

The EPA material below makes a very compelling case to require inert filter media for wood appliance testing; EPA's stack sampling method (Method 5) also notes this problem for certain circumstances.

EPA is aware of the acid gas artifact when sampling source PM with glass fiber filter media; see below from Method 5, section 7.1.1 [bolded]. The issue appears to be a “conventional wisdom” in the wood stack-testing community that there are no or negligible amounts of acid gases (SO<sub>2</sub> etc.) in wood smoke, and thus section 7.1.1 does not apply. That may be why Method 5G and 5H for wood stack PM tests specify the use of glass fiber filter media [below]. The ASTM method does as well.

Negligible S in wood may be a reasonable assumption for western US wood products (e.g., Douglas Fir or wood used in test labs like Omni in Portland OR), our measurements of many samples of wood pellets and chips [primarily eastern wood] show concentrations of S ranging from 8 to 175 mg/kg wood (ppm w/w), with a mean and median of ~75 ppm. See table 2 of: “Chemical Composition of Wood Chips and Wood Pellets” Srraam R. Chandrasekaran, Philip K. Hopke, Lisa Rector, George Allen, and Lin Lin Energy & Fuels 2012 26 (8), 4932-4937

This S analysis is also in our wood pellet and chip report to NYSERDA - as boxplot graphics:

<http://www.nyserda.ny.gov/-/media/Files/Publications/Research/Biomass-Solar-Wind/elemental-analysis-wood-fuel.pdf>

Woodsmoke from eastern wood, especially the northeast US where wet deposition of sulfur has historically been high, would be expected to have SO<sub>2</sub> and possibly other acid gases. Thus Method 5 Section 7.1.1's requirement for inert PM sample media may apply to wood burning appliance test methods. The expected variability of S in wood from different areas in the US and from different soils in the same region, and thus variation in the SO<sub>2</sub>-related PM artifact, could be a factor in the observed variability of wood burning appliance testing when cordwood is used. As the Q&A for Method 5 [below] says, this artifact becomes more important when testing cleaner (e.g., lower PM) devices such as those required by the proposed NSPS.

One candidate for an inert filter media suitable for these tests is Teflon-coated glass fiber media. This media can tolerate much higher particle loadings than the stretched membrane Teflon filter media commonly used for ambient PM sampling, such as for the PM<sub>2.5</sub> FRM sampler.

Background material follows.

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EPA test method 5, “Determination of Particulate Matter Emissions from Stationary Sources” specifies that glass fiber media be used for PM sampling.

<http://www.epa.gov/ttn/emc/promgate/m-05.pdf>

Specifically, methods 5G and 5H for measuring PM from wood burning appliances specify that glass fiber media be used for PM sampling.

But -- **Method 5, Section 7.1.1** states: “In sources containing SO<sub>2</sub> or SO<sub>3</sub>, the filter material must be of a type that is unreactive to SO<sub>2</sub> or SO<sub>3</sub>. Reference 10 in Section 17.0 may be used to select the appropriate filter.” However, that reference (Publication No. EPA-600/7-77-060. June 1977) is out of date.

#### **EPA's Method 5 Q&A:**

This issue is discussed in more detail in the EPA Q&A for Method 5 at:

<http://www.epa.gov/ttn/emc/methods/method5.html#dum>

which states: “The reaction of gaseous compounds such as SO<sub>2</sub> and SO<sub>3</sub> with filter media can result in large positive errors in mass on the filters. As the amount of particulate matter sampled using Method 5 decreases, it becomes increasingly important to ensure filter materials are unreactive to the constituents of the sample matrix.”



## SO2 Artifact References.

U.S. EPA, Air Quality Criteria for Particulate Matter, Volume I.

EPA/600/P-95/001aF, April 1996

Pages 4-30 and 4-31

[http://ofmpub.epa.gov/eims/eimscomm.getfile?p\\_download\\_id=219820](http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=219820)

The reactivities of filter substrates with the aerosol have been reported extensively. A common problem with glass fiber filters used on high volume samplers is the basic pH of the glass material and its effective conversion of SO<sub>2</sub> to particulate sulfates (e.g., Pierson et al., 1976). Appel et al. (1984) also reported similar conversions of nitrogen oxides to particulate nitrates on glass fiber filters.

Witz et al. (1990) reported losses of particulate nitrates, chlorides and ammonium (19, 51 and 65%, respectively) from quartz fiber filters during storage. No significant losses of sulfates were reported from quartz filters. Similarly, Zhang and McMurry (1992) reported the anomalous loss of fine particle nitrates from Teflon filters and noted that predictive loss theories were insufficiently accurate to permit corrections. Lipfert (1994) also observed that nitrate artifacts on glass fiber filters were difficult to quantify on a routine basis. Measurements of particulate nitrate using nylon filters by the IMPROVE protocols show, however, that such effects are minor except in California (Malm et al., 1994).

Eatough et al. (1993) found significant losses of particulate organic compounds on quartz filters due to volatilization, such that ambient concentrations of particulate carbon may be underestimated substantially. Lipfert (1994) investigated filter artifacts in a field study in New York and concluded that positive sulfate artifacts inflated PM<sub>10</sub> values from glass fiber filters by 6  $\Phi\text{g}/\text{m}^3$ . It was noted that the combination of sulfate and nitrate artifacts on glass fiber filters may inflate TSP measurements by as much as 10 to 20  $\Phi\text{g}/\text{m}^3$ .

Appel, B. R.; Tokiwa, Y.; Haik, M.; Kothny, E. L. (1984) Artifact particulate sulfate and nitrate formation on filter media. *Atmos. Environ.* 18: 409-416.

Lipfert, F. W. (1994) Filter artifacts associated with particulate measurements: recent evidence and effects on statistical relationships. *Atmos. Environ.* 28: 3233-3249.

Pierson, W. R.; Hammerle, R. H.; Brachaczek, W. W. (1976) Sulfate formed by interaction of sulfur dioxide with filters and aerosol deposits. *Anal. Chem.* 48: 1808-1811.

Pg. 428, *Methods of Air Sampling and Analysis*, 3rd ed., James Lodge, Jr. Editor, 1989:

**3.4 FILTER ARTIFACT FORMATION.** Sulfur dioxide, nitrogen oxides, nitric acid, and organic vapors can be absorbed on the filter medium along with the suspended particles thereby causing positive biases. Samples taken in the presence of high SO<sub>2</sub> concentrations have been shown to yield up to 10 µg/m<sup>3</sup> of excess sulfate on glass fiber filters (34,35). Quartz, Teflon membrane, and Teflon coated glass fiber filters have been shown to minimize NO<sub>x</sub> and SO<sub>2</sub> absorption (36,37), and denuder inlets (38) have been used to minimize nitric acid absorption. Very little information is currently available regarding organic artifacts.

34. Coutant, 1977. Effect of Environmental Variables on collection of Atmospheric Sulfate. Environ. Sci. Tech., 11:875.
35. Appel (1984), above.
36. Spicer and Schumacher, (1977). Interference in Sampling Atmospheric Particulate Nitrate. Atmos. Environ., 11:873.
37. Mueller et al. (1983). The Sulfate Regional Experiment: Report of Findings. Report EA-1901, EPRI, Palo Alto, CA