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ANALYTICAL PERFORMANCE OF THE PIEZOELECTRIC CRYSTAL DETECTOR

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SUMMARY

A piezoelectric crystal, which can be coated with various low-vapor-pressure materials, has been used as a detector in a gas chromatograph that can operate at room temperature using an air or nitrogen carrier gas. Performance data are presented on sensitivity, response and gas chromatographic peak parameters for a range of compounds from SO_2 to heavy hydrocarbons. The use of selective coatings to increase sensitivity is demonstrated.

INTRODUCTION

In the past, piezoelectric quartz crystals have been used successfully for many purposes, from frequency controllers to micro balances. Recently, a piezoelectric crystal has been effectively utilized in a gas chromatographic (GC) detector to provide a uniquely simple yet sensitive analytical instrument that can operate at room temperature and with an air or nitrogen carrier gas[1].

King[2] was the first to demonstrate that the principle of piezoelectric crystal oscillators could be applied in a GC detector. He coated quartz plates with the same partitioning liquids used in GC columns. The separated components were detected after leaving the column when they passed over the coated crystal and partitioned into the liquid coating, changing the natural resonance frequency of the oscillating quartz crystal. This frequency shift can be converted linearly to a voltage and displayed on a recorder to produce a chromatogram. In a more recent paper[3], King described many applications for the piezoelectric detector, including its ability to accomplish chromatography of high-boiling compounds at low temperatures. Both King[2] and Guilbault[4] have demonstrated that through the use of specific coatings the piezoelectric crystal becomes a sensitive and versatile detector. Guilbault and Lopez-Roman[5] have since shown its application to the detection of SO_2 in air. Janghorbani and Freund[6] have evaluated coated piezoelectric crystals as digital sensors and have suggested their use for continuous monitoring of gas streams.

We have recently been investigating the qualitative and quantitative performance of a chromatograph utilizing a piezoelectric detector (P/Z Chromatograph, Laboratory Data Control, Riviera Beach, Fla., U.S.A.), whose design is based on the work of Karasek and Gibbins[1]. It is the purpose of this paper to present data on the analytical performance of this detector and limits of detection for a number of compounds as well as data on the use of specific coatings to selectively increase sensitivity. Response factors and analytical results for a range of compounds from SO_2 to mixtures of heavy hydrocarbons indicate the scope of its analytical capabilities.

EXPERIMENTAL

Instrument design

Fig. 1 is a simplified scheme of the P/Z chromatograph. The sample to be analyzed is injected through a conventional injection port system onto a packed GC column, where separation of the components is achieved. Because component separation is accomplished at room temperature, the columns used are short (20 in.) compared to columns of conventional lengths. Immediately after leaving the column the components pass through a stainless-steel detector block that houses a suitably coated 9,000 MHz piezoelectric crystal. The components are sensed as a frequency change, the variation of which is determined by heterodyning the detector signal against a similar reference oscillating circuit. The audio signal representing the difference between the reference and detector circuits is amplified, clipped and differentiated; the resulting pulses are then rectified and filtered. The DC voltage produced, which is proportional to the frequency shift, is compared to an offset or zeroing control and is amplified and displayed on a millivolt chart recorder.

Generally the crystal partitioning coating is the same as that used on the column in order that column and crystal bleed compensate each other. The crystal coating is obtained by depositing an appropriate volume of a solution of known weight

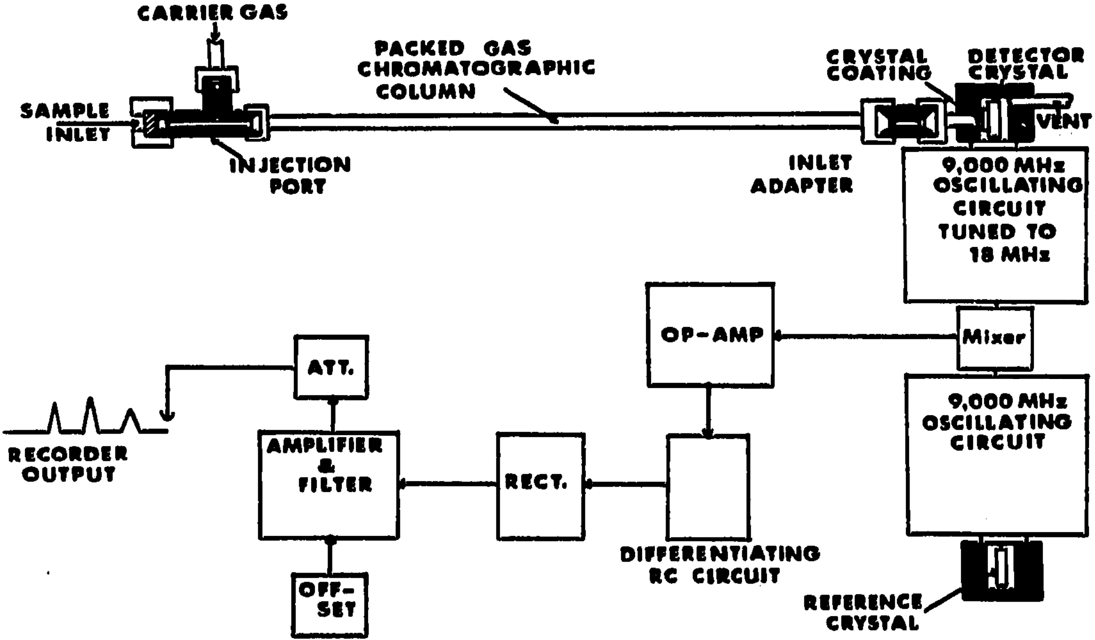

Fig. 1. Schematic diagram of P/Z chromatograph.

percent on the center of a clean crystal with a microsyringe. After an 8- to 10-h conditioning period at a temperature 25 to 100° below the maximum recommended temperature of the liquid support, this deposit forms a uniform layer over most of the electrode surface. The coated crystal detector is placed in the instrument where it is operated under a carrier flow of 20–40 ml/min until a stable baseline is achieved. This usually requires 1 to 2 h of operation. It has been observed that the prolonged heating of the crystal during the initial conditioning period does not adversely affect its performance but does reduce the time required for the detector to reach equilibrium stability.

All columns used in the instrument for this work were 20 in. long and constructed of 1/8 in. O.D. stainless-steel tubing packed with 5% loadings of either Carbowax 400 or UCON LB550X on 100–120 mesh Chromosorb W, or silicone fluid OV-17 on 80–100 mesh Chromosorb P. All columns provided adequate separation with short retention times for the compounds chromatographed. A 4-μg coating on the detector crystal was used throughout the investigation.

Procedure

A mixture of *n*-acetates in equal proportions by weight was chromatographed at room temperature to demonstrate component separation and detector response to increasing molecular weight.

In order to establish the precision and accuracy with which the instrument can perform quantitative analysis, response factors for the components of two typical mixtures were calculated. The procedure involved preparing an accurate weight percent mixture of the components, making 0.5-μl injections and then calculating the individual peak areas with the aid of a Sargent Model SRG recorder in conjunction with a Model 240 disc integrator. The response factors were calculated relative to ethanol for the first mixture using an average of six runs. The same procedure was followed for a series of normal hydrocarbons. In this case the factors were calculated relative to *n*-hexane using an average of ten runs. Kováts retention indices for benzene and toluene were calculated.

The minimum detectable quantity for a large number of compounds was determined. A dilute solution of each compound was prepared in a suitable solvent. Injections of decreasing volume were made until the signal produced by the component of interest measured twice that of the ambient noise level. The minimum detectable volume was then converted to mass units.

Improved detector sensitivity through the use of specific coatings was illustrated by redetermining the minimum detectable quantity for *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane using a rubber crystal coating. This coating was produced using commercial rubber cement (Carter's Clean Grip Rubber Cement, The Carter's Ink Company of Canada, Toronto, Canada).

Nitrogen samples containing low concentrations of SO_2 were also analyzed. Varying concentrations of SO_2 in N_2 were obtained by first filling a 1-ml Hamilton gas-tight syringe to capacity with anhydrous SO_2 and then evacuating it to the appropriate volume and refilling it to capacity with dry nitrogen. This procedure was repeated until the desired dilution was obtained. The gases were allowed to equilibrate between each dilution and before injection.

Reagents

The analytical standards used in the minimum detectable quantity study were obtained from kits Nos. 11A, 21A, 25A, 41A, and 62A (PolyScience Corp., Evanston, Ill., U.S.A.). All other compounds were reagent grade as specified by the American Chemical Society.

RESULTS AND DISCUSSION

A crystal coated with a liquid phase will respond when a critical mass is sorbed onto its surface. Fig. 2 illustrates the response of the piezoelectric detector to an equal weight percentage mixture of n-acetates. It can be observed that the response increases with increasing molecular weight, making the higher-boiling compounds at the end of the chromatogram more detectable. A plot of either log response *versus* boiling-point or log retention time *versus* boiling-point yields a straight line, indicating that the detector response is predictable. King[3] reports a detector response time in the 40-msec range. The rapid response time is reflected by the symmetry of the peaks and can be attributed to the small detector volume, minute mass of the crystal coating, and short component residence time in the detector. Because of the relatively low temperature operation, component separation can be achieved with the short 20-in. columns. Peak shapes are quite symmetrical with all the columns studied.

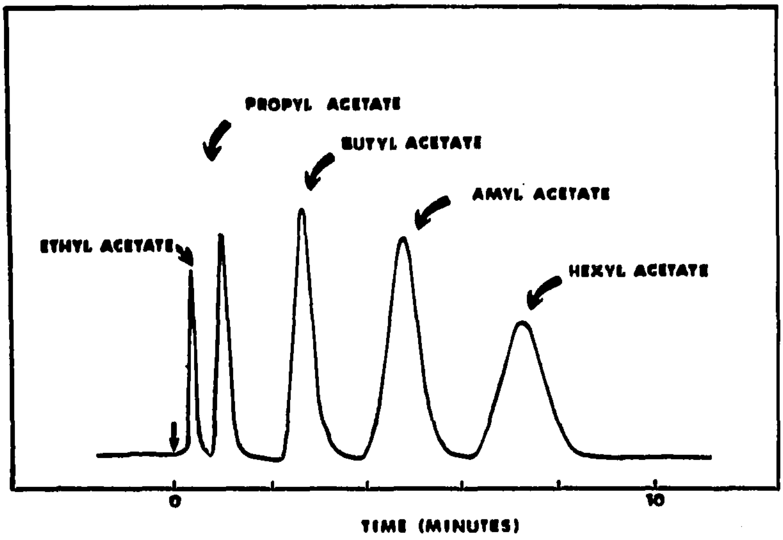

Fig. 2. Chromatogram of a mixture of n-acetates. Conditions: temperature, 25°; column: 1/8 × 20 in. O.D. stainless-steel column packed with 5% UCON LB550X on 100–120 mesh Chromosorb W; crystal coating, 4 μg UCON LB550X; sample size, 0.5 μl; carrier gas, air; flow-rate, 60 ml/min.

The following are some columns other than those already mentioned in this paper which have been used: 5% SF-96 on 80–100 mesh Chromosorb P, 5% Carbowax 20M on 100–120 mesh Chromosorb W, 5% SE-30 on 80–100 mesh Chromosorb P, 5% dinonyl phthalate on 100–120 mesh Chromosorb W, 5% Lexan on 100–120 mesh Chromosorb W, 5% Hallcomid M180L on 100–120 mesh Chromosorb W, 3% UC W-98 on 80–100 mesh Chromosorb W, and 5% diethylene glycol adipate on 100–120 mesh Chromosorb W.

A prerequisite for quantitative GC analysis is that the detector response be linearly proportional to the quantity of components injected on the column. Table I displays data resulting from the quantitative study of a simple alcohol mixture. Determined values are accurate to within ±0.1%. Fig. 3 shows a typical chromatogram displaying the elution of a series of normal alcohols at room temperature.

Table II presents response data for a similar quantitative study of a series of *n*-hydrocarbons. The error of the determination varies between 0.8 and 0.1%. The percent relative standard deviations quoted are those of the six individual runs relative to the average calculated weight percent.

TABLE I

QUANTITATIVE ANALYSIS OF A MIXTURE OF NORMAL ALCOHOLS

Sample	*Relative response*	*Known weight percent*	*Average calculated weight percent*	*Relative standard deviation (%)*
Ethanol	1.0	53.96	54.10	0.012
1-Propanol	2.26	32.48	32.35	0.005
Butanol	5.20	13.56	13.55	0.035

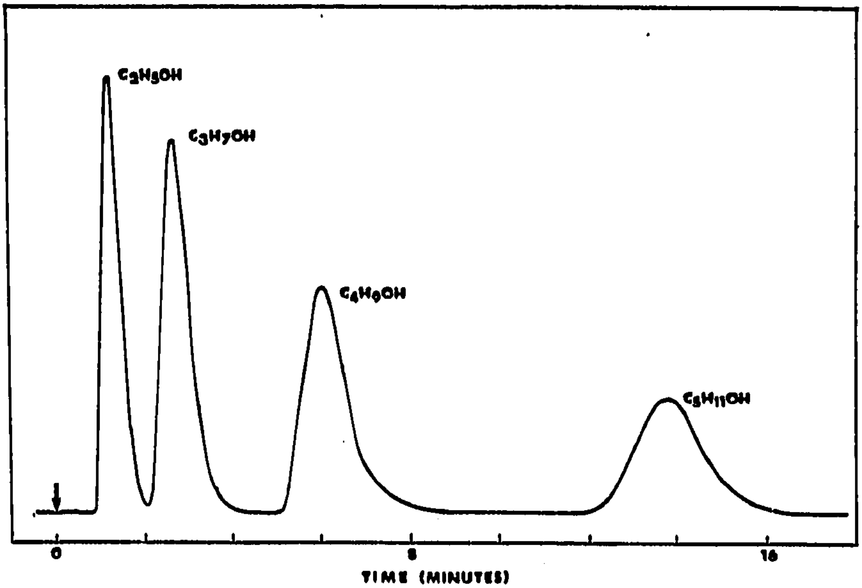

Fig. 3. Chromatogram of a mixture of *n*-alcohols. Conditions: temperature, 25°; column: 1/8×20 in. O.D. stainless-steel column packed with 5% Carbowax 400 on 100–120 mesh Chromosorb W; crystal coating, 4 μg Carbowax 400; sample size, 0.5 μl; carrier gas, air; flow-rate, 50 ml/min.

TABLE II

QUANTITATIVE ANALYSIS OF A MIXTURE OF HYDROCARBONS

Sample	*Relative response*	*Known weight percent*	*Average calculated weight percent*	*Relative standard deviation (%)*
n-Hexane	1.00	46.22	45.42	0.008
n-Heptane	2.60	10.41	10.92	0.037
n-Octane	7.09	27.62	28.10	0.007
n-Nonane	18.95	8.70	8.82	0.032
n-Decane	51.95	7.05	6.70	0.061

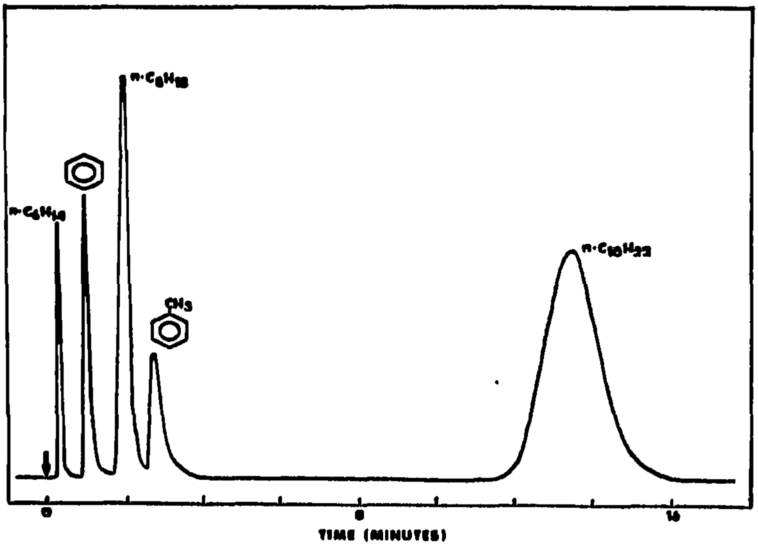

Fig. 4. Chromatogram of a mixture of normal and aromatic hydrocarbons. Conditions: temperature, 25°; column, 1/8 × 20 in. O.D. stainless-steel column packed with 5% OV-17 on 80–100 mesh Chromosorb P; crystal coating, 4 µg OV-17; sample size, 0.5 µl; carrier gas, air; flow-rate, 30 ml/min.

Fig. 4 shows a chromatogram of a mixture of normal and aromatic hydrocarbons. These compounds are all separated with a minimum resolution of 1.7. This permits the calculation of the Kováts retention index at room temperature for benzene and toluene.

Table III displays the results of the limits of detection study. It can be seen that in general the detection limit improves with increasing molecular weight. All compounds in this study were chromatographed at room temperature using a Carbowax 400 coating on the column packing and detector. This appears to be a very versatile coating and can be satisfactorily used for many compounds. Table IV illustrates the improvement in sensitivity which can be achieved by using coatings that are more specific to the compounds of interest. The four hydrocarbons were

TABLE III

LIMITS OF DETECTION OF THE PIEZOELECTRIC CRYSTAL DETECTOR FOR VARIOUS COMPOUNDS USING A CRYSTAL COATING OF CARBOWAX 400

Compound	*Molecular weight*	*Boiling-point (°C)*	*Minimum detectable quantity (g)*
n-Hexane	86.18	68.9	$2 \cdot 10^{-6}$
n-Heptane	100.21	98.4	$7 \cdot 10^{-7}$
n-Octane	114.23	125.6	$4 \cdot 10^{-7}$
n-Nonane	128.26	150.8	$4 \cdot 10^{-8}$
n-Decane	142.29	174.1	$3 \cdot 10^{-8}$
n-Undecane	156.32	195.9	$2 \cdot 10^{-8}$
n-Dodecane	170.34	216.3	$2 \cdot 10^{-8}$
Ethanol	46.07	78.5	$8 \cdot 10^{-6}$
Benzene	78.12	80.1	$4 \cdot 10^{-7}$
o-Xylene	106.17	144.4	$2 \cdot 10^{-7}$
Cumene	120.20	152.4	$3 \cdot 10^{-8}$
Mesitylene	120.20	164.7	$9 \cdot 10^{-8}$
p-Cymene	134.22	177.1	$9 \cdot 10^{-8}$
n-Hexylbenzene	162.28	277.0	$3 \cdot 10^{-8}$
2-Hexanone	100.16	128.0	$2 \cdot 10^{-7}$
2-Heptanone	114.19	151.5	$2 \cdot 10^{-7}$
2-Octanone	128.22	173.0	$2 \cdot 10^{-7}$
2-Nonanone	142.24	195.3	$2 \cdot 10^{-7}$
Ethyl acetate	88.12	77.1	$4 \cdot 10^{-7}$
Ethyl propanoate	102.13	99.1	$3 \cdot 10^{-7}$
Ethyl butanoate	116.16	124.0	$2 \cdot 10^{-7}$
Ethyl pentanoate	130.19	144.6	$2 \cdot 10^{-7}$
Ethyl hexanoate	144.22	168.0	$4 \cdot 10^{-8}$

TABLE IV

LIMITS OF DETECTION OF THE PIEZOELECTRIC CRYSTAL DETECTOR FOR SOME *n*-HYDROCARBONS USING A SPECIFIC CRYSTAL COATING PREPARED FROM RUBBER CEMENT

Compound	*Minimum detectable quantity (ng)*
n-Nonane	4
n-Decane	5
n-Undecane	2
n-Dodecane	4

chromatographed at room temperature with a Carbowax 400 column and a rubber crystal coating. This coating displays a larger component interaction specifically with hydrocarbons and consequently the sensitivity is increased by an order of magnitude.

One determination for which the piezoelectric detector is sensitive is the detection of SO_2 in air. Fig. 5 illustrates the linearity of response obtained when different concentrations of SO_2 by volume in nitrogen are chromatographed. The absolute limit of detection, corresponding to a signal-to-noise ratio of 2:1, is found to be in the range of 3–5 ppm using a 1-ml sample size.

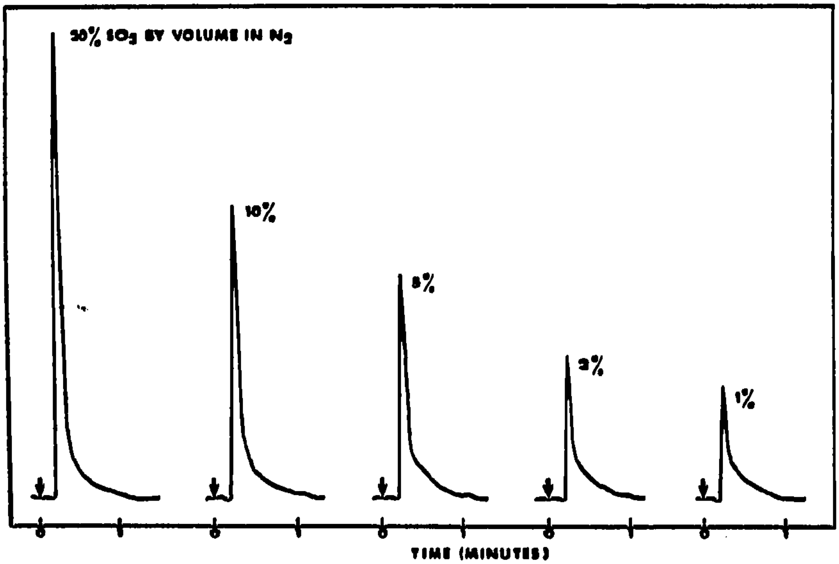

Fig. 5. Chromatograms of varying concentrations of SO_2 in nitrogen. Conditions: temperature, 25°; column, 1/8 × 20 in. O.D. stainless-steel column packed with 5% Carbowax 400 on 100–120 mesh Chromosorb W; crystal coating, 4 µg Carbowax 400; sample size, 1-ml; carrier gas, air; flow-rate, 60 ml/min.

CONCLUSIONS

From studies to date it appears that the scope of analytical capabilities of the piezoelectric detector are considerable. Based on its sensitive range of detection and high stability (noise < 0.05 Hz), the detector represents an effective means of detection of trace compounds. Perhaps its most exciting potential lies in the air pollution monitoring field. Further work is currently being done with specific coatings for light inorganic gases. It is expected that they will extend the useful range of this detector in qualitative and quantitative GC.

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