CHROMATOGRAPHIC DESIGN AND TEMPERATURE-RELATED CHARACTERISTICS OF THE PIEZOELECTRIC DETECTOR

F. W. KARASEK, P. GUY, H. H. HILL, Jr. and J. M. TIERNAY

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)

(First received December 8th, 1975; revised manuscript received February 17th, 1976)

SUMMARY

The design of a chromatograph with a piezoelectric detector capable of operating in the 25–100 °C range is described. The instrument permits studies on temperature-related behavior of the piezoelectric crystal and its coatings. The effect of temperature on the sensitivity and analytical characteristics of the detector are described. While detector sensitivity decreases with temperature and relative response of compounds changes, there is an increased scope of analytical capabilities.

INTRODUCTION

Piezoelectric (PZ) sorption detectors, first originated by King, exhibit a wide variety of applications in their use as relative humidity indicators, vacuum microbalances, air pollution monitors, hydrogen gas detectors, and gas chromatographic (GC) detectors[1-3]. In each case their principle of operation is similar. A quartz crystal vibrating with a constant frequency in the megacycle range exhibits a decrease in that frequency when substances are adsorbed directly on the surface of the crystal coated with a thin film of liquid or solid adsorbant.

When used as a detector for a gas chromatograph[4,5], the response is obtained by coating the crystal with a thin film of the same liquid phases commonly used in the column. Eluents partition into the liquid phase on the crystal to produce the response just as they partition into the liquid phase in the column to produce the chromatography.

The response of a PZ detector for a compound eluted from a GC column can be described by the relation:

$$A = C \frac{W}{\gamma P^{\circ} F} \tag{1}$$

where A = area response, W = total weight of the eluent, γ = activity coefficient of the eluent in the crystal coating, P° = vapor pressure of the eluent at the operating temperature, F = carrier gas flow-rate and C = a constant which is characteristic of the detector temperature, the crystal, and the liquid phase used to coat the crystal.

This equation, derived from one presented by Janghorbani and Freund[6], points out many of the salient characteristics of the PZ detector when it is used in conjunction with GC.

Since the use of PZ detectors has been limited to room temperature chromatography, studies on the temperature-related characteristics of coated PZ crystals are necessary to fully assess the merit of this detection method. To extend the analytical usefulness of the PZ technique for GC, a chromatograph and PZ detector cell capable of operating between 25 and 100 °C was constructed and its characteristics studied[7].

EXPERIMENTAL

Instrumental design

A chromatograph and detector designed for PZ detection above room temperature was constructed, since no such instrument is commercially available. The instrument, a Variable Temperature P/Z chromatograph (VT/PZ), is shown in Fig. 1. Quartz crystals used were 9-MHz AT-cut crystals held on a HC6/u base (International Crystal Mfg., Oklahoma City, Okl., U.S.A.). The reference crystal remained under vacuum in its protective housing, resulting in a reduced noise level and longer crystal life (Figs. 2 and 3). Complete details of the circuitry and construction of the instrument can be found in ref. 7.
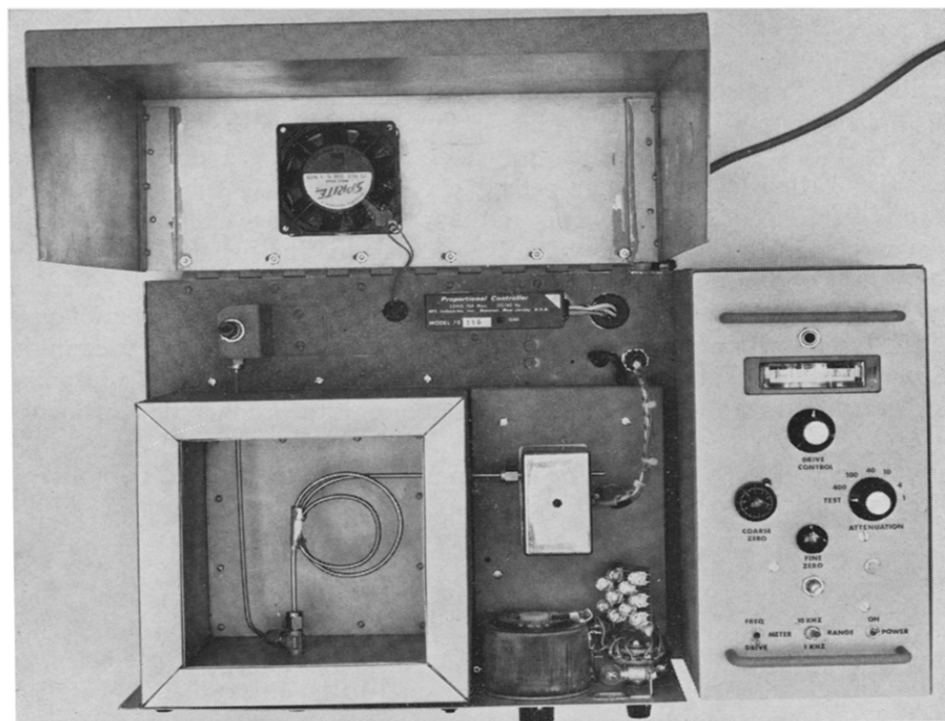

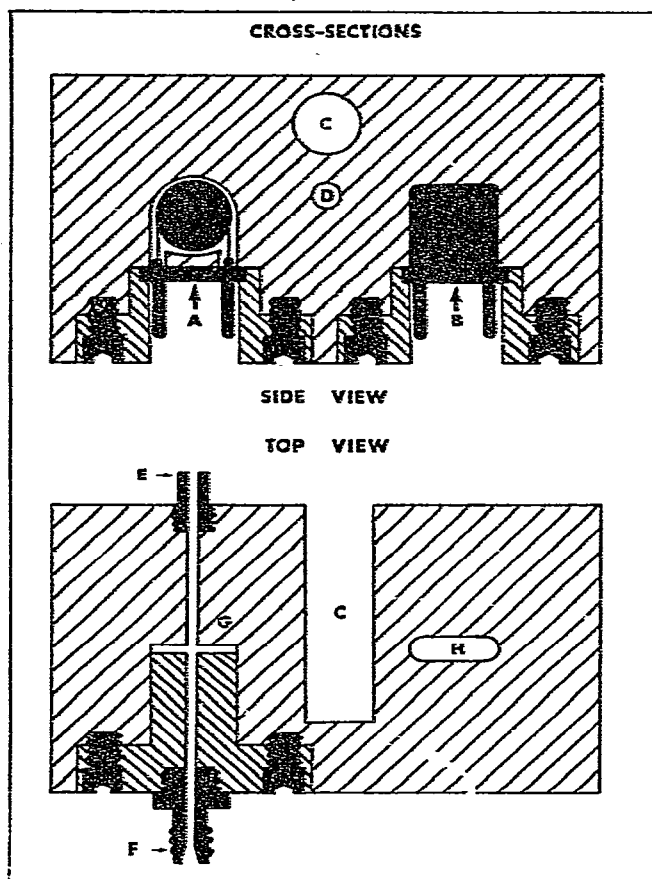Fig. 1. A top view of the VT/PZ gas chromatograph with the oven open.

Fig. 2. Cross-sectional views of the VT/PZ detector block with (A) sample crystal, (B) reference crystal, (C) heating cartridge well, (D) thermistor well, (E) detector exit, (F) detector entrance, (G) sample crystal cavity, and (H) reference crystal cavity.

Procedure

Crystals were coated with either Carbowax 400 or Hallcomid M 180 L using the procedure normally followed in this laboratory[4,5]. Chromatography was done with an 1/8 in. O.D. × 22 in. or 24 in. stainless-steel tubing packed with either 5% Carbowax 400 or 20% Hallcomid M 180 L on 100–120 mesh Chromosorb W. Injection port and column oven temperatures were the same and varied from 25 to 100 °C. The detector temperature was controlled separately and could also be varied from 25 to 100 °C. Air was used as the carrier gas. Exact conditions for each experiment are given with the figures. All reagents chromatographed were standards obtained from PolyScience (Evanston, Ill., U.S.A.).

RESULTS AND DISCUSSION

The design of the VT/PZ chromatograph and detector is delineated in Experimental and illustrated with Figs. 1–4. Frequency noise was in the order of 0.02 Hz,
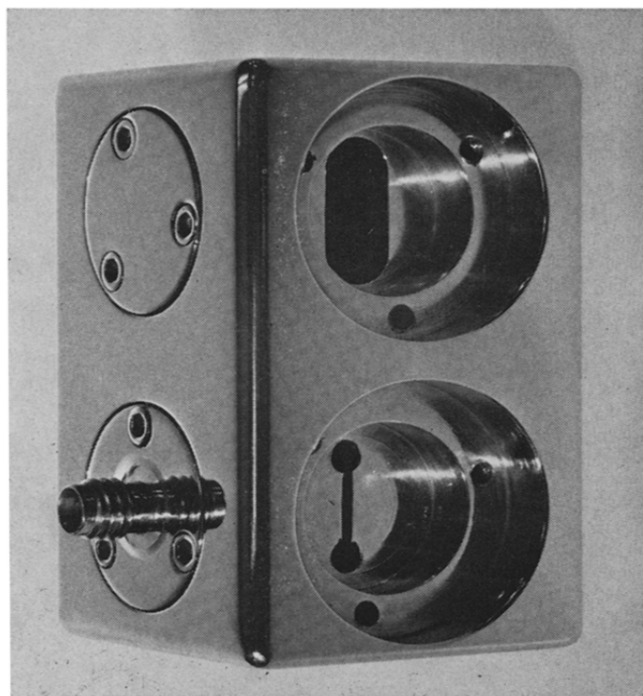
Fig. 3. Photograph showing construction details of the piezoelectric crystal detector cell.

and drift was less than 0.02 Hz/min. Note that quick fluctuations of frequency were filtered out in the frequence–voltage convertor. Overall stability of the oscillators was in the order of 1 part in 10^9 over a typical run of 5–10 min. Chromatographic peaks gave frequency deviations from about 100 Hz to less than the noise level, giving a dynamic range of 5000 or 10,000 to 1.

At room temperatures the detector behaved somewhat similar to previous models, except that it was considerably more stable and less erratic in operation. Signal-to-noise ratio for an injection of 3.5×10^{-7} g of benzene was found to be 7, establishing the minimum detectable amount of benzene as 1×10^{-7} g. This response is comparable to that of a commercially available chromatograph utilizing a PZ detector which operates only at room temperature (P/Z chromatograph; LDC, Riviera Beach, Fla., U.S.A.).

The effect of elevated detector temperatures on the response of a given compound is shown in Fig. 4. Area responses with respect to various detector temperatures between 40 and 100 °C were plotted for identical injections of benzene, n-decane and n-butanol. The response of each compound decreases as the detector temperature is increased. Furthermore, the relative responses of these three compounds are seen to be temperature dependent. At higher temperatures the compounds become more similar in response. Fig. 5 shows the theoretical response dependence upon temperature for the model compounds. Data points were calculated from the equation presented by Janghorbani and Freund[6]:

$$S = HTe^{A/T} \tag{2}$$

where S = the response per unit concentration of the eluent, H = a constant for a given set of detector and chromatographic conditions (arbitrarily set as 1×10^{-16} to approximate detector response at 40 °C), A = the molar heat of vaporization of the eluent in cal/mole (ref. 8) and T = the detector temperature in °K.

In general, agreement between the experimental data (Fig. 4) and the theoretical data (Fig. 5) is good. Absolute and relative responses vary essentially in the same manner. Yet the actual rate of decrease in response with temperature is not as great as that calculated from eqn. 2. This difference may be due to changes in H over the temperature range investigated or permitting the sample to impinge directly upon the crystal. The observed PZ detector response at elevated temperatures is higher than predicted from Fig. 5 and still adequate for many analytical uses. Furthermore, the detector's response is linear as was illustrated by sub-microliter injections of *n*-hexane (Fig. 6).

Nevertheless, the decrease in detector response for increased temperature requires that special consideration be given when selecting operating conditions. For a given temperature the PZ response increases with molecular weight and boiling
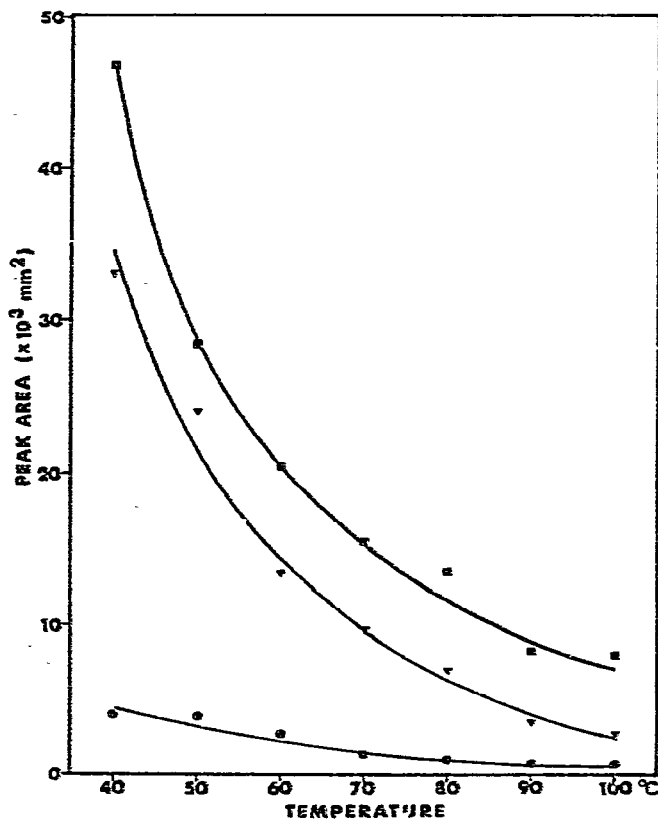

Fig. 4. Detector response *versus* temperature. Conditions: column temperature, 40°C; detector temperature, 40–100°C; column, 1/8 in. O.D. × 24 in. stainless-steel tubing packed with 5% Carbowax 400 on 100–120 mesh Chromosorb W; crystal coating, 7 µg Carbowax 400; sample, 0.1 µl of benzene (●), *n*-decane (▼) and *n*-butanol (■); carrier gas (nitrogen) flow-rate, 10 ml/min.
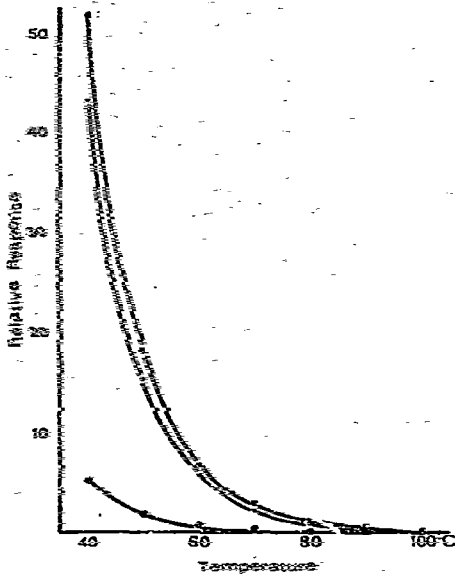
Fig. 5. Theoretical detector response *versus* temperature. Symbols as in Fig. 4.
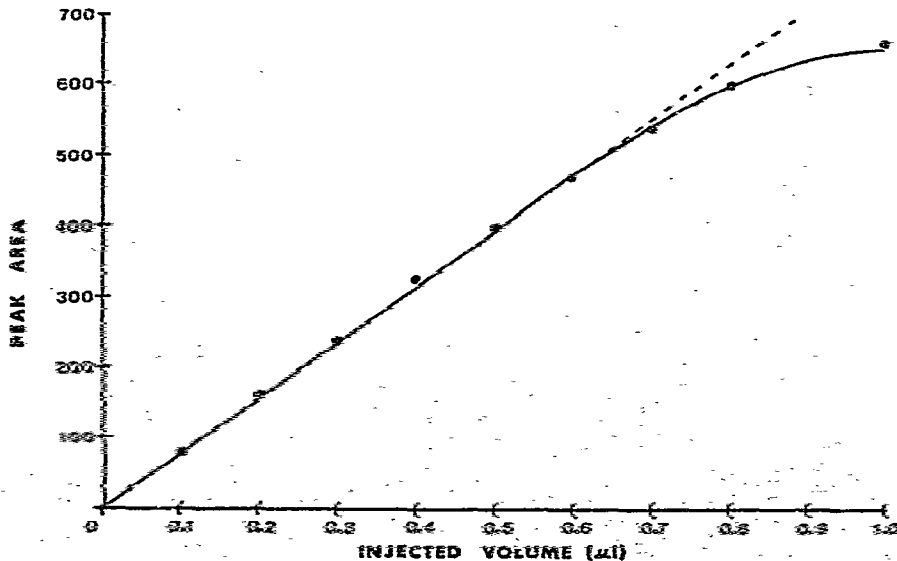

Fig. 6. Peak area *versus* volume of *n*-hexane injected. Conditions: column temperature, 80°C; detector temperature, 74°C; column, 1/8 in. O.D. × 20 in. stainless-steel tubing packed with 5% Carbowax 400 on 100–120 mesh Chromosorb W; crystal coating, 7 μg Carbowax 400; carrier gas (air) flow-rate, 5 ml/min.
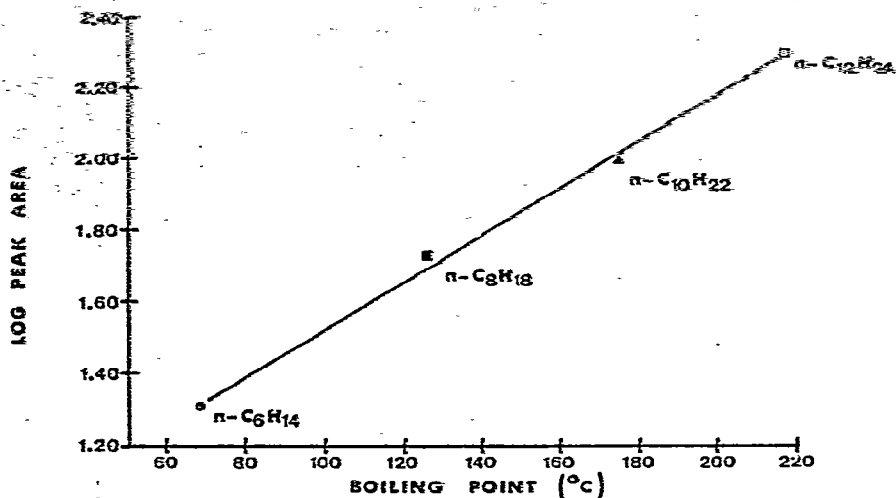
Fig. 7. Plot of log peak area *versus* boiling point. Conditions: Column temperature, 80°C; detector temperature, 74°C; column, 1/8 in. O.D. × 20 in. stainless-steel tubing packed with 5% Carbowax 400 on 100–120 mesh Chromosorb W; crystal coating, 7 μg Carbowax 400; sample, n-hexane, n-octane, n-decane and n-dodecane; sample size, 150 μg of each; carrier gas (air) flow-rate, 5 ml/min.

point of the eluting components. In Fig. 7 the logarithm of the VT/PZ detector's area response is seen to be proportional to boiling point of the compounds. As the vapor pressure of compounds decreases, their sensitivity in the PZ detector increases. Yet adequate component vapor pressure is a requisite for GC. Therefore, for each component there is an optimum temperature which is high enough to allow elution within a reasonable time but low enough to allow sensitive PZ detection.

CONCLUSIONS

The design for a chromatograph with PZ detection above ambient temperature was described and its major parameters discussed. It was found to have essentially the same characteristics (*i.e.*, sensitivity, linearity, etc.) as those with PZ detectors used at room temperature.

Detector temperature is an important parameter in PZ detection. Relative response of components vary with temperature so that there is less discrimination between compounds detected at higher temperatures. Absolute detector response for a given compound decreases with increasing temperature. This effect was found not to be as pronounced as is predicted from theoretical considerations. For optimum detector conditions, the column and detector temperatures should be kept as low as practical but sufficiently high to elute the component of interest in a reasonable time.

The VT/PZ chromatograph and detector extends the range of GC PZ detection to many compounds with vapor pressures too low for ambient PZ chromatography and provides the option of faster analyses at reduced sensitivities.

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