EVALUATION AND MINIMIZATION OF ORGANIC AEROSOL SAMPLING ARTIFACTS USING IMPACTORS AND QUARTZ FIBER FILTER DENUDERS

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(CE-CERT)

STUDY OBJECTIVES

- **Evaluate a simple denuder-impactor-filter combination to minimize collection artifacts when sampling for particulate organic carbon**
- **Compare with the EPA PM reference method and other state-of-the-art particulate organic carbon sampling methods**

MOTIVATION

- Quartz fiber filter denuders have been shown to minimize the positive adsorption artifact
- Impactors are expected to minimize the volatilization collection artifact
- Carbon coated denuders have been developed to remove interfering VOC followed by carbon coated filters to retain particulate SVOC
- If OC is to become a regulatory target, then an acceptable and simple sampling method is needed to minimize collection artifacts

QUARTZ FIBER FILTER DENUDER

- Fitz, D.R, (1990) Reduction of the positive organic artifact on quartz fiber filters. Aerosol Sci. Technol, 12, 142-148.
  - Parallel plate denuder constructed of the same quartz filter media used for particle collection
  - Denuder should remove gases that would be collected on the quartz filter
  - The OC on a quartz back filter should therefore be negligible.

QUARTZ FIBER FILTER DENUDER EVALUATION (CSMCS, 1987)

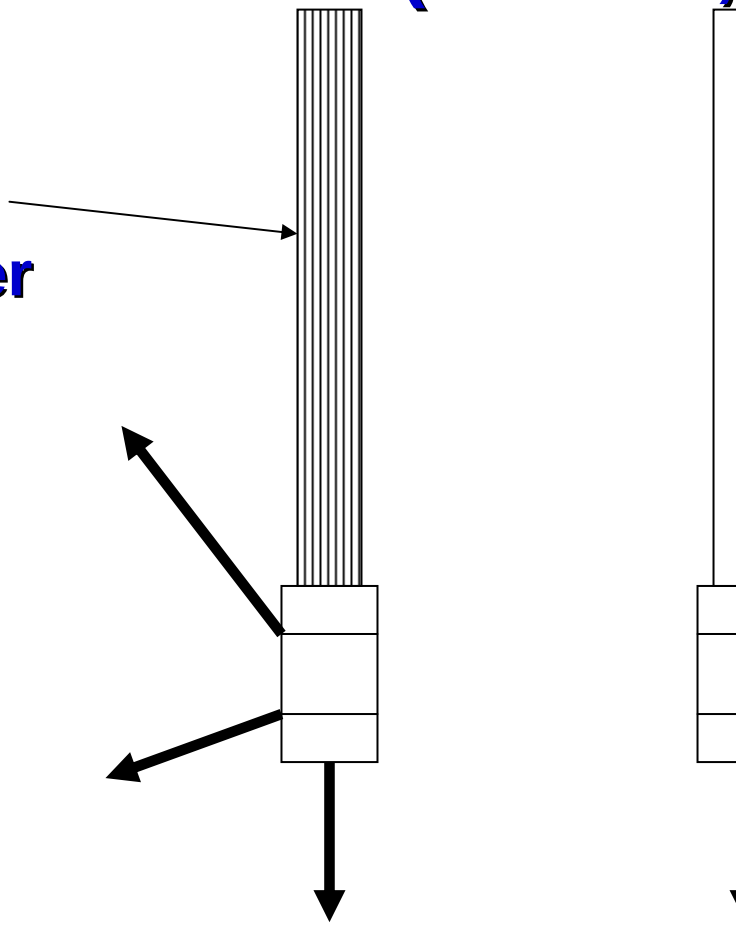
Parallel Plate QFF Denuder

OC = 14.6 ug/m3

EC = 1.51 ug/m3

OC = 0.60 ug/m3

EC = 0.01 ug/m3



Denuder Housing Only

OC = 16.6 ug/m3

EC = 1.53 ug/m3

OC = 2.73 ug/m3

EC = 0.01 ug/m3

IMPACTORS

- **Zhang, X.Q., and McMurry, P.H. (1987) Theoretical analysis of evaporative losses from impactor and filter deposits. Atmos. Environ. 21, 1779-1789.**
  - **Collected particles are rapidly covered with other particles and therefore removed from equilibrium processes with passing air**
  - **Impaction was theoretically shown to have potentially less evaporative losses compared to filtration**

SAMPLING CONFIGURATION

1.	____ Q	TOA	$PM_{2.5}$ POC
	____ Q	TOA	Adsorbed VOC, VPOC
2.	____ T	Mass	Federal Method $PM_{2.5}$ reference
	____ Q	TOA	Adsorbed VOC, VPOC
	____ Q	TOA	Adsorbed VOC, VPOC
3.	/Q/	none	Removes VOC that adsorb on quartz filter
	____ Q	TOA	POC w/o adsorbed gases
	____ Q	TOA	Indicates /Q/ efficiency or adsorbed VPOC
4.	------ I	TOA	POC w/o adsorption or volatilization
	____ Q	TOA	Very fine POC, adsorbed VOC, VPOC
	____ Q	TOA	Adsorbed VOC
	/Q/	none	Removes VOCs that adsorb on quartz filter
5.	------ I	TOA	POC w/o adsorption or volatilization?
	____ Q	TOA	Very fine POC, adsorbed VPOC
	____ Q	TOA	Adsorbed VOC

Q=quartz filter, T=Teflon filter, I=Impactor, /Q/=quartz fiber filter denuder, VOC=volatile organic carbon, POC=particulate organic carbon, VPOC=volatilized POC, TOA= thermal optical analysis

SAMPLING CONFIGURATION

6.	------ I	TOA	POC w/o adsorption or volatilization
	/Q/	none	Removes VPOC, VOC that adsorb on quartz filter
	____ Q	TOA	Very fine POC
	____ Q	TOA	Potentially very little OC
7.	____ T	none	Removes POC
	------ I	TOA	Dynamic POC blank
	____ Q	TOA	Adsorbed VOC, VPOC
	____ Q	TOA	Adsorbed VOC, VPOC
8.	/C/	none	Removes POC
	____ Q	TOA	POC, remaining VOC
	____ Q	TOA	Adsorbed VPOC, remaining VOC
	____ CIF	TPV	Remaining VOC, VPOC
9.	____ T	none	Removes POC
	/C/	none	Removes VOC
	____ Q	TOA	Absorbed remaining VOC+VPOC
	____ Q	TOA	As above, measure of Q breakthrough
	____ CIF	TPV	Remaining VOC+VPOC

Q=quartz filter, T=Teflon filter, I=Impactor, /Q/=quartz fiber filter denuder, /C/=carbon impregnated filter denuder, CIG=carbon impregnated glass fiber filter, VOC=volatile organic carbon, POC=particulate organic carbon, VPOC=volatilized POC, TOA= thermal optical analysis, TPV= temperature programmed volatilization

University of California, Riverside
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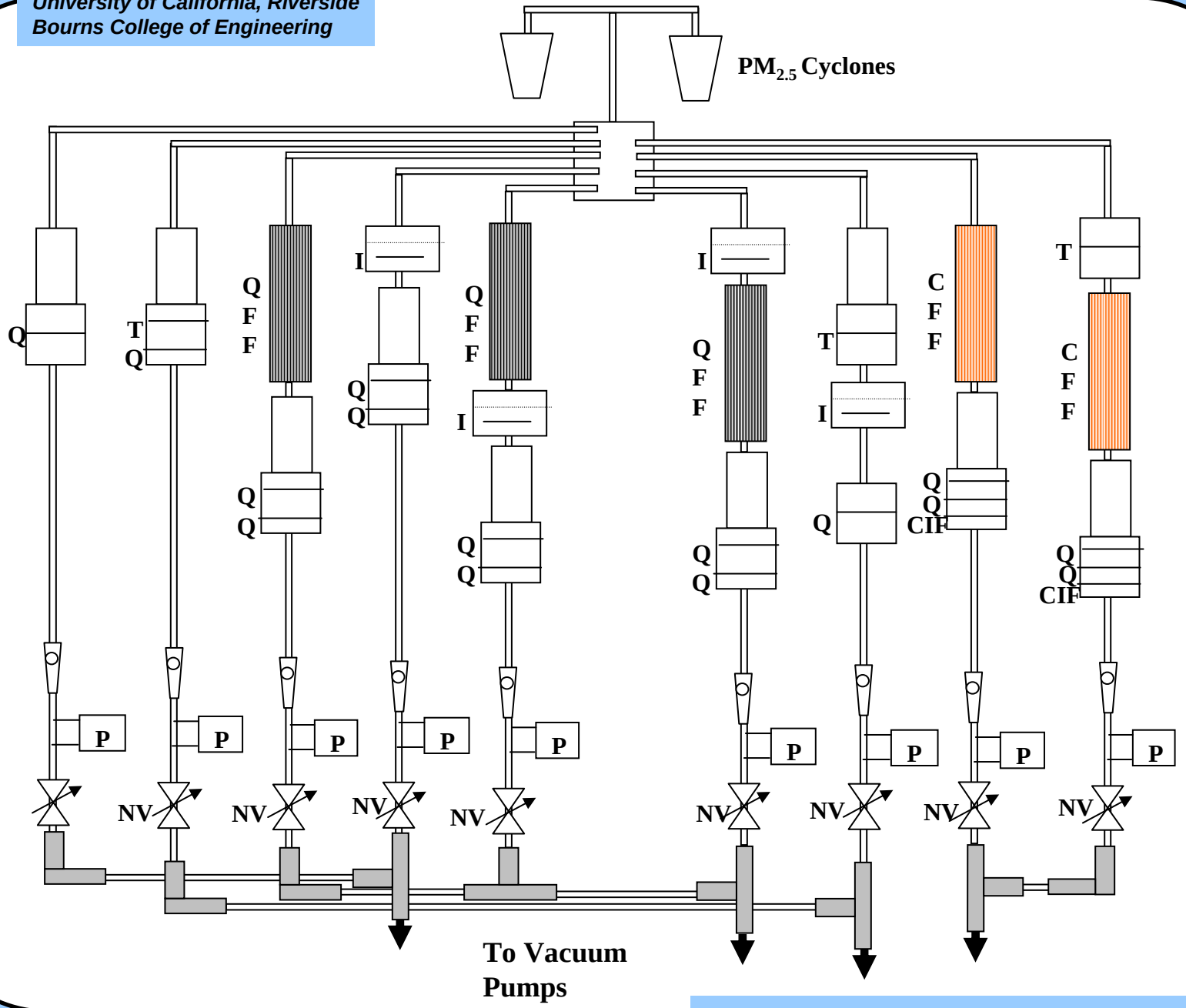


Center for Environmental Research and Technology

PARALLEL PLATE DENUDER DESIGN FOR FILTER MEDIA

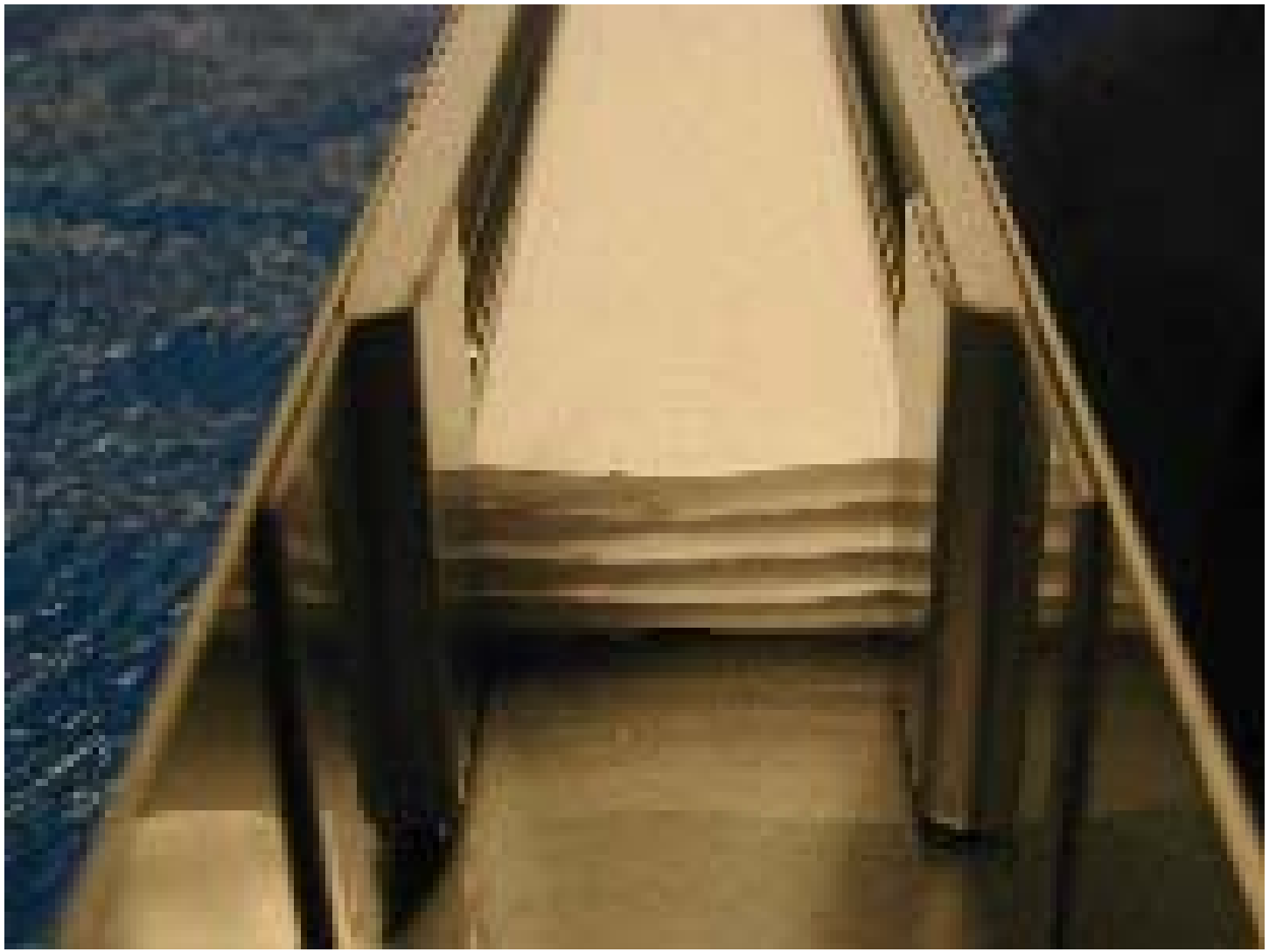
- **Improvements needed for routine use**
  - **Better seal was needed if used under the high pressure drop of an impactor**
  - **Changing filter strip substrates was difficult**
  - **Once loaded the denuder needed to be handled carefully**

PARALLEL PLATE DENUDER HOUSING FEATURES

- **Substrates are held firmly in place - can be shipped without damage**
- **Construction is all stainless steel, with a stainless steel crush ring for sealing**
- **Substrates can be reactivated at 550ºC without removing from the housing**
- **Relatively inexpensive to manufacture**

Parallel Plate Denuder Components

View of Parallel Plates (filter strips)



Photograph of Sampler-Denuders

Photograph of Sampler-w/o Denuders

Photograph of Sampler- Overview

Method Evaluation

- **Ambient Sampling**
  - 24-Hour sample collection periods per EPA FRM
  - Two initial test days in Riverside CA (receptor dominated area), October 2004
  - Month of sampling in Riverside as a part of SOAR, August 2005
  - Month of sampling in Pico Rivera, CA (source dominated area), September-October 2005)
- **Source Sampling**
  - 350 KW diesel generator steady state, 25% power
  - Emissions measured used standard techniques by the CE-CERT Mobile Emission Laboratory (MEL)
  - Dilution tunnel for 16:1 total dilution

Source Sampling

Substrate Analysis

- **Quartz filters analyzed by Sunset Labs Thermal Optical Method (NIOSH 5040)**
- **Aluminum substrates analyzed by placing on a quartz filter punch- no correction for charring**
- **Carbon impregnated filters analyzed by heating to 480°C in helium to obtain OC- no correction for charring possible**

Results Summary- Ambient Air

- The OC accounted for approximately 30% of the measured mass (using a factor of 1.4)
- More OC was observed on the quartz filter immediately following a Teflon filter (40% correction) than on the quartz filter immediately following a quartz particle collection filter (25%) correction
  - Conclusion:Nearly half the OC on the Qz front filter is artifact
- The OC on the quartz back filter below the denuder was only slightly less than the quartz back filter without a denuder.
  - Conclusion: The quartz fiber filter denuder was largely ineffective under these conditions
- The second quartz fiber on channels 1-7 showed similar amounts of OC and no EC,
  - Conclusion: The quartz fiber filter denuder was again largely ineffective under these conditions

Results Summary- Ambient Air

- The front quartz fiber on channels 2 and 7 on Teflon-filtered air gave similar results
  - Conclusion: The VOC causing a adsorption is largely unattenuated by the impactor
  - Conclusion:The after filter of a MOUDI impactor is primarily an adsorption artifact.
  - Conclusion: Although the results were similar to correcting front carbon OC by the OC on a quartz filter behind a Teflon filter, the most artifact-free method of sampling may to use and impactor and correct the after filter for artifact using the OC on a quartz filter that has a Teflon front filter.
- The total EC from the impactor channels tended to be erratic and higher than the quartz front filter.
  - Conclusion: The estimated OC-EC split is not “correct”
  - The EC from impactor channels should be calculated from TOC corrected for EC on a front quartz filter

Results Summary- Ambient Air

- The denuder consisting of carbon-impregnated strips had an efficiency of approximately 50%
  - The denuder design was insufficient to remove the VOC
- The OC on both the carbon impregnated filters was approximately three times higher than a standard quartz filter and equal to the total mass measured by weighing
  - Conclusion: Confirms that the denuder is not removing sufficient VOC to prevent artifact adsorption

Conclusions- Source Sampling

- The EC was four times higher than the uncorrected OC
- TC agreed well with measured mass (1.4 factor for OC)
- Despite concentrations approximately two orders of magnitude higher than ambient air, more OC was observed on the quartz filter immediately following a Teflon filter (30% correction) than on the quartz filter immediately following a quartz particle collection filter (15%) correction
  - Conclusion:Nearly half the OC on the Qz front filter is artifact
  - Conclusion: Quartz filters are not easily saturated by adsorbed VOC

Conclusions- Source Sampling

- The OC on the quartz back filter below any of the quartz fiber filter denuder channels was about half that of the quartz back filter without a denuder.
  - Conclusion: The quartz fiber filter denuder was approximately 50% effective under these conditions
- As with ambient sampling, the front quartz fiber on channels 2 and 7 on Teflon-filtered air gave similar results
  - Conclusion: The VOC causing a adsorption is largely unattenuated by the impactor
  - Conclusion:The after filter of a MOUDI impactor is primarily an adsorption artifact.
  - Conclusion: The most artifact-free method of sampling may to use and impactor and correct the after filter for artifact using the OC on a quartz filter that has a Teflon front filter, HOWEVER:

Conclusions- Source Sampling

- The total EC (and TC) from the impactor channels tended to be erratic and much lower than the quartz front filter.
  - There may be electrostatic losses in the impactor
  - The EC from impactor channels should NOT be calculated from TOC corrected for EC on a front quartz filter
- The denuder consisting of carbon-impregnated strips had variable efficiency of near zero to 50%
  - The denuder design was insufficient to remove the VOC
- The OC on both the carbon impregnated filters was approximately twice that of a standard quartz filter
  - Conclusion: Confirms that the denuder is not removing sufficient VOC to prevent artifact adsorption j

Overall Conclusions

- Artifact OC based on the amount on a quartz filter under a Teflon filter was nearly 50% for both source and ambient sampling
- Since the amount of VOC collected is the same on the first quartz filter, the correction for the MOUDI after filter is much higher (near 90%) than for a quartz front filter since most of the particulate mass has been collected by the MOUDI
- The most accurate method to measure ambient OC is to sample with and impactor/quartz after filter
  - Correct for the adsorption artifact on quartz after filters using a quartz filter behind a Teflon filter
  - Correct the OC/EC split bias and uncertainty by subtracting the EC on a quartz front filterfrom the total carbon collected by the impactor/filter

Overall Conclusions

- Since the above method gives results similar to correcting front OC by subtracting OC on a quartz filter behind a Teflon filter, it is unlikely that there is a significant volatilization artifact on quartz filters.
- Determining mass by the EPA reference method using Teflon filters is not likely to be affected by volatilization artifacts
- While the quartz fiber filter denuder was not effective under these conditions (30 L/min), it still may be useful research tool at lower flow rates (or with a redesign for 30 L/min)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