

# **Problems and Inconsistencies and Their Potential Solutions for Sampling and Analysis of EPA Method 202 Condensable PM Samples**

**Extended Abstract #91**

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## **INTRODUCTION**

As is the case with any scientific method, field practice will almost always reveal additional questions regarding the validity of a procedure. Since its inception, EPA method 202 has manifested varying levels of difficulty upon testing companies. Improper procedures were the typical culprit. In other instances, product and supply specifications were inadequate.

I make no attempt within the context of this paper to judge the validity of EPA Method 202. The data presented here reflect research that further tests the perceived limitations of EPA Method 202 and how best to adapt procedures to help “make it work.” The work presented here addresses two areas that testers have had a particularly difficult time with.

1. Importance of container material, both wash (or rinse) and storage bottles for use with hexane
2. Upper limitation of Teflon membrane filters in sampling high sulfur dioxide emission sources

## **USE OF DIFFERENT WASH BOTTLE MATERIALS AND THEIR EFFECTS ON WEIGHT RESIDUE**

### **Intro**

The promulgation of the “new” EPA method 202 has required a switch in impinger rinse and extraction solution from methylene chloride to hexane. Unfortunately, many testers than also switched from their use of teflon wash and storage bottles to polyethylene and other plastics. Hexane is, in general, a more accommodating chemical than methylene chloride (and other halogenated hydrocarbons), but the material of its container should still be an important consideration for the stack tester.

Several unusually high organic residues have been observed in our method 202 analyses over the past year. Most projects with high organic cpm results had consistently high residues throughout the project, including blank determinations! A quick resolution to this problem was obviously of paramount importance.

- Switch from methylene chloride to hexane (late 2010)

- Unusual (and high) organic cpm weight residues on some projects
- Was usually consistent throughout each project if “high” weights were observed
- Field and reagent blanks were also affected
- 6.2.2.(k) “Any container material is acceptable, but wash bottles used for sample and blank recovery must not contribute more than 0.1 mg of residual mass to the CPM measurements.”

Although concerned initially that the problem may be on our end, I eventually turned to the clients as internal QA tests proved that our procedures and instrumentation were within method criteria. Through a series of questions presented to clients that had high organic residues, it became clear that the choice of container material to store and utilize hexane rinse solution was certainly a problem. Polyethylene (both LD and HD) and polypropylene containers were each used by testers for projects where high organic residues were observed. Those using Teflon containers all had consistently low residues.

## Experimental Method

Our experimental design tested the gravimetric residue for hexane stored at three different time periods and in four different container material types. Two replicate analyses were performed for each set of parameters. The hexane tested was Macron Chemicals UltimAR<sup>®</sup> Hexane – a 99.5% min assay blend of mixed hexane isomers in which 95% minimum was n-hexane.

Gravimetric weights were determined at a relative humidity level of between 30-40% and a temperature of 67-72°F using a PI-240 Denver analytical balance with a resolution of 0.1 mg. Teflon<sup>®</sup> “baggies” were utilized for sample weighing containers as these are both inert and lightweight to minimize background weight. An electronic anti-static device was then used to remove static electricity from these containers during the weighing procedure.

- Container Materials
  - Polypropylene (PP)
  - Low-density Polyethylene (LDPE)
  - High-density Polyethylene (HDPE)
  - Tetrafluoroethylene (Teflon<sup>®</sup>)
- Time
  - 30 Minute
  - 24 Hours
  - 4 Days
- Other Factors
  - Unused containers
  - Used containers
- Different Manufacturers - Not tested

## Results

The gravimetric weights from this test are tabulated in Table 1. **Note:** These weights have not been blank corrected. In practice these results would be reduced by weight residues obtained from a field blank run of a maximum of 2.0 mg total cpm.

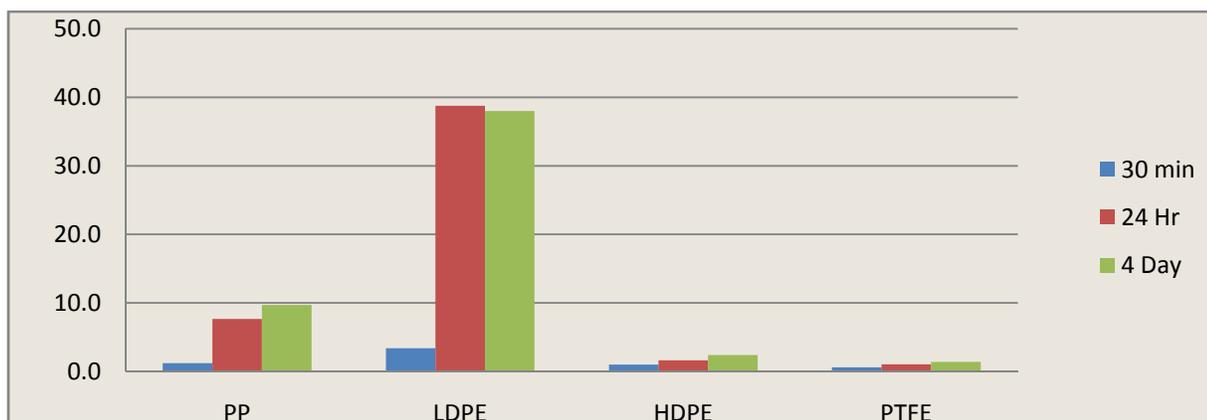
**Table 1.** Gravimetric Residue Weights

	Polypropylene		LD Polyethylene		HD Polyethylene		Teflon <sup>®</sup>	
	New	Used	New	Used	New	Used	New	Used
30 minutes	1.2 mg 1.4 mg	1.2 mg 1.3 mg	5.3 mg 5.0 mg	1.8 mg 1.6 mg	1.2 mg 0.8 mg	0.7 mg 1.1 mg	0.7 mg 0.7 mg	0.5 mg 0.5 mg
24 hours	8.1 mg 7.6 mg	6.8 mg 8.1 mg	38.9 mg 41.5 mg	37.9 mg 36.8 mg	1.1 mg 1.8 mg	1.9 mg 1.7 mg	0.7 mg 1.2 mg	1.4 mg 0.9 mg
4 days	13.8 mg 14.7 mg	4.4 mg 6.0 mg	45.0 mg 28.1 mg	53.2 mg 25.5 mg	2.5 mg 2.7 mg	2.2 mg 2.0 mg	1.7 mg 1.1 mg	1.3 mg 1.3 mg

## Discussion & Summary

These results demonstrate that a significant residue contamination can be directly linked to the choice of container material used for containing hexane rinse solution. This is by no means an exhaustive research project. There are certainly many other container material types available, but these are the most commonly used by stack testing companies.

**Figure 1.** Gravimetric Residue Weights, mg



- High-density polypropylene and Teflon the better choices, Teflon slightly better
- Low-density polypropylene was the worst

- 2 areas of significant differences for used vs unused
  - LD Polyethylene at 30 minutes - increased ~3.5 mg from 1.5-2.0 mg
    - Probably due to film on material surface
- Polypropylene at 4 days - increased ~9 mg from 4.5-6 mg
  - Breakdown of material surface resulting in “deeper” material degradation ??

As a result of these findings I would highly recommend the use of Teflon containers for the storage of hexane solution. (Although not specifically investigated in our study, it is generally believed by container suppliers that fluorinated polyethylene containers also contribute near zero levels of residue artifact.)

## **VARYING CONCENTRATIONS OF FLUE GAS SO<sub>2</sub> AND MOISTURE AND THEIR EFFECTS ON FILTER FOULING RATES ACROSS A VARIETY OF MANUFACTURERS’ TEFLON® MEMBRANE FILTERS AND PORE SIZES**

### **Introduction**

The fundamental difference between membrane filters and the typical quartz or glass fiber depth filters used by most PM methods is the nature of their permeation. Depth filters utilize a network or web of tightly woven material that embeds or otherwise prevents the permeation altogether of particulate matter.

Membrane filters typically utilize one or two layers of material with discrete and uniform size pores through which smaller material or molecules may pass through. Because their efficiency relies entirely on the size of these pores, they tend to be very small. This low porosity, when used in the presence of certain compounds such as sulfur dioxide, metal oxides, and caustics - combined with high moisture, can foul membrane filters. Sulfur dioxide in water, for instance, becomes sulfurous acid, which like its brother sulfuric acid, is oily and not amenable to passing through small pores.

The intent of this project is to determine the limitations of these membrane filters specifically with regards to pore size and varying levels of moisture and sulfur dioxide. It was hoped to find a “magic” formula that could be used to calculate a minimum filter porosity given a level of SO<sub>2</sub> and stack moisture.

Sulfur dioxide was chosen as a surrogate for these congealing compounds simply because it is more commonly found under stack testing conditions. Other compounds could differ significantly from these results.

- Membrane vs Depth Filters
- Small, discrete pore size of membrane filters can foul easily
- Method 202 currently specifies a minimum efficiency rating, not a specific pore size

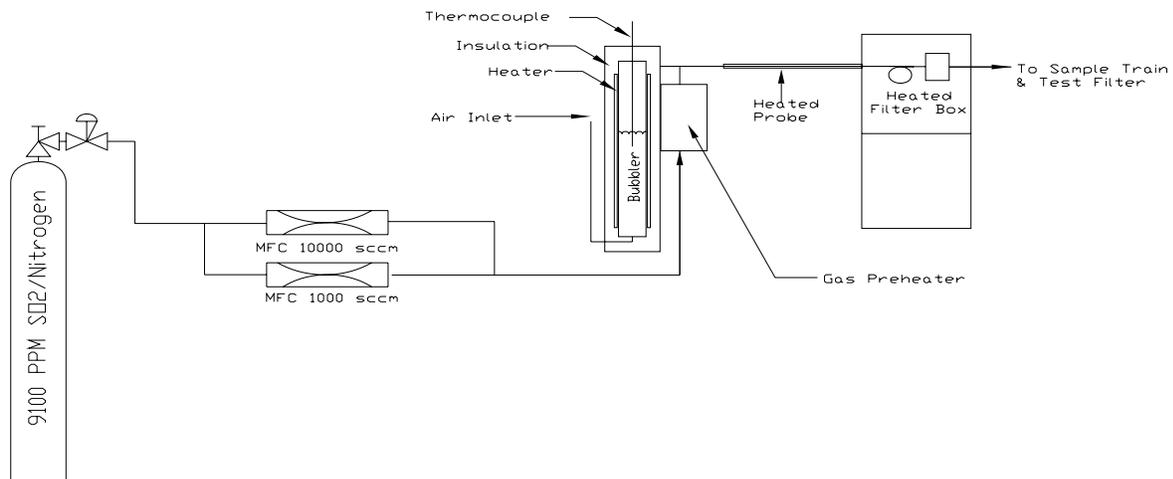
- $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$  ( $\text{H}_2\text{SO}_4$  with oxidation) Oily!
- $\text{SO}_2 + \text{H}_2\text{O} + \text{Cationic gases} \rightarrow \text{Sulfur oxide salt formation ??}$

## Experimental Method

Our study utilized four different Teflon membrane filters from two manufacturers with varying levels of pore size at varying  $\text{SO}_2$  concentrations. Filters were tested at a temperature of  $66^\circ\text{F} - 82^\circ\text{F}$  at saturated moisture levels, approximately 7-8%. Sampling rate was 21 L/min for approximately 30 minutes. Two replicates were performed for each set of conditions.

- Membrane Filters
  - Tisch  $1.0 \mu\text{m}$
  - Tisch  $0.45 \mu\text{m}$
  - Tisch  $5.0 \mu\text{m}$
  - Pall Corp “Zefluor”  $3.0 \mu\text{m}$
- $\text{SO}_2$  Concentrations
  - 0 ppm
  - 100 ppm
  - 500 ppm
  - 1000 ppm
- Other Parameters
  - Bubbler Temp  $100^\circ\text{F} - 117^\circ\text{F}$  (varied to maintain saturation after  $\text{SO}_2$  injection)
  - $\text{SO}_2$  9100 ppm (in  $\text{N}_2$ )
  - Flow 21 L/min

**Figure 2.**  $\text{SO}_2$  / Moisture System Schematic





## Results

- Pressure at exit of CPM filter housing was 8-9½ in Hg and did not change after sampling for 30 minutes regardless of filter type/porosity (except 0.45  $\mu\text{m}$ ) or  $\text{SO}_2$  concentrations!
- Pressure at exit of CPM filter housing when testing with 0.45 $\mu\text{m}$  filter was 9½-12 in Hg. Also did not change after sampling for 30 minutes, regardless of  $\text{SO}_2$  concentration!

## Discussion & Summary

Although  $\text{SO}_2$  emissions may under certain conditions form salts on a sampling filter surface,  $\text{SO}_2$  concentrations under 1000 ppm alone are not enough to foul Teflon membrane filters, even under full moisture saturation and when using a 0.45  $\mu\text{m}$  filter!

- SO<sub>2</sub> emissions up to 1000 ppm at saturated moisture levels (7-8% at 65°F - 85°F) are not enough to foul Teflon membrane filters at 0.45 µm porosity and higher.
- Parameters outside the scope of this test that may foul Teflon membrane filters
  - Moisture condensation at filter surface
  - CPM filter temperature below 65°F
  - Other species present in gas stream
  - Longer sampling rates

## **Acknowledgments**

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**Ken Schmaltz**                Membrane filter samples  
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**Chris Dale**                    Membrane filter samples  
**Environmental Supply, Inc.**

## **REFERENCES**

1.        EPA Method 202, U.S. Environmental Protection Agency, Rev 2010