

Short Communications

The effect of the column tubing composition on the recovery of chlorinated hydrocarbons by gas chromatography

Recent discussions^{1,2} on the effect of the type of metal used in gas chromatographic columns for the quantitative analysis of some halogenated compounds prompts us to submit data obtained with columns of different tubing composition including one designed from quartz. Little data was presented to accurately show these effects. The following study was designed to present carefully measured recovery values of microgram quantities of several chlorinated hydrocarbons. The compounds selected were considered relatively difficult to chromatograph and were also considered to be important in certain commercial fields.

All of the metal columns were 6 ft. long and 1/4-in. O.D. The quartz column was 6 ft. long, 6 mm O.D. and 4 mm I.D. Although all of the metal tubings were purchased as 1/4-in. O.D. tubing, it will be noted in Table I that the variation of the I.D. affected

TABLE I
COLUMN PACKING DATA

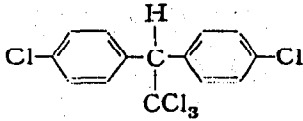
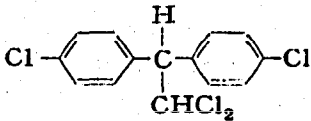
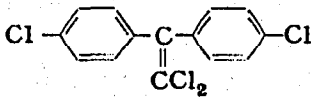
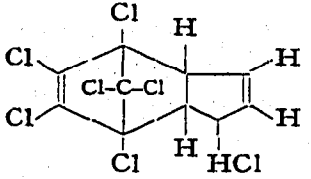
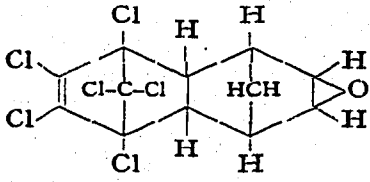
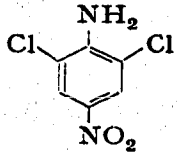
<i>Tubing</i>	<i>Copper</i>	<i>Stainless steel</i>	<i>Aluminum</i>	<i>Quartz</i>
Column length	6 ft.	6 ft.	6 ft.	6 ft.
Column packing	15 g	17 g	19 g	10 g
Packing per column-foot	2.50 g	2.83 g	3.16 g	1.66 g

the amount of column packing per foot of column, but had no effect on the amount of recovery of the compound (Table II).

The liquid phase for the chromatographic column was prepared from Dow-Corning No. 11 silicone compound. The silicone was dispersed in ethyl acetate and filtered on a Whatman No. 1 filter paper. The clear filtrate was concentrated in a rotary evaporator, the concentrate was added to absolute ethyl alcohol, and the mixture was refrigerated 16 h. The resultant precipitate, which was water-clear and fluid, was separated from the supernatant layer and washed several times with absolute ethanol, air-dried, and used as the stationary phase for the chromatographic column. Twenty grams of the silicone was dispersed in chloroform and added to 100 g of acid-washed, 40-50 mesh, Chromosorb P. The chloroform was removed from the slurry by a rotary vacuum evaporator, followed by drying the packing with an infrared lamp.

The gas chromatograph was a Dohrmann Model 100 equipped with a pyrolysis train (825°) and a microcoulometric detector. The injection block and column temperatures were each 250°. The nitrogen and oxygen flow rates were 100 ml/min.

TABLE II
GAS CHROMATOGRAPHY RECOVERY DATA

Compound	Common name	Percent recovery			
		Column tubing			
		Copper	Stainless steel	Aluminum	Quartz
	<i>p-p'</i> -DDT	53	56	65	77
	Technical DDT*	50	56	66	77
	DDD	78	77	77	85
	DDE	83	87	86	86
	Heptachlor	24	36	68	79
	Endrin	72	77	87	88
	Dicloran	—	—	84	97

* An isomeric mixture, plus related halogenated compounds.

Results and discussion

The data in Table II are characteristic of a number of determinations. With the compounds studied, copper tubing was the least desirable and quartz tubing the most efficient. Exercising extreme care in the sampling and the control of temperature conditions, reproducibility of results on a given day were within a variation range of $\pm 3\%$, with the exception of the compound, heptachlor. It should be noted that the effect of the metal on the compound is not the only factor to be considered in the analysis of these compounds. For example, the degree of purity of the compound may not be accurately known. Endrin³ and DDT² are subject to degradation at high temperatures. Another type of stationary phase on the column might possibly be more applicable for a given compound. For example, heptachlor, which is considered to be

relatively stable, gave very erratic results with the various columns (see Table II), suggesting that it could not be efficiently resolved with the column packing that was used.

The aluminum block of the gas chromatograph was "preconditioned" with 100 μg quantities of the halogen compound to be tested, as suggested by the manufacturer of the instrument. The results of such treatment were not conclusive. Subsequently, the block was modified to include a quartz tube insert in the injection port area. However, since the vaporized sample component could still come in contact with sections of the metal block, this modification did not materially improve the degree of recovery of the compound.

Finally, the block and the columns were pretreated with tris-(2-biphenyl) phosphate² which has been suggested as an inhibitor of the Friedel-Crafts type of catalysis. Indiscriminate application of this reagent to the chromatographic instrument can produce adverse effects because of its low vapor pressure at 250°. Excess amounts may accumulate in the block and tangibly interfere with the analytical results. None of the above treatments materially improved the analytical results.

In conclusion, our experiences indicate careful sampling is necessary (accuracy is limited by the present type of syringes available), strict temperature control is essential, pin-hole leaks in the chromatographic systems must be avoided, and an all-glass or all-quartz system—including the sample injector area—seem to be preferable.

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¹ D. M. COULSON, *Technical Report No. II, Report No. 5*, Stanford Research Institute, Menlo Park, Calif., *SRI Project No. P-3198*, (1961) 7.

² F. A. GUNTHER, R. C. BLINN AND G. K. KOHN, *Nature*, 193 (1962) 573.

³ D. D. PHILLIPS, G. E. POLLARD AND S. B. SOLOWAY, *J. Agr. Food Chem.*, 10 (1962) 217.

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An unusual ninhydrin reaction with inorganic cations

Ninhydrin, triketo-hydrindene hydrate, is universally used as a very sensitive reagent for amino-nitrogen in amines, amino acids and peptides.

ZACHARIUS AND TALLEY¹ reported recently that certain non-nitrogenous keto acids in eluates from ion exchange columns were found to react with ninhydrin to give coloured compounds. Although the colour thus obtained was mostly red, the danger of ascribing a colour reaction to the presence of certain nitrogenous compounds was pointed out. Nothing, however, is known about a reaction of ninhydrin with inorganic cations, except $(\text{NH}_4)^+$.

It was therefore greatly surprising to discover in a recent investigation of amino acids by high-voltage paper electrophoresis that some inorganic cations present in the sample produced a colour reaction similar to that of amino acids. Since under the chosen experimental conditions² the positions of K^+ and Na^+ almost coincided with

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