Facile Elimination of Sulfur Interference in Pesticide Analysis by Gas Chromatography

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The presence of interfering co-extractives in pesticide analysis is a well-recognized problem that often necessitates extensive cleanup of extracts prior to the determinative gas-liquid chromatographic (GLC) analysis. The electron-capture (EC) detector is probably the most prevalent detector used for pesticide analysis because of its high sensitivity, especially to organochlorine compounds, but it is only relatively specific. Unless care is exercised in pesticide determinations by GLC-EC, peaks may be misidentified with potentially serious consequences. (ANONYMOUS 1969).

A number of workers have reported spurious GLC-EC responses from extracts of various media (FRAZIER et al. 1970; PEARSON et al. 1967; SANS 1967). PEARSON et al. (1967) found a soil extract to contain three peaks by GLC-EC with the earliest peak to mimic BHC (isomer unspecified) and the latest and largest peak to mimic aldrin. They identified these interferences to be due to elemental sulfur. Others also have found this interference to be characterized by three peaks (CHEN et al. 1973; OSADCHUK and WANLESS 1968; SCHUTZMANN et al. 1971; STRUBLE 1972). This interference is characteristic of samples from anaerobic sites such as bottom muds from lakes, streams and estuaries (GOERLITZ and LAW 1971), marine sediments (CHEN et al. 1973) and sewage sludges (MILLSON 1970) as well as samples that have received sulfur as a fungicidal treatment (PEARSON et al. 1967).

Researchers have addressed the problem of sulfur interference in various ways. OSADCHUK and WANLESS (1968) oxidized aldrin to dieldrin and thus separated aldrin from sulfur by GLC-EC. GOERLITZ and LAW (1971) used a drop of metallic mercury shaken with the extract to remove sulfur. Others have used various GLC parameters to separate sulfur from compounds of interest (LESTER and SMILEY 1972; STRUBLE 1972 and 1974).

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SCHUTZMANN et al. (1971) removed sulfur by refluxing extracts on a steam bath for 3-4 hours with a copper-aluminum alloy. They found copper and nickel turnings successful only with extracts containing small amounts of sulfur.

CHEN et al. (1973) found the first sulfur peak to be due to S_4 (probably the BHC mimic), the second and smallest peak to be S_6 and the third and largest peak to be S_8, presumably the aldrin artifact. They and STRUBLE (1972) showed that GLC-EC is sensitive to sulfur in sub-nanogram quantities.

In an EPA manual (THOMPSON 1972), sulfur interference was addressed directly to sediment analysis and it was stated that not only was GLC-EC affected but also GLC using flame photometric and Coulson electrolytic conductivity detectors. The use of acid-washed copper powder was recommended that converts sulfur to copper sulfide on the copper surface. This method entails extract concentration and at least two extract transfers making it a time consuming process. It was reported that copper degrades certain insecticides, such as organophosphates and heptachlor, but these are not encountered generally in sediment samples and degradation was not as extensive as when metallic mercury was used.

Our laboratory has used acid-washed copper ribbon for several years in removing sulfur interferences from soil, sediment and sewage sludge extracts. A minimum of extract manipulation is used since the final extract ready for GLC is treated with milligram amounts of copper ribbon. If sulfur is present, the ribbon turns black almost instantaneously. Additional ribbon is added until no further reaction is apparent and some bright copper color remains. The extracts are ready to inject within an hour unless several additions of copper are made. In many of our samples, we have seen not just a single or several interfering peaks but rather a broad, diffuse and often off-scale "peak" from about 30 seconds to four minutes after injection indicating a high sulfur concentration. With a Tracor MT-220 GLC, this phenomenon is common using columns of 3% SP-2100, 1.5% SP-2250 + 1.95% SP-2401 or 4% SE-30 + 6% SP-2401 and a flow rate of about 60 ml N_2/min. In Figure 1, chromatograms of an extract of digested sewage sludge, containing primarily the polychlorinated biphenyl (PCB) Aroclor 1254, are shown before and after copper treatment. This procedure also enables one to determine the presence of sulfur by an exploratory injection followed immediately, if positive, by the addition of copper ribbon. Thus one can determine

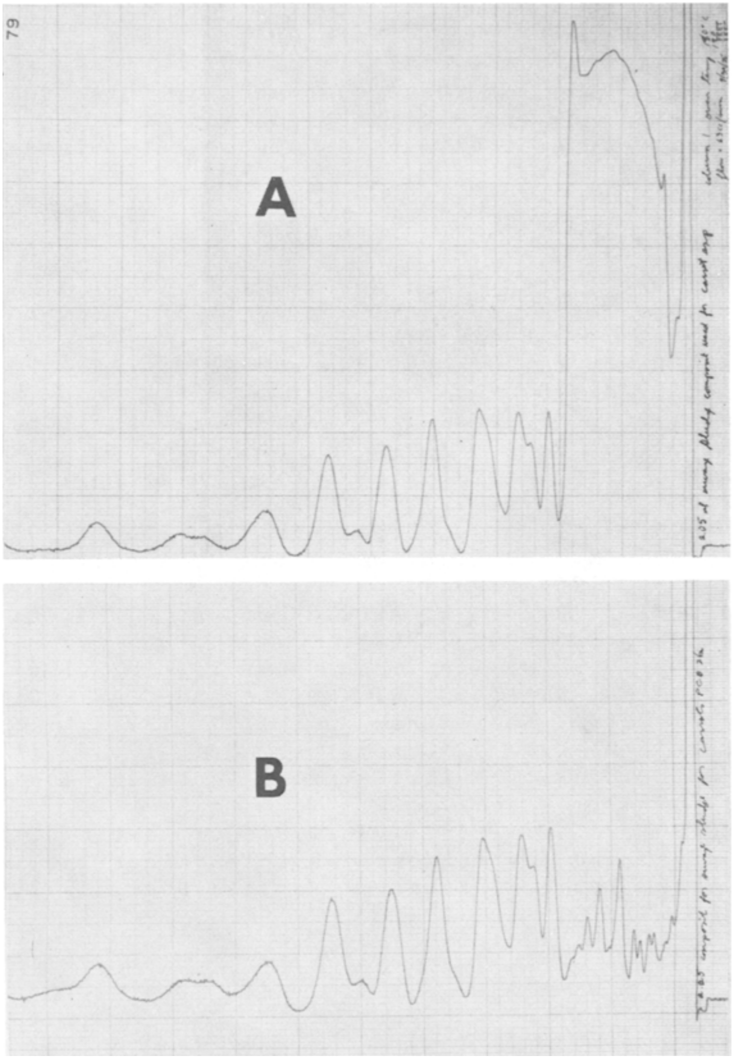

Figure 1. Gas chromatograms of an extract of digested sewage sludge before (A) and after (B) treatment with acid-washed copper ribbon to remove elemental sulfur.

readily the before and after effects of sulfur removal on the chromatogram. Since we have been concerned primarily with the analysis of DDT residues and PCBs, no degradation of these compounds by this treatment has been evident. Possible degradation of other compounds by this copper treatment should be determined by the potential user.

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