Note

Improved analysis of sulphur gases on porous polymers

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Porous polymer beads were first used as a column packing in gas chromatography by Hollis[1] for the separation of gaseous mixtures, while later reports demonstrated applications to a wide range of organic compounds[2,3]. The general utility of porous polymers has been reviewed by Dave[4] and by Hollis[5].

The polymers, originally developed for gel permeation chromatography[6], are prepared by modified suspension polymerization[7,8] of styrene, divinylbenzene and ethylvinylbenzene. Pore size is regulated by the solvent used and by the degree of cross-linking achieved during the copolymerization. Polymers of increased polarity are achieved by incorporation of a comonomer containing polar functional groups.

Considerable difficulty has been experienced with the analysis of highly polar compounds, notably sulphur dioxide and hydrogen sulphide, on porous polymer columns due to the apparently irreversible adsorption of the gas molecules onto active sites within the column. This adsorption is observed as a gradual increase in peak area with successive injections, until the active sites are saturated and the column stabilizes.

In the case of a column packing with no polar functional groups, adsorption may take place on metal connections, particularly copper and aluminium, and onto silanol (Si–OH) groups that are present on the surface of glass columns and on glass wool stoppering.

The reason for the increased polarity of some of the porous polymers is not known with certainty but has been the subject of speculation[9]. Zado and Gabecic[9] have indicated the various possible physical mechanisms, although the polarity has also been suggested to be due to functional groups containing acidic hydrogen atoms, *i.e.*, –OH and –SH, –COOH, –NH$_2$ and =NH groups which would account for the significant degree of adsorption of compounds such as sulphur dioxide and hydrogen sulphide.

To decrease the adsorption, and hence the time required for column stabilization, it is necessary to saturate the active sites before an analysis is carried out. This can be achieved simply by repeated injections of the sample, or a more concentrated mixture of the same gas, until column stabilization is achieved[10]. The usual method, however, is to saturate the column material with a species that is preferentially ad-

sorbed onto the active sites, such as phosphoric acid in the treatment of Carbowax and porous polymer columns[11].

A common treatment is the injection of a high concentration of a silanizing reagent onto the column. This method has been used successfully for some time in the treatment of silica supported columns in which the active sites are silanol groups[12]. One of the most common silanizing reagents is dimethyldichlorosilane (DMCS) which deactivates a silanol group in the following manner[13]:
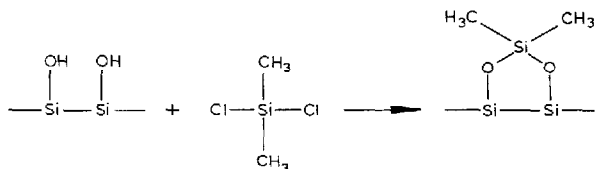
Silanizing reagents have also been shown to improve the effeciency of columns employing the Chromosorb series of porous polymers[12]. Pre-silanized columns in the Porapak series are commercially marketed and have been shown to give improved performance over untreated columns in the analysis of polar organic · compounds[14,15]. Separations of mixtures of the highly polar sulphurous compounds such as sulphur dioxide, hydrogen sulphide and carbonyl sulphide in low concentrations have been achieved on a silanized and acid-washed Porapak Q column[16].

It is the purpose of this study to improve the efficiency of sulphur dioxide analysis on porous polymer columns by silanization with dimethyldichlorosilane. Rather than directly inject the reagent onto the column however, it is proposed to achieve stabilization through silanization by incorporation of low concentrations of the silane into the nitrogen carrier gas.

EXPERIMENTAL

The chromatography was carried out using Gow Mac and Tracor 550 instruments equipped with a Spectrophysics Autolab System IV Reporting Integrator. Both employed Tracor flame photometric detectors with the Tracor 550 instrument being more stable. The oven temperature used was 70°C and the carrier gas flow-rate approximately 100 ml/min in both cases.

Six 0.5-m columns were prepared from 1/8 in. PTFE tubing. The following packings were used to provide a grood cross-section in terms of the extent of sulphur dioxide adsorption and the effect of the silanizing agent; Porapak T, Q, P; Porasil C, B; Chromosil 310.

All phases were obtained from Waters Associates except Chromosil 310 which is produced by Johns-Manville.

RESULTS AND DISCUSSION

The effectiveness of silanization was evaluated by comparing the stability of the column response with and without DMCS included in the carrier gas. Concentrations of 200 ppm and 400 ppm DMCS were used. Silanization was carried out by

passing the carrier gas containing DMCS through the column overnight. Column stability was evaluated over ten injections of 100 ppm of sample.

For assessing the column stability, two criteria were used: the standard deviation of the peak area over ten injections of sulphur dioxide, and the number of injections required to achieve stable operation. The latter value was obtained by calculating the mean peak area obtained over the last few injections when the response appeared to have stabilized. The number of injections for stable operation was simply the number required for the peak area to reach 98 % of this value.

Standard deviations, obtained as a percentage of the mean peak area over ten injections, were used to assess the degree of fluctuation in response.

Porasil B appeared to be the worst of the columns examined for the analysis of low levels of sulphurous gases. With pure carrier gas, the peak area responses to 100-ppm injections of SO_2 were less than 1000 counts, and there appeared to be no evidence of stabilization after ten injections. These effects can be attributed to almost complete adsorption of SO_2. After treatment with 200 ppm of DMCS, adsorption of SO_2 was dramatically reduced to the extent that the area response rose to approximately 500,000 counts.

Chromosil 310 without DMCS in the carrier gas gave the sharpest response of the six materials tested. Particularly low variability in response to 100 ppm SO_2 indicated a negligible extent of adsorption. As expected, the variability was not significantly influenced by treatment with DMCS.

A drop in response, however, was observed, which may be due to combustion of DMCS with lowering of the sensitivity of the flame. It was generally noted with all columns (except Porasil B) that the sensitivity was slightly decreased with DMCS treatment.

When untreated carrier gas was used with Porapak Q significant SO_2 adsorption was observed as a gradual rise in area response with increasing number of injections of 100 ppm SO_2. The response did not appear to have stabilized after ten injections. With 200 ppm DMCS in the carrier gas, the response to 100 ppm SO_2
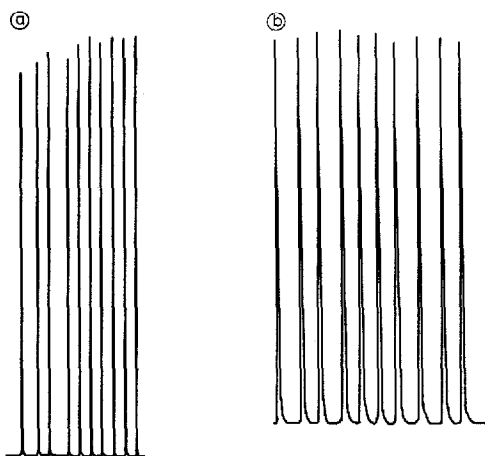

Fig. 1. Chromatograms of repetitive injections of sulphur dioxide on Porapak Q: a, untreated; b, treated with DMCS.

TABLE I

EFFECT OF DIMETHYLDICHLOROSILANE ADDITION ON COLUMN STABILITY

Amount of SO_2: 100 ppm in each case.

Column	DMCS (ppm)	No. injections for stability	S.D. (%)
Porasil B	0	>10	14.6
	200	10	3.9
Chromosil 310	0	3	1.8
	200	0	0.7
Porapak Q	0	>10	4.1
	200	1	1.1
Porapak T	0	6	17.8
	200	1	1.6
Porapak P	0	4	3.0
	200	1	2.1
Porasil C	0	>10	4.4
	200	4	2.3

stabilized after only one injection, and the overall standard deviation was decreased. Fig. 1 shows the chromatograms for the 100-ppm SO_2 injections.

Significant adsorption of SO_2 was indicated with Porapak T by the number of injections required for stabilization and the standard deviation of the response to 100 ppm SO_2. Treatment with DMCS dramatically improves column stability in terms of the variability of response, and the number of injections required to achieve steady response as shown in Table I. Increasing the DMCS concentration to 400 ppm appeared to have little further effect. Chromatograms for the 100-ppm injections are shown in Fig. 2.

With pure carrier gas, minor adsorption of SO_2 at 100 ppm concentration occurred with Porapak P. Use of 200 ppm DMCS in the carrier gas reduced the
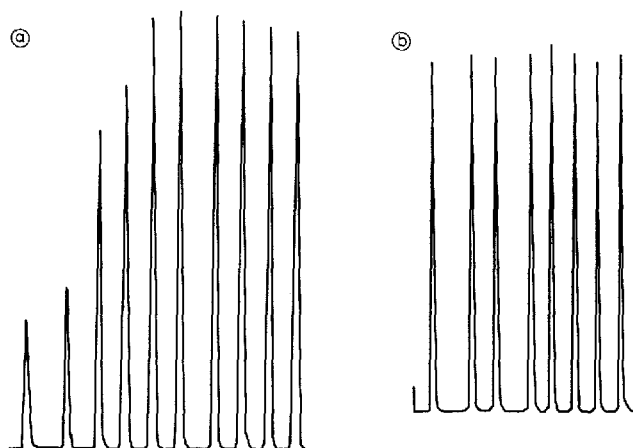

Fig. 2. Chromatograms of repetitive injections of sulphur dioxide on Porapak T: a, untreated; b, treated with DMCS.

number of injections required for stability and the standard deviation of the response.

With pure carrier gas, the response to injections of 100 ppm SO_2 with Porasil C did not stabilize after ten injections. The use of 200 ppm DMCS in the carrier gas reduced the response variability and the number of injections necessary to achieve stability. While the results reported in Table I and demonstrated in Figs. 1 and 2 all refer to sulphur dioxide, essentially identical behaviour is observed with the analysis of hydrogen sulphide.

CONCLUSION

The destabilizing effect of SO_2 adsorption has been illustrated for a number of column packings, most notably Porapak T and Q. Incorporation of 200 ppm of DMCS in the nitrogen carrier gas has been shown to contribute significantly towards the stability of those columns where sulphur dioxide adsorption is a major problem.

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