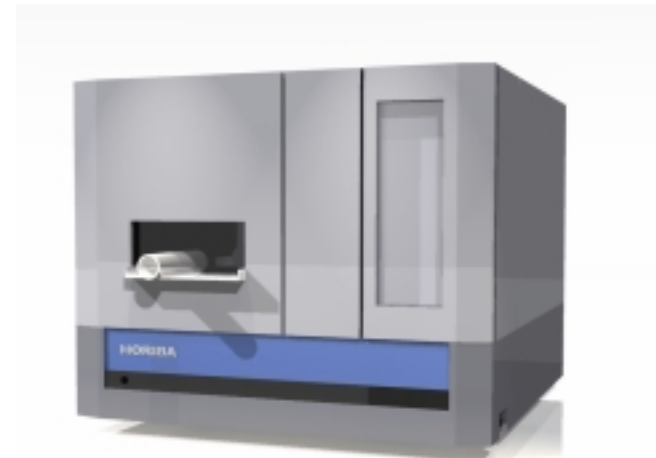
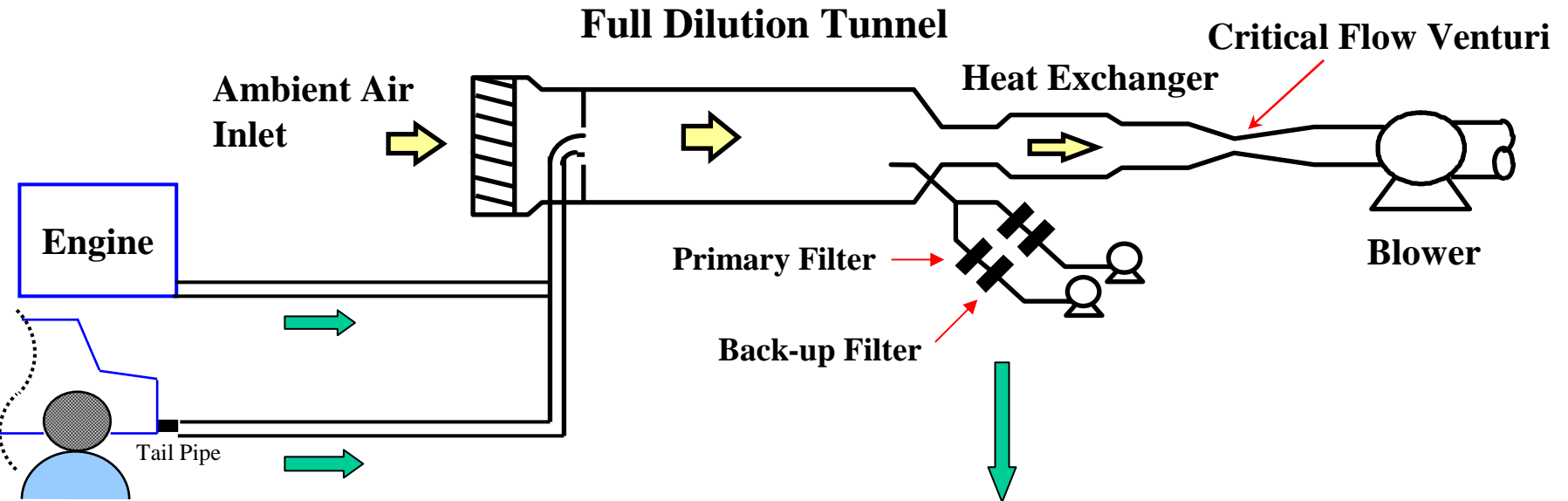


# Improvements in the Thermal Mass Measurement Technique for Mass and Characterization of Low Levels of Diesel Particulate Matter

Michael Akard and Tomoshi Yoshimura  
HORIBA Instruments, Inc.



# Particulate Measurement



$$\text{PM Mass} = \text{Filter Mass after Sampling} - \text{Filter Mass before Sampling}$$

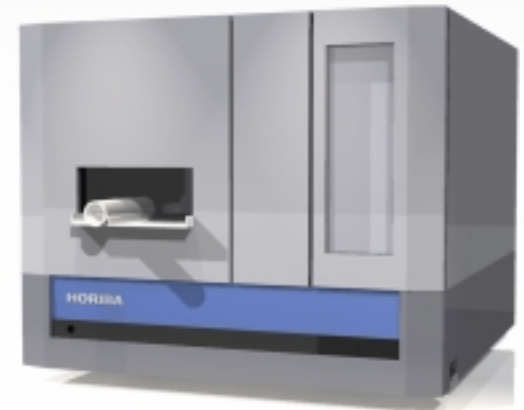


- Time Consuming Process
- EPA Requirements
  - 100  $\mu\text{g}$  of Particulate
  - 100 mg (100,000  $\mu\text{g}$ ) filter weight
  - +/- 2.5  $\mu\text{g}$  or better
  - Balance measure within +/- 25 ppm (1/400,000)
- Replicate Measurement
- 30 Minute Minimum Stabilization Time
- Clean Room with Humidity Control
- Changes in Barometric Pressure-buoyancy of filter

- Solvent Organic Fraction (SOF)
  - Sample Preparation – Soxhlet Extraction
- Sulfates
  - Sample Preparation – Extraction (H<sub>2</sub>O/Isopropyl Alcohol)
  - Analysis – Ion Chromatography
- Residual Carbon Particulate (RCP)
  - Remaining particulate weight
  - Ash + Soot

# Thermal Mass Measurement

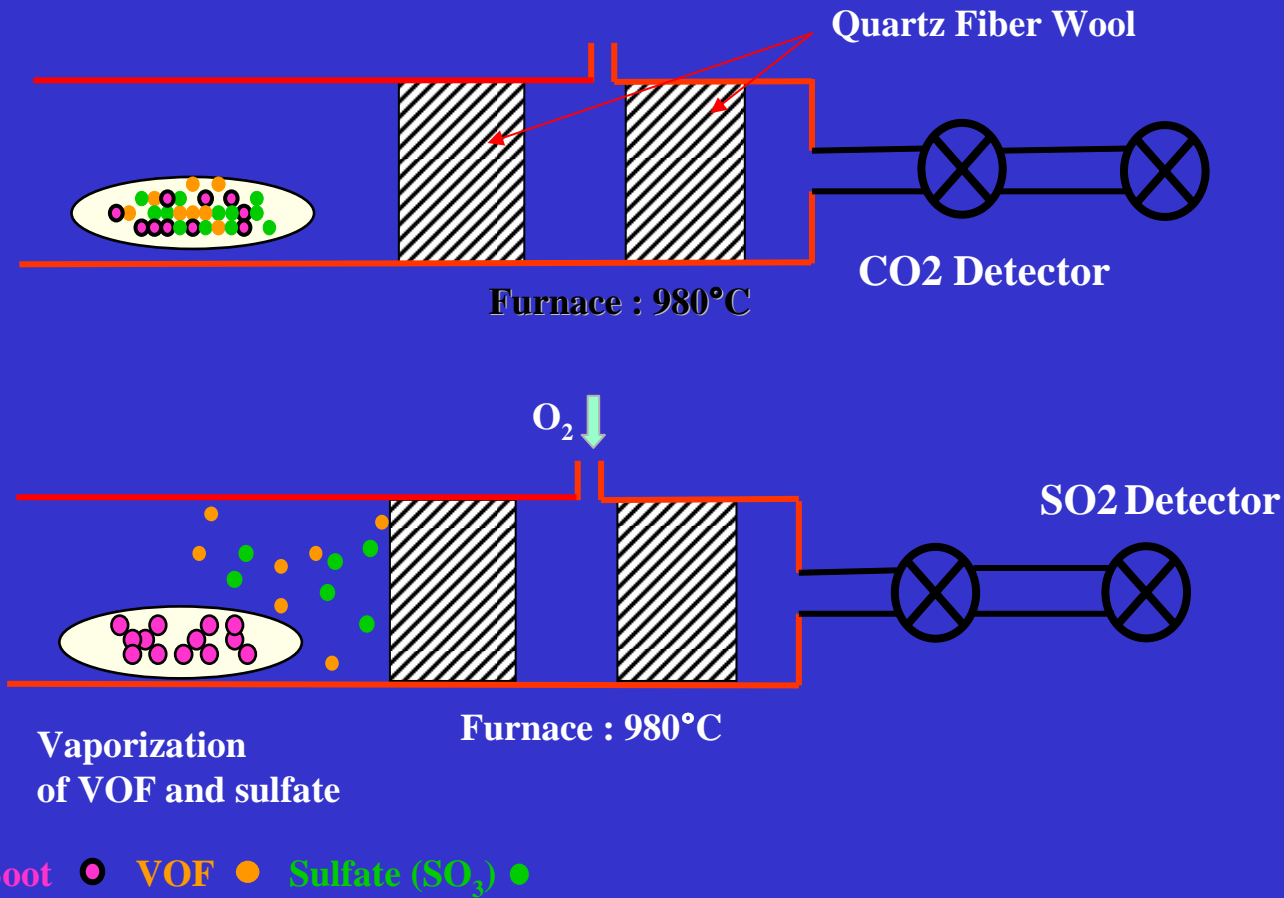
- Filter Collection Method same as Current
- Filter Rolled onto Quartz Holder
- Holder with Filter Purged with Nitrogen
- Insert Holder with Filter into Furnace at 980°C
- Analysis Time from 4 – 6 Minutes Typical



- Filter Media must be Quartz
- Vaporize Hydrocarbons (SOF) and Sulfates
  - First phase
  - Oxidation of SOF in second furnace
  - Conversion of all sulfur into SO<sub>2</sub>
- Oxidize Soot
  - Second phase
  - Occurs in first furnace on filter
- Detection by NDIR (CO<sub>2</sub> and SO<sub>2</sub>)
- Ash and Nitrate not detected

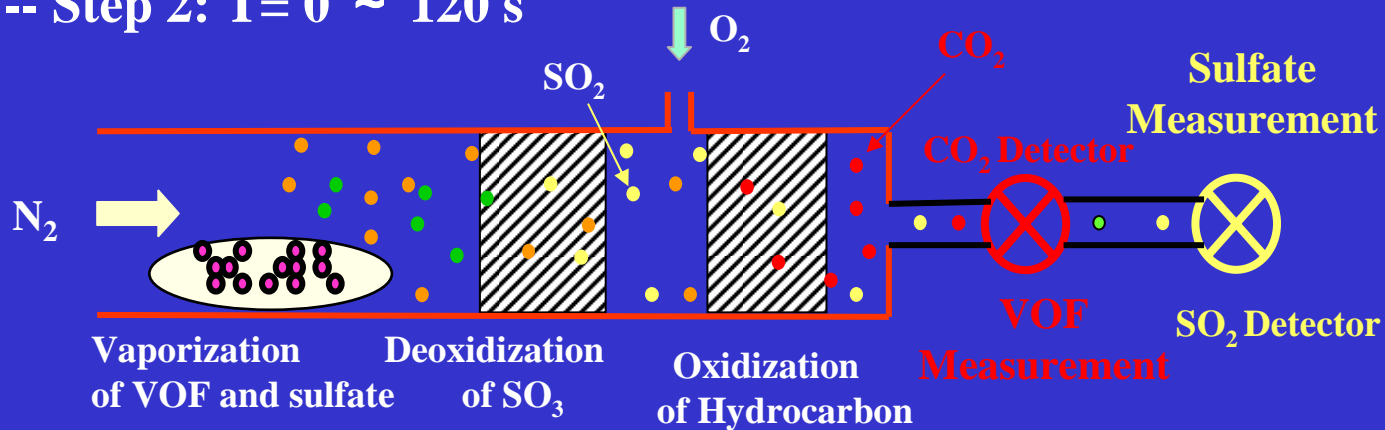
# Vaporization – First 60 seconds

## Phase 1 -- Step 1: Place Filter in the Furnace

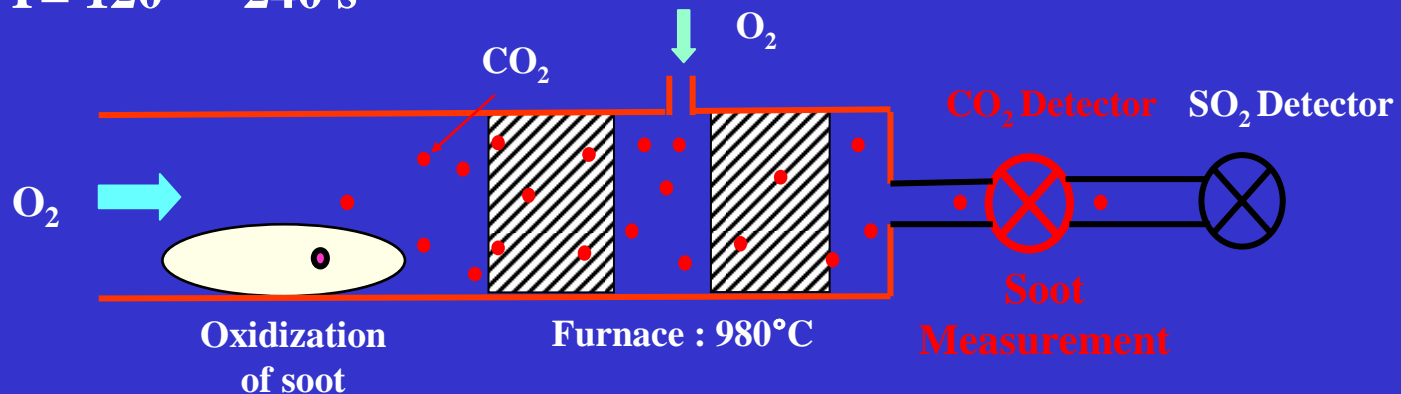


# Measurement – SOF and then Soot

Phase 1 -- Step 2: T= 0 ~ 120 s



Phase 2: T= 120 ~ 240 s



Soot ● VOF ● SO<sub>3</sub> ● CO<sub>2</sub> ● SO<sub>2</sub> ●

# Instrument Specifications

## MEXA 1370PM

Measurement	:	Soot / SOF / Sulfate / Total PM
Detectors	:	NDIR – CO <sub>2</sub> & SO <sub>2</sub>
Detection Limits	:	0.2 µg VOF 0.2 µg Soot 8.0 µg Sulfate
Total Analysis Time	:	4-6 minutes
Duty Cycle Time	:	12-15 minutes
PM Filter	:	Quartz 47 mm or 70 mm (Advantec)
Weight	:	~90 kg (Analyzer)
Dimensions		
Analyzer	:	690(W) × 577(H) × 803(D)
EY-80	:	100(W) × 230(H) × 280(D)
Display & Control	:	360(W) × 280(H) × 428(D)

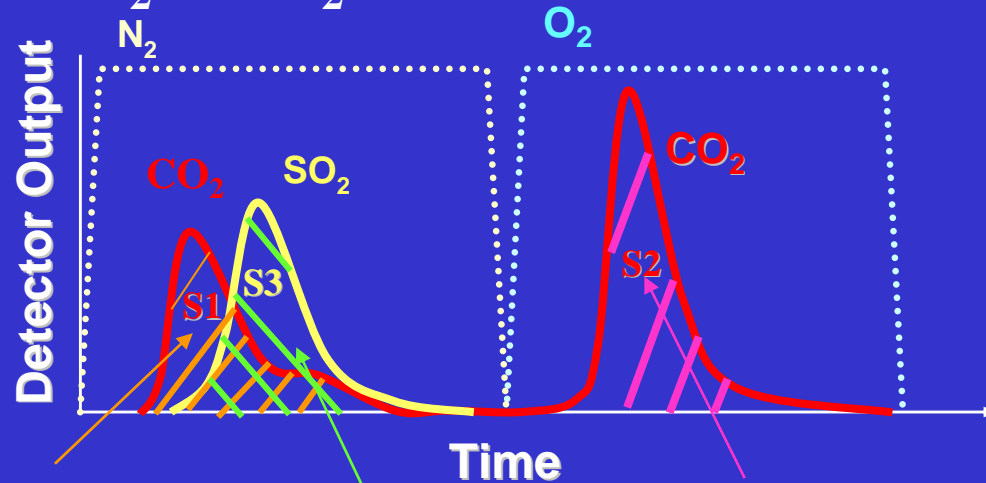
# MEXA 1370PM Advantages

- Only PM Analyzer that Measures Sulfate
- Gives User Clear Difference between Soot and VOF (not just a temperature profile)
- Measures Mass as Required by EPA
- Fast 2 - 4 minute analysis
- Simple Operation
- Uses Existing Particulate Sampling System
- Less Expensive Overall than Weigh Room
- Single Measurement (no pre-weighing filters)

- Quartz filters required
  - Must tolerate temperature of 980°C
  - R&P and Sunset also use quartz
- Collection efficiency must be comparable for teflo and other filters (99% min. for particles > 1.0µm)
- Quartz will adsorb hydrocarbons
  - Optional muffle furnace to condition (bake) filters
  - Conditioned filters typically last couple of days but is dependent upon storage conditions

# Mass Calculations (1 of 2)

## 1. Generate CO<sub>2</sub> & SO<sub>2</sub> Mass Measurement



### VOF Information

$$\text{CO}_{2\text{mass}} = k_{\text{CO}_2} * \text{S1}$$

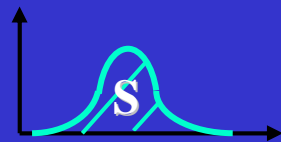
### Sulfate Information

$$\text{SO}_{2\text{mass}} = k_{\text{SO}_2} * \text{S3}$$

### Soot Information

$$\text{CO}_{2\text{mass}} = k_{\text{CO}_2} * \text{S2}$$

Fixed Volume  
Std. Gas  
Calibration



Signal Integration

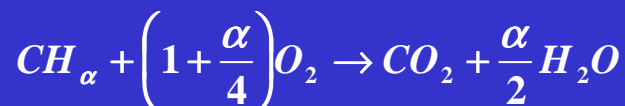


Mass of Gas

$$k = \text{Mass of Gas} / \text{Signal}$$

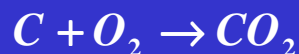
## 2. Determination of VOF, Soot and Sulfate using mass relations

**VOF: Volatile Organic Fraction ( $\alpha=1.8$ )**



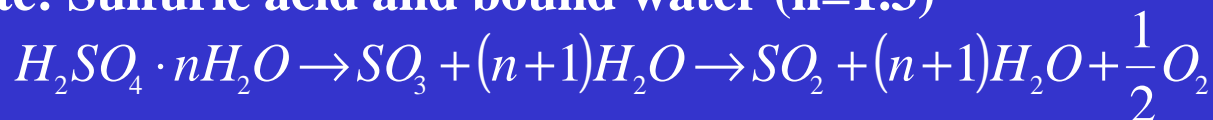
$$VOF_{mass} = \frac{MW_{HC}}{MW_{CO_2}} CO_{2mass} = \frac{12.01 + 1.008 \times \alpha}{12.01 + 16.00 \times 2} CO_{2mass}$$

**Soot: Elemental Carbon**



$$Soot_{mass} = \frac{MW_C}{MW_{CO_2}} CO_{2mass} = \frac{12.01}{12.01 + 16.00 \times 2} CO_{2mass}$$

**Sulfate: Sulfuric acid and bound water ( $n=1.3$ )**



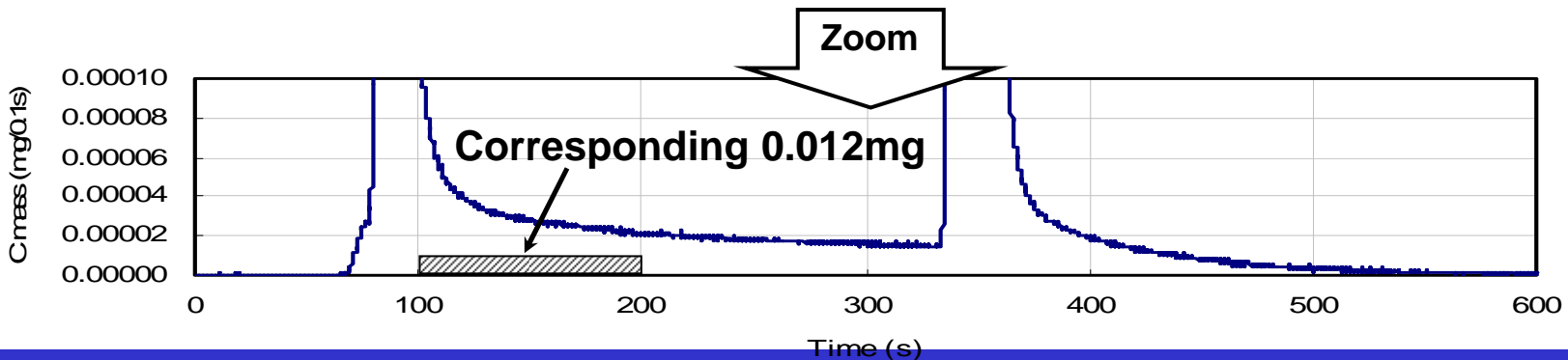
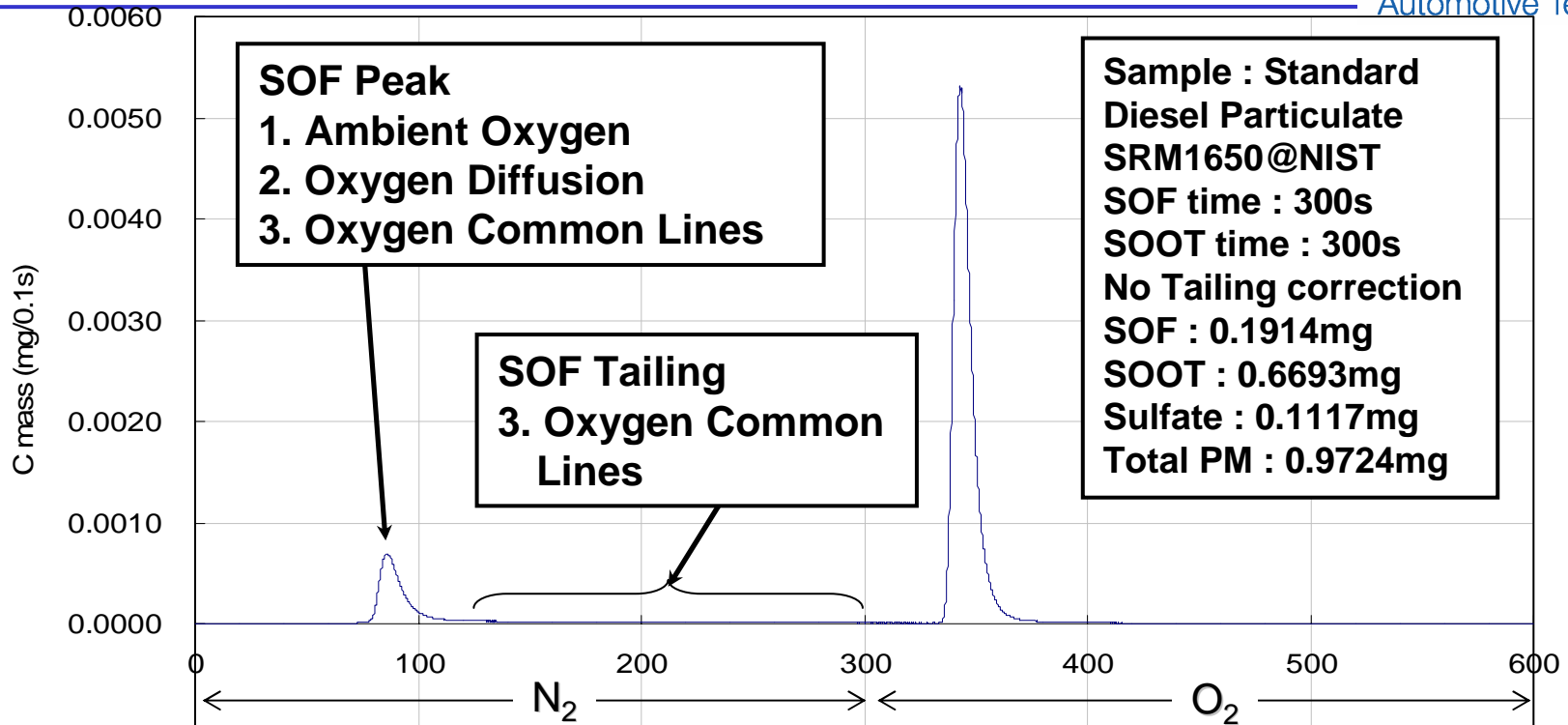
$$Sulfate_{mass} = \frac{MW_{H_2SO_4} \times (1+n)}{MW_{SO_2}} SO_{2mass} = \frac{98.08 \times (1+n)}{64.06} SO_{2mass}$$

# Need for Improvements

- Significant Tailing of SOF Peak
  - Initially thought to be dead volumes – diffusion limited portion of SOF
- Evaluation of Tailing
  - Tailing ended after soot peak
  - Tailing increased with increases in soot
  - Soot/SOF ratios variable with different oxygen introduction times (beginning soot measurement)
- Soot is Oxidized before Scheduled Oxygen Introduction into Furnace
- Apparent at PM Masses below 1 mg

- Oxygen from Ambient when Shutter opens to Furnace
- Oxygen Diffusing in from Second Furnace
- Residual Oxygen from Previous Run
- Oxygen Introduced through Common Oxygen and Nitrogen Lines
- Oxygen not Completely Purged from Filter

# Preliminary SOF Tailing



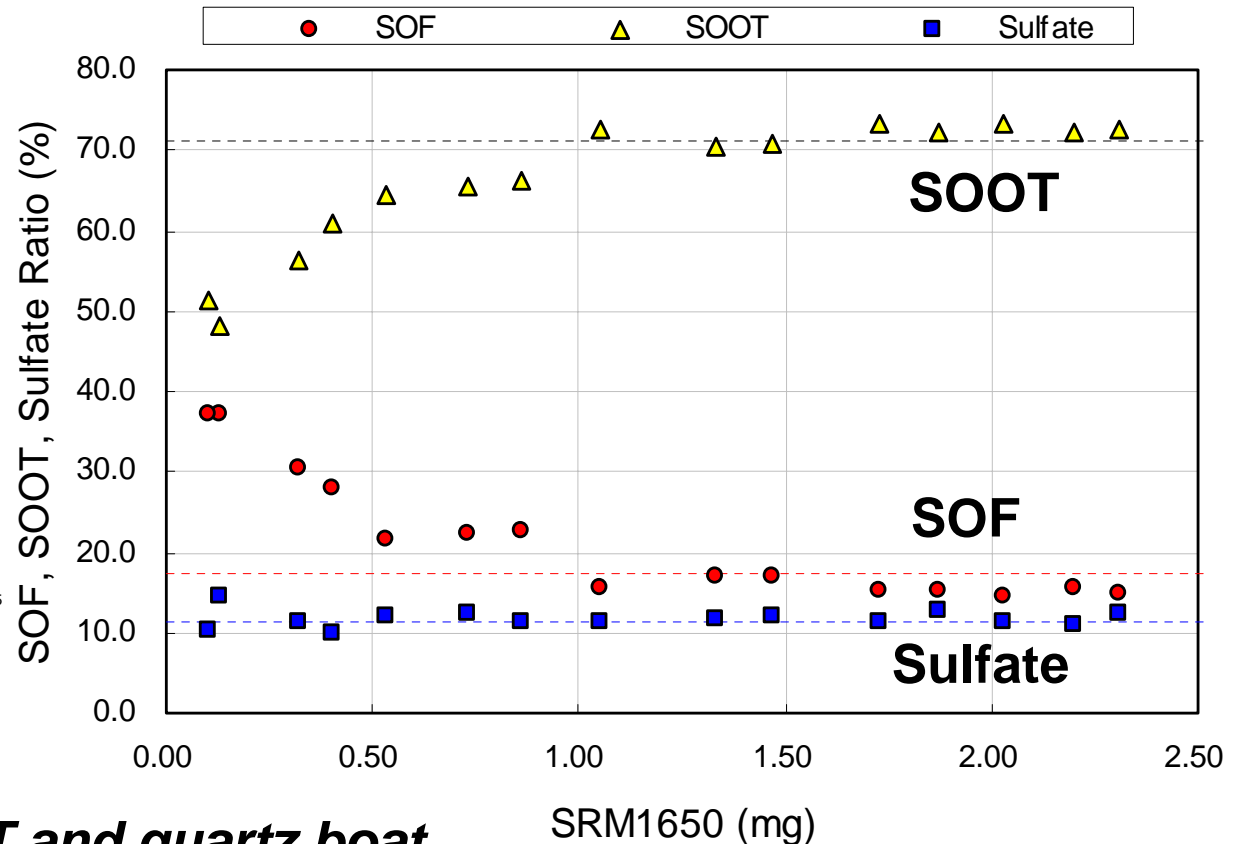
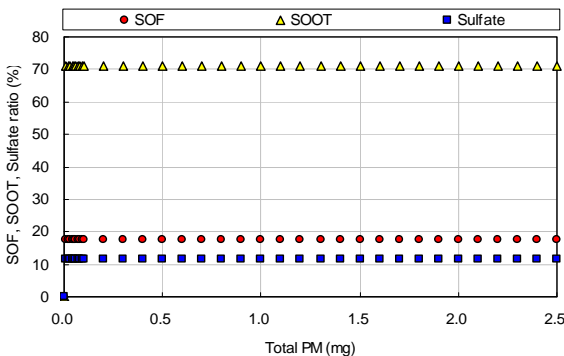
# Preliminary SOF/Soot Ratio of Standard

Sample = SRM1650

SOF Measure Time = 300s

SOOT Measure Time = 300s

**Ideal**

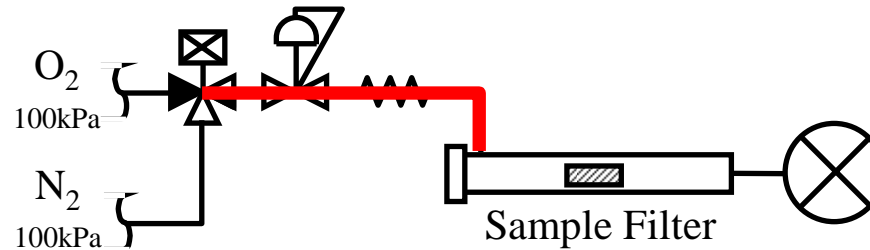


- ***SRM1650@NIST and quartz boat***
- ***SOF, SOOT ratio is not constant under 1.0 mg***
- ***Sulfate ratio is constant***

- Eliminate oxygen in first furnace until soot measurement
  - Replace all nitrogen carrying lines with 3 mm stainless steel tubing
  - Reduce shared plumbing for nitrogen/oxygen
  - Improve purging flow to eliminate trapped air/oxygen volumes
- Insure sufficient oxygen in second furnace during SOF measurement
  - Adjust valve timing in software

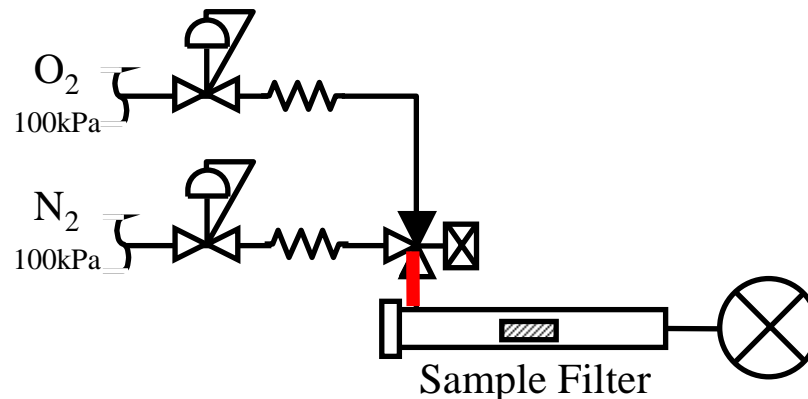
# Plumbing Modification

*Original*



*\* Shortened N<sub>2</sub>, O<sub>2</sub> common carrier line*

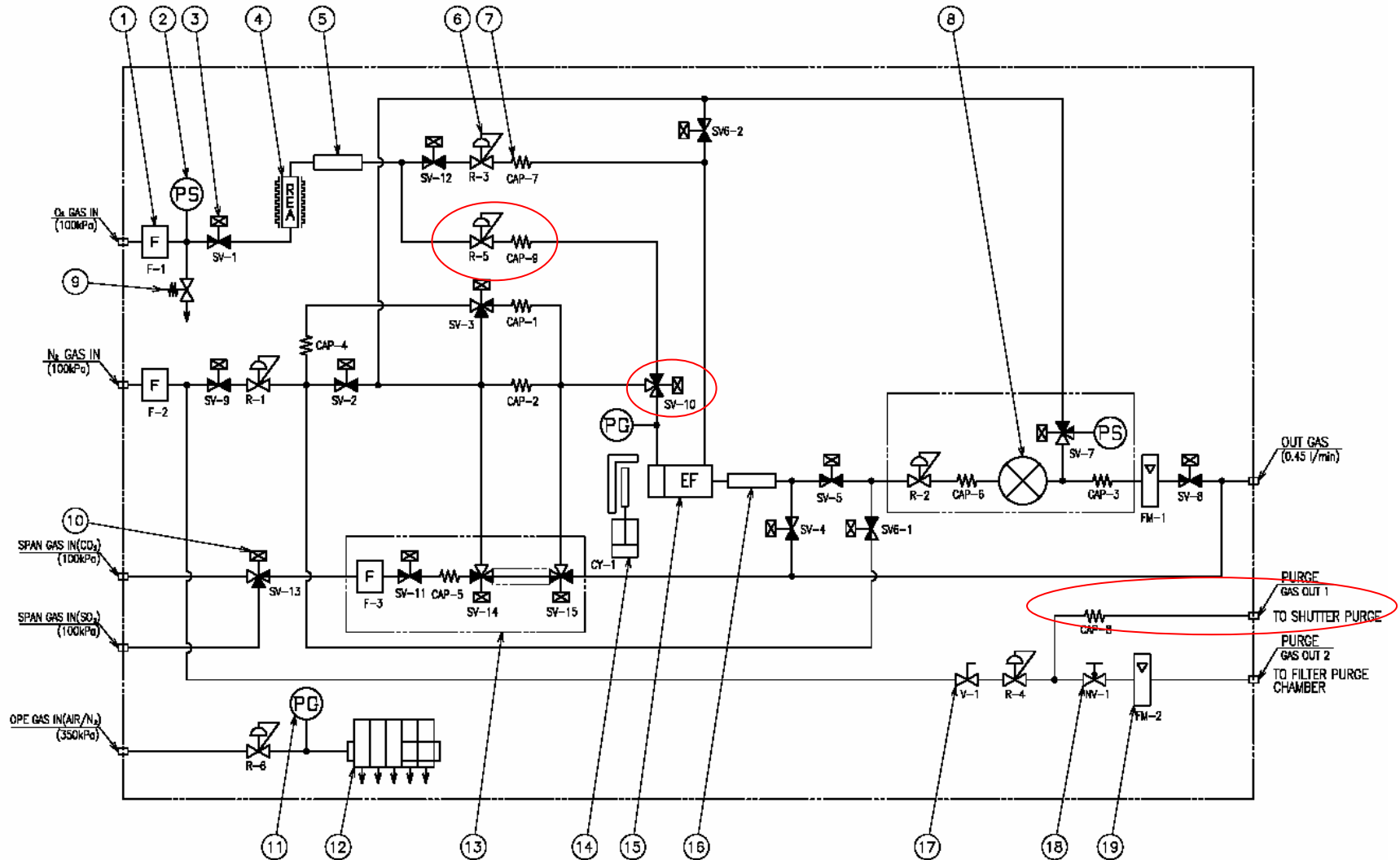
*Modified*



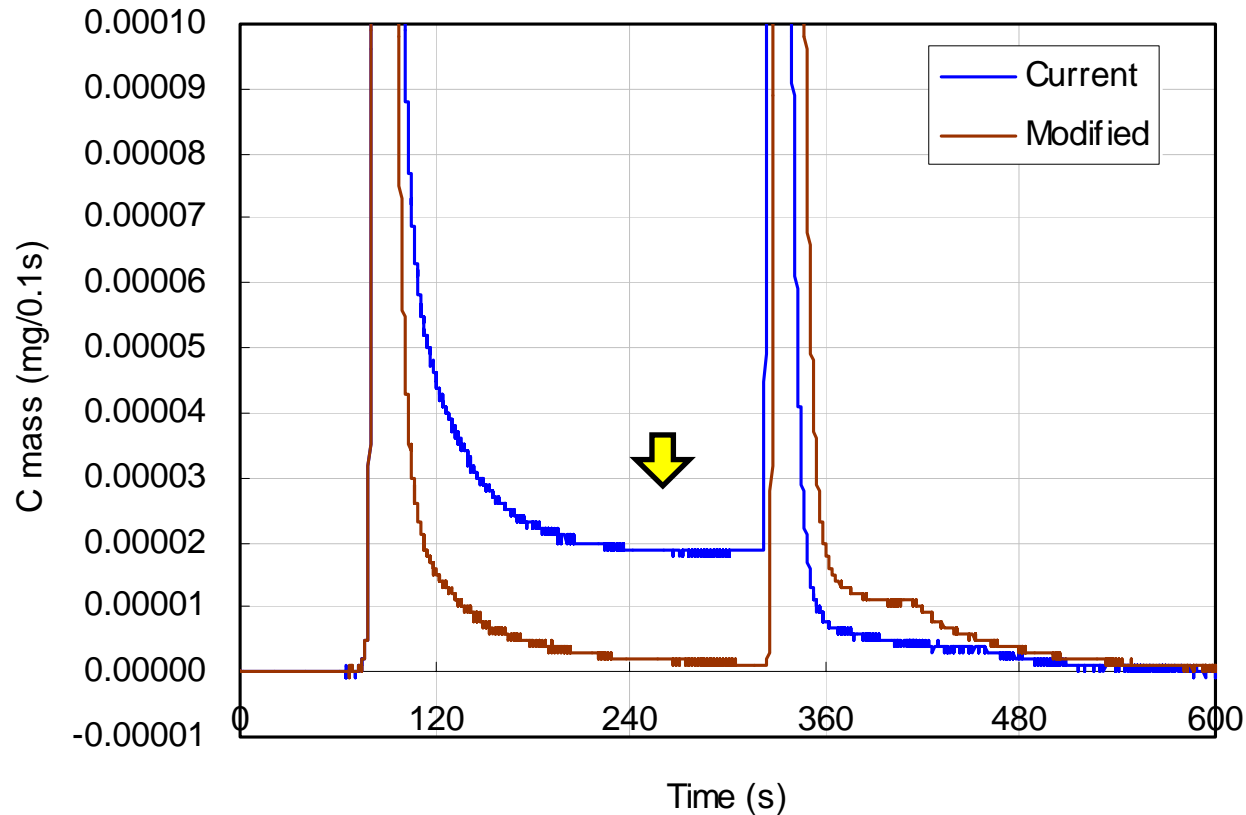
***Additional independent oxygen carrier line to avoid SOOT reaction in SOF measure sequence***



# New Flow Schematic



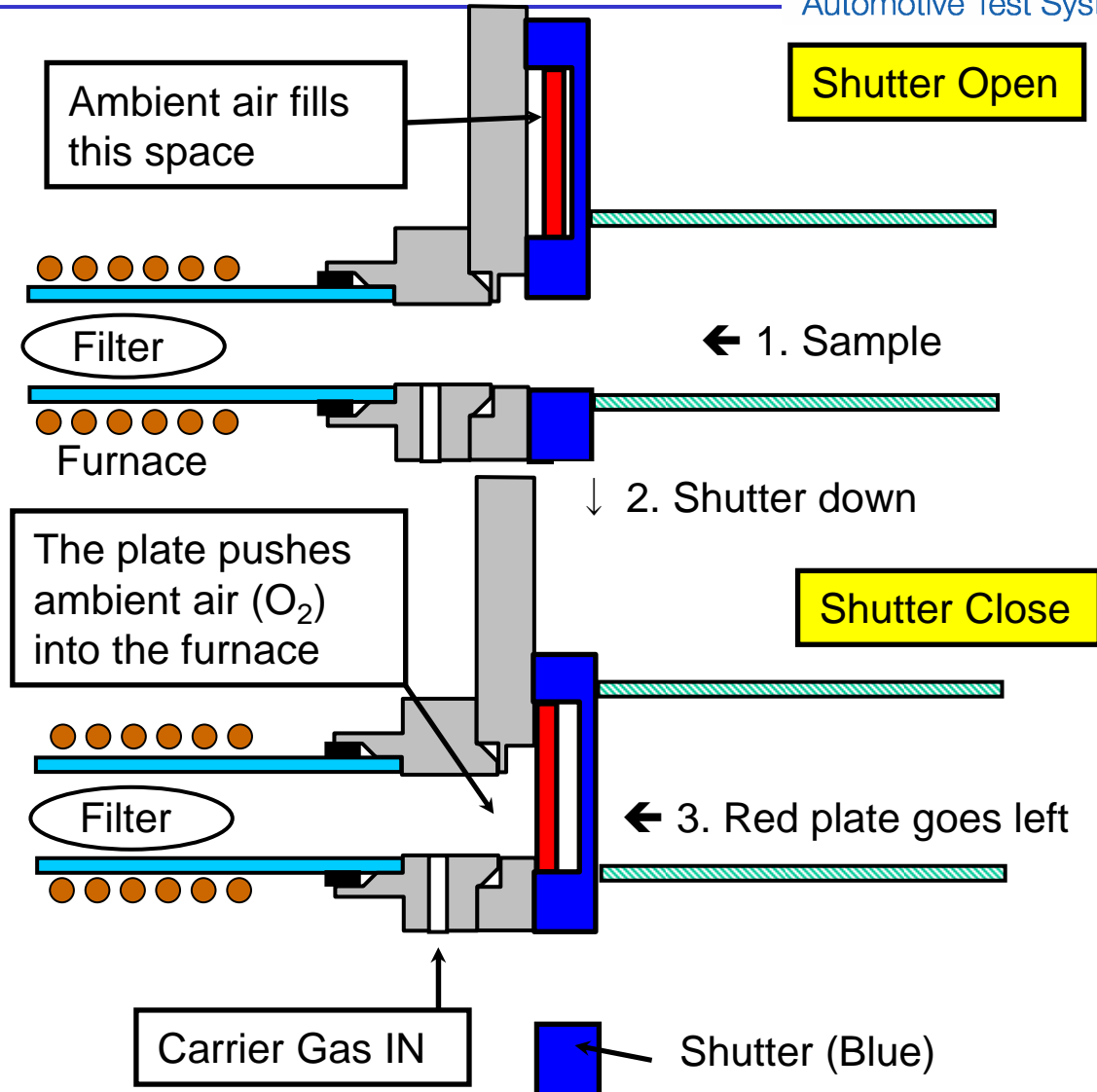
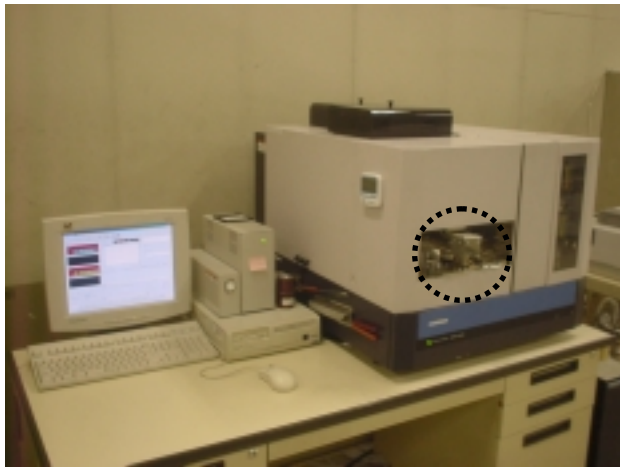
# Results from Plumbing Modification



■ ***SRM1650 + Quartz Filter (Total amount of SRM is approx. 0.3mg)***

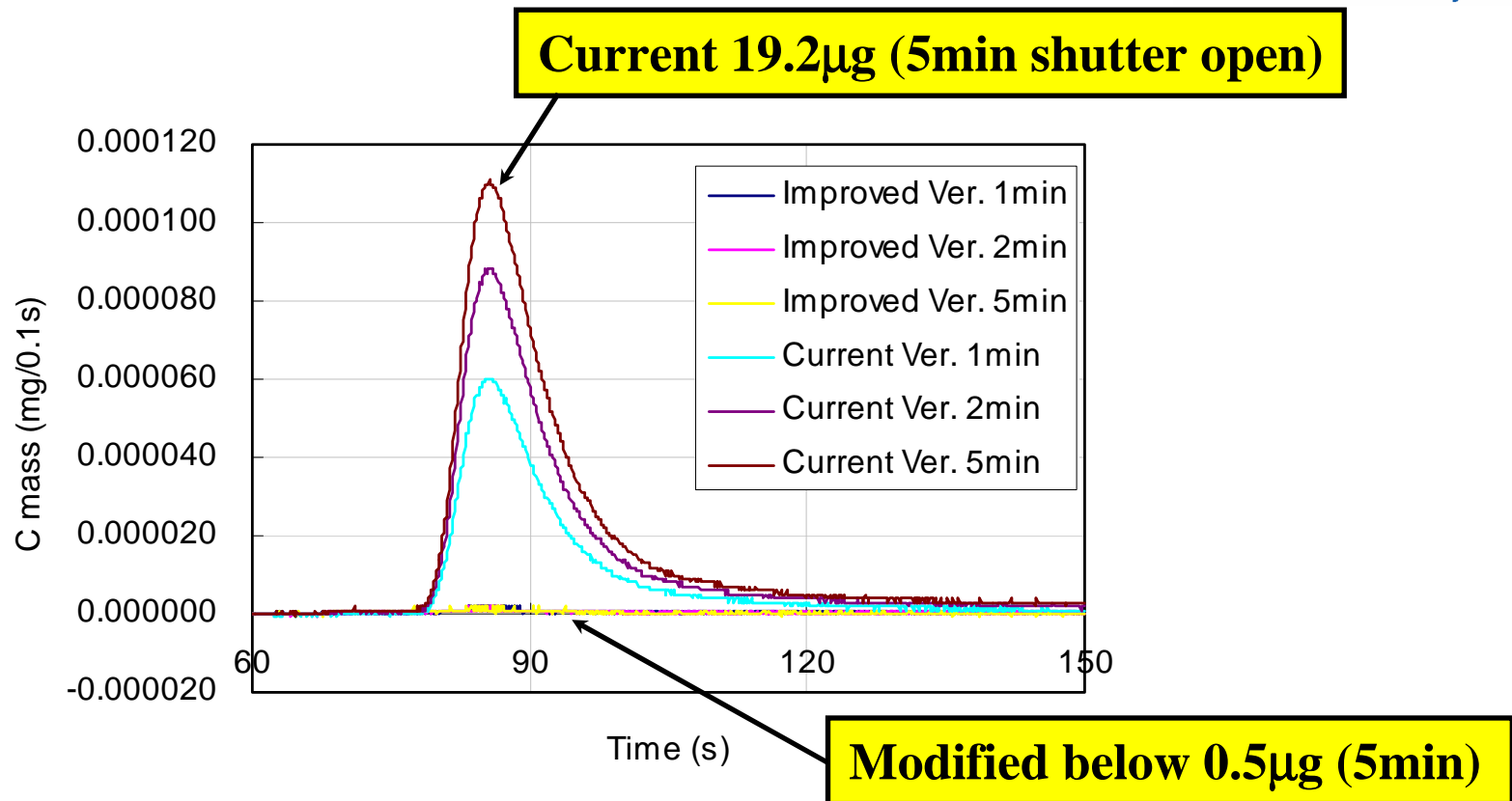
# Shutter Purge

Center cross section  
of the front shutter



***Additional  $N_2$  purge will prevent ambient air entering the shutter while open***

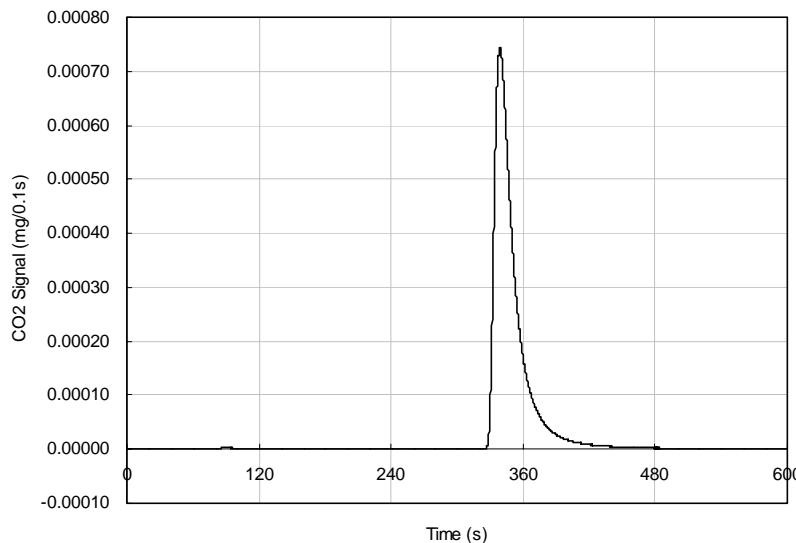
# Results Shutter Modification



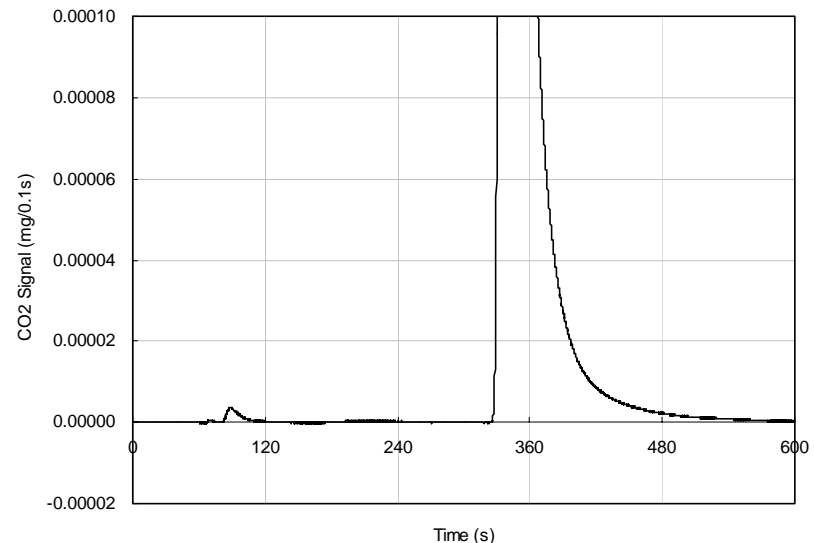
- ***These ambient oxygen could be used for SOF oxidization in the case of real PM.***

# Graphite Measurement

Carbon Graphite Measurement



Scaled up of the left graph



**Sample Boat = Carbon Graphite + Quartz**

**SOF = 0.0009mg**

**SOOT = 0.1914mg**

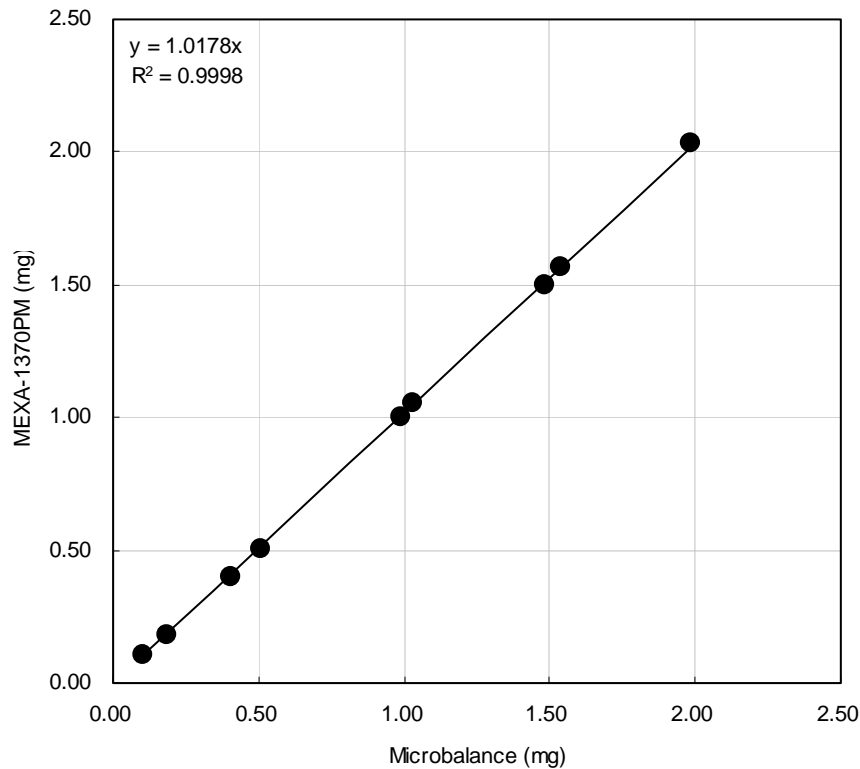
**SULFATE = 0.0107mg**

**TOTAL PM = 0.2030mg**

■ ***VERY small SOF peak***

■ ***SOF tailing is minimal***

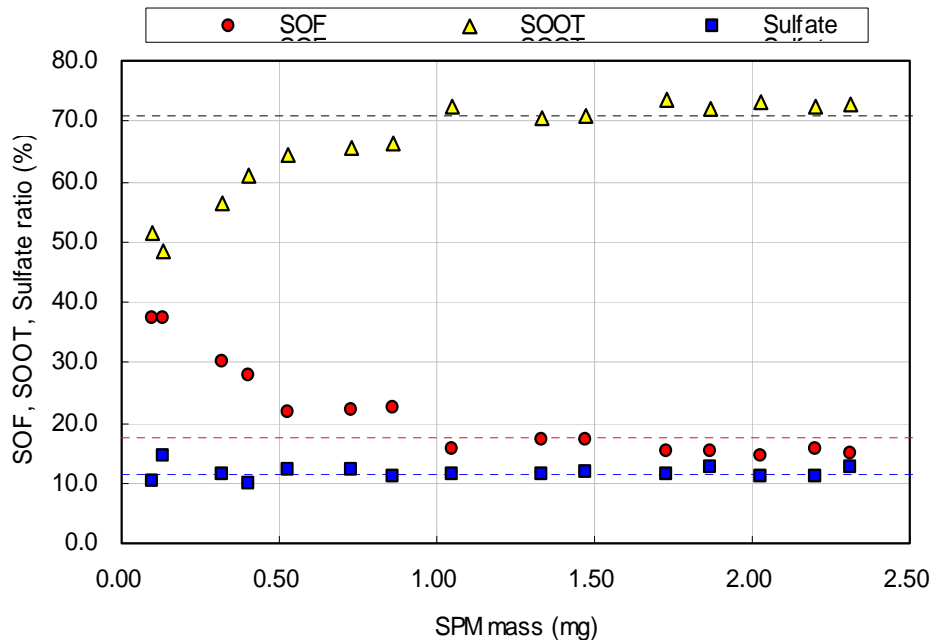
# Comparison with Gravimetric



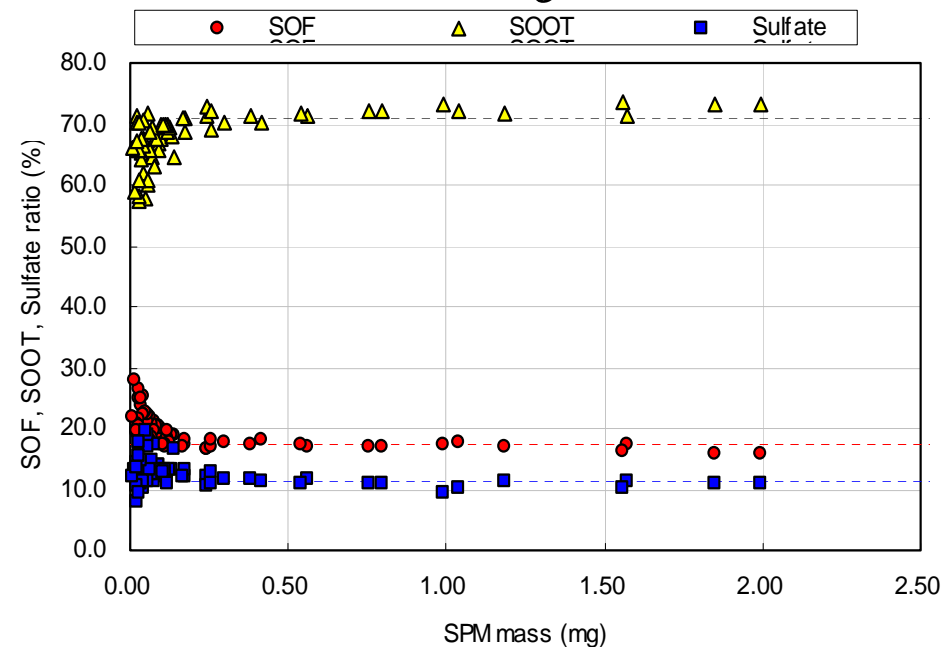
- ***Good correlation with gravimetric result***
- ***Good linearity***

# Modified Soot/SOF Ratio of Standard

## Original

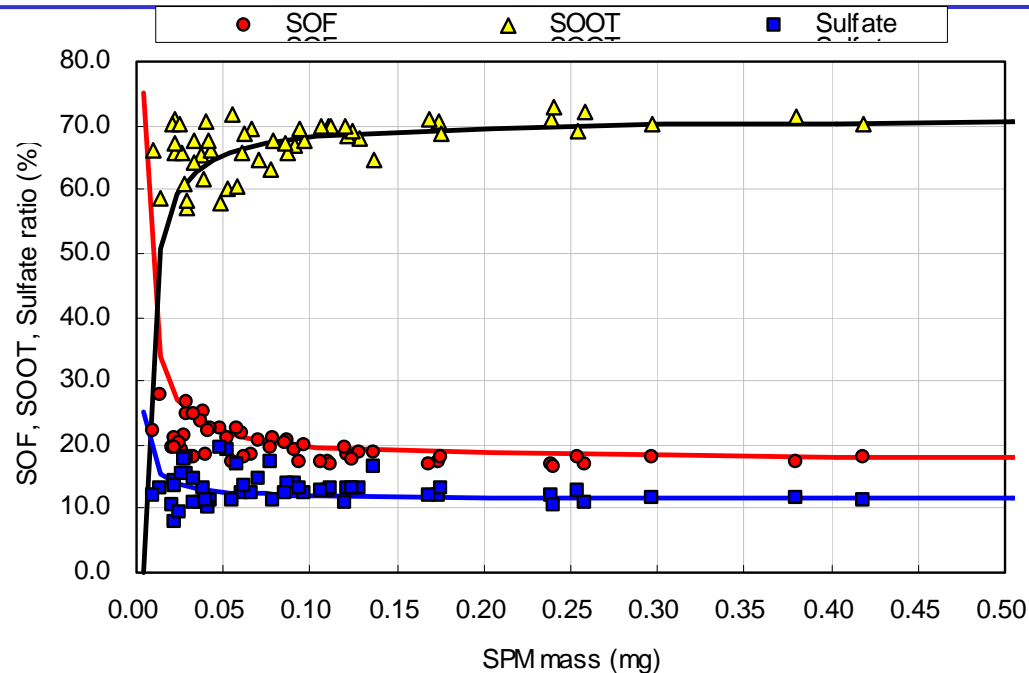


## Modified



- **Component ratio stabilized significantly.**
- **It is hard to see the component ratio below 0.1mg**
- **A very short common line for both  $N_2$  and  $O_2$**

# Very Low Mass Measurements



**Each Solid line shows calculated value with estimated background/system noise and/or SOF contamination shown below:**

**SOF : 0.003 mg**

**Sulfate : 0.001 mg**

**Calculated values shows similar trend as the experimental result**

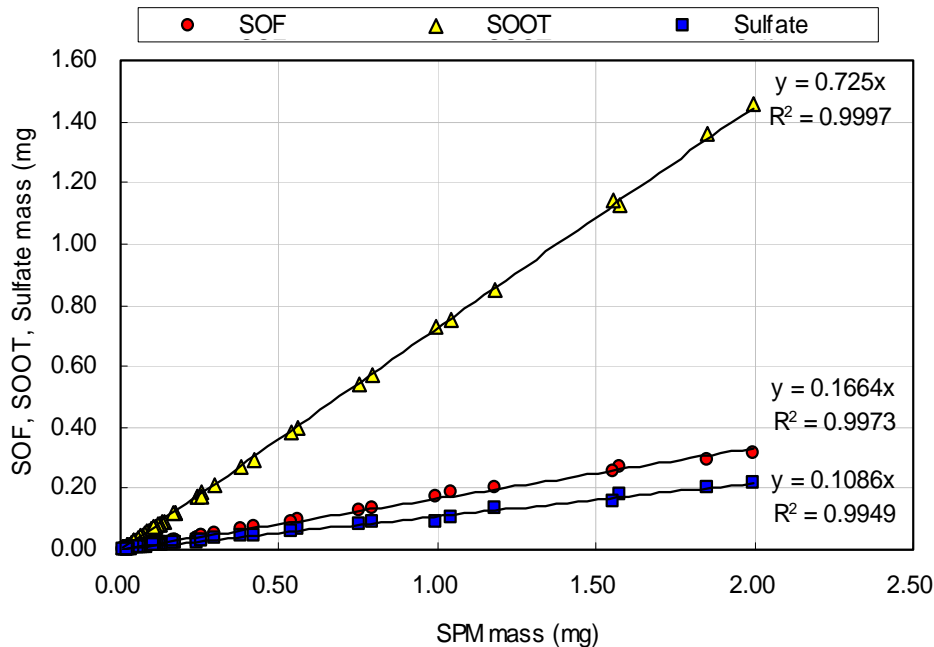
**These numbers are realistic because of SOF contamination or integrated noise**

**A couple of  $\mu\text{g}$  background effects on the (percentage) results significantly**

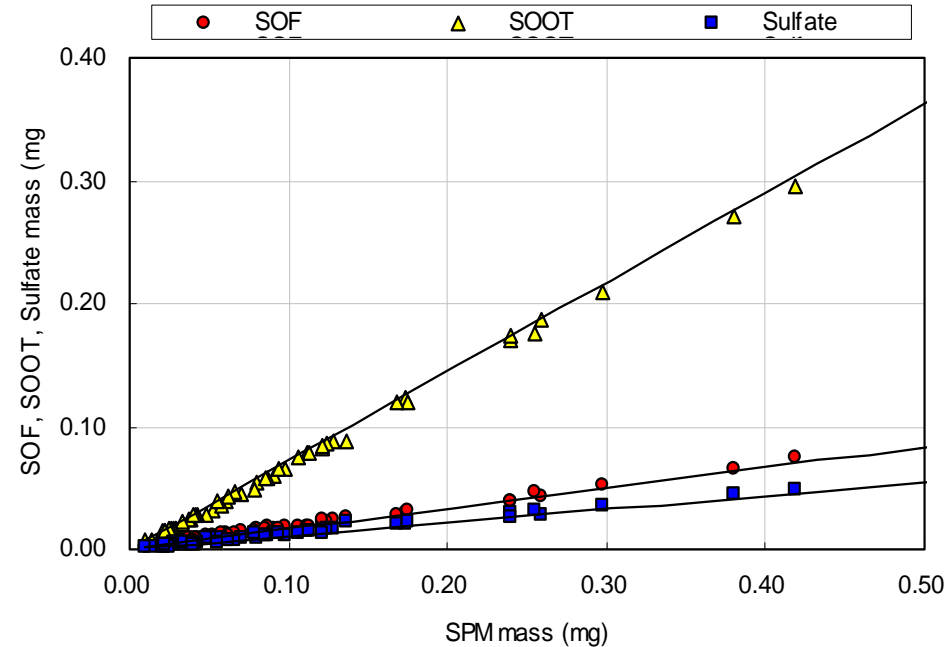
**These errors may be unavoidable...**

# High to Low Range Extrapolation

High range 0 ~ 2.5 mg



Low range 0 ~ 0.5 mg



- **Extrapolated values from High range to Low range for SOOT result is a small negative difference. This difference is due to SOF contamination, system background/noise and remaining soot to SOF by residual oxygen**

- Unexpected oxygen from the instrument is the main cause of SOF tailing.
- The oxygen introduced during the first phase is significantly reduced.
- SOF tailing is eliminated in testing with standard sample (Carbon graphite, Standard PM SRM1650).
- Modification is recommended to get better performance for division performance of SOF and SOOT.

- MEXA 1370PM
  - Fast Alternative to Labor Intensive Gravimetric Method for PM Mass Measurement
  - True Mass Measurement
  - Laboratory Instrument
  - Soot, VOF, Sulfate, Total PM Values
- References
  - SAE 2001-01-0218 (H. Fukushima, et. al.)
  - SAE 2004-01-0589 (M. Akard, R. Chase, et. al.)