COMMENTS ON SAMPLING AND ANALYTICAL METHODS

Minor comments are on the original NIOSH draft.

General comments: In using trade names, the document should be consistent. Any shorthand such as dropping registration notation should be documented at the earliest opportunity and then a standard format adopted thereafter e.g. Aroclor ®
Florisil ®

Environmental Sampling and Analytical Methods

3714 ....evaluated under laboratory conditions using aerosol generation techniques. Field studies were also performed in a PCB environment containing aerosol and vapor components.

The statement as it stands leaves open the question of aerosol or vapor studies. The document should be completed by inclusion of this information in a manner similar to the above amended statement, and expressing the true nature of the exercise. Both aerosol and vapor concentrations must be included.

3724 -3726 Earlier in the text, 2 solvents are mentioned along with the use of single and multiple impingers.

/ Which solvent was used should be clarified (toluene or ethylene glycol) and the number of impingers.

The conclusions reached imply a study using an aerosol of PCBs or an equilibrated vapor environment. Is this true?

3737 to use when personal sampling for PCBs.

This circumvents other techniques such as area monitoring for calculating effective exposures.

3738 NIOSH has not tested all available solid sorbents (e.g. porous polymers). Hence, this line should be reworded to reflect only those methods tested.

3752 Electron capture gas chromatography is the most widely used method, but not necessarily the "preferred" method. For example, the wide variance in response factors referred to in Table I is a distinct disadvantage.

3801 -3803 In this day, it is not possible to eliminate a method based on the lack or expense of a computer. In many small companies, the OSHA requirements will rapidly force the purchase of such a unit for many applications.

3809 -3810 One might prefer NBS as a repository for "standard" samples.

3824 Perchlorination should definitely not be used to quantitate PCBs. We have confirmed that not only biphenyl, but also substituted biphenyls, cause large positive errors. At least one of the replacement fluids for PCBs in capacitors is a substituted biphenyl (Chemical and Engineering News, p. 25, Nov. 15, 1976). Hence this interference is already present in the manufacturing facility and precludes use of perchlorination. See attached copy of letter from J. Coleman Meber to Dr. I. E. Wallen.

3834 -3835 See comments on alternate standardization procedure, line 5354.

3843 -3845 See above comments on perchlorination.

APPENDIX I

5248 Samples collected must be representative of the personal exposure of individual workers.

5252 -5253 Records should include: Pump model & Serial no.
Sampling Tube type and no.
i.e. sampling equipment details

5258 -5260 Calibration data should also be recorded.

5266 -5268 The aim of sampling is to permit determination of the personal exposure level primarily. This leads to a decision on compliance/non-compliance situations. It cannot lead to the "lowest feasible level" without other major input beyond the scope of sampling and analysis.

5273 Airflow through the pump shall be controllable within ±5% of the desired rate during the entire sample period.

5291 A more frequent requirement for pump calibration is required. At least monthly and preferably in the method for a daily setup calibration.

5292 -5293 Spot-checked is an open statement and means nothing.
For digital readout pumps specify parity check between expected stroke count versus actual.
For pump with rotameters specify before and after readings. We would prefer a calibration after flow stabilization and again before pump is turned off, for each sample.

5303 The sorbent tube should not be vertical.
Pointing down - loses glass wool and Florisil
Pointing up - dust from overhead, hard hat, etc. enters.
Suggest a close to horizontal location, attached to the collar of the worker.

5304 Air being sampled should pass directly into the open inlet of the sorbent tube
This precludes filters.

5308 The recommended sample volume for this method is 50 liters (U.S. spelling)

5310 The sorbent tubes should be labelled. At this point it should reiterate checking label and I.D. Number.

5320 A bulk air sample is of no value unless the restraints required to obtain a good and recoverable sample are fully documented.

5324 Throughout Appendix II nomenclature for PCB and PCBs is confused. In general, PCBs should be used as a noun describing a PCB mixture, while PCB is an adjective.

5346 This reads more smoothly if written, "This would correspond to a detection limit of 40 ng ~~of~~ in 5 ml of desorbent".

5354 This alternate standardization procedure is of highly questionable utility. As pointed out in line 535B, it has not been evaluated in NIOSH laboratories. As correctly stated in the draft, the reason an alternate procedure is needed are two-fold. First, most of the GC peaks in a chromatogram of a PCB product contain more than one component. Secondly, electron capture detector response differs significantly for different PCB isomers (See Table I of the draft). These two factors indicate that the absolute quantity of PCB represented by a given peak containing unresolved components varies depending on the relative amounts of the components.

The relative composition of a given peak can vary for the following reasons:

1. PCBs with a given degree of chlorination (i.e. 42%) from different manufacturers contain different isomer ratios.

2. Component ratios vary for products with different degrees of chlorination. For example, from Table XII - 6, the ratio of dichloro- to trichlorobiphenyls for the peak with RRT 28 in Aroclor 1221 is 85:15. From Table XII - 8, the same peak in Aroclor 1242 has a ratio of 25:75. Similarly, for peak RRT 70 in Aroclor 1242 and 1254, the tetrachloro-to pentachlorobiphenyl ratios are 90:10 and 25:75.

3. Vapor pressure differences alter the composition of vaporized PCBs relative to the liquid. (See attached figure showing chromatograms of liquid and vapors from Aroclor 1016).

4. Interfering components may be present which distort the sample chromatogram. This is likely to be a major problem in capacitor and transformer manufacturing facilities because several of the PCB replacement products (i.e. phthalate esters and chlorobutyl-diphenyl ether) have similar GC retention times to PCBs and give an electron capture response.

   The weight factor technique of Webb and McCall does not adequately account for these difficulties.

   For those situations where the sample chromatogram closely matches the chromatogram of a reference PCB mixture, the Standard Analysis described in 5554 ff should be followed. However, if the chromatograms do not match, we believe the only satisfactory analytical method which will yield accurate results is gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring (SIM). The detection limit of this technique for Aroclor 1016 is about one nanogram of PCB injected into the instrument. Considering the environmental limit of 0.05 mg/m^3 recommended in this document, it might be possible to reach this lower detection limit for the total procedure by sampling as outlined in the draft, evaporating the hexane desorbent and analyzing the concentrate by GC/MS.

Alternatively, thermal desorption from a suitable solid sorbent directly into the GC/MS can be used. This well documented technique analyses the entire collected sample at once, rather than only an aliquot at a time. Response factors vary only slightly for different PCB isomers and most interferences are eliminated.

5381 The bulk sample must not be shipped in the same container as the sample tubes.

5396 The volume of air sampled can be measured to within at least ±5%. Delete next sentence.

5410 Delete 100% and conclude sentence with ".... recovered with a relative standard deviation of 4.4% for 27 spiked samples". Delete next sentence.

5460 Type of electron capture detector is not important.

5515 rinsing with pesticide grade acetone and hexane should follow the water rinses.

5533 Argon/methane is also a suitable GC carrier gas. The flow rate for either carrier gas should be only about 30 ml/min for a 2 mm id column.

5590 Actual retention times should be used in calculations if available. If not available, then the measurements described here can be used.

6118 The vapor pressures in Table XIII - 5 appear to be too high. What is the source of these data, and has their accuracy been verified?