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Anomalous Gas Chromatogram Due to the Oxidation of Porous Polymer Beads by a Sample Containing Oxygen Gas

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By the gas-chromatographic analysis of the organic vapor in the air by means of a Porapak column, a broad peak accompanied by long tailing was observed at column temperatures above a certain value with a flame-ionization or an electron-capture detector. The cause of that peak was investigated using various gases and columns by changing the column temperature. The conclusion was that oxygen in air reacted with polymer beads even at temperatures lower than that cited in the catalogue as temerature to be employed, and the reaction products gave the anomalous broad peaks. The reaction was considered to consist of the oxygenation of polymer beads to produce carbon monoxide, carbon dioxide, formic acid, and the other organic compounds. For Porapak Q and P, the maximum temperature which can be used in safety may be 120°C for an analysis of a sample which consists in greater part of air.

In the field of occupational health, the analysis of toxic gases in very low concentrations is necessary in order to estimate the contamination of the ambient air by the gases, and many analytical methods have been developed. Of these methods, gas chromatography is one of the most reliable and useful methods.[1–6] For the analysis of relatively higher concentrations of toxic gases in the air, a gas sampler attached to a gas chromatograph can be used to introduce the sample air directly into the column. For example, 1 m*l* of air which contains 1 ppm of benzene is sufficient to obtain a satisfactory chromatogram with an ordinary flame-ionization detector. A Porapak column is suitable for the analysis of those samples.[7] Furthermore, the characteristics of columns are not weakened, for no stationary liquid phase is used. Stationary liquid frequently is eluted, even if very slowly, and causes noise.[8] Therefore, a Porapak column is very useful for an analysis of gases in the ambient air in an industrial environment and in the atmosphere.

By the practical use of a Porapak column for the analysis of gases in the air, sometimes an anomalous broad peak has been observed, and it has interfered with the other peaks of the minor components to be determined. For instance, in a sample of organic solvent vapors in the air, a satisfactory chromatogram has been observed at relatively lower temperatures, but with a rise in the temperature an anomalous broad peak has been found, as is shown in Fig. 1. With a Porapak Q column, a few ppm of hexane present in the air has shown a good chromatogram with a clear peak at a column temperature of 132°C. However, for the xylene air sample a broad peak has followed the xylene peak at 183°C. That broad peak has appeared under those experimental conditions at temperatures higher than 160°C and has been enhanced with an increase in the column temperature.

The cause of that broad peak has been investigated in order to avoid such an unfavorable phenomena.

Experimental

Materials. The gases used were nitrogen, carbon monoxide, air, and oxygen, all of which were supplied from a gas cylinder without any purification except in special cases, when air was purified by several methods. The

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[1] R. Van Houten and G. Lee, *Am. Ind Hyg. Ass. J.*, **30**, 465 (1969).

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[3] L. D. White, D. G. Taylor, P. A. Mauer, and R. E. Kupel, *ibid.*, **31**, 225 (1970).

[4] F. H. Reed and W. R. Halpin, *ibid.*, **29**, 390 (1968).

[5] J. Novak, V. Vasak, and J. Janak, *Anal. Chem.*, **37**, 660 (1965).

[6] I. H. Williams, *ibid.*, **37**, 1723 (1965).

[7] O. L. Hollis *ibid.*, **38**, 309 (1966).

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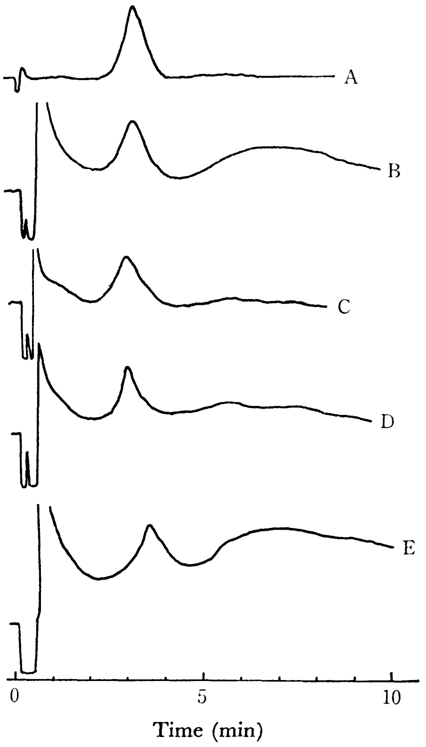

Fig. 1. Gas chromatogram of organic solvent vapor in the air by Porapak Q column of 1/8 in (o.d.) with flame ionization detector.

Flow rate of carrier gas was 30 m*l*/min and volume of gas sampler 4 m*l*.

Samples and column temperatures were with (1) column length of 47 cm, (A) *n*-hexane and 132°C; and (B) *o*-xylene and 183°C; with (2) column of 3 ft, (C) 2,3-dimethyl butane and 164°C; (D) benzene and 174°C; and (E) toluene and 192°C, respectively.

polymer beads were Porapak P and Q (50 to 80 mesh) of Water Associates Co.

Gas Chromatograph. Two types of gas chromatographs were used in the present experiment. The main experiment on the oxygen effect on the column was carried out by means of an Ohkura gas chromatograph Model 6000 equipped with a flame-ionization detector. The column used was made of U-shaped stainless steel tubing. The sample was injected into a chromatograph with an automatic gas sampler (1 m*l*), the temperature of which was regulated at 60°C. A few chromatograms were obtained by means of a Perkin Elmer Model 800 Vapor Fractometer equipped with a dual flame-ionization detector or an electron-capture detector. The column used consisted of coiled stainless steel tubing. The volume of the gas sampler was 4 m*l*. The latter instrument was also used to analyze the pyrolytic products of Porapak P and Q. The column was washed with hydrochloric acid and water, and then dried by nitrogen flushing. Polymer beads were packed into the column by means of a vibrator.

Infrared Spectrometer. A Hitachi EPI G 2 infrared spectrometer was equipped with a 10-cm gas cell and used to identify the gaseous components of pyrolytic products.

Differential Thermal Analysis. The differential thermal analysis and thermogravimetric analysis of polymer beads were done by means of a Rigakudenki DTA, compact-type TGA thermoflex. The temperature was programmed from room temperature to about 500°C at the rate of 5°C/min. For each polymer beads, one curve was observed in a nitrogen-gas flow environment and another in an air flow in the same temperature range.

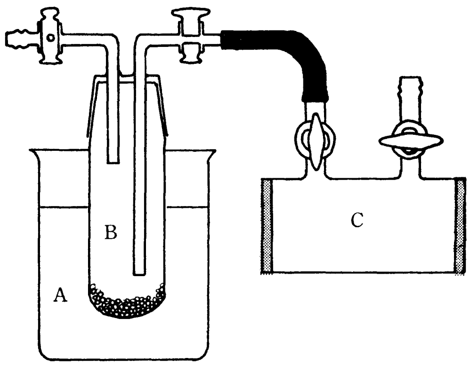

Fig. 2. Schematic diagram of vessel for pyrolysis and sampling of products in a gas cell.

A, Silicone oil bath; B, Vessel for pyrolysis of polymer beads; C, Infrared gas cell.

Analysis. Polymer beads were pyrolyzed in the specially-prepared vessel shown in Fig. 2. The vessel was immersed in an oil bath heated at from 190 to 210°C. The gaseous product in the vessel was introduced into a infrared gas cell which had previously been evacuated at 1 mmHg. The product was also collected in a 10-m*l* hypodermic syringe in order to be introduced into the gas sampler of the gas chromatograph. In this case, the column temperature was maintained at about 120°C, because below 120°C the anomalous chromatogram was not observed by means of a Porapak column.

Results

Any sample the major component of which was air showed an anomalous chromatogram with a highly sensitive detector like a flame ionization or an electron capture at column temperatures above a certain limiting value. As a chromatogram obtained with a flame ionization detector was similar to that obtained with an electron capture detector at the column temperature of 170°C, this paper summarized the results obtained with a flame ionization detector. Air was introduced only into the gas chromatograph with a gas sampler, and chromatograms were taken at various column temperatures. The experimental results are summarized in Fig. 3 for the Porapak Q and P columns. Chromatograms of column temperatures lower than about 140°C did not show any anomalous peaks. For the Porapak Q column, above 170°C broad and long tailed peaks were observed, while for Porapak P above 160°C a large and broad peak with a long tail was observed. If those peaks were caused by a pressure drop or by some other shock of the sampling process, similar phenomena might be observed upon the use of nitrogen gas through a gas sampler. However, that possibility can be excluded on the basis of Fig. 4, where the chromatogram of nitrogen gas shows a little peak with a short interval by injection and no other large or broad peaks appeared. It was considered reasonable that no impurity in the sample or contaminant in the gas sampler caused the anomalous chromatogram, because inactive gases, like nitrogen or carbon monoxide, did not show a broad peak and the braod peak with the air sample could not be removed by the purification of the air.

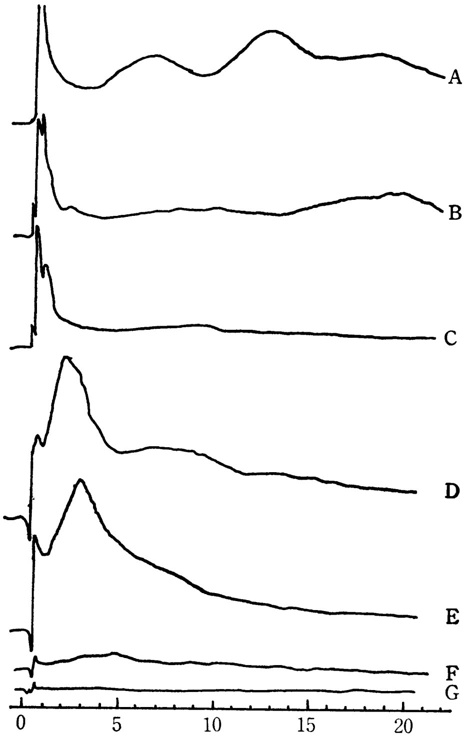

Fig. 3. Anomalous chromatogram by air and column temperature.

Porapak Q column of 6 mm (o.d.) and 200 cm (length) was used for (A), (B), and (C), and Porapak P column of 6 mm and 150 cm for the others. Volume of the gas sampler was 1 m*l*. Column temperature and carrier flow rate were, (A) 182°C and 50 m*l*/min; (B) 170°C and 48 m*l*/min; (C) 137°C and 45 m*l*/min; (D) 180°C and 62 m*l*/min; (E) 164°C and 46 m*l*/min; (F) 144°C and 52 m*l*/min; and (G) 122°C and 48 m*l*/min, respectively.

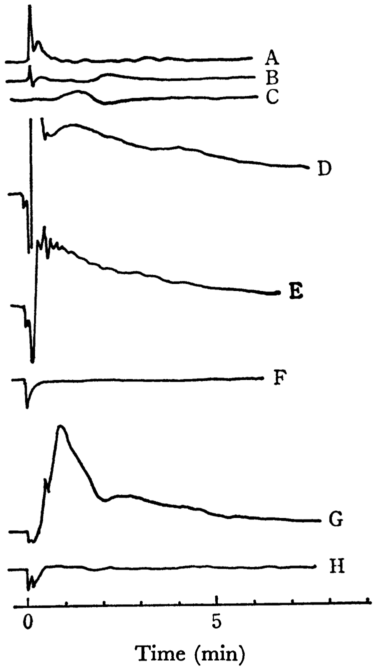

Fig. 4. Chromatograms of a few kinds of gases by Porapak P column, and gas sampler of 1 m*l*.

Column temperature, column size and carrier flow rate were; (1) 116°C, 6 mm (o.d.) and 50 cm (length), and 36 m*l*/min, respectively for samples of (A) oxygen, (B) air, and (C) nitrogen; (2) 170°C, 1/8 in and 6 ft, and 30 m*l*/min, respectively for samples of (D) oxygen, (E) air, and (F) nitrogen; (3) 192°C, 6 mm and 150 cm, and 47 m*l*/min, respectively for samples of (G) air and (H) nitrogen.

The main components of air are oxygen and nitrogen. The former reacts possibly with polymer beads to cause an anomalous broad peak. In fact, the peak with an air sample was enhanced by oxygen at 170°C, as is shown in Fig. 4. The anomalous chromatogram was considered to be due to the pyrolytic product of the polymer beads in the column produced by oxygen at higher temperatures, as organic acid, aldehydes and degraded compounds. The elution of those products could be changed by connecting the Porapak column and another column, like an active carbon, a molecular-sieve, or a silica gel column, in series. The connection of those columns before the Porapak column did not produce any chromatogram different from that produced by the Porapak column only, but in connection after the Porapak column, the active carbon column did not show any detectable broad peaks in the present experiment, and the molecular sieve column greatly delayed the elution of the main broad peaks.

In order to confirm the above estimation, polymer beads were pyrolyzed and the product was analyzed. The temperature at which polymer beads were pyrolyzed was determined by a DTA experiment. By the DTA of a sample in a nitrogen atmosphere, the degradation or decomposition started about 250°C for Porapak Q and about 230°C for Porapak P. However, in oxygen or air the decomposition was observed above 160°C for both polymers. The DTA curve passed a maximum near 210°C. Therefore the pyrolysis was carried out at from 190 to 210°C, and the gaseous product was analyzed by gas chromatography and infrared spectrometry. The infrared spectrum is shown in Fig. 5. The spectrum showed bands of water near 3800, 1600, and 600 cm^{-1}, bands of carbon dioxide near 3800, 2350, and 660 cm^{-1}, band of carbon monoxide near 2100 cm^{-1}, and bands of formic acid near 1780, 1100, and 630 cm^{-1}. Peaks of other many components were observed by gas chromatography, as is shown in Fig. 6. At present, not each component has been identified gas-chromatographically.

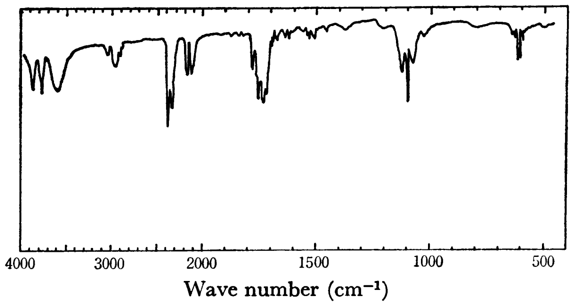

Fig. 5. Infrared spectrum of gaseous product from pyrolysis of Porapak Q.

Temperature of pyrolysis was 210°C.

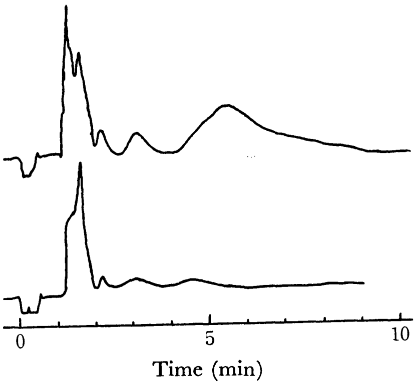

Fig. 6. Chromatograms of gaseous product by pyrolysis of polymer beads at 195°C.

Porapak Q column of 1/8 in (o.d.) and 3 ft (length) was used at 125°C. Flow rate of carrier gas was 30 m*l*/min and volume of gas sampler 4 m*l*. Flame ionization detector was used.

Upper chromatogram was observed with gaseous product of pyrolysis of Porapak P and lower with Porapak Q.

Discussion

An anomalous chromatogram of a sample containing air has been observed with a Porapak column at temperatures higher than about 160°C. Considering the cause of the chromatogram in the basis of the experimental results, it is deduced that the oxygen in the air reacts with polymer beads. Some of the reaction products (mainly oxides) may be identified as carbon monoxide, carbon dioxide, formic acid and other oxidized organic compounds. The Porapak column is stable below the temperature cited in the catalogue only when an inactive carrier gas is used. However, if a sample contains more air or oxygen gas than the components to be analyzed, the chromatogram inevitably produces an anomalous broad peak with a long tailing at temperatures which do not exceed the maximum temperature cited in the catalogue as stable.[9] That chromatogram is not successful for use in determining minor components because of the interference of the broad peak.

Barta and Gordon have reported that Porapak Q has active sites which caused an exchange of hydrogen in ketones.[10] Active sites may also possibly react with oxygen to produce the pyrolytic compounds.

At present not all substances produced by pyrolysis have been identified and experiments are easy in only a few cases. Nevertheless, several significant pieces of information can be obtained from the results. Below 120°C, Porapak P and Q columns apparently do not react with oxygen and no anomalous chromatogram is found. More precisely, the temperature limit of no anomalous peak may be 130°C for the Porapak Q column and 120°C for the Porapak P column, both column materials of 50 to 80 mesh.

The cause of the anomalous peak is apparently the reaction of the polymer beads in the column with oxygen. Several procedures are considered to avoid such unfavorable chromatograms, which frequently interfere with the peak to be observed. These considerations are necessary in making an analysis to monitor the concentration of gas in the air continuously. One procedure is a temperature programming, *i.e.*, air passes through the column at a lower temperature, 120°C or so, and then the temperature is raised at a suitable rate. This temperature programming procedure may avoid the effect of oxygen on the chromatogram when the Porapak column is used. Another method is to make the column shorter. When the particular components to be analyzed are one or two, and when their retention times are far from those of the other peaks, it is possible to make the column shorter than that used usually for the analysis of a sample containing many components, and the column temperature can be lowered. Figure 1 shows one example. When the Porapak Q column 3 ft long is used, the retention time of 2,3-dimethylbutane is about 3 min when the temperature is 164°C and the carrier gas flow rate is 30 m*l*/min. However, the present results show that the retention time becomes shorter (2.6 min) with the 47-cm column at 132°C, and the separation of the peaks is sufficient. By lowering the column temperature with shorter column, it is thus possible to suppress the anomalous chromatogram.

The process of concentrating a sample in the air may also preclude those effects of oxygen on the chromatogram, but the process is rather complicated compared with the direct analysis of the air without any concentration procedures. Furthermore, the procedure of concentrating the samples to be determined involves several problems, such as the efficiency of concentration for each component, the contamination of the sampling apparatus, and the recovery process of the collected compounds.[3–6]

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[9] The booklet on Porapak, Water Associates, Inc., Framingham Mass. (1965), pp. 5, 19.

[10] C. I. Barta and A. S. Gordon, *J. Chromatog. Sci.*, **8**, 63 (1970).