Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

# An analytical investigation of 24 oxygenated-PAHs (OPAHs) using liquid and gas chromatography–mass spectroscopy

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The following figure is a representative OPAH calibration curve on the GC-EI/MS method. Concentration curves used in the study spanned 4 orders of magnitude using a 9-point curve, so all compounds were quantitated using quadratic models from ChemStation (Agilent) software. All OPAHs showed at least some non-linearity over the concentration range used in the study.

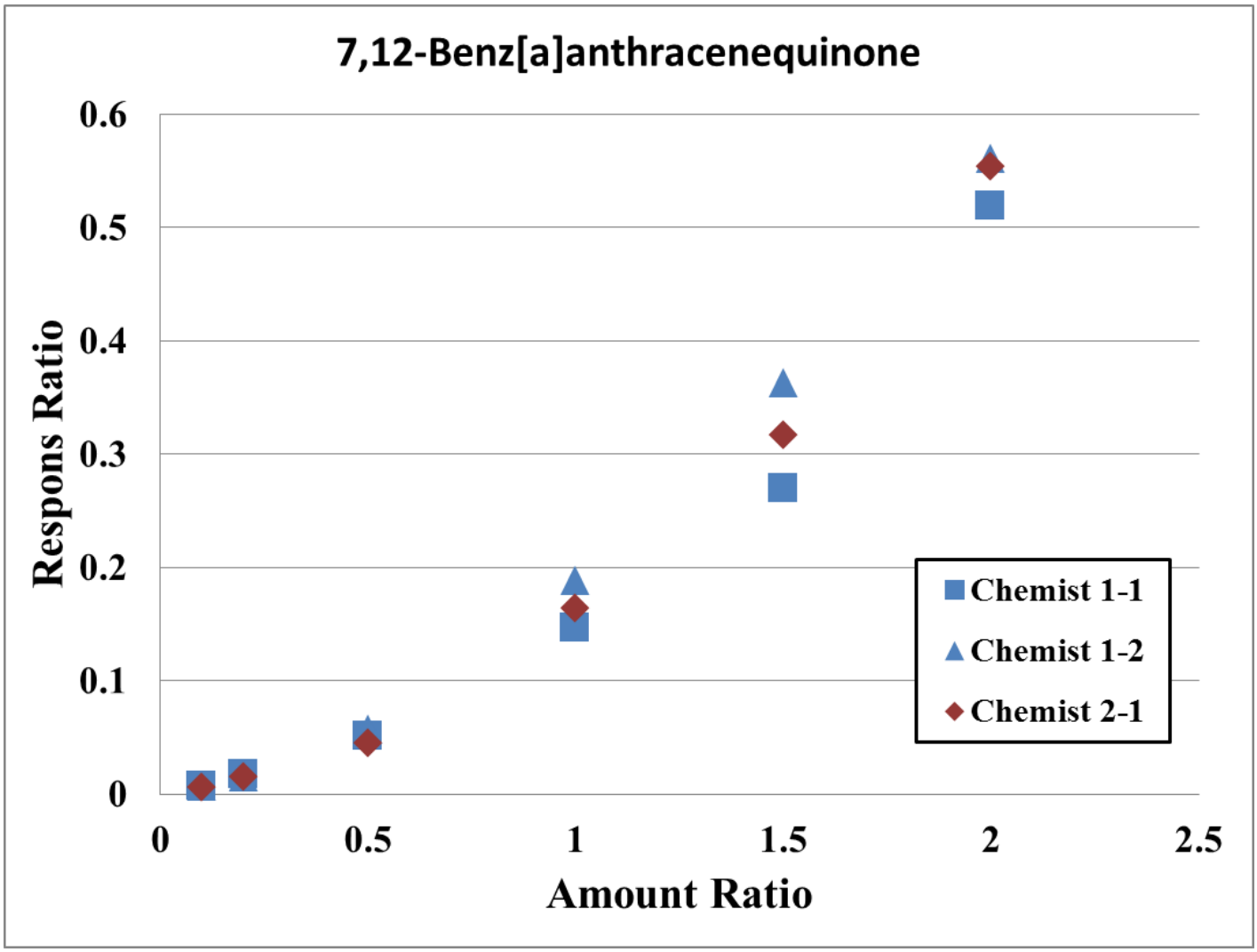


**Fig. S1.** Three independent calibration series from two chemists using the GC-MS. Colors correspond to the individual who made the calibration series, and each symbol represents a separately prepared series. The concentration range shown is 50-1000 ng $mL^{-1}$ to show non-linearity within an order of magnitude

The following figure shows average stability over 17 weeks for each individual OPAH on each method. Each time point consisted of three individual aliquots except for time point (0) for the LC-MS (n=1). Variability is represented by one standard deviation, and SigmaPlot™ (Systat Software, Inc., San Jose, CA) was used to model linear regressions for each stability series. Only 1,2-ANAPQ showed a significant decrease over the study period ($p<0.05$), but this result was later refuted by the data shown in Figure 2d and described in the main text.

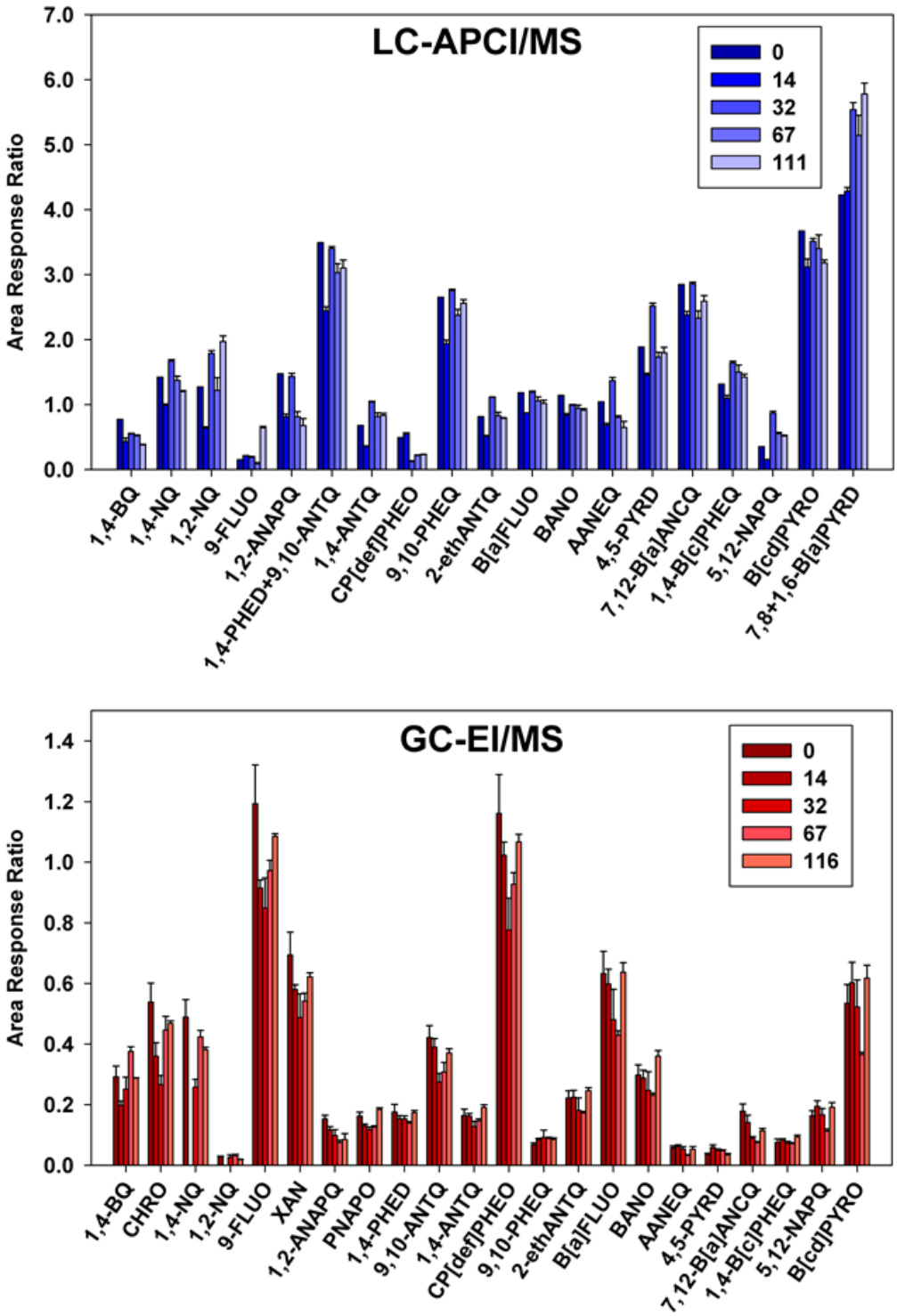


**Fig. S2.** Average stability (n=3) of OPAHs on the GC and LC-MS methods over 116 and 111 days respectively

The following table lists quantitated values in mg $Kg^{-1}$ of OPAHs for each method compared to NIST certificate of analysis values (COAs) [28] and to Layshock et al. 2009 [17]. Our purpose here is to show current individual quantitated values, comparisons made between the three bodies of work, and to demonstrate each method in our research as able to quantitate OPAHs in real matrices. Comparisons to NIST COAs have been originally documented in Layshock et al., 2009 [17], and extracts shown here were re-quantitated in 2012 from the original extraction date in 2009.

**Table S1.** Comparison to Layshock et al., 2009 and NIST informational values in mg $Kg^{-1}$ of sample. Compounds and values highlighted in green have not been published in either Layshock et al., 2009 or in NIST certificates of analysis (COA)

| | Urban Dust SRM 1649b | | | | Diesel Extract SRM 1975 | | | Diesel Particulate Matter SRM 1650b | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **OPAHs** | This Study GCMS | This Study LCMS | Layshock et al. 2009 | NIST | This Study GCMS | This Study LCMS | Layshock et al. 2009 | This Study GCMS | This Study LCMS | Layshock et al. 2009 |
| 1,4 Benzoquinone | <LOQ | <LOQ | N/A | N/A | <LOQ | <LOQ | N/A | <LOQ | <LOQ | N/A |
| Chromone | <LOQ | N/A | N/A | N/A | <LOQ | <LOQ | N/A | <LOQ | <LOQ | N/A |
| 1,4 Naphthoquinone | (0.25) | 0.30 | N/A | N/A | <LOQ | 0.51 | N/A | <LOQ | 1.1 | N/A |
| 1,2-Naphthoquinone | (2.8) | <LOQ | N/A | N/A | (5.2) | <LOQ | N/A | <LOQ | <LOQ | N/A |
| 9-Fluorenone | 0.76 | 1.2 | 0.74 | 1.4 | 2.6 | 2.3 | 2.6 | 19 | 18 | 25 |
| Xanthone | 0.19 | N/A | N/A | N/A | <LOQ | <LOQ | N/A | 6.2 | <LOQ | N/A |
| Acenapthenequinone | <LOQ | <LOQ | <LOQ | N/A | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| Perinaphthenone | <LOQ | N/A | N/A | N/A | <LOQ | <LOQ | N/A | 150 | <LOQ | N/A |
| Phenanthrene-1,4-dione | <LOQ | <LOQ | <LOQ | N/A | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| 9,10-Anthraquinone | 2.6 | 1.3 | 1.5 | 1.8 | 8.1 | 2.2 | 5.4 | 64 | 21 | 54 |
| 1,4-Anthraquinone | <LOQ | <LOQ | <LOQ | N/A | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| 4H-cyclopenta[def]phenanthren-4-one | 0.73 | 1.5 | 0.60 | N/A | 7.0 | 6.0 | 7.5 | 9.2 | 7.6 | 3.4 |
| 9,10-phenthrenequinone | <LOQ | <LOQ | <LOQ | N/A | <LOQ | <LOQ | <LOQ | <LOQ | 2.6 | <LOQ |
| 2-Ethylanthraquinone | (0.51) | 0.93 | N/A | N/A | <LOQ | 0.51 | N/A | 4.4 | 19 | N/A |
| Benzofluorenone | 0.78 | 0.97 | 1.6 | N/A | 1.8 | 1.7 | 3.2 | 18 | 17 | 16 |
| Benzanthrone | 1.18 | 0.62 | 3.9 | 1.6 | 1.5 | 0.62 | 4.8 | 23 | 13 | 39 |
| Aceanthracenequinone | <LOQ | <LOQ | <LOQ | N/A | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| Pyrene 4,5 dione | <LOQ | <LOQ | N/A | N/A | <LOQ | <LOQ | N/A | <LOQ | <LOQ | N/A |
| 7,12-benz[a]anthracenquinone | 1.4 | 1.1 | 3.0 | 3.6 | 3.4 | 2.1 | 6.9 | 5.7 | 5.1 | 9.2 |
| Benzo[c]phenanthrene-[1,4]quinone | 0.20 | 0.32 | <LOQ | N/A | <LOQ | <LOQ | <LOQ | <LOQ | 27 | <LOQ |
| 5,12-Napthacenequinone | 0.72 | 0.80 | 2.0 | N/A | <LOQ | <LOQ | 0.81 | <LOQ | 7.1 | <LOQ |
| Benzo(cd)pyrenone | 0.56 | 0.33 | 1.7 | N/A | 0.71 | <LOQ | 2.2 | 5.0 | 2.5 | 10.4 |
| Benzo[a]pyrene-7,8+Benzo[a]pyrene-1,6 | N/A | <LOQ | N/A | N/A | N/A | <LOQ | N/A | N/A | 1.6 | N/A |
| **OPAHs** | **13** | **9.0** | **15** | **8.4** | **30** | **16** | **33** | **304** | **140** | **158** |

Abbreviations: SRM – Standard reference material, <LOQ – below limit of quantitation for that study, N/A – Not applicable

The following figure represents additional evidence of suppression of GC-EI/MS data by silicone PSD background in an un-deployed sample. Standard addition values for all 5 OPAHs originally suppressed in Figure 5 in the main text are all within 20% of the true value. However, IS quantitated values are all below 80% of the true value, and in the case of 1,4-B[c]PHEQ, an order of magnitude lower (IS-50 ng $mL^{-1}$; true value-500 ng $mL^{-1}$). Current work with silicone PSDs in our laboratory have shown more efficient cleaning processes as effective for removing silicone suppression of OPAHs (data not shown).

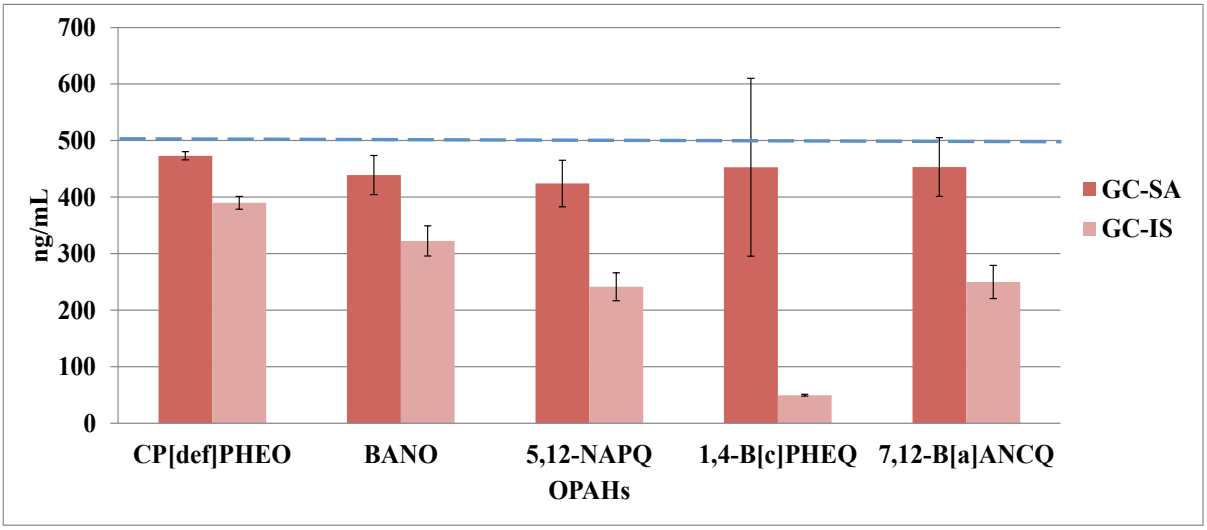


**Fig. S3.** Standard addition and internal standard quantitation on a non-deployed silicone sample using the GC-EI/MS method. Since the silicone had no background, the true value of the overspikes and addition should be 500 ng $mL^{-1}$, and is represented by the dashed blue line