

Interfering GLC Peaks from Materials and Chemicals in Pesticide Residue Analysis

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Several years of testing cereal grains for organochlorine pesticide residues by G.L.C. has disclosed the fact that analyses are occasionally plagued by spurious peaks. Many of these spurious peaks have glc retention times similar to pesticide chemicals and will interfere with analyses in the p.p.b. range. Attempts to eliminate pseudo-pesticide peaks have resulted in the identification of several sources of glc-ecd interferences from some of the materials and chemicals commonly used in pesticide residue analysis.

Some contaminants which may occur in various analytical methods have been discussed in the literature. Bevenue, Kelley and Hylin(1) reported that organic solvents, glassware, plastic ware, cellulose, extraction thimbles, filter paper, and silica gels yielded spurious gas chromatographic peaks which interfered with water analyses for pesticide residues. Bevenue(2) mentioned that reagent grade sodium sulfate produced a significant pseudo-pesticide glc peak which eluted from a clean-up column containing florisil and sodium sulfate.

This paper discusses many materials and chemicals which can contribute contaminants that may interfere with glc-ecd analysis of cereal grains for organochlorine residues. These include anhydrous sodium sulfate analyzed reagent; filter paper, 2V folded unwashed and #42 double-acid washed; wash bottles, Unitized 1000 ml. and wash bottles all glass assembly with glass stoppers and side-arm pump; soiled (used) teflon gaskets; silane-treated glass wool; Blendor mixer and Omni mixer; rubber gloves; and talcum powder. Suggestions are offered for eliminating these peaks or minimizing them to an acceptable working level.

Experimental

The five experiments in this section describe ethyl ether + hexane washings of the respective material. The data for the experiments are discussed in the next section.

(1) Contaminants from Sodium Sulfate

Anhydrous granular sodium sulfate, analyzed reagent was tested for glc-ecd peaks. Twenty-five grams of sodium sulfate was washed with 150 ml. of 3% ethyl ether + hexane in a clean-up

column fitted with a fritted glass disc. The eluant was concentrated to 5 ml. A 2.5 μ l injection was made into a 3% SE-30 column in a MT-220 gas chromatograph with a Ni⁶³ detector.

(2) Contaminants from Filter Paper

Folded 2V unwashed and #42 double-acid washed filter papers were tested for peaks. Filter paper was placed in a 4" glass funnel. Each was washed with 100 ml. of the solvent mixture. The filtrate was concentrated to 5 ml. A 5 μ l injection was made into the G.C.

(3) Contaminants from Wash Bottles

Unitized 1000 ml. wash bottles and 1000 ml. all glass bottles with glass stopper and side-arm pump assembly were tested for interfering peaks. The bottles were filled with the solvent mixture and allowed to stand for several days. Two hundred ml. of solvent was removed from each bottle and concentrated to 5 ml. Aliquots of 2.5 μ l were injected into the G.C.

(4) Contaminants from Soiled Teflon Gaskets

Soiled (used) teflon gaskets were tested for spurious peaks. Extraction tube caps as described in the Levi *et al*(3) technique were assembled with unused (new) teflon gaskets. Other assemblies were fitted with used (soiled) teflon gaskets. Three stainless steel balls were placed in an extraction tube with 25 ml. of the solvent mixture. Each cap was secured to the tube by a stirrup connector and ball-milled for one hour. The washings were concentrated to 5 ml. Aliquots of 2.5 μ l were injected into the G.C.

(5) Contaminants from Glass Wool

Silane-treated glass wool was tested for spurious glc peaks. A small piece of glass wool was inserted into the stem of a 4" glass funnel. The glass wool was washed with 20 ml. of the solvent mixture. This filtrate was not concentrated. A 5 μ l aliquot was injected into the G.C.

Results

1. Figure 1 shows a chromatogram for sodium sulfate. This chromatogram shows a very wide solvent peak, two very high early eluting peaks, a large later peak and a small peak fused to the leading shoulder of the highest peak.
2. Chromatographic results for filter paper are shown in Figure 2. Folded filter (2V) paper is shown in Figure 2A and (#42) acid-washed paper in Figure 2B. The chromatogram for 2A shows many high peaks and numerous smaller ones. The chromatogram for Figure 2B shows two peaks both off-scale deflection, one high peak and numerous smaller peaks.

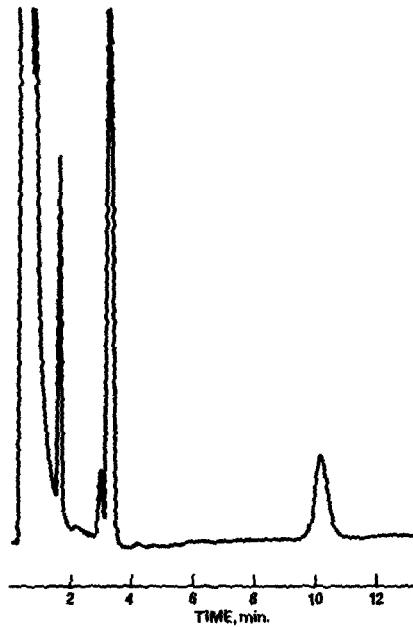


Figure 1. Gas chromatogram of solvent washings from sodium sulfate.

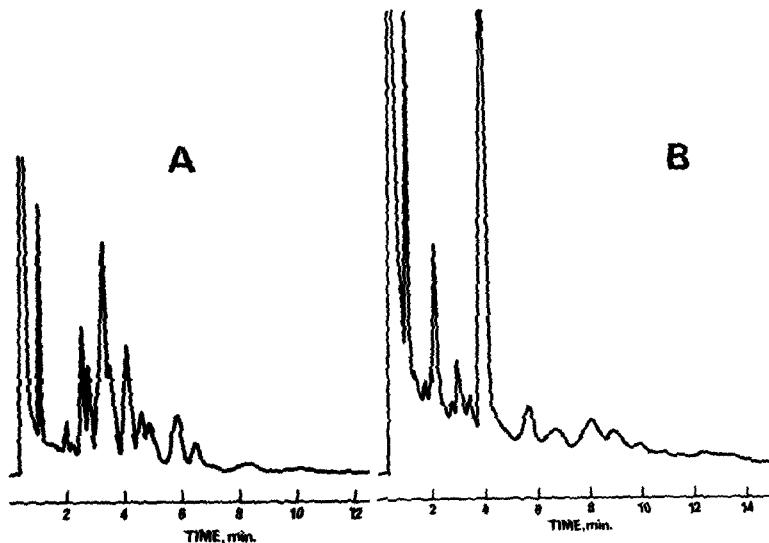


Figure 2. Gas chromatograms of solvent washings from filter paper (A) folded (2V); (B) acid-washed (#42).

3. A chromatogram for wash bottle contents is shown in Figure 3. This chromatogram shows one very high peak and several smaller peaks. This chromatogram is typical for either the solvent from the Unitized bottle or for the solvent from the all-glass bottle with the side-arm pump.

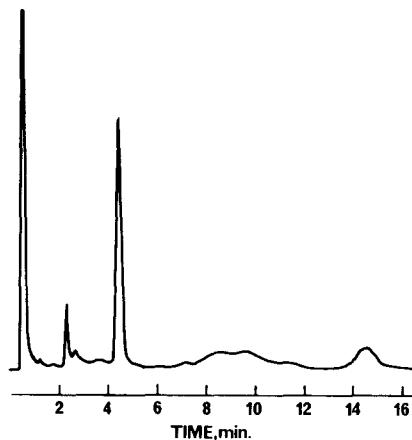


Figure 3. Gas chromatogram of solvent from wash bottles.

4. The chromatogram for soiled (used) teflon gaskets is shown in Figure 4. This chromatogram shows a very high peak and two lower significant peaks. The chromatogram for an unused (new) teflon gasket is not shown. This chromatogram had only minute peaks and is exactly similar to the chromatogram of Figure 6A.

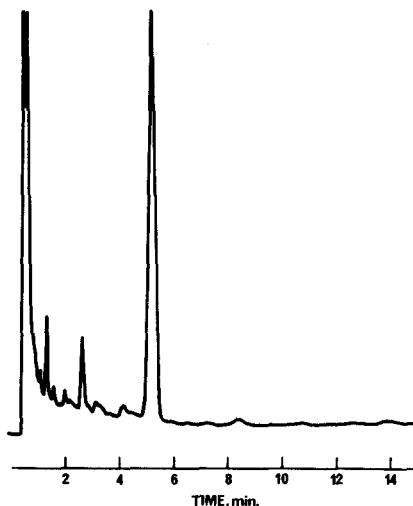


Figure 4. Gas chromatogram of solvent washings from teflon.

5. The chromatogram for glass wool is shown in Figure 5. This chromatogram shows one very large peak and three smaller ones.

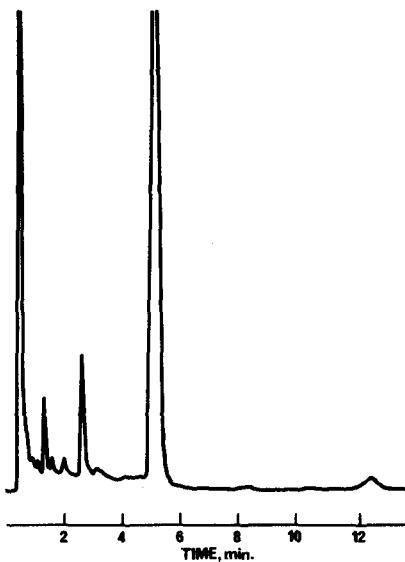


Figure 5. Gas chromatogram of solvent washings from glass wool.

Discussions and Observations

It is evident that the data in this paper indicate that sodium sulfate, filter papers, solvent from wash bottles, teflon gaskets and glass wool can produce interfering glc peaks.

Volatile organic impurities in sodium sulfate can be removed by heating at 600°C for two hours or by washing with a solvent system. Conditioned sodium sulfate will give only extremely small non-interfering glc peaks.

Filter paper should be soaked in a solvent system overnight and then washed three or four times with more solvent. This reduces spurious peaks to a minimum level, but does not eliminate them.

Spurious glc peaks cannot be eliminated from Unitized glass bottles. Spurious peaks can be eliminated from an all glass assembly wash bottle with side-arm pump by removing the rubber pump. A rubber bulb with rubber tubing connection is substituted. This is removed when refilling the bottle. With both types of bottle the fumes of the solvent attack rubber parts and impurities may collect in the solvent.

Conder(4) has reported that teflon contains a significant number of minute pores of less than 100 Å and can therefore absorb impurities. In pesticide analysis teflon gaskets can absorb peak producing contaminants from unconditioned sodium sulfate and from contaminated samples. With continued use contaminated teflon gaskets gradually release these contaminants into further analyses. Washing contaminated teflon gaskets with solvents, boiling water, boiling water and detergent has little effect. Contaminated teflon gaskets should be discarded and new teflon substituted.

Glass wool should be heated at 600°C for two hours to eliminate organic materials. It is then suitable for use in clean-up columns or other apparatus.

Additional precautions should be exercised when using the Bertuzzi *et al*(5) method or any other method employing Blender mixers or Omni mixers. In the Blender mixer the rubber gasket should be removed and a fluoro-silicone rubber gasket substituted. Rubber gives several later eluting peaks. For the Omni mixer the rubber gasket should be removed and teflon gaskets substituted. As noted earlier teflon must also be monitored but will pose less of a problem than rubber.

Analysts in pesticide residue analysis must use rubber gloves in handling strong organic solvents. They must be used carefully for organic solvents may dissolve rubber. Such washings may accidentally fall into a test. In addition cross-contamination may occur with rubber gloves from one sample to another. Furthermore, with rubber gloves, if talcum powder is used for easier donning of gloves, traces of powder in a test will give rise to large spurious peaks.

Using all the precautions recommended in this paper, contaminant peaks, that may interfere with trace analysis of cereal grains for organochlorine residues, can be avoided. Pesticide free wheat should give chromatograms containing a fairly straight baseline with few insignificant peaks. To illustrate this, Figure 6 has been included. Figure 6 shows chromatograms for a pesticide free wheat sample analysed by: (A) the method of Levi *et al* a glc-ecd technique for organochlorine analysis of wheat; and (B) the method of Bertuzzi *et al*, also a glc-ecd technique. Neither of these chromatograms contain peaks which would interfere with the analysis of organochlorines in the parts per billion range.

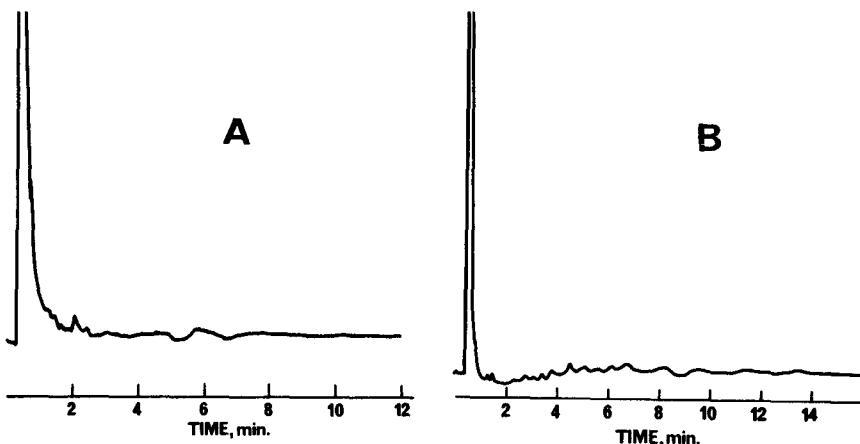


Figure 6. Gas chromatograms of wheat analysed by
 (A) Levi et al; (B) Bertuzzi et al.

Acknowledgment

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References

- (1) BEVENUE, A., KELLEY, T. W., and HYLIN, J. W.: Problems in Water Analysis for Pesticide Residues. *J. Chromatog.* 54 71-76. 1971.
- (2) BEVENUE, A. Zweigs "Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives", Vol. 5 41-2. Academic Press. 1967.
- (3) LEVI, Iser, MAZUR, P. B. and NOWICKI, T. W.: A Rapid Method for the Determination of Organochlorine Residues in Wheat by G.L.C. with E.C.D. Manuscript in preparation (1971).
- (4) CONDER, John R.: Teflon, A Noninert Chromatographic Support. *Anal. Chem.* 43 367-370. 1971.
- (5) BERTUZZI, P. F., KAMPS, L., MILES, C. W. and BURKE, J. A.: Extraction of Chlorinated Pesticide Residues from Nonfatty Samples of Low Moisture Content. *J. A. O. A. C.* 50 623-627. 1967.