

To:

From:

Subject: Comments from review of NIOSH Methods 9106 and 9109

Date: November 17, 2005

I have completed a review of the draft NIOSH Methods 9106 and 9109, and I have the following comments:

Methods 9106 and 9109

The SIM tuning and data acquisition requirements are not specified. Presently, instruments may be tuned in any manner at the discretion of the laboratory, and may include tuning to Scan mode requirements with an accompanying loss in sensitivity. I have observed that the tuning algorithms proposed are designed to maximize the 69 atomic mass unit ("amu") ion for the tuning compound perfluorotributylamine ("PFTBA") inherently produce a better signal to noise ratio, and a lower detection limit. These tuning algorithms are typically referred to as the "Autotune" instrument option. The proposed tuning specifications are ambiguous, and may produce ambiguous data. In analyzing data produced from these methods, the agency will require that tuning be accomplished by way of Autotune protocols, and the following conditions must be met: (1) The operator must confirm that the 69/70, 219/220, and 502/503 isotope ratios occur at the proper ratios of 1 percent (+/- 50 %), 5 percent (+/-25 %), 10 percent (+/- 10 %) respectively.; (2) The peak width at half height for the 502, 219, and 69 PFTBA isotopes be 0.5 amu +/- 0.2 amu: and (3) The operator must confirm the correct mass assignment of these isotopes to a tolerance of 0.1 amu (e.g., 69.0 amu +/- 0.1 amu).

Once tuned, these instruments have acceptable electronic drift; such that, operators must verify that the tuning is stable at a minimum of once per operating day to insure correct mass axis alignment, and eliminate data accumulated with contaminated ion sources. These instrument tuning requirements specify the minimum acceptable performance goals which are easily verified.

I observed an apparent typographic errors in the existing tuning requirements, Suggested Tuning Requirements for the Scan Mode, Table 7 each method (9106/9109):

- m/z 119 should be m/z 219
- The Scan Rate at 2 /second is not performance based. Consistant with other specifications, the agency will require a minimum of 10 scans across a peak, and this scan rate may need to be adjusted on certain instruments.

Both of these methods, in Table 8, footnote (3) proposes a dwell time of 50 milliseconds. It is clear that this suggestion does not optimize the data acquisition for maximum sensitivity, nor will this recommendation meet a minimum of 10 scans across the peak. This acquisition parameter must be adjusted to optimize the response.

In tabular form these are the minimum performance specifications for the use of this method in Colorado in support of agency projects:

Minimal acceptable requirement for analysis of wipe samples

<u>Activity</u>	<u>Specifications</u>	<u>Documentation needed</u>
GC/MS Tuning	Autotune or equivalent. Acceptable Isotopic ratios (1, 5, 10 %) Peak width at half height (0.5 amu +/- 0.2) Correct mass assignment (+/- 0.1 amu) 10 scans across a peak	Printout of tune report. Demonstration.

Confirmed Positive detections: (REPORT: Concentration, qualify quantitative estimates with a "J")

- ion relative retention time tracks that of standards (+/- 0.10 RRT)
- characteristic ion abundance ratio tracks ratio of standards (+/- 25 %)
- characteristic ions maximize within +/- one scan

Unconfirmed detections: (REPORT: Detected not confirmed, specify reason. Qualify quantitative estimates with a "J")

- ion relative retention time tracks that of standards (+/- 0.10 RRT)
- characteristic ion abundance ratio fails to track ratio of standards (+/- 25 %)
- characteristic ions do not maximize within +/- one scan

Method 9109

This method, as written, suggests the concurrent use of MSTFA and MBHFBA as a combined derivatizing reagent scheme. This does not make sense to me. I think the intent was to promote either MSTFA, or MBHFBA since each reagent develops a unique derivative. Table 8 in this method includes suggested ions for Heptafluorobutyryl-Tri methyl silyl derivatives. When I reconcile the suggested ions present in Table 8, I deduce the ions in the table refer to Heptafluorobutyryl derivates from the use of MBHFBA. There is not an equivalent table for Trimethyl-silyl derivatives produced from MSTFA.