

RGM: What happens when good analytical chemists breathe toxic vapors

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Observations of 'Reactive Gaseous Mercury' are now widespread in the US and throughout the world. The method relies on a KCl coated annular denuder to collect RGM, followed by thermal desorption into a cold-vapor atomic fluorescence detector. However there are three problems with the method: 1) The chemical form of RGM in the atmosphere is not known, nor is it known whether commonly used surrogates (e.g. HgCl₂) are representative; 2) There is currently no standard method to calibrate; and 3) Very few tests have been made to evaluate interferences. These three problems severely limit our ability to use RGM data.

Our group has focused on development of a new method using thermal decomposition to measure total airborne Hg (TAM). Taking the difference between TAM and Hg^o should give a signal that is comparable to RGM. However a comparison of the new method with the annular denuder method has revealed a significant bias (see Swartzendruber *et al.* 2009). To better understand this bias, we have conducted lab tests using HgCl₂ and HgBr₂ in the presence or absence of O₃. The results show that RGM is lost from the denuder surface in the presence of O₃ at concentrations of 6-100 ppbv. These tests have been conducted several ways and the results appear to be robust. Overall, our tests indicate an underestimate of RGM of 20-50% due to O₃ at ambient concentrations. Very recent tests on RGM collected from ambient air suggest the loss is less, on the order of 10%, however these tests have not yet been repeated nor have they examined RGM from different environments. It should also be noted that there are other possible interferences, both negative and positive, that need to be evaluated. While it is not our intent to completely indict the KCl denuder method, the obvious message is 'caveat emptor'. In our opinion, the Hg measurement community needs to get back to basic analytical chemistry by expending more effort to fully characterize our methods.

As a final note, we are continuing to develop and evaluate our airborne instrument. We are testing several alternate methods to measure TAM and Hg^o without interference from O₃. Results to date are promising and will be shared at the meeting.

Photochemical reactions of manufactured Carbon nanomaterials in the aquatic environment

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The photochemical reactivity of nC₆₀ and carboxylated single walled carbon nanotubes (SWNT-COOH) in aqueous suspensions under natural sunlight (West Lafayette, IN, 40° 26' N) and lamplight ($\lambda = 300-410$ nm) have been investigated. The phototransformation of aqueous nC₆₀ in sunlight produces singlet oxygen (¹O₂) as a key transient species, as indicated by decay of the singlet oxygen scavenger furfuryl alcohol [1, 2]. Phototransformation products include more water soluble species; however, LDI-TOF mass spectrometry indicates that most of the photoproducts formed after 947 h of summer sunlight irradiation retain the 60-carbon structure. The FTIR spectrum of sunlight-irradiated nC₆₀ reveals the complete loss of the sharp absorption peaks of the parent C₆₀ and appearance of new absorption bands at frequencies consistent with C-O stretching (1060 cm⁻¹); C-O-H in-plane bending and/or carboxylate asymmetric stretching (1390 cm⁻¹); and C=C stretching and/or carboxylate symmetric stretching (1600 cm⁻¹). Irradiation under sunlight and under lamplight of carboxylated SWNTs (SWNT-COOH) dispersed in water also produces ¹O₂ (as indicated by furfuryl alcohol [FFA] decay). In air-equilibrated suspensions, the loss of 0.2 mM FFA in 10 mg/L SWNT-COOH was ~85% after 96 hours. Additionally, changes in the overall rate of FFA decay, upon performing the experiment with added azide or in deuterium oxide, were mechanistically consistent with ¹O₂ as the intermediate. By using other radical scavengers, the potential photo-generation of O₂⁻ and •OH under sunlight also is indicated, suggesting several reactive oxygen species (ROS) are produced simultaneously. Irradiation at pH 3 results in aggregation, indicating transformation reactions had occurred, with aggregation suggesting that de-carboxylation or other reaction leading to a less colloiddally stable materials had occurred. The significance of these reactions and of related work on phase distribution of C₆₀ [3, 4] will be discussed.

[1] Hou & Jafvert (2009) *Environ. Sci. Technol.* **43**, 362-767.
[2] Hou & Jafvert (2009) *Environ. Sci. Technol.* **43**, 5257-5262. [3] Chen & Jafvert (2009) *Environ. Sci. Technol.* **43**, 7370-7375. [4] Jafvert & Kulkarni (2008) *Environ. Sci. Technol.* **42**, 5945-5950.