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Letter to the Editor: Preparation of respirable crystalline silica samples for subsequent analysis

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Dear Sir

We respectfully disagree with the conclusion in the paper by Lee, R.J. et al. (2016) that: "… muffle furnace preparation of [respirable crystalline] silica samples be discontinued" because the authors data and the results of previously published studies do not support this assertion. Muffle furnace treatment and low-temperature plasma ashing are regarded as equivalent sample preparation steps for respirable crystalline silica analysis in NIOSH Manual of Analytical Methods 7500 (NIOSH, 2003a) and 7602 (NIOSH, 2003b). Muffle furnace ashing is also used for sample preparation in several international standard methods (ASTM International, 2014; HSE, 1984; INSHT, 2005; INS, 2013; ISO, 2015). A previously published study by Cox et al. (2015) obtained results that indicated "under-reporting" of silica mass on test filters. Lee, R.J. et al. (2016) examines two possible reasons, "shipping" and "level of effort", as to why results were low in the Cox et al. study. Although Lee, R.J. et al. (2016) correctly state that "OSHA (2016) reviewed the Cox et al. study and identified several deficiencies associated with filter generation and quality control testing that OSHA believes invalidates the Cox et al. findings", they follow this with the statement that their study "addresses OSHA's comments and finds the deficiencies cited did not contribute to the results of the Cox study". This latter statement is surprising in that the major deficiency noted by OSHA in their criticism of the Cox et al, (2015) study involved "filter generation and quality control testing", not "shipping" or "level of effort".

Lee, R.J. et al. (2016) used different levels of quartz on filters obtained from the National Institute of Standards and Technology (NIST), i.e. Standard Reference Materials® (SRM) 2953, 2954 and 2955 (NIST, 2007). Lee, R.J. et al. (2016) found no problems with sample loss during shipping after analysis of the results using five statistical tests (section 2.3). This conclusion confirms the findings of a large round-robin carried out by the United Kingdom's

Health and Safety Laboratory (McLister et al., 2001). On the other hand, Lee, R.J. et al. (2016) believed they had uncovered issues with what they termed “level of effort” based on statistical “analysis by JMP® software” (the specific statistical tests were not reported). One issue was with partial scraping and non-scraping of the samples in the crucibles after the ashing procedure, where they found poor and inconsistent recoveries. This is not a new finding, and NIOSH 7500 (XRD) stipulates: “scrape the crucible with a glass rod to loosen all particles” (NIOSH, 2003a), while NIOSH 7602 (IR) requires that potassium bromide be added to the sample in the crucible. This latter method further requires standards to be run through the entire preparation process, including ashing, “to monitor for contamination and losses” (NIOSH, 2003b).

The other issue with the processes considered by Lee et al. (2016) under “level of effort” is purported differences in the use of: 1) low temperature plasma ashing (LTA), 2) muffle furnace with new crucibles (MF-new), and 3) muffle furnace with used crucibles (MF-used). Their only statistically significant finding (test results and probability not reported) for these processes when properly implemented (complete scraping of the crucible) was between the pooled means (all loadings) of the reference materials and the different processes (LTA, MF-new and MF-used). However, we believe this analysis to be inappropriate as pooling the different loadings conceals the underlying variances in the dataset. The NIST SRM’s have narrow coefficients of variation (CV) around their average compositions, while the experimental CVs from the analyses of the different treatment processes are much larger, so that any comparisons with just a few samples in each loading level for each process (n=5) can lead to misleading assumptions about the significance of differences. As an example of the inconsistency of the data, the results for LTA and MF-new at the highest loading are similar to the reference values, and so are the results for MF-new at the middle loading, while the results for LTA at this middle loading are not.

We have examined the differences between the processes at each loading statistically by analysis of variance (ANOVA) in SAS® (Carey, NC). The data are presented in box-plot format in Figure 1. The “recoveries” follow these statistically significant rankings: lowest loading (19.4 μg): LTA = MF-new = MF-used; middle loading (48.6 μg): LTA > MF-new = MF-used; highest loading (96.1 μg): LTA = MF-new > MF-used. There is no consistent pattern in the comparisons between either the different processes against the reference values or the different processes against each other, which indicates that the processes are not the source of the variability observed.

Overall, the CV of LTA in the Lee, R.J. et al. (2016) study is a little better than MF (new or used; used is slightly lower than new), and a similar observation was noted in the method ruggedness tests performed for NIOSH (Anderson, 1983). Ruggedness tests were applied as part of the respirable crystalline silica methods development, to determine any significant differences from sample preparation techniques, including parameters within-technique such as temperature (for MF) or wattage (for LTA), and time (for both), and between the techniques of x-ray diffraction (XRD) and infra-red (IR) analysis. In the 1983 test report, a larger variance for MF is indicated as a reason for preferring LTA for IR analysis. However, a similar difference was not observed in the corresponding tests for XRD analysis. The combined data can be found on p77 of Anderson (1983) where the difference in absolute

average values for LTA-IR and MF-IR (7.5%) does not indicate major losses through the use of MF, especially since the XRD average result falls between the LTA-IR and MF-IR average results. The 16% CV for MF-IR analysis was considered fit-for-purpose and thus MF is included as an option in method 7602. The pooled CV's from the data in the work of Lee, R.J. et al. (2016) are below 16% – being 13% for MF-new and 11% for MF-used.

In addition to the ruggedness tests (Anderson, 1983) other reports corroborate our objection to the conclusions in Lee, R.J. et al. (2016). In our laboratory, Lee, T. et al. (2012) deposited reference coal dust (two different particle sizes) with consistent quartz content on filters and prepared 90 samples by LTA and 90 by MF for IR analysis. The percentages of quartz in the coal dust measured were then compared for each process. Quartz contents obtained by the different ashing methods were 7.0 ±1.3 (LTA) and 7.5 ±2.1 (MF) percent, with no significant difference between them (see the last two columns in Fig 7 of Lee et al., 2012). If muffle furnace samples had lower recovery of quartz than LTA, this would have shown up as a significant difference in the quartz content of the two coal dusts between the two preparation techniques. Also, Harper et al. (2014) evaluated the analyses of proficiency test samples of laboratories participating in the program administered by the American Industrial Hygiene Association Proficiency Analytical Testing (PAT), LLC. The data from IR analyses were not found to have scatter that could be attributed to bias between different procedures, and there was no significant difference between IR results and XRD results. In an examination of one specific PAT round of testing (Eller et al., 1999) there was no significant difference between processes in the PAT round tested, which is why that information was not included in the publication (Key-Schwartz, NIOSH – personal communication). In addition, 56% of respondents used MF for sample preparation and this proportion was not likely very different in the larger study of Harper et al. (2014). A significant bias in this process compared to others would have been obvious in the scatter of the data in Harper et al. (2014).

The conclusions reached in the Lee, R.J. et al. (2016) paper: "the data do show a low recovery when muffle furnaces are used in the sample preparation" cannot be supported by statistical analysis of the data presented, provided that scraping is complete per NMAM 7500. Nor is there any evidence from previous studies that muffle furnace will produce low results. Thus there is not any basis on which to recommend a substantive change to the methods per the manuscript: "These data suggest the method should be modified to mandate plasma ashing rather than permitting the use of a muffle furnace".

One other statement in the abstract of Lee, R.J. et al. (2016) regarding the relationship of this work to OSHA Standards concerning respirable crystalline silica should also be questioned. OSHA takes its own samples for compliance purposes are these are prepared by digestion in tetrahydrofuran and not by LTA or MF ashing, so this work is not fully relevant "in light of OSHA's proposed reduction in the PEL and action level proposed by OSHA" (sic).

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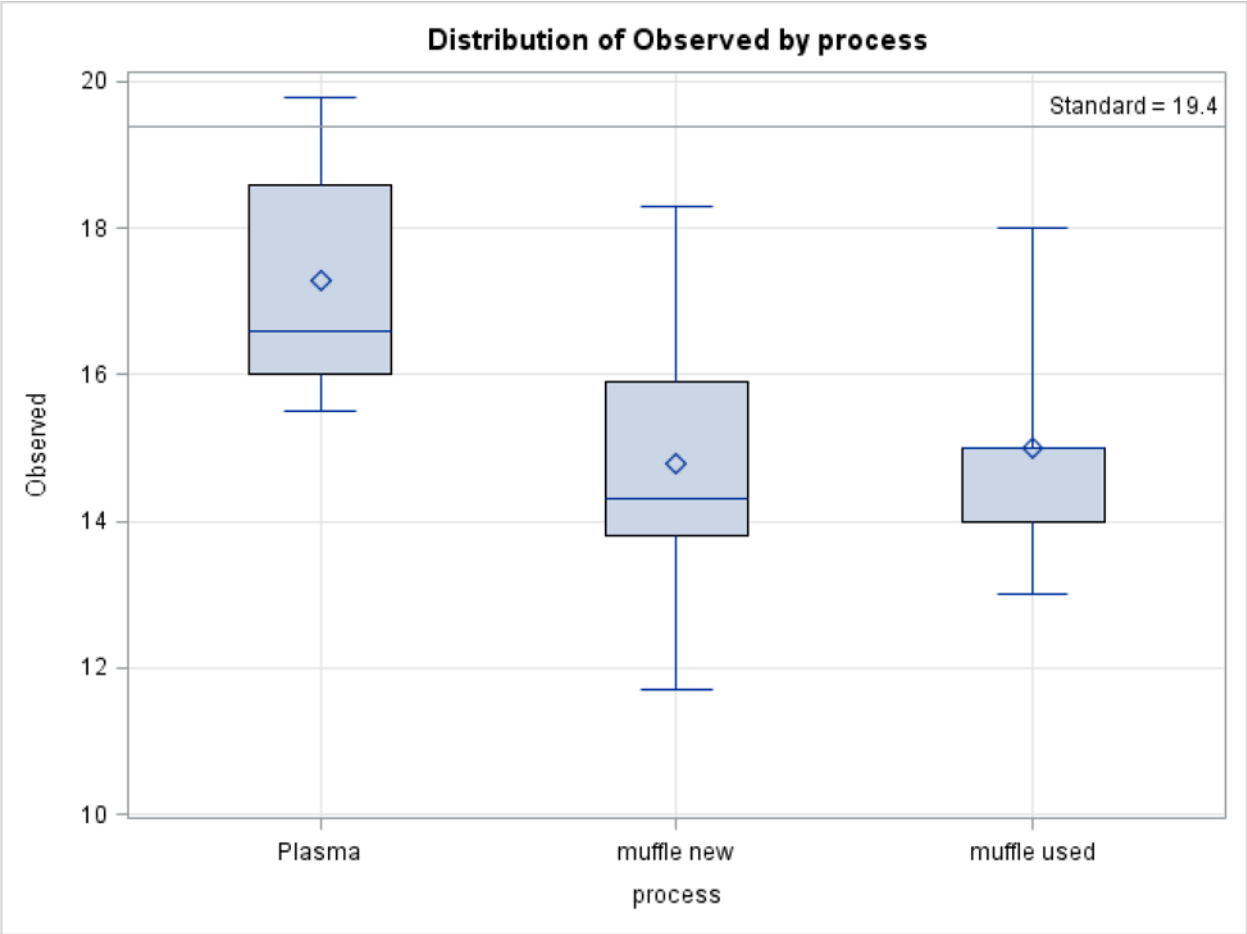
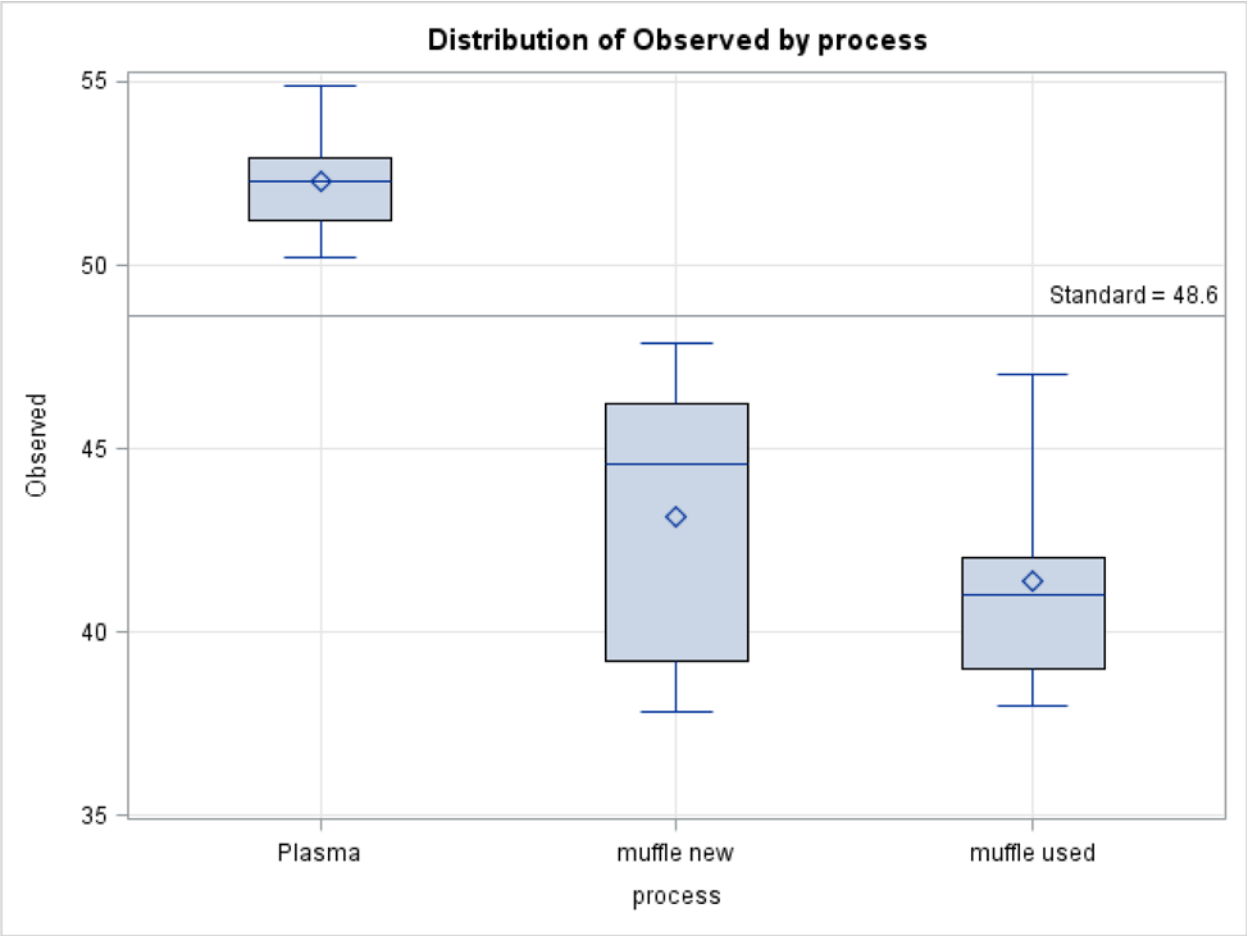


(a)



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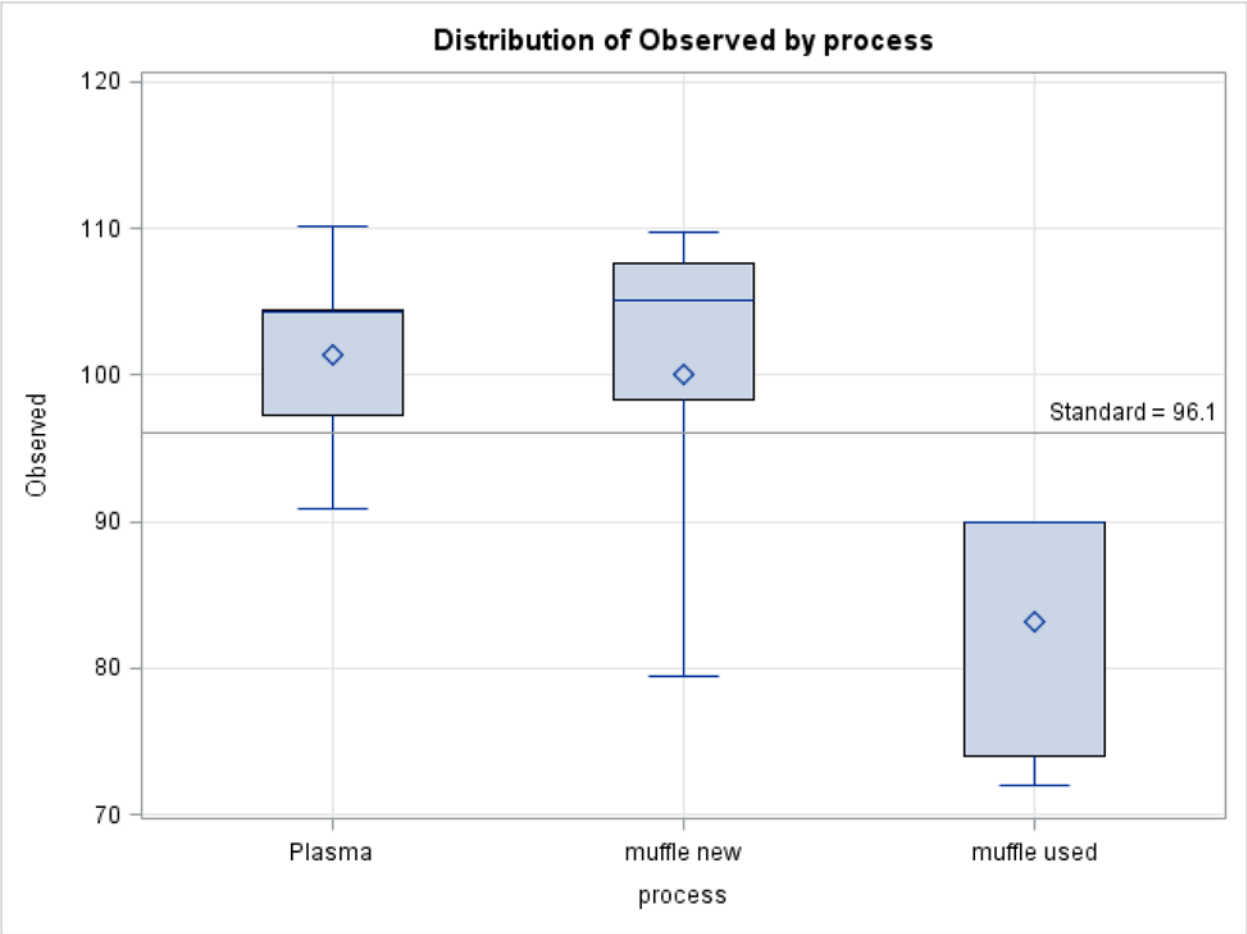

(c)

Figure 1.

(a) Standard mass of respirable silica on filter = 19.4 μg.

Length of the box represents the interquartile range; diamond in the box interior represents the mean horizontal line in the box interior represents the median; vertical lines issuing from the box extend to the minimum and maximum values of the analysis variable.

(b) Standard mass of respirable silica on filter = 46.8 μg.

(c) Standard mass of respirable silica on filter = 96.1 μg.