A one-piece all-glass injection block and gas chromatographic column for the microanalysis of halogenated hydrocarbons

Reports of high-temperature decomposition of halogenated hydrocarbons resolved by gas chromatography have implicated the metallic surfaces of the column tubing as the site and the cause. We have recently shown[1] that improved recovery of this class of compounds may be obtained by replacing the metallic columns with a quartz column. This modification, however, did not completely eliminate contact of the compound with the metal parts of the instrument; *i.e.*, the injection area was largely metallic.

An all-glass, one-piece, injection block and chromatographic column has been designed and applied to the Dohrmann Model 100 gas chromatograph (Dohrmann Co., San Carlos Calif., U.S.A.), as illustrated in Fig. 1. The system is one piece up to the connection with the quartz pyrolysis tube, thereby eliminating all contact of the compound with a metal surface. It has been our experience that the slightest pin-hole leak will cause a measurable loss of the sample. This one-piece design has removed this problem.

The column is filled with the chromatographic packing prior to sealing it to the system and it must be cut off for refilling. However, the column will be efficient for a large number of samples provided that an efficient "cleanup" procedure has been applied to the sample prior to chromatography. This is especially true when agricultu-

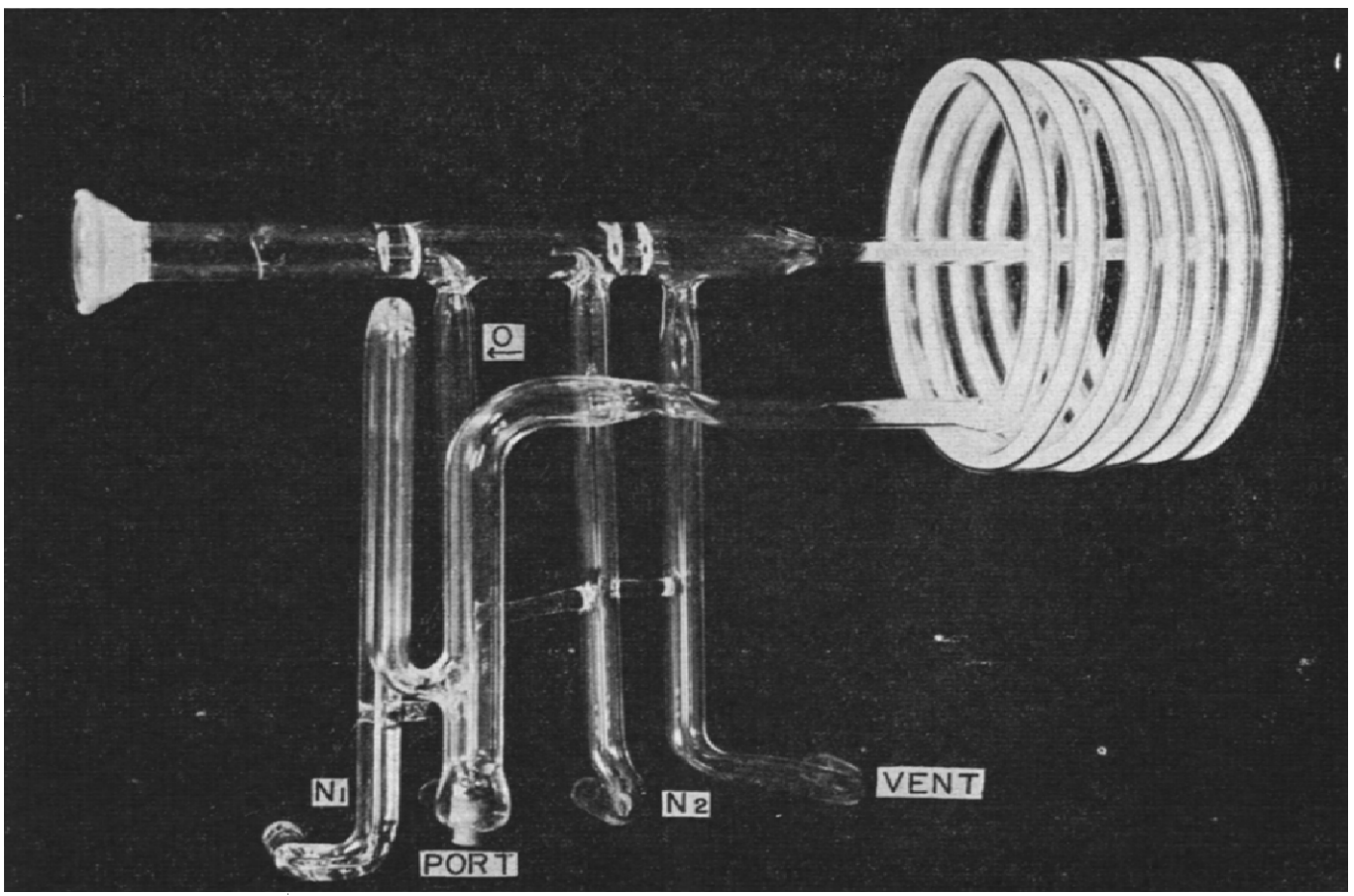

Fig. 1. All-glass, one-piece injection port and gas chromatographic column.

ral commodities are analyzed for trace amounts of halogenated organic contaminants.

The column packing was a portion of the same supply described previously, *i.e.*, 20% "purified" Dow-11 silicone oil on 40–50 mesh Chromosorb P. Therefore, the recovery data (Table I) may be directly compared with that previously reported[1].

TABLE I

GAS CHROMATOGRAPHY DATA ON HALOGENATED HYDROCARBONS USING AN ALL-GLASS SYSTEM

	Recovery (%)
p,p'-DDT (dichlorodiphenyltrichloroethane)	78
Technical DDT (isomeric mixture)	74
DDD (dichlorodiphenyldichloroethane)	82
DDE (dichlorodiphenyldichloroethylene)	89
Heptachlor (3,4,5,6,7,8,8-heptachlorodicyclopentadiene)	79
Heptachlor epoxide	95
Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethano-naphthalene)	84
Dicloran (2,6-dichloro-4-nitroaniline)	98
2,4-DMe (2,4-dichlorophenoxyacetic acid methyl ester)	100

In Fig. 1, N_1 is the gas inlet that supplies the nitrogen carrier gas for the chromatography column; N_2 is the inlet for auxiliary nitrogen to propel the column effluents through the pyrolysis tube; O is the gas inlet that supplies oxygen to support combustion in the pyrolysis tube. The "vent", as marked in Fig. 1, allows the solvent vapors to be released to the outside through a valve, since it is unnecessary to combust the solvent. The vent valve is closed prior to the elution of the higher boiling halogenated compounds. The injection port is constructed of heavy-wall tubing to provide a sufficient reservoir of heat for complete vaporization of all materials injected into the system. Similarly, the tubing for the N_1 gas supply is of heavy-wall construction to provide preheated nitrogen to the injection chamber. Construction and directional jets are provided within the system to insure proper flow of gas streams throughout the system.

It has been noted that solvent vapors will ignite in the pyrolysis tube if they are not released through the vent port. This ignition can be observed as a flashback that permeates the entire system, back to the column including the oxygen and auxiliary nitrogen ports. Therefore, it is recommended that small volumes, 10 μl or less, be used and an ample vent period be allowed to avoid the flashback. This effect undoubtedly takes place in a metal system, but goes unobserved. Variable data could be ascribed to this effect.

Increased retention times (desirable with some compounds) and improved resolution of a mixture of some halogenated hydrocarbons have been observed if a large temperature differential can be maintained between the sample injection area and the chromatograph column, *i.e.*, high-temperature injection and a cooler column. This may be accomplished by inserting an asbestos-cement disc, 1/4-in. thick, between the injection and column areas of the all-glass system. The disc contains two slots in positions corresponding to the column spacing connection so that the disc may be easily inserted or removed without disturbing the system. The use of the asbestos disc

provides a temperature differential of as much as 100° between the sample injection and column areas.

If necessary, the injection port can be designed to include a removable pyrex or quartz tube insert which may be periodically removed for cleaning because of the possible accumulation of undesirable condensation products obtained from samples of plant, animal, or soil origin.

The recovery data obtained with the all-glass system are similar to those obtained with a quartz column and a metal injection block. The continued inability to realize better recoveries from some of the compounds studied suggests that other factors are involved in addition to contact of the compound with metallic surfaces. It must also be pointed out that the all-glass system was fabricated from borosilicate glassware. This was done for ease of construction as compared to an all-quartz piece. Since quartz was previously found to allow improved recoveries, the same effect may be true for an all-quartz system.

A combination of conjectural possibilities contributing to low recoveries may include formation of elemental chlorine, hydrogen chloride, adsorption of the compound or its decomposition products on the glass surface and reactivity with the column packing support. The first two possibilities seem the most logical in view of the fact that the recoveries shown are in direct molar ratio of the chlorine content of the compounds studied assuming the loss of one or more chlorine atoms. The loss of hydrogen chloride would show the same approximate values. This thesis will be studied further.

If the apparent loss does in effect show these phenomena to be true, then the only further improvement in the system would be to change the column packing material in such a way as to avoid the decomposition. It shows that the all-glass one-piece system has accomplished its purpose of providing optimum conditions for the recovery of these high-boiling halogenated compounds by avoiding leaks.

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[1] H. BECKMAN AND A. BEVENUE, *J. Chromatog.*, 10 (1963) 231.

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