Journal of Chromatography, 168 (1979) 202–207

CHROM. 11,392

Note

Volatility range of liquid-phase bleed constituents in gas–liquid chromatography

VELUPPILLAI PARAMASIGAMANI and WALTER A. AUE
5637 Life Sciences Center, Dalhousie University, Halifax, N.S. (Canada)
(Received August 14th, 1978)

In recent years we have made frequent use of a particular two-column configuration, which permits single peak processing by a variety of degradation techniques such as photolysis[1], electron capture[2], catalyzed reductive dehalogenation[3] and Penning ionization[4]. Although the instrumental design differs for each of these cases, the principal function remains the same: one component of a mixture separated by the first column is transferred to a reactor where degradation takes place. The products of degradation plus residual parent compound flow on to the second column, where they are separated.

It is inherent in such a procedure that bleed from the first column enters the reactor and the second column, together with the peak of interest. Depending on chromatographic conditions and the chosen modes of degradation and detection, it is conceivable that bleed components could pose as minor products of the degradation reaction. As frequently-run blanks indicate, this is not a common occurrence. Yet, it was desirable to find out more about the characteristics of bleed from some frequently-used packings, especially about its distribution into volatility ranges.

Of particular interest to us was the question whether bleed included typical gases or low-boiling liquids as constituents, since the existence of such products would generally not be recognized by routine gas chromatographic (GC) techniques. Our concern is illustrated by Fig. 1, which shows, as a typical example, the neutral, volatile products of *n*-hexylbenzene as degraded in a β-stimulated, mild argon plasma[4], then separated on a surface-modified[5] silica gel 62. The distribution of products is, within limits, characteristic of the degraded sample, and includes a number of gases and volatile liquids. If such were to be also present in column bleed in significant amounts, structural information contained in the degradation pattern may be obscured.

It is well known that such compounds are formed in larger amounts in the pyrolysis of organic polymers; however, the connection between pyrolysis and bleed production appears tenuous. The temperature ranges are very different —typically some 300 to 400° apart— and pyrolysis is more likely than bleed to involve secondary reaction of the many radicals formed. On the other hand, a wide variety of chemical interactions (with oxygen or water in the carrier gas, with metal ions and other active sites on the support, with sample decomposition products, etc.) are believed to contribute to bleed beyond straight-forward thermal decomposition. At least in the

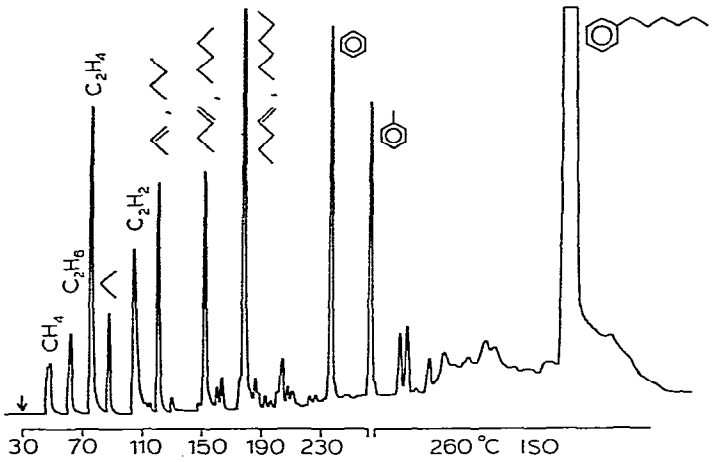

Fig. 1. Degradation pattern of *n*-hexylbenzene in a mild argon plasma[4], 3400 V.

beginning of a column's life, bleed is thought to involve mainly the volatile, lower molecular-weight fractions of a polymeric liquid phase. It is probably for this reason that most chromatographers tend to think of bleed from a well-conditioned column as being composed of compounds with relatively high molecular weight.

The occurrence of bleed in gas chromatography may be a nuisance, but its influence can be felt in many ways. Bleed will affect (in general: degrade) the performance of several types of selective detectors, and the limitations it places on GC–mass spectrometric (MS) studies are well known. Bleed, at least in the case of Carbowax 20M, is also an effective deactivation agent[6,7]. A few serious studies of bleed exist[8], but the subject is generally treated in a lighter fashion[9].

This study of bleed is likewise a somewhat superficial one: none of its constituents are isolated and positively identified. However, beyond the obvious value to our own peak degradation work, we thought it interesting for colleague gas chromatographers to scan the approximate distribution of bleed; in this case from three popular liquid phases: Apiezon L, OV-101 and Carbowax 20M.

EXPERIMENTAL

The apparatus designed for Penning ionization[4] was used, but the reactor was, of course, inactive. Bleed was generated at around 250° from three packings installed in "first column" position: 10% Apiezon L, 5% OV-101 and 5% Carbowax 20 M. All liquid phases had been coated on Chromosorb W AW (45–60 mesh) and were, except as noted, well-conditioned before use. Bleed was collected by the cool "second column" for extended periods of time as specified in the figure legends.

In second column position, a 200 × 0.4 cm I.D. coiled glass tube filled with 5% Carbowax 20 M on Chromosorb W AW (45–60 mesh), was used for high boilers; and a 125 × 0.4 cm I.D. aluminum column filled with silica gel Davison grade 62 (60–40 mesh), deactivated by a bonded layer of Apiezon L (made similar to procedures described in ref. 5) served to separate the low boilers. The entrance section of the latter column, bent in U-shape, could be immersed in LN_2 to ensure collection of

early peaks produced during long bleed periods. Removal of the LN_2 trap (at the end of collection and begin of analysis), resulted in an extinguished detector flame. Relighting the flame could usually not be achieved fast enough to catch the fastest eluting peak, methane.

"Blanks" are included with all chromatograms. These were generated by repeating the collection procedure, but keeping the first column at low temperature (70–100°). Early peaks measured on the Carbowax column are broadened by the long sampling times (and inadequate retention at the column head); their retention temperature is therefore different from that of the same compound under regular GC conditions. The *I* (Kováts index) scale was produced by injecting the *n*-alkane standards on the first column, with "collection time" being equal to that used for bleed.

The carrier gas, nitrogen, of "high-purity" grade, was further cleaned by passage through activated carbon, silica gel and molecular sieve 5A at room temperature and a heated scavenger cartridge for O_2 and water (Supelco, Bellefonte, Pa., U.S.A.).

RESULTS AND DISCUSSION

The results are given by Figs. 2–6, which are largely self-explanatory. Figs. 2 and 3 show the behavior of Apiezon L (a petroleum product obtained by molecular distillation, showing some evidence of unsaturated and aromatic structures[10]).

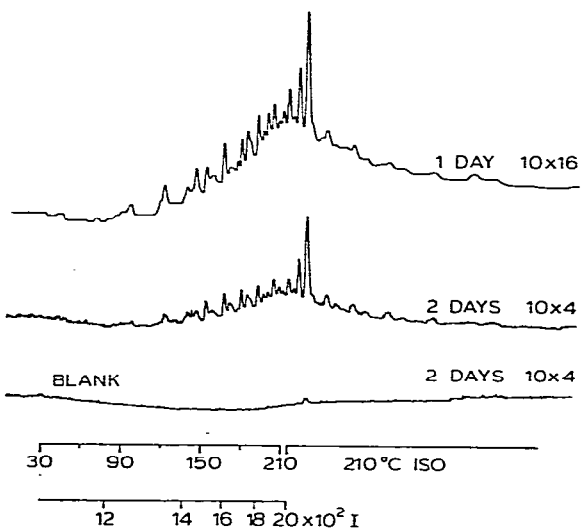

Fig. 2. Apiezon L bleed, at 250 and 255°, separated on Carbowax 20M, after one and two days of conditioning at 250°, respectively. Blank at 90°. Collection times: 45 min ("one day"), 90 min ("two days"), 45 min (blank); 45 min (*I* scale).

On the Carbowax column, which samples the higher boilers, a homologous series is clearly discernable. The units are methylene, as can be seen from a comparison with the Kováts indices given on the second abscissa. (This axis, due to sampling conditions, should be considered approximate.) Since very little bleed was produced from a well-conditioned column in this region, the patterns shown here were ob-

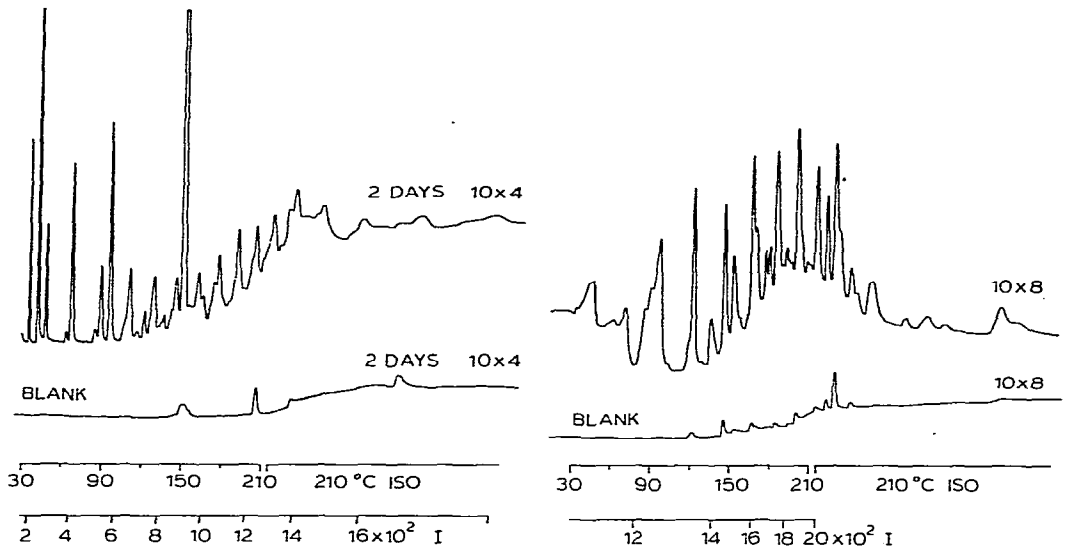

Fig. 3. Apiezon L bleed at 250° for 60 min, separated on modified silica gel 62. Blank at 80°.
Fig. 4. OV-101 bleed at 250° for 45 min, separated on Carbowax 20M. Blank at 70°.

tained from a new column after one and two days of conditioning, respectively; note the different attenuations and the long sampling times. Bleed components of high volatility were more prominent, as shown on the silica gel column (Fig. 3). Again, the homologous nature of most of the compounds is evident The retentions of the two major peaks outside the homologous series correspond, within experimental

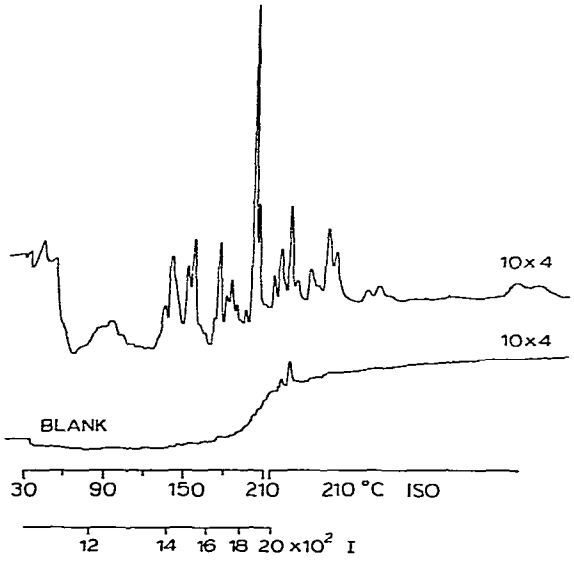

Fig. 5. Carbowax 20M bleed at 245° for 45 min, separated on Carbowax 20M. Blank at 95°.

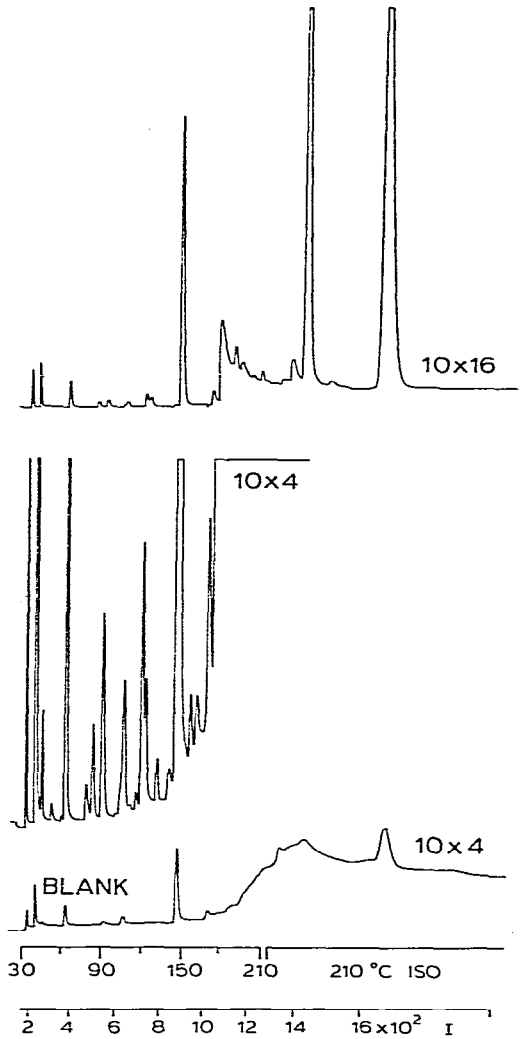

Fig. 6. Carbowax 20M bleed at 242° for 60 min (upper trace) and 246° for 90 min (middle trace), separated on modified silica gel 62. Note different attenuations. Blank at 73° for 60 min. *I* scale: 60 min.

limits, to those of ethylene (43°), and benzene (153°). Clearly, quite a number of light molecules were produced. Note that methane could not have been seen due to experimental conditions.

Fig. 4 shows the high boilers from OV-101; in accord with its dimethylsilicone structure only very small amounts of low boilers were present. The chromatogram contains one major (and perhaps one minor) series of peaks, whose units are different from that of the homologous *n*-alkane series. Such behaviour is expected from the degradation of a silicone; similar series of compounds, most likely of a cyclic nature[11], can also be obtained from injection of strong acids.

Fig. 5 shows the high boilers of Carbowax 20 M, a compound formed from two polyethyleneglycol chains linked by a proprietory diepoxide[12]. The amounts are small compared to those of the low boilers shown in Fig. 6. The latter picture is particularly striking with its strong, singular peaks; taken for the sake of clarity at two attenuation levels. These peaks may be related to the cross-linking agent and, to add another, purely speculative thought, may be responsible for the deactivating effect[6,7] of Carbowax 20M bleed.

While some of the peaks displayed in Figs. 2 to 6 are quite prominent, it must be remembered that these were collected from columns run at high temperatures for long periods of time. For our purpose, *i.e.* for use under typical conditions of single peak degradation by plasma processing[4], bleed peaks (that could be mistaken for product peaks) are negligible —provided, of course, that well-conditioned packings with liquid phases of high thermal stability are employed.

The two-column technique used in this study was well-suited for the investigation of GC liquid phase bleed generated under authentic conditions. It would have been easy and interesting to monitor, in this manner, the qualitative and quantitative changes in bleed engendered by carrier gases containing different levels of oxygen, water, and possibly various acidic and basic components. A variety of important polymer structures could have been thus tested and the resulting patterns (augmented by identification of important peaks by coupled mass spectrometry) may have given information about contributions of different degradation mechanisms, liquid phase stability and stabilizers, most advantageous support surface treatment, etc.

Clearly, this approach would have led far beyond our limited interest. It is unfortunate from a general point of view that only three liquid phases could be investigated in this study; however, the fact that two of these three produced bleed predominantly of low molecular weight, should be of some chromatographic interest.

ACKNOWLEDGMENT

This research was supported by NRC grant A-9604. We appreciate a gift of silica gel 62 by Davison Chemical, W. R. Grace & Co., Baltimore, Md., U.S.A.

REFERENCES

1 W. A. Aue and R. Aigner, *ANAL-064, Abstract of Papers, 172nd ACS Meeting, San Francisco, August 1976*, Port City Press, Baltimore, Md., 1976.
2 W. A. Aue and S. Kapila, *Anal. Chem.*, 50 (1978) 536.
3 S. Kapila and W. A. Aue, *J. Chromatogr. Sci.*, 15 (1977) 569.
4 W. A. Aue, V. Paramasigamani and S. Kapila, *Microchim. Acta*, I (1978) 193.
5 M. Daniewski and W. A. Aue, *J. Chromatogr.*, 147 (1978) 119.
6 N. F. Ives and L. Giuffrida, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 973.
7 J. J. Franken, R. C. M. de Nijs and F. L. Schulting, *J. Chromatogr.*, 144 (1977) 253.
8 W. Gerrard, S. J. Hawkes and E. F. Mooney in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, pp. 199.
9 W. A. Aue, *Intern. J. Environ. Anal. Chem.*, 5 (1977) 6.
10 F. Vernon and C. O. E. Ogundipe, *J. Chromatogr.*, 132 (1977) 181.
11 H. Rotzsche in R. P. W. Scott (Editor), *Gas Chromatography 1960*, Butterworths, London, 1960, p. 210.
12 H. E. Persinger and J. T. Shank, *J. Chromatogr. Sci.*, 11 (1973) 190.