Investigation of Gaseous Pollutant Transport Efficiency as a Function of Tubing Material

Study Design and Experimental Results

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Reinventing tomorrow.

Agenda

Background

- General information regarding Reference and Equivalency Program
- Information regarding the study

Study

- Study Goals
- Experiment setup
- Results

Summary

- Recommendations

Background

- Reference and Equivalent Methods Designation Program
  - The Equivalency Program has assumed the responsibility of technically interpreting:
    - 40 Code of Federal Regulations (CFR) Part 50, Appendixes A, B, C, D, F, G, J, and L
    - 40 CFR Part 53
    - 40 CFR Part 58, some provisions of Appendix C
    - The Program may also share, with Office of Air Quality Planning and Standards (OAQPS), in joint responsibility for some related provisions of 40 CFR Part 58, Appendixes A and C.

  - The Equivalency Designation Program operates out of the Office of Research and Development (ORD).
  - The program utilizes professional researchers, Quality Assurance staff and Quality Assurance Project Plans (QAPP) to ensure that research is performed with scientific integrity.
    - Task Order R-20F0311 under the Research Laboratory Support Contract with Jacobs Technology, the on-site contractor for US EPA allows the EPA to utilize independent researchers allowing autonomy from results.

Background Continued

- Reference and Equivalency Designation Program has been receiving inquiries regarding the use of alternative materials regarding 40 CFR, Part 58
  - 40 CFR, Part 58, Appendix E: Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring
  - Section 9: Probe Material and Pollutant Sample Residence Time
    - "...EPA has specified borosilicate glass or Fluorinated ethylene propylene (FEP) Teflon™ (or their equivalent) as the only suitable probe materials for delivering test atmospheres in the determination of reference or equivalent methods."
    - "...sampling probes for reactive gas monitors at National Core Monitoring Stations and at Nitrogen Dioxide (NO_2) sites must have a sample residence time less than 20 seconds."
- These specifications have been the guiding principles of network sampling design over the last several decades.

Background Continued

- Quality Assurance (QA) Handbook for Air Pollution Measurement Systems: Ambient Air Quality Monitoring Program, Volume II, Jan. 2017

- Section 7.3: Sampling Probes and Manifolds

  - "… EPA has specified borosilicate glass or FEP Teflon™ (or their equivalent) as the only suitable probe materials for delivering test atmospheres in the determination of reference or equivalent methods."

Background Continued

- "Questions have been asked about perfluoroalkoxy (PFA)…a newer formulated Teflon ™ than FEP…it has been accepted as equivalent to FEP Teflon™."

- Appendix F (QA Handbook): Sample Manifold Design
  - "…if the sample lines are manufactured out of polytetrafluoroethylene (PTFE), PFA, or FEP Teflon™, this is acceptable to EPA."
  - "…One manifold feature must be consistent: the probe and manifold must be constructed of borosilicate glass or Teflon™ (PFA or PTFE). These are the only materials proven to be inert to gases."

- Anecdotally
  - Region 3, Region 4, Region 9, and Clean Air Markets Division of EPA may already be using Kynar® (Polyvinylidene Fluoride [PVDF]) sampling lines in their compliance networks. Kynar® is not mentioned anywhere in 40 CFR nor in the QA Handbook.

Background Continued
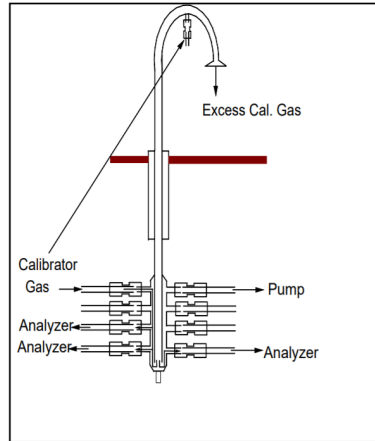
Manifold Systems
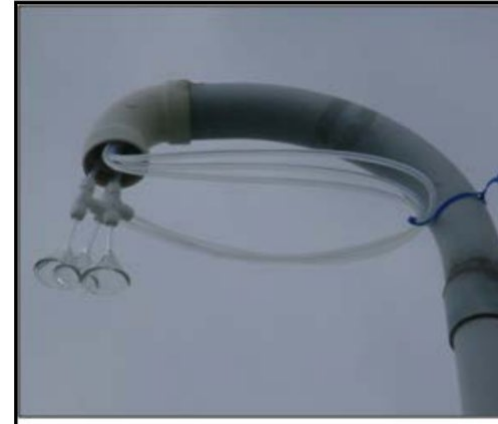
Individual Sampling Lines

- Both systems have advantages and disadvantages, but the individual sampling line systems are favored because they are straightforward and less prone to failure

- In the networks, residence times in both systems are typically 10 seconds or less

- Sample line lengths are typically 5 to 15 feet but may be significantly longer in some compliance networks and in special research studies
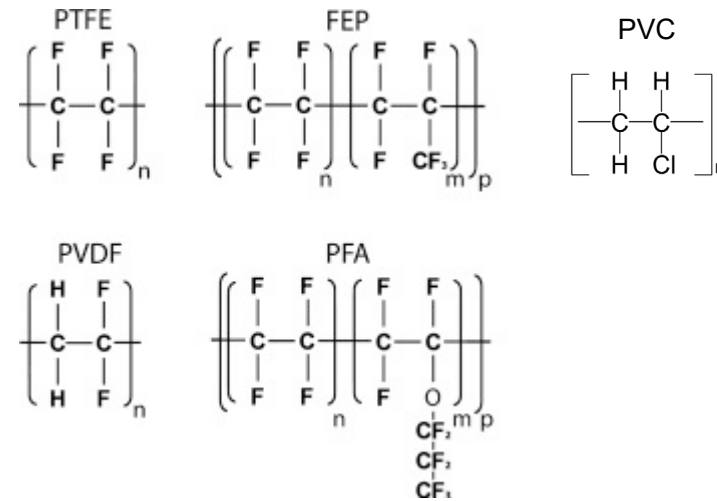
Study Goals

- **Conduct literature review**
  - Citings from the CFR and other literature pointed to testing performed on cylinder coatings as well as other environmental sampling setups
    - Not a direct comparison of materials
- Identify and purchase commercially available probe materials based on theoretical considerations and literature review
- Design experimental test setup for determining transport efficiency as a function of pollutant type for Ozone (O_3), NO_2, Carbon Monoxide (CO), and Sulfur Dioxide (SO_2)
- Determine the repeatability of the transport tests
- Determine the fractional transport efficiency versus pollutant concentration
- Conduct tests to determine the need to passivate (i.e., pre-condition) new tubing prior to its use in order to maximize pollutant transport efficiency
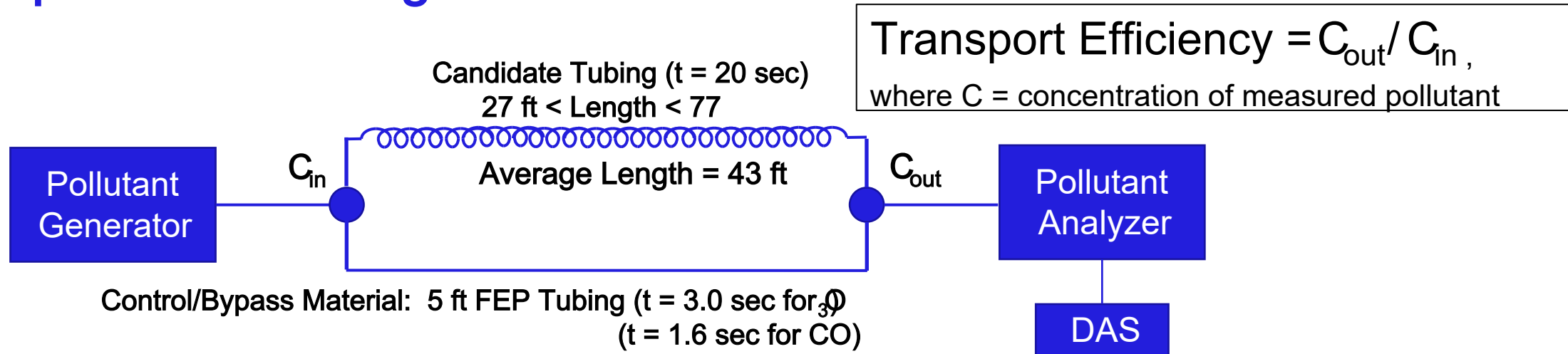
Selected Probe Materials

- Fluorinated ethylene propylene (FEP)
- Polytetrafluoroethylene (PTFE)
- Polyvinylidene Difluoride (PVDF)
- Perfluoroalkoxy (PFA)
- 316 Stainless Steel (316 SS)
- Silconert®-2000 Coated Stainless Steel
  - Internally and externally coated with a proprietary non-reactive amorphous silicon coating
- Polyvinyl chloride (PVC) Tygon® S3 Tubing

- Tubing: ¼ inch Outer Diameter (OD) and nominal 3/16 inch Inner Diameter (ID)
- For Ozone (Flowrate [Q]= 0.560 liters per minute [Lpm]),
- $L = 4*Q*time[t]/(\pi *ID^2)$, L = 34 feet (ft) to 36 ft for a 20 second residence time, depending upon exact ID.

- The 20 second residence times used during the laboratory tests were used to simulate worst-case loss conditions during field sampling.

Experimental Design

Candidate Tubing (t = 20 sec)
27 ft < Length < 77

$$\text{Transport Efficiency} = C_{out} / C_{In} ,$$
where C = concentration of measured pollutant

C_{In}

Average Length = 43 ft

C_{out}

Pollutant Generator

Pollutant Analyzer

DAS

Control/Bypass Material: 5 ft FEP Tubing (t = 3.0 sec for O_3)
(t = 1.6 sec for CO)

- Control valves are switched automatically, and data is collected by a Data Acquisition System (DAS) system
  - Each test takes roughly 1 hour to complete
  - A test contains multiple rounds of valve switching and reading to ensure that the gas is at the target concentration in the bypass material

- 3 replicate tests were each conducted at 20%, 50%, and 120% of the NAAQS value. For O_3, this equated to test concentrations of 15 parts per billion (ppb), 35 ppb, and 85 ppb, respectively.

- Each test was conducted using new tubing (unconditioned). In addition, ozone line loss tests were conducted using new tubing conditioned with ozone at 450 ppb for 1 hour prior to testing.

- Acceptance criteria were based on those of the National Performance Audit Program (NPAP) ozone line loss test:

  Maximum acceptable transport loss = 2.5% (i.e., minimum 97.5% transport efficiency)

Experimental Design

Wait….Did you just say that your experimental matrix includes 7 different tubing, 3 replicates, 3 concentrations and 4 gases?

Yes…it did…don't forget conditioning experiments as well….

- Tubing required for ozone tests (L = 34 to 36 ft):
  - For 7 tubing materials x 3 replicates x 3 test concentrations x 2 testing conditions = 4,488 ft = <u>0.85 mile</u>

Pollutant	Flow Rate (Lpm)	Required Tubing Length (miles)
O_3	0.560	0.85
SO_2	0.470	0.71
CO	1.026	1.55
NO_2	0.900	1.36
		Total = 4.5 mile

Total Tubing Cost = $71,000 (United States Dollars)

Time required ~10.5 months

FEP Test Results - Ozone

Material	Conc. (ppb)	Transport Efficiency, %	
		Unconditioned	Conditioned
	15	99.7	100.5
		97.7	99.9
		97.6	99.5
		98.4	**99.9**

- Transportation efficiencies are the average of the 3 replicates at each concentration
- Residence time of 20 seconds

- Test results confirm FEP's high ozone transport efficiency as well as confirming the CFR's requirement to use FEP and/or borosilicate glass.

Test Results- Ozone

Material	Conc. (ppb)	Transport Efficiency, %	
		Unconditioned	Conditioned
316 SS ($164 United States Dollars [USD] per 100 ft)	15	-0.31	0.13
	35	-0.29	-0.01
	85	-0.15	-0.15
	Mean	-0.25	-0.01
Silconert®-coated SS ($1,009 per 100 ft)	15	-0.06	68.0
	35	-0.49	87.2
	85	9.4	92.4
	Mean	2.95	82.5
Tygon® ($56 per 100 ft)	15	3.93	0.09
	35	8.57	-0.15
	85	19.59	0.17
	Mean	10.7	0.04

⬅ No Change!

⬅ Dramatic Improvement!

⬅ Got worse!

Test Results – Ozone, continued

Material	Conc. (ppb)	Transport Efficiency, %	
		Unconditioned	Conditioned
FEP ($280 per 100 ft)	15	99.7	100.5
	35	97.7	99.9
	85	97.6	99.5
	Mean	**98.4**	**99.9**
PTFE ($185 per 100 ft)	15	97.2	99.0
	35	97.2	98.7
	85	97.5	98.9
	Mean	**97.3**	**98.9**
PVDF ($182 per 100 ft)	15	94.5	99.4
	35	95.1	99.4
	85	95.2	99.0
	Mean	**95.0**	**99.3**
PFA ($317 per 100 ft)	15	94.2	99.1
	35	99.0	99.0
	85	95.3	99.6
	Mean	**96.2**	**99.2**

All four increased beyond 97.5% threshold utilizing a conditioning step.

Test Results, remaining gases

Tubing Material	Mean Transport Efficiency for 20 Second Residence Time (%)				
	SO_2 (Unconditioned)	SO_2 (Conditioned)	NO_2 (Unconditioned)	NO_2 (Conditioned)	CO (Unconditioned)
FEP	100.6	99.8	98.7	99.8	100.1
316 SS	3.0	77.0	-0.7	40.1	99.5
Silconert®-Coated SS	100.1	-	95.6	98.5	100.1
Tygon®	88.9	87.7	79.9	85.1	100.4

Even with conditioning, the 316 SS and Tygon® tubing were unacceptable materials for SO_2 and NO_2 transport. Silconert®-coated SS displayed acceptable performance although conditioning was required when measuring NO_2.

Test Results, remaining gases

Tubing Material	Mean Transport Efficiency for 20 Second Residence Time (%)		
	SO_2 (Unconditioned)	NO_2 (Unconditioned)	CO (Unconditioned)
FEP	100.6	98.7	100.1
PVDF	100.0	99.4	100.5
PTFE	100.4	99.2	99.6
PFA	100.5	99.1	100.3

Fluoropolymer tubing performed exceptionally well for the remaining reactive gases, even without conditioning.

Summary of Fluoropolymer Tubing Performance

Tubing Material	Mean Transport Efficiency for 20 Second Residence Time (%)				
	O_3 (Conditioned)	SO_2 (Unconditioned)	NO_2 (Unconditioned)	CO (Unconditioned)	Average
FEP	100.0	100.6	98.7	100.1	99.9
PVDF	99.3	100.0	99.4	100.5	99.8
PTFE	98.9	100.4	99.2	99.6	99.5
PFA	99.2	100.5	99.1	100.3	99.8
Fluoropolymer Average	99.4	100.4	99.1	100.1	

Summary

- Ozone was the most reactive of the Criteria gases and conditioning with 450 ppb ozone for 1 hour was required to obtain maximum transport efficiency. The 3 candidate fluoropolymers (PVDF, PTFE, and PFA) displayed transport efficiencies close to that of FEP. Even with conditioning, there was zero transport efficiency of ozone through 316 SS and Tygon®. Ozone losses through Silconert®-coated SS improved with conditioning but not to an acceptable degree.

- Transport efficiency of SO$_2$ was acceptably high for all tubing materials except for 316 SS and Tygon®. Losses through these materials were not acceptable following their conditioning.

Summary continued

- For NO_2, the 3 candidate fluoropolymers displayed transport efficiencies close to that of FEP. Even with conditioning, there was zero transport efficiency through 316 SS and Tygon®. NO_2 losses through 316 SS and Tygon® improved with conditioning but not to an acceptable degree.

- The transport efficiency of CO was acceptably high for all tubing materials

Repeatability

- With the exception of 316 Stainless Steel, Silconert®-coated Stainless Steel, and Tygon®, replicate test results showed that tests were generally quite repeatable under the same test conditions.

- The three candidate fluoropolymers (PVDF, PTFE, and PFA) displayed high transport efficiency independent of criteria gas and pollutant concentration. Repeatable results were obtained for these fluoropolymers during 3 replicate tests for each tubing type and concentration.

Recommendations

- Based on the results of this study, ORD recommends that Part 58 Appendix E Section 9 be revised to add PVDF, PTFE, and PFA as approved probe materials to the currently approved borosilicate glass and FEP Teflon materials.

- Test methods, results and recommendations will be available in EPA Report EPA/600/R-22/166 once approved.

Any Questions?

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Thank you for your attendance!

Supporting Materials – Literature Search

▪ 1. Altshuller et al. (1961), 2. Hughes (1975), 3. Wechter (1976), and 4. U.S. EPA (1971) *Field Operations Guide for Automatic Air Monitoring Equipment*, No. APTD-0736, Research Triangle Park (RTP).

1. Experiments from Altshuller (et al. 1961) indicated that Teflon® and glass tubing were the most satisfactory materials to use in O_3 sampling. Stainless steel and polyethylene tubing were less satisfactory and polyvinyl chloride (PVC) tubing was considered unsatisfactory.

2. Hughes (1975) provided the standard preparations and overview of the storage pollutant reference standard gases and the proper types of cylinders to use for the storage of these gases. Hughes also investigated Teflon® permeation tubes and other reference gases including NO_2 and SO_2. The materials described in the Hughes article provided specific storage applications of the criteria pollutants.

3. Wechter (1976) further reviewed the storage of gases in cylinders. The article sought to review a treated aluminum cylinder in the hopes of guiding the gas industry to provide a more stable and accurate calibration standard. Three of the four gaseous criteria pollutants, CO, SO_2 and NO_2 were used in this research. The treatments on the aluminum cylinder walls aided in maintaining the stability of the reactive calibration gases during the long-term performance testing of the cylinder. The treatment was described as a two-part process; the first part was to enhance the aluminum oxide layer, and the second part was listed as "proprietary in nature".

4. The U.S. EPA *Field Operations Guide for Automatic Air Monitoring Equipment* (1971) stated specifically that only borosilicate glass and FEP Teflon® are to be used for inlet materials, citing Wohler's research from 1967, and appears to be the most commonly referenced research in the entire CFR section 58. The article referenced the adsorption and desorption of glass, plastic, and metal tubing regarding CO and SO_2 (Byers and Davis, 1970) and provided a schematic of the testing apparatus and test results.

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Supporting Materials – Sample Gas Flow Path and Data Flow Path
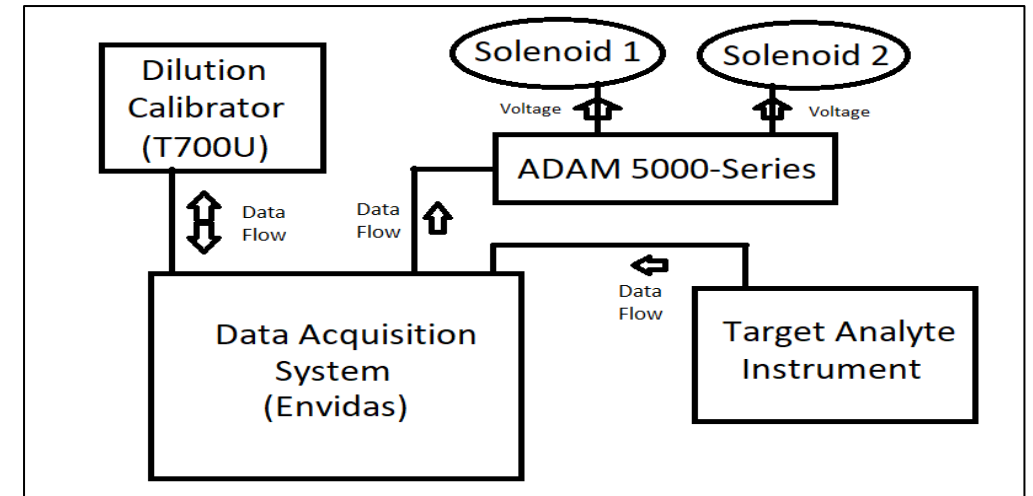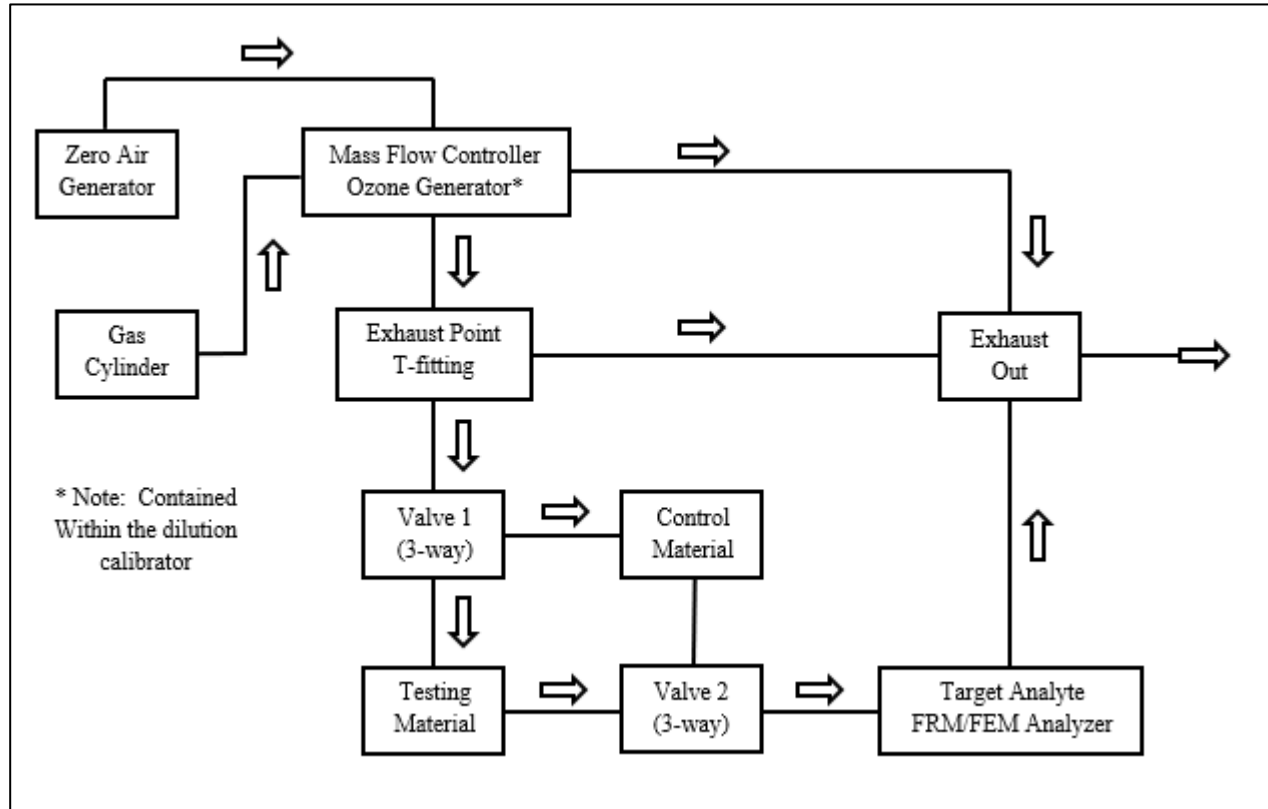
Supporting Materials – Valve Switching and Timing Sequences