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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A smart nanofibrous material for adsorbing and real-time detecting elemental mercury in air" *by* Antonella Macagnano et al.

Anonymous Referee #1

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A review of the manuscript acp-2016-1077

Journal: ACP Title: A smart nanofibrous material for adsorbing and real-time detecting elemental mercury in air Author(s): Antonella Macagnano, et al. MS No.: acp-2016-1077 MS Type: Research article Special Issue: Global Mercury Observation System – Atmosphere (GMOS-A)

General comments The task of the atmospheric mercury monitoring network developing is very important for understanding the scale of emission, regional and global transfer, and deposition of this environmental pollutant. Existing system of background monitoring is based on AFS and AAS instrumental observations requiring high investments for set up of any new monitoring point. That's why creation of new low-cost, hands-

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off measurement systems is an imperative topical issue. The manuscript presents the results of the development of a novel sensor for air mercury measurements based on original manufacturing technology. The title reflects the contents of the paper, the main results are outlined in the Abstract. Introduction gives a comprehensive, 3.5 pages, review of the atmospheric mercury, speciation, mercury transfer, existing publications on the mercury sensors development. Principal part of the manuscript is devoted to description of a new sensor design and manufacturing technology, study of the absorptivity of the new material exposed to mercury vapour. Sensitivity of the new sensors is far not sufficient for the task of mercury monitoring declared in Introduction (see Specific comments, 1). No data on mercury measurement in ambient air, selectivity, and possible interferences are presented.

Specific comments 1) Commonly, in regulatory and scientific literature, the weight concentration units are used (ng/m3, pg/m3) for atmospheric mercury and mercury speciation. The authors use these units in Introduction, but different units: ppm, ppb, ppt in parts describing sensors. It is not explained what these units are related to: volume, mass, or number of molecules? We suppose the volume units are used. It is inconvenient, because a comparison with conventional concentration units requires recalculation to the normal condition (P, T). Besides, the “tiny” ppb values can create a false impression of enabling background Hg concentration measurements. For example, mercury concentration of 1 ng/m3 is about 0.1 ppt (vol). It turns the achieved “low” detection limit (LOD) and measurement range of “20 -100 ppb (LOD 1,5 ppb)” (see lines 23-24) to a quite high figures in conventional units: 200,000 – 1,000,000 ng/m3 (LOD = 15,000 ng/m3). For comparison, the concentration of saturated Hg vapour is 12,000,000 ng/m3 at 18 oC. Such sensitivity gives no possibility to monitor mercury in ambient air, as the LOD is 10,000 times larger than the average background mercury concentration of 1.5 ng/m3 (see line 75).

2) How the LOD value was determined and at what exposure time? There is no description in the text. Different figures of LOD are presented in Abstract and Conclusion

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(compare lines 23-24 and 390-391).

3) Lines 69- 70 “Since automated measurement methods of Hg require power, argon gas, and significant operator training, they are difficult to apply. . .” Argon is not required for AAS systems.

4) Lines 105-107 “ decorated with gold nanoparticles (AuNPs) to obtain nanostructured materials capable of adsorbing GEM as a useful alternative system for making regional and global estimates of air Hg concentrations”. Gold adsorbs not only GEM.

5) Lines 116-118 This is true that: “sampling rates (SRs) using the same passive samplers may depend on environmental conditions and atmospheric chemistry at each site. Moreover, it has been also highlighted that the performance of passive samplers may be influenced by meteorological factors (e.g., T °C, RH, wind speed) therefore inducing bias for the result of passive sampling (Plaisance et al.,. 2004; Sderstrm et al., 2004).” However, there is no evidence that the developed samplers are independent of meteorological factors (e.g. humidity) and interference of trace gases and aerosols, especially under long exposure time.

6) Lines 121-124 “In this work we describe an alternative approach adopted in the place of conventional ones demonstrating that the combination of gold affinity for Hg with a nanoscale sized framework of titania provided the chance to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte.” See note (1). Besides, the technology of real-time monitoring is not described.

7) Lines 128-131. “The TGM/GEM sensor surface described here could be deployed in a global network such as GMOS; a permanent network of ground based monitoring sites and observations of Hg and/or related species on a global scale and with remote sensors would in fact be highly desirable”. Again, see note (1). The achieved sensitivity is insufficient for background measurement at the level of few ng/m3 provided by GMOS stations, and for speciation study at the level of pg/m3.

8) Lines 333-338. For better understanding of sensing measurements: “The sensor was exposed to a flow of Hg0 336 in air with a concentration of 800 ppb for 1 min (Fig. 7, right)” In terms of standard units, we see that the sensor was exposed to almost saturated Hg vapour at 8 mg/m3. Thereby it is not clear how such high concentration was measured? Earlier (line 234), it was mentioned, that “The Hg0 concentration was checked by Tekran®2537A analyser”. Tekran 2537 is not capable of measuring such high concentration.

Technical corrections 1). Numerous misprints: “fibers” instead of “vapour”:

Lines 91-91: “cold-fiber atomic absorption spectroscopy .... cold-fiber atomic fluorescence spectroscopy”

Line 141: ”Morphological, optical, electrical aspects and sensing measurements of fibers of GEM in air”

Line 144: “adsorbing and removal Hg fiber”

The same mistakes in the Reference list:

Lines 412-414 “Ferrua, N., Cerutti, S., Salonia, J. A., Olsina, R. A. and Martinez, L. D., 2007. On-line preconcentration and determination of mercury in biological and environmental samples by cold fiber-atomic absorption spectrometry. J. Hazard. Mater. 141 693–699” In the original Cold Vapour, see: http://www.sciencedirect.com/science/journal/03043894/150

Lines 412-414 “Determination by Cold Fiber Atomic Absorption Spectroscopy. Analytical Letters 39” In the original Cold Vapour, see: http://www.tandfonline.com/doi/full/10.1080/00032710600622167

2) Lines 73 -76 The sentence “Previous research highlighted that Hg-concentration levels in air vary greatly across different environmental locations, remote as the Polar Regions, background or rural, and urban locations with an average range between 1.5

ngm-3 (GEM) and 1 pgm-3 (GOM and PBM), depending on the speciation" should be revised: probably just by replacing "between" with "of".

Conclusion Obviously, an advanced comprehensive research has been done for the novel sensor design and manufacturing technology development. However, the sensitivity is far not sufficient to achieve the declared goal "to create promising sensors for environmental monitoring in real time, characterised by high sensitivity to the analyte" (lines 123-124). Probably, the new sensors can be used for other applications involving measurement of high mercury concentrations, such as technological or mercury exposure control. I would suggest that the manuscript No acp-2016-1077, after suggested corrections, can be redirected for publication in a journal dedicated to sensor technologies, which will be more suitable for this kind of research than Special Issue "Global Mercury Observation System – Atmosphere" (GMOS-A). The proposed novel Hg sensor may be made more suitable for the use in the GMOS project upon its further development and improvement.

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