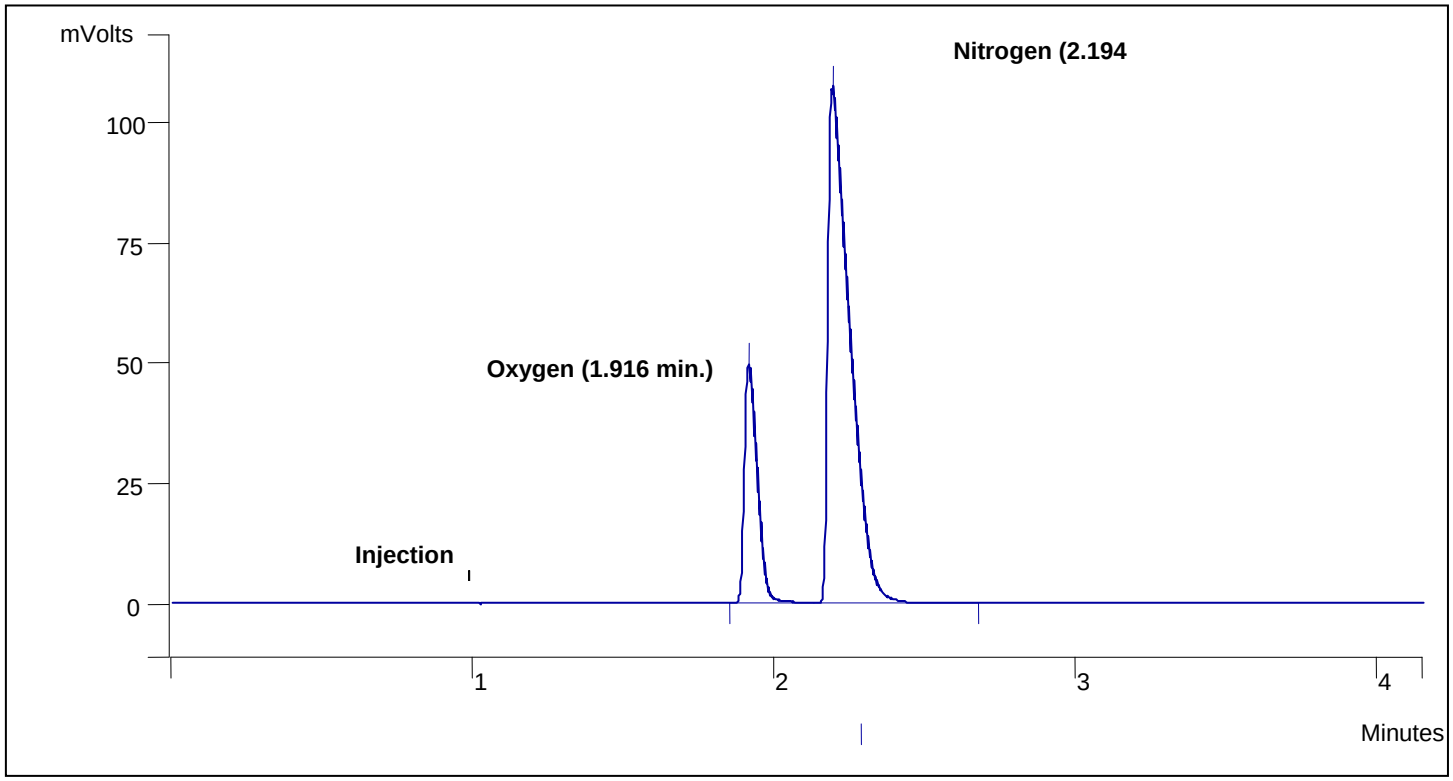
Major concentrations of Carbon Dioxide remain problematic, even with the modifications added to the standard methods. The tail of the Carbon Dioxide peak can still linger within the interconnecting tubing after the column set and contribute improperly to the non-methane measurement. To minimize this problem, paths for the foreflush and backflush are isolated after the column. The foreflush flow is directed to a reduction catalyst and the Front Flame Ionization Detector. Carbon Dioxide can be quantified with this chromatogram. The backflush flow goes to an oxidation catalyst, to a second reduction catalyst and finally to the Middle Flame Ionization Detector. Once Carbon Dioxide exits the column set in the foreflush, it cannot contribute to the non-Methane quantitation in the backflush as the two paths are completely separated. The backflush occurs after the foreflush elution of the Ethanes. The Ethanes are measured separately and can be mathematically added to the C_3+ result.



NMOC chromatogram of 89 ppmC Propane. Column temperature – 100 ^{o}C, ramped to 150 ^{o}C @ 7 minutes ; injection volume – 1.0 ml; blank baseline subtracted



Foreflush chromatogram of 15% Carbon Dioxide. Column temperature – 100 ^{o}C; injection volume – 1.0 ml; blank baseline subtracted.



TCD chromatogram of Room Air. Column temperature – 100 ^{o}C; injection volume – 250 μl; detector – TCD. Baseline is not subtracted.

SPECIFIC ENHANCEMENTS WITH LOTUS CONSULTING NMOC ANALYZER

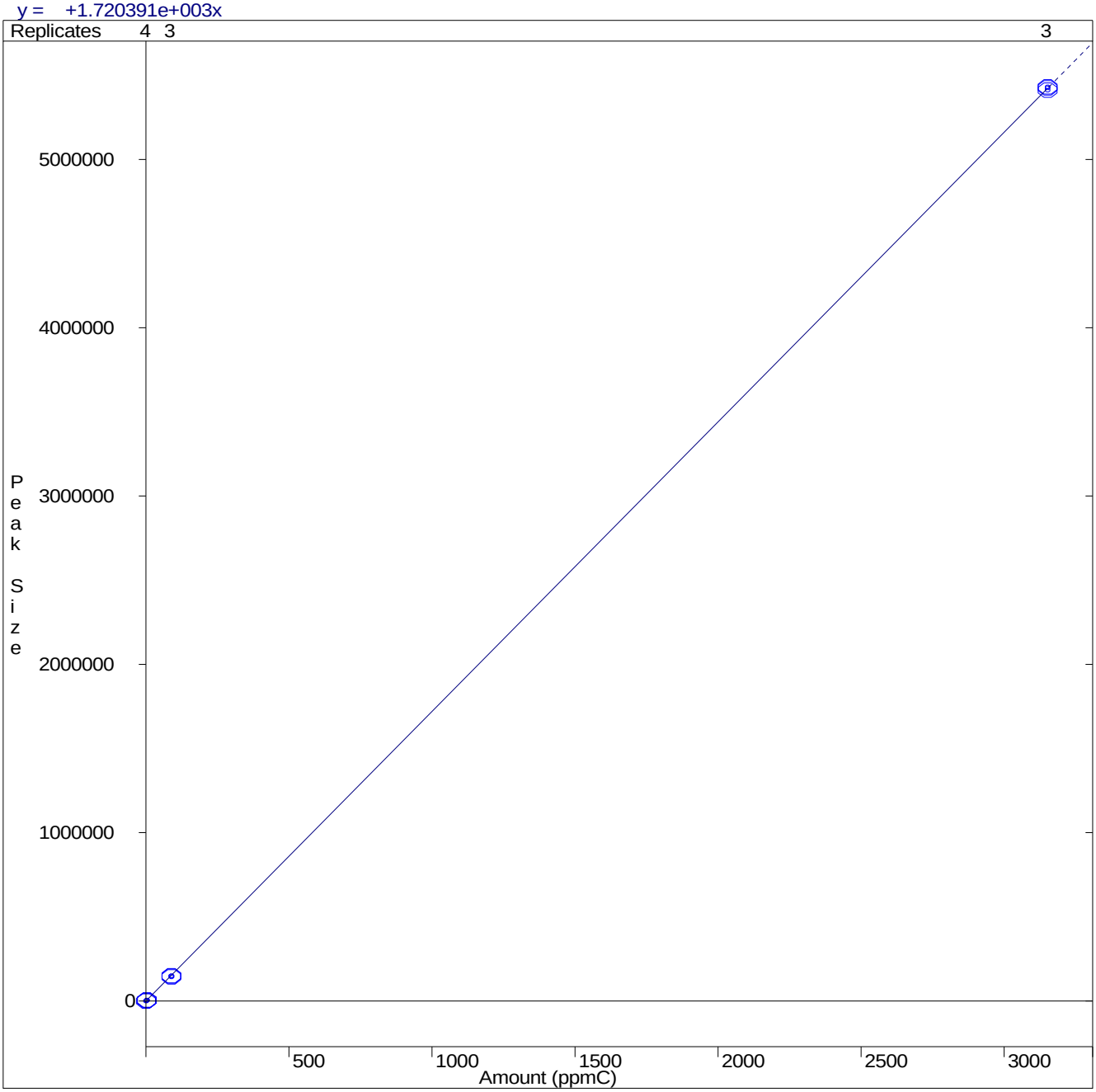
- **Dual Flame Ionization Detectors** - after separation of CO2 from NMOC with the analytical column, the two sample streams are kept apart by directing flows to two Flame Ionization detectors.
- **Simultaneous Operation with Thermal Conductivity Detector** - for measurement of fixed gases, including Oxygen, Nitrogen, Carbon Monoxide and Methane.
- **Dual, Independent Flows for NMOC Carrier Gases** - permits faster flow for backflush resulting in sharper peaks and faster analysis.
- **Dual Reduction Catalysts** - after separation of CO2 from NMOC with the analytical column, the two sample streams are kept apart by directly flows to two separate reduction catalysts.
- **Oxidation Catalyst on Backflush Only** - foreflush components (CH4, CO and CO2) need not be oxidized as their response with Reduction Catalyst and FID correctly accounts for all of their carbons.
- **No Oxygen In-Line with Oxidation Catalyst during Normal Operations** - Chromia/Alumina is fully efficient without constant recharge during operations, especially with NMOC below 50 ppmC. Too much Oxygen into reduction catalyst can greatly interfere with the reduction process.
- **Included Automated Valving to Facilitate Recharge of Oxidation Catalyst with Air**.
- **Appropriate Valving to Easily Check Catalysts Performance,** as required in methods.
- **Automatic Doses of Air to Both Reduction Catalysts** at start of run to eliminate carbon build-up on catalysts.
- **Two Valves with Balancing Restrictors for backflush operations** - better valving operation than the valves setup indicated in the SCAQMD method. Restrictors greatly improved baseline upsets during valve actuations and provide better maintenance of flows through the scheme.
- **Operation of EPA Method 25 or SCAQMD 25.3 without hardware changes** - appropriate columns are selected by an automated column switching valve.
- **Enhanced Detection by Automatically Selecting One of Two Sample Volumes Without Hardware Changes.**
- **Pressure Regulators Plumbed in Parallel with Flow Controllers** - pneumatic configuration greatly improved baseline upsets during valve actuations and provide better maintenance of flows through the scheme.
- **Flame-out/Reignition and Balancing Restrictors Reduce Need for Flame-out Restrictors** - reduces peak broadening; sharper NMOC improves detection.
- **Argon Carrier for NMOC** - results in accurate measure Oxygen concentration as Argon in sample is not detected with Thermal Conductivity Detector. Argon carrier yields larger FID response (factor of 2 over Helium) for better detection of NMOC.
- **Columns Filled to Ends** - minimizes peak broadening due to dead volume; sharper NMOC improves detection.
- **High levels of Carbon Dioxide accurately reported** - with an additional gas sampling valve with a small 100 µL sample loop.

Calibration Curve Report
File: c:\... \chromatograms\4-9-00 10;30;07 24.78 ppmc toluene-middle.mth
Detector: 3800 GC, Address: 44, Channel ID: Middle

C3

External Standard Analysis
Curve Type: Linear
Origin: Force
y = +1.720391e+003x

Resp. Fact. RSD: 3.266%
Coeff. Det.(r^2): 0.999996



Typical linearity for multipoint calibration with Propane.
Injection volume: 1.0 ml.

Specifications

NMOC

Injection Volume: 3 ml, 1 ml or 0.1 ml, method selectable by automated valving

Detection Limit: < 0.1 ppm C (3 ml loop)

Linear Range: < 1 ppm C to > 50,000 ppm C (within +/- 5% of linearity)

Area Reproducibility – typically < 2% RSD (when >10X detection limit)

Calibration Reproducibility – typically < ± 3%

Typical Recovery of Hexane: > 99%

Typical Recovery of Acetone: > 80%

Typical Recovery of Benzene: > 99%

Typical Recovery of Toluene: > 98%

Oxidation Catalyst – proprietary material, similar to Chromia/Alumina

Typical Oxidation Catalyst Efficiency: > 99%

Dual Reduction Catalysts – 10% nickel nitrate coated on Chromosorb GAW, 100/120 mesh, 3 cm by 1/8" OD nickel tubing in oven controllable by the gas chromatograph to 450 °C

Typical Reduction Catalyst Efficiency: > 95%

Columns –

EPA Method 25 - 0.3 meter Unibeads IS, 60/80 mesh, in 1/8" OD stainless steel tubing; and 0.6 meter Carbosieve G, 60/80 mesh, in 1/8" OD stainless steel tubing.

SCAQMD 25.3 – 0.3 meter Tenax GC, 80/100 mesh in 1/8" OD stainless steel tubing; and 2 meters Chromosorb 106, 80/100 mesh in 1/8" OD stainless steel tubing.

Column Switching – column sets are method selectable by automated valving

Fixed Gases

Injection Volume: 250 µl

Detection Limit – O_2, N_2, – <10 ppm V/V; CO, and CH_4 – <1 ppm

Linear Range: <10 ppm V/V to 100% V/V

Columns – Hayesep N, 60/80 mesh, 6' X 1/8" SS plumbed as foreflush/backflush to vent, and Molecular Sieve 5A, 45/60 mesh, 6' X 1/8" SS.

Miscellaneous

Detectors – Flame Ionization Detector, 2 each; Thermal Conductivity Detector.

Electrometers – Two each included, with single range from 100 μVolts full scale to 1000 Volts full scale with Star Workstation.

TCD Electronics – 20X amplification of signal, constant mean-temperature filaments, filament protection circuit.

Carrier Gas Flows – Primary carrier flow for Fixed Gases is controlled with Electronic Flow Controllers Type 3. All column carrier gases for NMOC controlled by Electronic Flow Controllers plumbed in parallel with Pressure Regulators. Other flows are set with Digital Flow Controllers. Most pressures for carrier gases are displayed on gauges visible from front of instrument.

Detector Gases Controls – Two FID Detector Electronic Flow Controllers for FID air, FID hydrogen and catalyst hydrogen, and one TCD Detector Electronic Flow Controller for both make-up and TCD reference.

Sample Introduction – Tedlar™ bag, pressurized canister or gas-tight syringe (for fixed gases only) all standard and fully operational with no hardware changes; Multi-position Automated Sampler (up to 16 positions) with micro-electric actuation and control through Star Workstation included.

Valving – All valves are high performance, low volume design by Valco Instruments and all valves involved in chromatography are heated.

Valve Actuation – All valves utilized in routine operation are fully automated under timed control of the gas chromatograph with micro-electric actuation.

Temperature Probes – All temperature zones within the gas chromatograph monitored with self-calibrating Platinum Probes and controlled with Fully Proportional Heating.

Flameout-Sensor – A continuous internal monitor to provide an error message if the Flame Ionization Detector suffers a flameout. When the error occurs, reignition is attempted three times and the system is prohibited from coming to “Ready” until reignition occurs.

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