

CHROM. 21 588

NEW METHOD FOR SURFACE CHARACTERIZATION BY GAS CHROMATOGRAPHY

L. J. ANTHONY* and R. A. HOLLAND

AT&T Bell Laboratories, 600 Mountain Avenue, Room 1A-320, Murray Hill, NJ 07974 (U.S.A.)

(First received January 31st, 1989; revised manuscript received April 20th, 1989)

SUMMARY

We report the development of a new chromatographic method for surface characterization, based on the principle of gas chromatographic intermediate surface testing. In this method, the chromatograms are obtained in parallel in a dual-oven chromatograph with a pneumatic switching valve. This is an unusual application of a dual-oven gas chromatograph and column switching, not previously reported. The method is fast, produces data that are more readily interpretable, and can provide information difficult or impossible to obtain with the previously developed single-oven, unswitched, sequential test. These new attributes make intermediate surface testing a simple, straightforward, and generally applicable method for studying chemical interactions at the gas-solid interface of low-surface-area materials.

INTRODUCTION

Dual-oven gas chromatographs and column flow switching devices are typically used to enhance the separation of complex mixtures through multidimensional chromatography¹⁻⁵. We have developed an additional, novel application for these instruments by using them for intermediate surface testing⁶. This work is a result of the combination of successes and failures we experienced in using conventional intermediate surface testing to evaluate capillary tubing surfaces with a wide range of properties^{7,8}. While the successes clearly demonstrated the power of intermediate surface testing for characterizing the surface chemistry of low surface area materials (which often can be studied only indirectly from analogous high surface area powders), the failures pointed out the several circumstances in which it is difficult or impossible to obtain meaningful information from a conventional intermediate surface test. In this paper we first describe the new two-oven, column-switched method we have developed, and we then present examples to illustrate the limitations of the conventional method and how the new one overcomes them.

THE NEW TWO-OVEN, COLUMN-SWITCHED METHOD

Basic principles

The new, dual-oven, column-switched method is shown schematically in Fig. 1a, and the conventional single-oven method⁶ is shown for comparison in Fig. 1b. The upstream capillary (A) is a conventional gas-liquid chromatography column, the downstream capillary (B) is the material whose surface properties are to be characterized. Although the experimental procedures differ in the two methods, the basic principles are the same: The test consists of comparing the chromatograms obtained on column A alone and on A and B connected in series.

In both the conventional and the new methods, the function of upstream column A is simply to separate the components of a test mixture into a series of elution

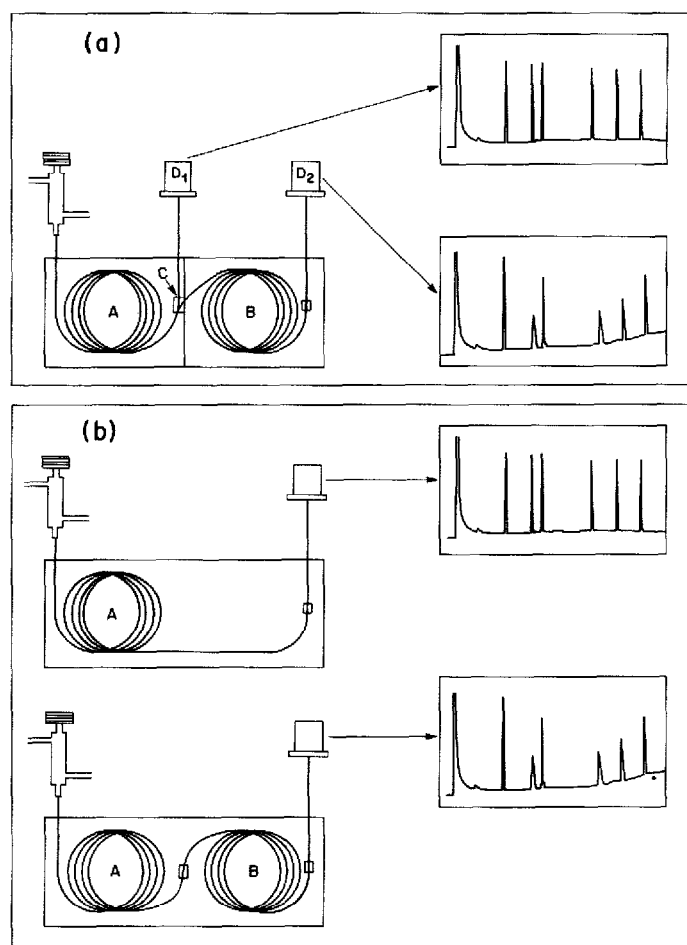


Fig. 1. (a) New dual-oven, column-switched method of intermediate surface testing. (b) Conventional method of intermediate surface testing. A = reference column; B = column to be tested; C = pneumatic switch; D₁, D₂ = detectors.

bands that have symmetrical peak profiles and are well-separated from the solvent band. (These "perfect" reference peaks could not be produced if the test mixture were injected directly onto the uncoated capillary to be tested.) If downstream capillary B is inert, these peaks elute from the coupled capillaries unchanged except for some symmetric band broadening and with an increased retention time corresponding to the dead time of the downstream capillary. However, if the downstream capillary is not inert, then changes in the shapes, areas, and relative retention times of the peaks provide information about both the nature and the strength of the components' interactions with the surface.

In the new method, the two capillaries are placed in different ovens of a dual-oven gas chromatograph and are connected to the six-port coupling device (C) of a pneumatic switch⁹. The switch diverts a small portion of the effluent of upstream capillary A to a detector (D_1), while transferring most of the material onto downstream capillary B, which is monitored by a second detector (D_2). The test mixture is injected onto the upstream column, and both the reference and test chromatograms are generated in the same experiment. The two ovens may be operated under different temperature conditions.

In contrast, in the original method, since column switching is not employed, the reference and test chromatograms must be obtained in separate, sequential experiments. After the reference chromatogram is obtained on the upstream capillary alone, the capillary to be tested is installed between it and the detector, and the test mixture is chromatographed again. In addition, since only one oven is used, temperature conditions obviously must be the same for the two experiments.

Rationale for developing the new method

As the results below will show, the dual-oven, column-switched method has distinct advantages and, in retrospect, would seem to be the best approach to intermediate surface testing whenever the objective is to obtain specific information about capillary surface properties. However, it should be emphasized at the outset that the original single-oven method is quite adequate for the purpose for which it was originally developed, that is, as a quick and simple screening test to distinguish "good" from "bad" capillaries in the course of multi-step surface deactivation treatments⁶. For this purpose, interactions of simple one- or two-component test mixtures can be studied under isothermal conditions (see, for example, ref. 10).

However, when the objective of intermediate surface testing is to study capillary surface properties, test mixtures contain several components with a range of polarities and functional groups, and information about the surface chemistry of the downstream capillary is deduced from the behaviour of specific components¹¹. With conventional single-oven testing, one is always constrained to choose between conflicting optimal temperature conditions for the upstream and downstream capillaries. For studying the downstream capillary, isothermal conditions are preferred so that all interactions of test components with the surface occur under identical conditions. In contrast, for generating the upstream reference chromatogram, temperature programming is preferred for two reasons: (1) so that test mixtures with several components encompassing a range of volatilities/polarities can be separated in a reasonable time in a single experiment, and (2) so that peaks elute from the upstream capillary with approximately constant widths. This makes the reference chromatogram a dis-

tinctive "fingerprint", so that additional band broadening and peak tailing caused by interactions with downstream column are easy to detect. (The most distinctive fingerprints can be obtained when the amount of each compound is adjusted for its detector response so that all peaks have equal areas. Under temperature programming, all peaks in the reference chromatogram will then have equal heights as well^{12,13}.)

In practice, for some applications, appropriate compromises can be made, and either isothermal or temperature-programmed conditions can be successfully applied^{7,11,14,15}. However, this was not the case in our research program on the development and characterization of new capillary surfaces with a wider range of surface properties^{7,8}. Two inherent limitations of the single-oven unswitched method became significant disadvantages: First, for a number of studies, it was impossible to find even a "compromise" temperature condition with which the test components of interest could be effectively separated on the upstream capillary and studied on the downstream one as well. Second, because it is necessary to disconnect the downstream capillary and generate a new reference chromatogram whenever either a test mixture or the temperature conditions are modified, the testing procedure became increasingly inefficient and time consuming.

It became clear that both of these problems could be overcome by using gas chromatographic instruments that have been developed for multidimensional techniques. Specifically, a dual-oven instrument would permit separate temperature control for the upstream and downstream column, and a column flow switch would enable test and reference chromatograms to be generated in the same experiment rather than sequentially.

EXPERIMENTAL

The chromatograph, a Sichromat 2 (Siemens, Karlsruhe, F.R.G.), was equipped with two flame ionization detectors, two split/splitless capillary inlets, and the requisite pneumatic components so that each oven can be operated separately as well as with column switching. Both ovens were equipped with auxiliary cryogenic cooling (liquid nitrogen) to assist in the maintenance of sub- and near-ambient temperatures. The upstream oven was equipped with a solenoid and needle valve for backflushing, which were not used for this application.

The six-port coupling piece of the pneumatic switch was located in the upstream oven and was used without modification. For this application, the switch was maintained in the "open" state, and the pressure drop across the switch was adjusted to divert about 10% of the effluent of the upstream column to the upstream detector, while transferring the remaining 90% to the downstream column. The principles of pneumatic switching are more fully described elsewhere^{4,9,16}.

Carrier gas (helium) flow was pressure-controlled at the inlet to the upstream column and at the midpoint of the system (pneumatic switch). The column dead time (retention time for an unretained peak^a) was approximated from the retention time

^a Clearly, the concept of a non-retained peak is meaningless for a highly adsorptive capillary. If such a capillary is to be used in the downstream position, the necessary pressure drop must be calculated, or the linear velocity established experimentally by first substituting a non-adsorbing capillary (*e.g.* high-purity fused silica) of identical dimensions.

for *n*-butane. Inlet and mid-point pressures were adjusted to provide a linear velocity of 28 cm/s in both columns. The upstream oven was temperature-programmed from 40°C to 150°C at rates of 2.5°C, 5.0°C or 25°C/min. The downstream oven was operated isothermally at temperatures ranging from 40°C to 150°C. The injector and detector temperatures were 200°C and 250°C, respectively.

The upstream column was a standard 15 or 25 m × 250 μm I.D. capillary with a 0.2-μm film of immobilized methyl silicone stationary phase [*e.g.* Ultra 1 (Hewlett-Packard, Avondale, PA, U.S.A.) or SPB-1 (Supelco, Bellefonte, PA, U.S.A.)]. Uncoated capillary tubing tested in the downstream position was also 15 m × 200–250 μm I.D. Conventional fused-silica capillary tubing was obtained from several suppliers, and had been manufactured by Polymicro Technologies (Phoenix, AZ, U.S.A.) or Spectran (Sturbridge, MA, U.S.A.). Other capillary tubing, both pure and specifically doped fused silica, was manufactured in our laboratory, using the modified chemical vapor deposition process to prepare the preforms from which the capillaries were drawn⁸.

The Grobs' "comprehensive standardized quality test" mix^{12,13} and a "non-polar test mix"⁷ were purchased pre-mixed from Supelco. Other test mixtures of alkanes and ketones were prepared in-house from reagent-grade chemicals purchased from Aldrich (Milwaukee, WI, U.S.A.) and Burdick and Jackson (Muskegon, MI, U.S.A.). All samples contained 0.1–0.5 mg/ml per component in methylene chloride. Sample volumes were 1–2 μl, and the splitting ratio was 50:1–100:1 to deliver on-column approximately 2–5 ng per component. Sample components and their abbreviations are listed in relevant figure captions.

Signals from the detectors were recorded simultaneously on a dual-channel strip chart recorder (Model 7100B; Hewlett-Packard, Palo Alto, CA, U.S.A.) and either computing integrators (Model 3393; Hewlett-Packard, Avondale, PA, U.S.A.) or a PC-based (AT&T PC6300) chromatographic data system (System 2600, PE-Nelson, Cupertino, CA, U.S.A.).

RESULTS

The following four examples illustrate the limitations of the conventional method and the advantages of the new dual-oven column-switched method.

Studying adsorptive surfaces

When a downstream capillary surface is strongly adsorptive, high temperatures may be required to elute components of interest. However, these temperatures may exceed those at which good peak separations can be maintained on the upstream capillary. Conversely, if the test is performed at the lower temperatures or slower programming rates necessary to separate a test mix on the upstream capillary, components of interest may be totally adsorbed on the downstream capillary, and the intermediate surface test will provide little useful information.

This situation occurred in our studies of neodymia-doped fused silica, as illustrated in Fig. 2. Fig. 2a–c shows results for two different pure fused-silica capillaries (a, b) and a neodymia-doped capillary (c); Fig. 2d is the upstream reference chromatogram. All four chromatograms were obtained under identical temperature programmed conditions^{7,8}. Note that three key test components, 2,6-dimethylphenol

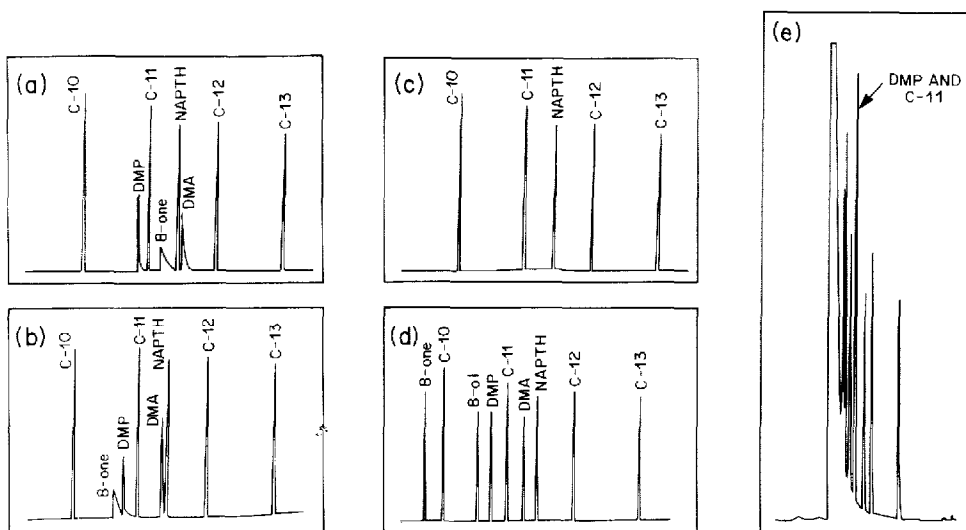


Fig. 2. (a-c) Conventional single-oven, unswitched intermediate surface tests of fused-silica capillaries, obtained under temperature-programming conditions as in refs. 7 and 8; a, b, two different samples of commercially available fused silica; c, neodymia-doped fused silica. (d) Upstream (reference) chromatogram obtained under same conditions as a-c. (e) Upstream (reference) chromatogram obtained isothermally at 150°C. Abbreviations: C-10 = *n*-decane; C-11 = *n*-undecane; C-12 = *n*-dodecane; C-13 = *n*-tridecane; DMP = 2,6-dimethylphenol; DMA = 2,6-dimethylaniline; 8-ol = *n*-octanol; 8-one = 2-octanone; NAPTH = naphthalene.

(DMP), 2,6-dimethylaniline (DMA), and 2-octanone (8-one), were totally adsorbed on the neodymia-doped capillary. Without peaks for these components, information cannot be deduced about acid/base properties (*e.g.* DMP/DMA ratios) and surface heterogeneity (peak shapes, esp. 8-one). Hence very little specific information is available about the neodymia-doped material.

Although the three compounds of interest could be eluted from the neodymia-doped capillary isothermally at 150°C, the results could not be easily interpreted because the upstream reference chromatogram (Fig. 2e) was poor. All test components eluted on the shoulder of the solvent peak, and C-11 and DMP co-eluted. To continue to study neodymia-doped surfaces with single-oven testing would have required the development of adequate reference chromatograms, for example by using longer and/or thicker-film columns and/or changing the components of the test mixture.

With the dual-oven, column-switched method, it was possible to raise the temperature of the neodymia-doped fused-silica capillary *without* changing either the composition of the test mix or the temperature program for the upstream capillary. Results are shown in Fig. 3. The upstream reference column was temperature programmed from 40°C to 150°C at 2.5°C/min, and the downstream column was held isothermally at 150°C. Peaks for DMP, DMA and 8-one can now be seen in the chromatogram. Since the reference chromatogram is unchanged (*cf.* Fig. 2d), the results may be compared with those obtained for the undoped fused silicas in Fig. 2a and b.

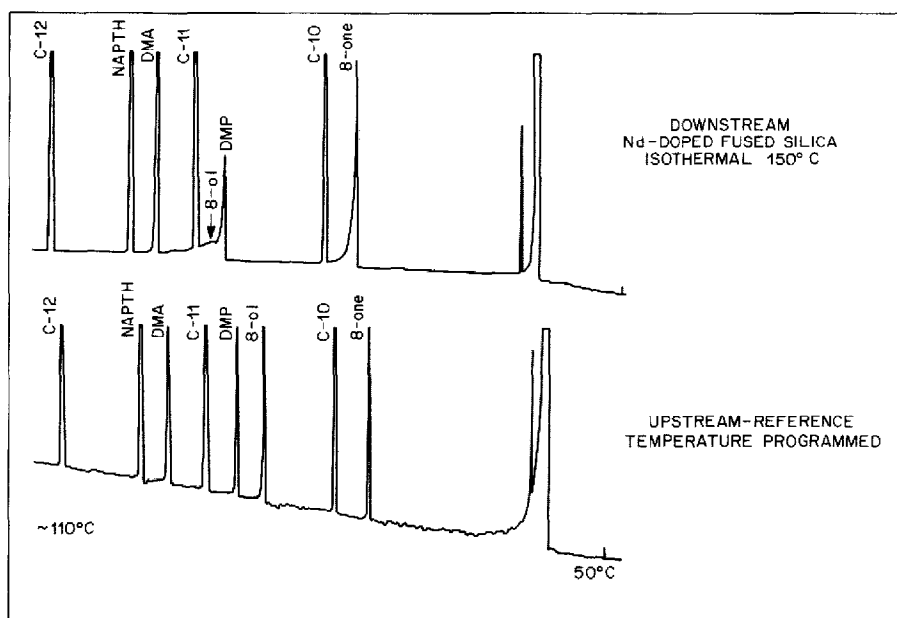


Fig. 3. Dual-oven, column-switched intermediate surface test of neodymia-doped capillary obtained isothermally at 150°C; upstream (reference) chromatogram temperature programmed as in Fig. 2c. Abbreviations as in Fig. 2.

Studying inert surfaces; studies at near-ambient temperatures

Single-oven intermediate surface testing also suffers from limitations when the downstream capillary must be studied at relatively modest temperatures—for example to study an inert surface, a weak adsorbate, or an adsorbent intended for operation at ambient conditions. When the downstream capillary imposes a relatively low upper temperature limit, low initial temperatures and/or slow programming rates must be used. Since the upstream capillary is constrained to the same conditions, either the reference chromatogram will be inordinately long, or the choice of test compounds will be limited to those which can be eluted from the upstream capillary in a reasonable time.

With two separately controlled ovens, significant time savings can be realized because the reference chromatogram can now be obtained at temperatures that exceed those permitted for the downstream capillary. For example, Fig. 4a and b shows chromatograms of the standard “non-polar test mix” obtained at programming rates of 25°C and 2.5°C/min. The corresponding temperature profiles are compared in Fig. 4c, with the elution temperatures of each component marked with a vertical tick-mark. For studies in which the temperature of the downstream capillary should not exceed *ca.* 100°C, only the slower temperature program can be used in a single-oven test. With two ovens, at least a fivefold savings in time can be achieved by using the faster programming rate to obtain the reference chromatogram, while still examining the downstream capillary at temperatures of 100°C or less.

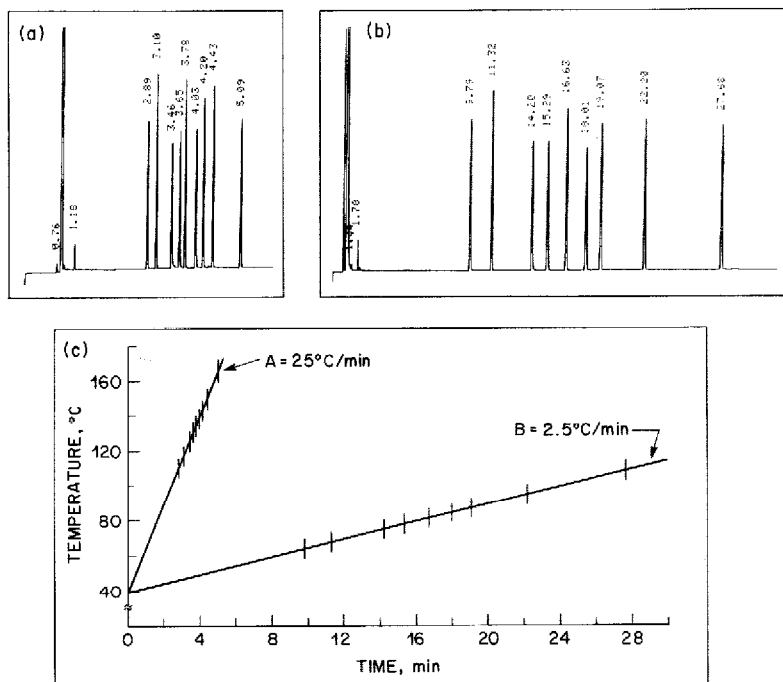


Fig. 4. (a, b) Upstream (reference) chromatogram obtained with initial temperature of 40°C and temperature-programming rate of 25°C/min (a) and 2.5°C/min (b). Numbers at the peaks indicate retention times in min. (c) Oven temperature profiles for the above programming rates, with elution time of each peak designated by vertical tick-mark.

Characterizing a surface at more than one temperature

In single-oven testing, it is difficult to study the temperature-dependence of surface properties in the downstream capillary because the upstream (reference) chromatogram also changes whenever the temperature and/or temperature program are changed. Even if one can account for the changing reference chromatograms, the study is time consuming, because one must repeatedly disconnect and reconnect the two columns to obtain a pair of reference (upstream alone) and test (upstream and downstream) chromatograms at each temperature. The dual-oven, column-switched method overcomes both of these problems. The temperature dependence of surface properties can be studied simply by changing the temperature of the downstream oven, without continually disconnecting and reconnecting the columns. Since the reference chromatogram remains constant, both qualitative and semi-quantitative data can be easily obtained from simple visual comparison of the chromatograms.

For example, Fig. 5 compares the intermediate surface tests of the neodymium-doped capillary at 100°C (a) and 150°C (b) obtained with the dual-oven, column-switched method. The reference chromatogram, obtained with temperature programming, is identical in both chromatograms. Differences in the downstream chromatograms at the two temperatures are immediately obvious: Both the retention time and peak shape improve much more for 8-one than for DMP and DMA when the

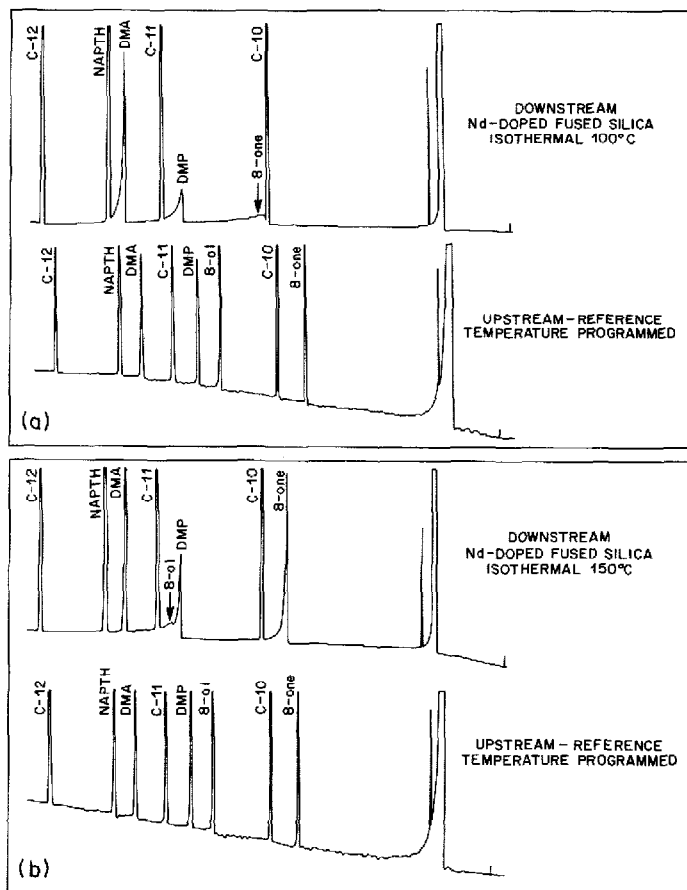


Fig. 5. Dual-oven, column-switched intermediate surface tests of neodymia-doped fused-silica capillary obtained at 100°C (a) and 150°C (b).

temperature is raised. For comparison, Fig. 6 shows the two significantly different reference chromatograms that would have been generated at 100°C and 150°C if the study had been done in one oven. Note that the pronounced tailing of the 8-one at 150°C would have been obscured in the solvent peak in the single-oven test although it is clearly visible in the dual-oven test.

Developing new test mixtures and optimizing test conditions

Obviously, if one wishes to change a test mixture or develop a new one, one must obtain a new reference chromatogram as well. In the old method, to do this requires repeatedly disconnecting and reconnecting the downstream capillary to obtain pairs of reference and test chromatograms. In the new method, the use of the column switch to couple the columns means that the reference and test chromatograms can be obtained in parallel in the same experiment. This results, in a minimum 50% reduction in the time required to complete the testing. Moreover, since the

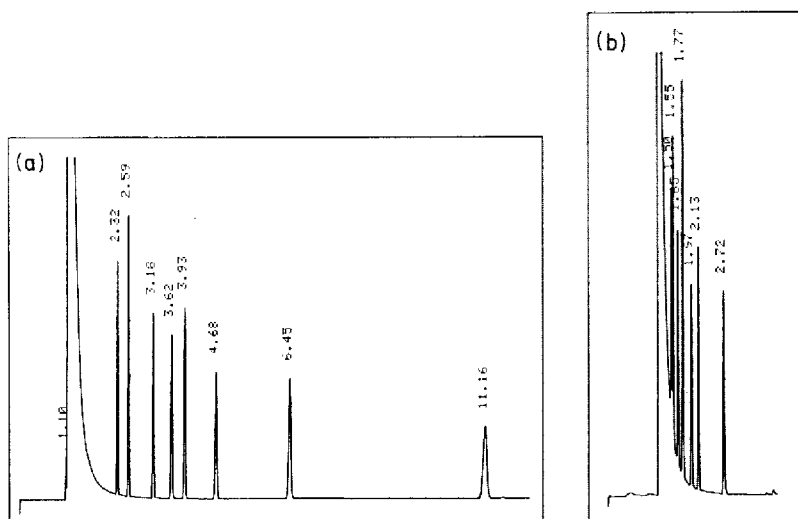


Fig. 6. Upstream (reference) chromatograms obtained isothermally at 100°C (a) and 150°C (b).

two columns remain coupled throughout testing, the possibility of making a "bad" butt-connection, with either excess dead volume or active sites, is virtually eliminated.

This feature of the new method was advantageous in our study of the adsorption of ketones on fused silica. It was of interest to determine if steric hindrance around the carbonyl group influences the adsorption. Fig. 7 compares results for 4-methyl-2-pentanone (a) and 2,4-dimethyl-3-pentanone (b) on a fused-silica capillary at 75°C. The stronger adsorption of the less substituted ketone (a) is immediately

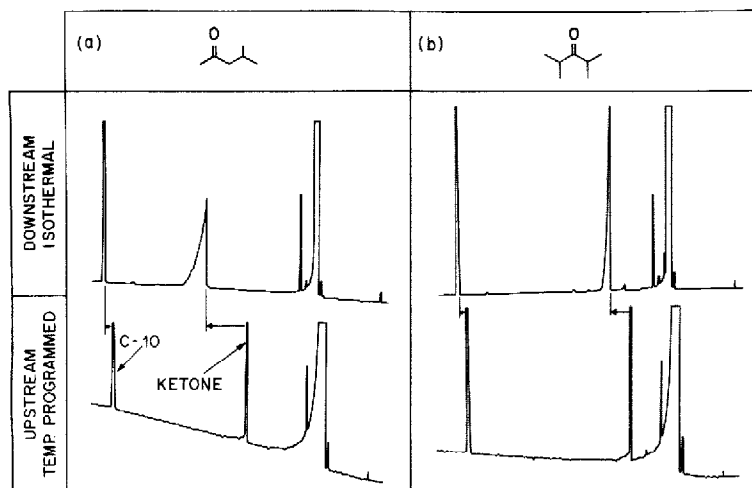


Fig. 7. Dual-oven, column-switched intermediate surface tests of 4-methyl-2-pentanone (a) and 2,4-dimethyl-3-pentanone (b) on commercially available fused-silica capillary at 75°C; *n*-decane included in test mixture; upstream (reference) chromatogram temperature programmed as in Fig. 2.

obvious in the longer retention time and greater broadening of the peak. (The rising baseline in the reference chromatogram of (a) is an artefact, as noted under *Instrumental performance*.) These results were obtained in two sequential experiments without disconnecting the columns. In contrast, to do this in a single-oven instrument would have required a minimum of four experiments, as well as the disconnecting and reconnecting of the two columns. Thus, a greater than 50% savings of time and effort was realized.

DISCUSSION

Instrumental performance

Just as in the original method, the new method requires that whatever device is used to couple the upstream and downstream capillary must not contribute either dead volume or adsorptive sites. The six-port coupling piece is significantly more complex than the simple butt connectors that can be used in the original method, and we were therefore concerned that it might be a source of significant adsorption. However, our experience is consistent with previously published reports^{17,18}. Specifically, the coupling piece does not contribute to band broadening and adsorption or solvent tailing unless the upstream capillary is improperly installed. When this problem occurs, it affects the upstream chromatogram much more than the downstream one. Consequently, it is immediately obvious on the reference chromatogram and cannot be mistaken for a real result on the downstream column. For example, the rising baseline in the reference chromatogram in Fig. 7a was caused by organic contamination at the inlet to the coupling piece. Note that the downstream chromatogram is not similarly affected.

In the particular chromatograph we chose to use, the two ovens share a common raisable mantle. Oven temperature control is accomplished by raising and lowering the mantle, and the control mechanism always operates with the values of the upstream oven. For studies of adsorptive surfaces, in which the downstream oven is warmer than the upstream, problems can arise if the temperature difference between the ovens is greater than about 150°C. Heat conduction from the downstream oven overheats the upstream oven, causing the mantle to open and close periodically to keep the upstream temperature as close as possible to its set-point. The periodic changes in the temperature of the downstream oven cause corresponding fluctuations in the baseline signal, in which small peaks can be lost.

In principle, the problem can be circumvented by exchanging the electronics modules so that the temperature control mechanism is directed by the downstream oven. However, the analogous problem will then occur for applications in which the downstream oven is significantly cooler than the upstream. In either event, auxiliary cryogenic cooling can minimize the problem. Clearly, the problem can be eliminated by using an instrument in which each oven is equipped with a separate venting mechanism and temperature control. (Such an instrument was not commercially available when this study was undertaken.)

Since the primary function of the column switch is to serve as an effluent splitter, and no flow switching takes place during the chromatogram itself, it may appear that the use of the pneumatic switch is an overly complex approach. Although an effluent splitter could be implemented using a simple tee-piece and restriction capil-

lary, such an approach would be practical only if one were always investigating capillaries of identical dimensions. The pneumatic switch offers the advantage of being able to control the pressure at the midpoint of the system, and hence affords a simpler and more flexible means of studying capillaries with different dimensions.

Future directions; physico-chemical measurements

The capability of separate temperature control in the upstream and downstream ovens now provides the possibility of using intermediate surface testing to generate the data for physico-chemical measurements, such as isotherms, adsorption rates, and heats of adsorption. Our initial results show that this approach offers several advantages over existing gas-solid chromatographic methods in which the adsorbing surface is studied directly in a one-column experiment¹⁹.

In a conventional one-column experiment, test compounds (and solvent, if any) are injected directly onto the surface to be tested. With intermediate surface testing, the upstream capillary separates test components from each other and from the solvent before they interact with the downstream capillary. Consequently, a number of compounds can be studied in the same experiment even if the adsorbing surface does not have sufficient selectivity to separate them itself. Additionally, the effects of solvent-adsorbate interactions or adsorbate-adsorbate interactions are minimized. Also, because the solvent peak passes down the capillary to be tested well in advance of all test components, the possibility that the solvent is perturbing the surface is minimized. (In addition, one could in principle use the pneumatic switch to dump the solvent to the upstream detector so that it would not influence the downstream column at all.)

With intermediate surface testing, information is obtained from the perturbation of an ideal or near-ideal peak by the surface of the downstream capillary. Therefore, changes in the peak profile arise only from interactions with the downstream capillary, and not from extra-column effects such as injection problems, which cannot be ruled out in one-column tests. In addition, small changes arising from weak interactions are easier to detect and quantitate on symmetric peaks than on the non-ideal peaks often obtained in one-column gas-solid chromatograms.

An obvious potential problem arises because when the column flows are pressure controlled, as is the case in most instruments. Because flow-rate varies inversely with temperature, retention time measurements obtained at different temperatures must be corrected for the changing dead-times. To overcome the problem, flow-controllers could be incorporated in an instrument, or the dead times could be measured, if a suitable non-adsorbing component were used.

With respect to the scope of the method, any material which can be drawn into capillary tubing can be studied. This can be an advantage: because of the large surface area of the capillary, low-surface-area materials such as glasses can be studied directly, rather than indirectly from analogous powdered samples (*e.g.* fused silica *vs.* silica gel). For the method to be as widely useful as possible, it should be applicable also to materials that are typically powders. Hence, the possibility of using packed micro-columns rather than capillaries in the downstream position is also being explored²⁰.

CONCLUSION

Intermediate surface testing is an unusual application for a dual-oven gas chromatograph and column switching, not previously reported. The new method has several significant advantages over single-column unswitched methods:

(i) Reference and test chromatograms are obtained in parallel rather than sequentially, thereby making possible the continuous, on-line monitoring of the upstream column. Consequently, results of true adsorption on the downstream column can be immediately distinguished from artefacts caused by a bad injection, sample degradation, etc.

(ii) When it is necessary to develop new test mixtures or to change chromatographic conditions, the new reference chromatogram is readily obtained without disconnecting the columns and reinstalling the upstream column alone.

(iii) Temperatures and temperature programs for the upstream and downstream capillaries can be set independently. The upstream capillary can be operated with temperature programming to generate a distinctive reference chromatogram in a reasonable amount of time. The downstream capillary can be operated isothermally, so that all components of the test mixture interact with it under identical conditions. Thus, both capillaries can be operated under optimal conditions, whereas with single-oven testing, the chosen conditions are always a compromise.

(iv) The downstream capillary can be studied as a function of temperature, with conditions for the upstream reference chromatogram held constant. This opens up the possibility of using intermediate surface testing to obtain physico-chemical data such as isotherms, heats of adsorption, etc.

In short, the new dual-oven, column-switched method is fast, produces data that are more readily interpretable, and can provide information difficult or impossible to obtain with a single-oven unswitched test. These new attributes make intermediate surface testing, originally developed solely to follow deactivation and coating steps in glass capillary chromatography columns, a simple, straightforward, and more generally applicable method for studying chemical interactions at gas-solid interfaces.

ACKNOWLEDGEMENTS

We thank Robert Slack and Rick Dougherty of ES Industries, Marlton, NJ, U.S.A., and Aachim Hein of Siemens AG for their assistance in optimizing the pneumatic switching system for our particular application.

REFERENCES

- 1 G. H. Schomburg, H. Husmann and F. Weeke, *J. Chromatogr.*, 112 (1975) 205.
- 2 E. L. Anderson, M. M. Thomason, H. T. Mayfield and W. Bertsch, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 335.
- 3 F. Mueller, *Am. Lab. (Fairfield, Conn.)*, 15 (1983) 94.
- 4 G. H. Schomburg, F. Weeke, F. Mueller and M. Oreans, *Chromatographia*, 16 (1983) 87.
- 5 S. M. Sonchik and J. Q. Walker, *Am. Lab. (Fairfield, Conn.)*, 17 (1985) 58.
- 6 G. H. Schomburg, H. Husmann and F. Weeke, *Chromatographia*, 10 (1977) 580.

- 7 L. J. Anthony, R. A. Holland and S. A. Heffner, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 167.
- 8 L. J. Anthony, L. Soto, S. A. Heffner, R. A. Holland, J. R. Simpson and S. G. Kosinski, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 395.
- 9 F. Mueller and M. Oreans, *Analytical Application Note No. 282*, Siemens, Karlsruhe.
- 10 M. W. Ogden and H. M. McNair, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 326.
- 11 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 302.
- 12 K. Grob, Jr., G. Grob and K. Grob, *J. Chromatogr.*, 156 (1978) 1.
- 13 K. Grob and G. Grob, *J. Chromatogr.*, 219 (1981) 13.
- 14 W. Bertsch, V. Pretorius and K. Lawson, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 568.
- 15 G. Rutten, J. de Haan, L. van de Ven, A. van de Ven, H. van Cruchten and J. Rijks, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 664.
- 16 D. R. Deans, *Chromatographia*, 1 (1968) 18.
- 17 B. M. Gordon, C. E. Rix and M. F. Borgerding, *J. Chromatogr. Sci.*, 23 (1985) 1.
- 18 F. Weeke and G. Schomburg, in P. Sandra (Editor), *Proc. 8th Int. Symp. Capillary Chromatography, Riva del Garda, May 19-21, 1987*, Hüthig, Heidelberg, 1987, p. 550.
- 19 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, New York, 1979.
- 20 L. J. Anthony, A. J. Muller and R. A. Holland, *J. Non-Cryst. Solids*, submitted for publication.