Gas-Liquid Chromatographic Separation of Sulfur from Chlorinated Pesticide Residues in Wastewater Samples

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The presence of colloidal sulfur and organo-sulfur compounds in wastewaters and sediments due to bacterial reduction of sulfates and oxidation of sulfides, human and animal wastes, industrial discharge, mineral sources, and agricultural run-off has been well documented (NAGANO, 1950; AULENBACH and HEUKELEKIAN, 1955; MASON, 1962; McKEE and WOLF, 1963). The interferences of sulfur in the analysis of extracts containing certain chlorinated pesticides (e.g., *o,p'*-DDE, *p,p'*-DDE, aldrin, lindane, heptachlor) by gas-liquid chromatography (GLC) has been reported (AHLING and JENSEN, 1970; SCHUTZMAN, *et al*, 1971) when electron capture detectors were employed. Liquid phases were those normally recommended (DOMINICK, 1971) for pesticide analysis: DC-200, QF-1, OV-17, OV-210, coated on a support of Gas-Chrom Q.

The techniques employed for routine sample clean-up using acetonitrile-hexane or hexane-ether partitioning and adsorption chromatography (alumina, silica gel, Florosil) (DOMINICK, 1971) prove inadequate for the separation and removal of large amounts of sulfur, although it has been found in this laboratory that trace quantities can be removed. The problem may be attributed largely to the solubility of sulfur in the solvents hexane and ether and the relatively large amounts of sulfur present in some samples.

Various techniques have been recommended to overcome this problem. Chemical desulfurization has been found effective (SCHUTZMANN, *et al*, 1971) when sample extracts were refluxed over a copper-aluminum alloy catalyst in the presence of water for 4 hours. The advantage of this procedure was that the sulfur interference (up to 50 ppm) was eliminated while affording reasonable recovery of most of the chlorinated pesticides. The obvious disadvantage is that more than four hours is added to the analytical time of each routine sample. Since the sulfur concentration observed in discrete samples

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varies widely, the interference is not observed in all extracts. In this majority of samples, then, the extra time becomes a needless expenditure of effort.

The use of a microcoulometric detector or an electrolytical conductivity detector for chloride specificity has been described (DOMINICK, 1971) and recommended (COULSON, 1969) as a means of overcoming the sulfur problem. Besides being quite expensive, these highly selective detectors are considerably less sensitive than electron capture detectors (COULSON, 1969). This requires the extraction of a much larger sample prior to analysis (∿3 liters instead of the 200 ml routinely extracted in this laboratory). The routine extraction and clean-up of this size sample is cumbersome at best, and needless if large amounts of sulfur are not present.

This note proposes a column packing mixture which the authors feel alleviates the sulfur interference problem without significantly adding to analytical time, yet affords the necessary resolution for quantitative identification of chlorinated pesticides.

Experimental

Sulfur was verified using thin layer chromatography for the separation of components in the sample extract and re-extracting the TLC spots with 24% ether-hexane: after combining several of these isolates, evaporation and cooling of the solvent yielded yellow crystals having a melting point of 114°C (rhombic S_8 has a m.p. = 113°C). Sulfur was dissolved in ether-hexane and injected into the chromatograph, yielding a chromatogram identical to the interfering substance, thus offering further verification of sulfur.

The column packing was composed of a mixture of 4.4% (w/w) OV-17, 4.7% QF-1, and 1.0% DC-200, all on 80/100 mesh Gas-Chrom Q solid support. Each liquid phase was coated separately on a portion of the support. The individually coated portions were combined before packing into 6' x 1/8" I.D. glass columns. After packing, the columns were conditioned at 250°C for 8-10 hours before use.

The gas chromatographs employed were Hewlett-Packard Model 5755-B instruments fitted with electron capture detectors (Ni^{63}). Carrier gas was 5% methane/argon at a flow rate of 40 ml/min. Detector, oven, and injection port temperatures were 250, 220, and 235°C, respectively.

Results and Discussion

The resolution obtained with the new column packing for thirteen chlorinated pesticides may be compared to that of the previously used material (5.5% QF-1, 5.5% OV-17 on Gas-Chrom Q) in Figures 1 and 2. The effect of the 1% DC-200 addition was to shift the major interfering sulfur peak between those of *o,p'*-DDE and *p,p'*-DDE, thus eliminating the sulfur interference with the analysis of these compounds without diminishing the resolution of the remaining pesticides of interest. Figures 3 and 4 compare chromatograms of the same sample extract injected on the two different columns: Figure 3 demonstrates a typical masking of *p,p'*-DDE by sulfur, while Figure 4 exhibits the effects of DC-200 on the sulfur peak relative to the DDE's.

The results of the routine use of this mixed column have demonstrated that satisfactory analysis of sulfur-containing wastewaters and sediments may be performed without lengthy and, often needless, chemical desulfurization or extraction of large quantities of sample followed by detection with a highly selective detector.

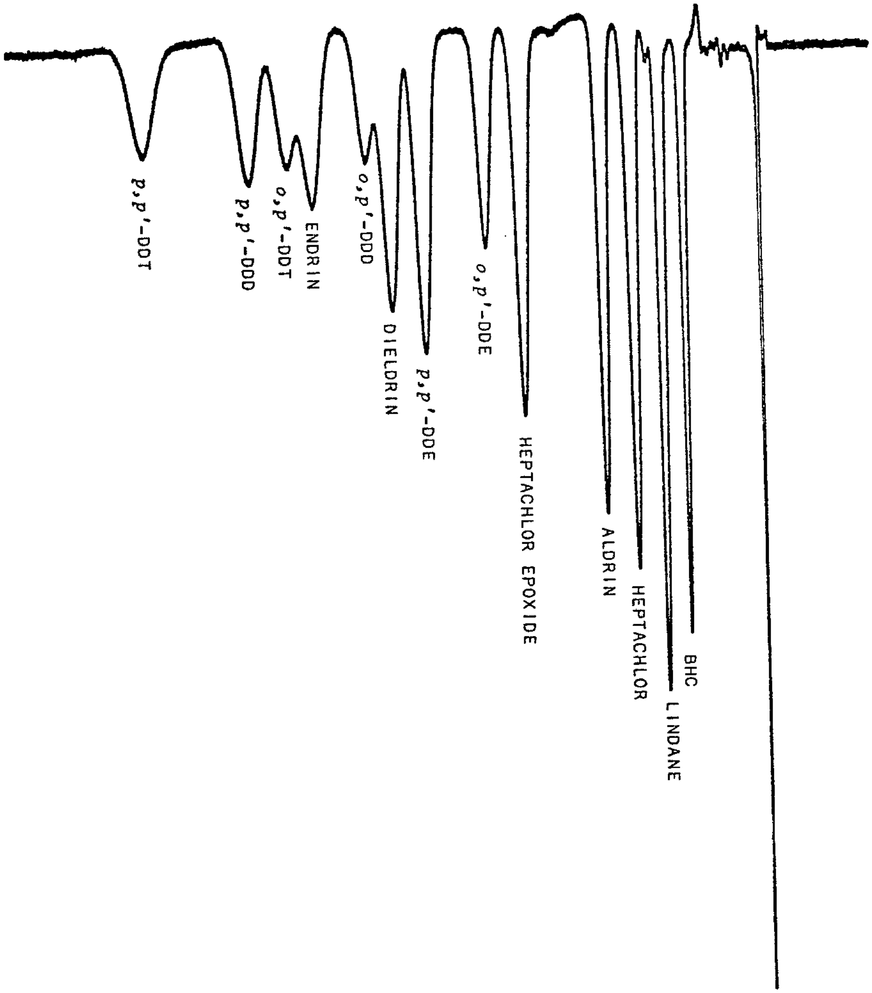

Figure 1. Resolution of 13 organochlorine pesticides by the mixture 4.4% OV-17/4.7% QF-1/1.0% DC-200 on Gas-Chrom Q.

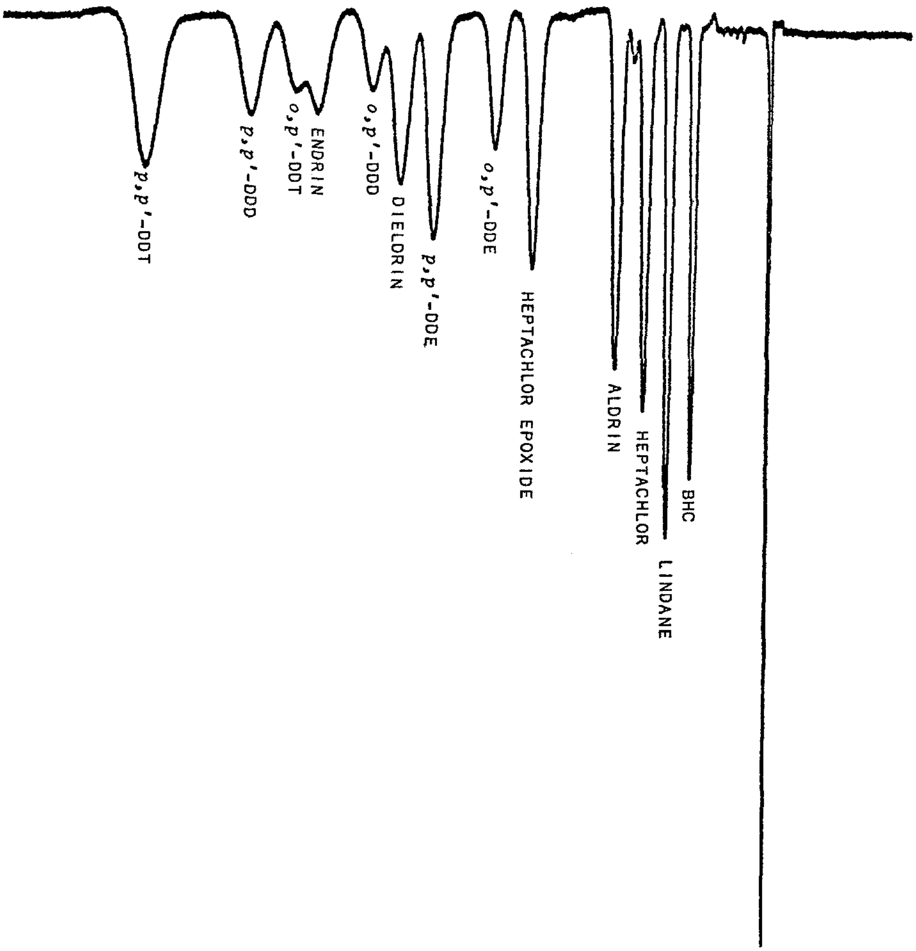

Figure 2. Resolution of 13 organochlorine pesticides by the mixture 5.5% OV-17/5.5% QF-1 on Gas-Chrom Q.

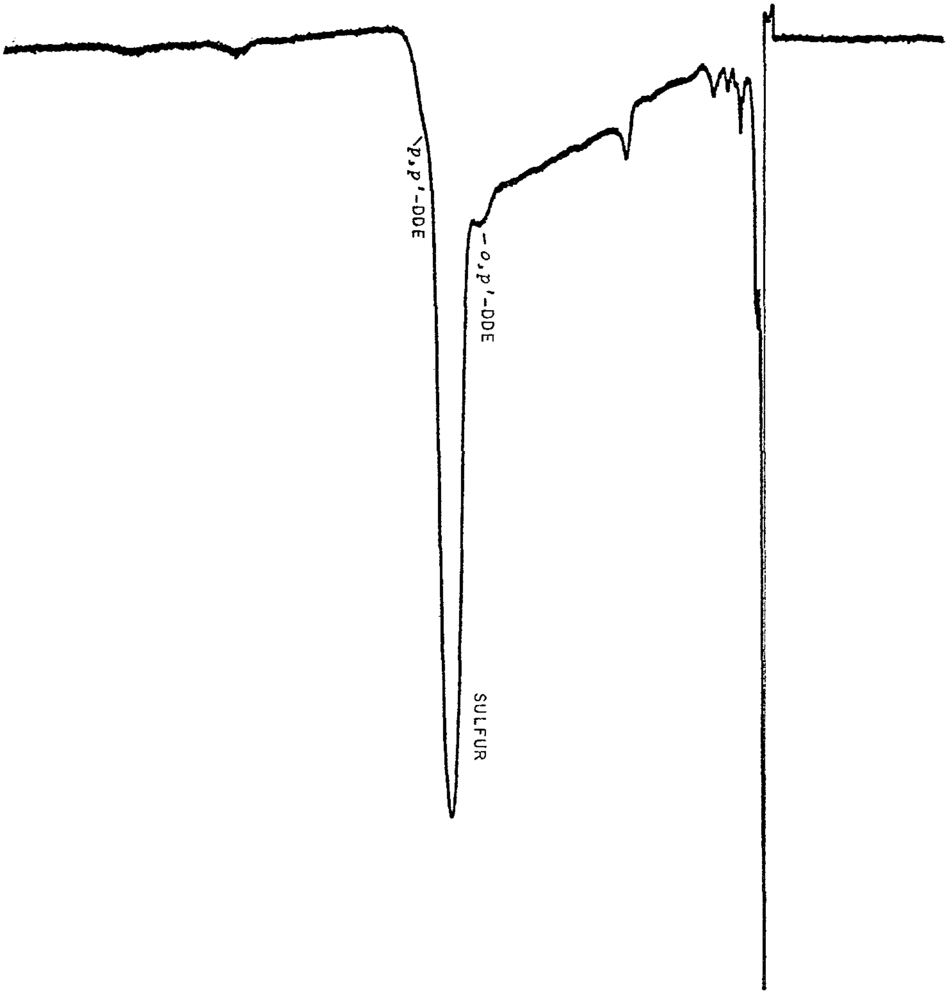

Figure 3. Raw sewage sample #9383 exhibiting Sulfur masking of p,p'-DDE: 5.5% OV-17/5.5% QF-1.

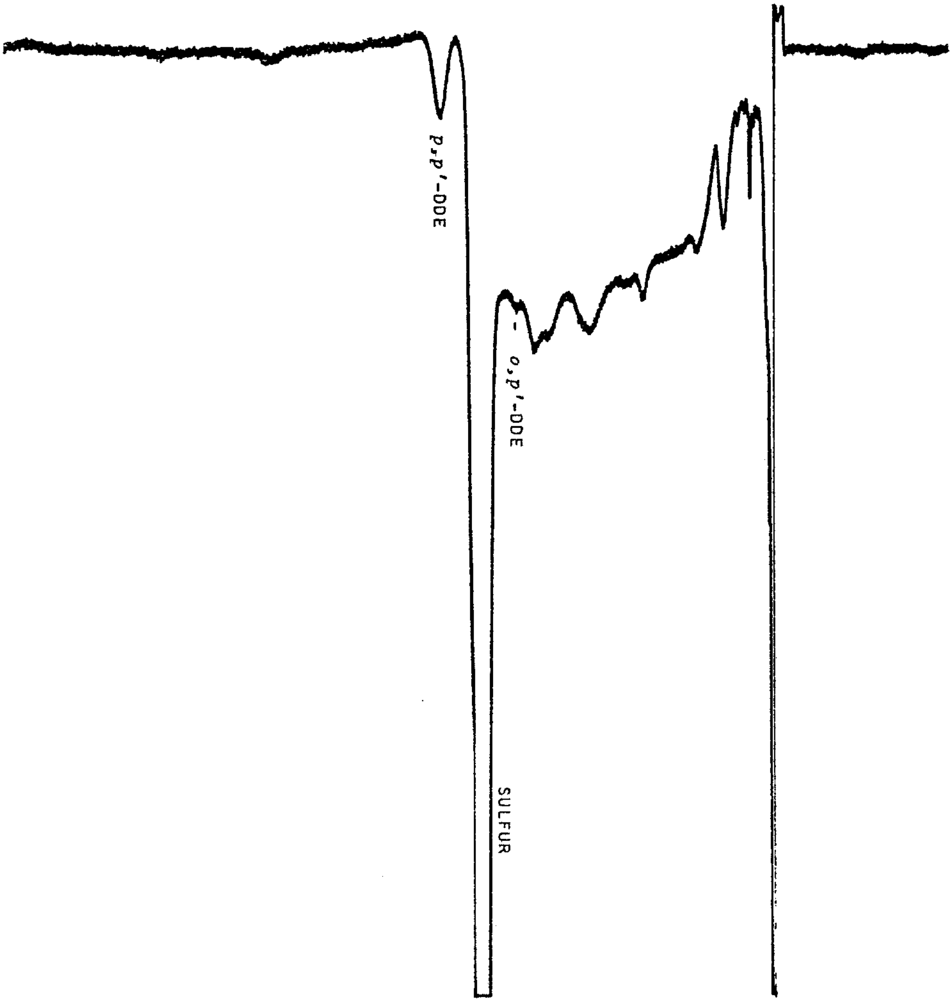

Figure 4. Sample #9383 exhibiting resolution of the DDE peaks on 4.4% OV-17/4.7% QF-1/1% DC-200.

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