WORKING DRAFT

PCB ANALYTICAL METHODOLOGY

We have no reason to doubt that the recommended EPA PCB test method is capable of detecting ppt levels of PCBs in waste waters. However, our experience with analyzing industrial waste waters for PCBs at the ppt level prompts us to be concerned about the following areas, some of which are not covered adequately in the test procedure.

I. Sampling Procedures

II. Correction for Laboratory and Reagent Background

III. Correction for Non-PCB Sample Interferences

IV. Absolute Verification

V. Quantitation

VI. Precision and Accuracy

Our concern lies in the fact that any method, especially one as complex as a PCB analytical method, which is to be used for enforcement purposes must be thoroughly evaluated. If this is not done, the enforcement and hence effectiveness of any effluent limit, no matter what the level, will prove to be difficult if not impossible.

For example, we have found that if waste water streams are not sampled properly, the PCB levels found depend on the sampling procedure employed and bear no relationship to the amount of PCBs discharged. For this reason, sampling procedures used must be designed for the discharge in question and clearly stated. To our knowledge, this has not been done.

We also note that no provisions are recommended for correcting the apparent PCB level found in a sample for laboratory and reagent background. It is our experience that as one approaches the ppt level, this background can significantly affect the observed PCB level.

With regard to correction for non-PCB sample interferences, we feel that while the procedure notes many of the possible interferences, it does not really address itself to the ones which are more likely to be in industrial waste water streams. For this reason, if the electron capture chromatogram does not match the PCB being manufactured or used, complete absolute identification of all components counted as PCB must be validated via GC/mass.

While the scheme proposed for estimation (quantitation) of PCBs is logical, it suffers from the same shortcoming as do the multitude of other procedures which have been proposed. It is an empirical estimate and only a reflection of the real PCB level. Therefore, it should be determined via an alternate more elaborate procedure

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how closely the calculated PCB levels (for each of the cases) are to the real PCB levels so that they may be corrected.

Last, but not least, the precision and accuracy of any procedure proposed as a standard method should undergo a thorough intra-laboratory evaluation. If this has not already been done, it must be carried out prior to the use of the procedure for enforcement purposes. The accuracy and precision of the Monsanto PCB procedure has been subjected to a preliminary evaluation. Prior to this evaluation, we probably would have over-estimated the precision and accuracy of our procedure. The exact details of the evaluation are available. Briefly, samples were prepared by spiking distilled water with 500 ppb PCBs. Individual preparations include blanks (no PCBs), Aroclor 1242 only, Aroclor 1254 only, Aroclor 1260 only, all 50-50 two component mixtures, and a 1/3, 1/3, 1/3 preparation containing all three components. Six samples of each mixture were prepared and analyzed by two analytical laboratories. Each result, expressed in ppb of the individual Aroclor, was converted to per cent of the total added. Analysis of variance was run on all data taken together and on each laboratory independently.

- The 95% confidence limits observed for individual results were:

Either Lab	87.5 ± 55.2%
Lab A	81.3 ± 46.4%
Lab B	93.7 ± 19.2%

- The repeatability for the individual labs, based on repeat tests of samples having identical prepared compositions was:

Lab A	± 42.0%
Lab B	± 11.6%

We feel that these results demonstrate the importance of evaluating the precision of any PCB procedure. Especially, if you consider that the test did not include sampling problems, used distilled water free of interferences, and was carried out at a relatively high PCB level (500,000 ppt) by two experienced laboratories. It is expected that, if sampling problems were included and the PCB level was decreased by a factor of 10,000 to say 50 ppt in actual waste water effluent, the accuracy and precision of any PCB method would degrade considerably.

E. S. Tucker/db
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