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September 4, 1970

Dr. Bennet C. Kwan
Environment Chemistry
Industrial Bio-Test Laboratories, Inc.
1810 Frontage Road
Northbrook, Illinois 60062

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I. B. T.

Dear Dr. Kwan:

I have found all three of the manuscripts which you submitted for review to be in accord with current knowledge and practices regarding the analyses of chlorinated pesticides. While the methods are not original, the outlined extraction procedures, Florisil cleanup procedures, and GLC conditions are well established in organochlorine research.

All three manuscripts may be criticized in that they do not emphasize the fact that the procedures are not specific for the chlorinated pesticides mentioned. To be sure, many other chemical species can be extracted from water with nonpolar solvents, eluted from Florisil, and detected by electron capture GLC. One of the more significant classes of interferring chemicals, particularly in Lake Michigan, is the chlorobiphenyls. The mixtures of chlorobiphenyls (prepared commercially as plasticizers by Monsanto Company under the name "Aroclor") contain components which have GLC elution volumes similar to many common pesticides and may cause interferrences in pesticide analyses. The analytical difficulties can be somewhat resolved by using a Florisil cleanup procedure which is a slight modification of the procedures outlined in the manuscript. I am enclosing copies of recent summaries of some of our work in which the analytical interferences between the chlorobiphenyls and chlorinated pesticides are discussed.

Current evidence indicates that the chlorobiphenyls (and perhaps chloronaphthalenes) are more widespread in natural waters than was first anticipated. It is apparent that the biota, sediments, and water from southern Lake Michigan contain the chlorobiphenyls in addition to the more common chlorinated hydrocarbon pesticides. For example, in Lake Michigan fish, the low levels of chlorobiphenyl isomers in addition to the several micrograms per gram of DDE could lead to the conclusion that pp'DDT, op'DDT, pp'DDD, and heptaclor epoxide are present unless the samples are examined more explicitly. Preliminary screening of extracts for the presence of chlorobiphenyls can be achieved by examining chromatograms of the concentrated extract for approximately ten components which have respective retention volumes similar to those of chlorobiphenyl mixtures. Since the chlorobiphenyls exist as complex mixtures, it is

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unlikely that they will be observed in water in less complex mixtures. Therefore, if a component is suspected of being a chlorobiphenyl based on GLC retention volume, there will also be at least ten other isomers present in the extract and the characteristic GLC chromatogram should be observed.

As I stated above, the Bender manuscript is certainly in agreement with current practices. I feel some sections have been written with a few too many short sentences which could be expanded and/or joined with preceeding discussions. For example, in section A under the topic of extraction, the discussion on handling emulsions may be rewritten and expanded. I would suggest that the water/hexane emulsion be included in the sample extract rather than expending considerable time and effort with persistent emulsion. Generally, if the emulsion is carried with the extract, the water can be effectively removed by the Na_2SO_4 column.

In paragraph H on page 4, apparatus is misspelled.

The discussion in the gas chromatography section on page 6 should be expanded or qualified. First, it is seldom possible to identify a chlorinated hydrocarbon using GLC. Generally, specific separations or chemical reactions must be used in addition to the multiple GLC columns. Without supporting data, the qualitative analyses contain uncertainties, particularly if the chlorobiphenyls or other interferences may be present.

In many instrumental analyses, information with a signal to noise ratio greater than two is generally considered to be significant if it can be reproduced. However, under proper GLC conditions, the noise level may be no greater than the width of the recorder pen and certainly not greater than a few percent of the working range. Therefore, it may not be meaningful to retain all information from signal/noise greater than two. It is unlikely that accurate measurements of peak heights and peak widths at half height can be obtained unless the peak height is substantially greater than twice the noise level.

Regarding the data on page 9, I would be somewhat skeptical of the significant digits in the analyses reported, particularly at the nanogram per liter levels in water. If three replicate water samples are taken, the relative error should also be reported.

The Bonderman manuscript contains several very important points concerning the handling of equipment and the use of retention data. The four points in section B on page 16 could be included in the Bender manuscript. Also, the fact that relative retention data may not be reproducible should be stressed.

The Burttschell and Boyle (1964) and Porter (1964) papers are not listed in the bibliography in the Bonderman manuscript.

The FWPCA method is well presented. However, the TLC step may become undesireable due to the time requirements when large numbers of samples are analyzed. Furthermore, quantitative TLC is difficult due to errors which are inherent in spotting procedures. The FWPCA methods may be criticized because of their recommendation to evaporate extracts at 70°C. This temperature is higher than necessary and may result in the increased oxidation or vaporization of species of interest. Lower temperatures (30 to 35°C) can be used to evaporate extracts if hexane and ethers are employed rather than chloroform or carbontetrachloride.

I will be happy to answer any questions you may have regarding my comments on the three manuscripts.

Sincerely yours,

Gilman D. Veith
Assistant Professor

jv/GV
Enclosures