Journal of Chromatography, 128 (1976) 35–43

CHROM. 9226

DETERMINATION OF THE LOSS OF STATIONARY PHASE IN GAS-LIQUID CHROMATOGRAPHY FROM THE CHANGE IN RETENTION VOLUME

ANNE-MARIE OLSSON, LENNART MATHIASSON, JAN ÅKE JÖNSSON and LARS HARALDSON

Department of Analytical Chemistry, Chemical Centre, University of Lund, S-220 07 Lund 7 (Sweden)

(Received March 5th, 1976)

SUMMARY

The effects of liquid-phase bleeding on the determination of gas chromatographic quantities are important, especially when using a high-precision gas chromatograph. Equations are developed in which changes in solute retention volume are used to correct for losses of stationary phase. The method gives the best precision when frequent measurements are made of solute retention volume and of the corresponding total volume of carrier gas that has passed through the column, and is therefore most suited to chromatographs coupled to an on-line computer. It has been found that the change in solute retention volume with accumulated carrier gas flow is constant with *n*-octadecane and 3,3′-oxydipropionitrile as stationary phases; no influence of flow-rate has been observed in the range 25–85 ml/min. Pressures of octadecane at 333 and 371 °K, and of 3,3′-oxydipropionitrile at 373 °K, have been calculated from the bleeding. The values obtained agree well with literature values for the saturated vapour pressure. Thus, in many cases, the change in volume of the stationary phase with accumulated flow can be calculated from the saturation vapour pressure.

INTRODUCTION

If the bleeding of the stationary phase is ignored during extended use of a column, then an error due to the change in the stationary phase volume is introduced into the calculations of partition coefficients. When using a high-precision gas chromatograph this error can be of the same magnitude as the sum of all of the other errors in the measurements. Hence there is a need to know the correct stationary phase volume at the time of an experiment. The possibility of using the retention volume of the solute to correct for weight losses from the stationary phase in gas–liquid chromatography (GLC) was shown by Keller *et al.*[1,2]. Later Berezkin *et al.*[3] studied the thermal stability of stationary liquid phases in a similar way, by assuming partition as the only mechanism responsible for solute retention. In the theoretical section below, equations are developed in which measured changes in the solute retention volume can be used to correct for losses in stationary phase at any time during the lifetime of a column. When the carrier gas is saturated with the vapour of the stationary phase, the equations can also be used to determine the vapour pressure of the organic compound used as the stationary phase.

THEORY

The retention volume, V_N, corrected for pressure drop for a solute on a stationary phase when partition is accompanied by adsorption phenomena can be written, according to Conder *et al.*[4] and Suprynowicz *et al.*[5], as

$$V_N = V_l K_l + V_s K_s + V_i K_i \tag{1}$$

where K_l, K_s and K_i are the partition coefficients for bulk liquid solution, support surface adsorption and liquid surface adsorption, respectively, V_s and V_i are volume expressions for the surface zones in which the support surface and liquid surface adsorption occur and V_l is the volume of the stationary phase. During column use, V_l decreases because of bleeding of the stationary phase. If the change in V_l with the accumulated carrier gas flow is constant, then the volume of the stationary phase at any accumulated flow is given by

$$V_l = V_l^{\mathrm{B}} + \frac{\mathrm{d}V_l}{\mathrm{d}V_{\mathrm{acc}}} \cdot V_{\mathrm{acc}} \tag{2}$$

where V_{acc} is the total volume of carrier gas that has passed through the column since it was inserted into the chromatograph and V_l^{B} is the volume of the stationary phase when V_{acc} is zero.

The terms $V_s K_s$ and $V_i K_i$ in eqn. 1 can be considered as constants, provided the loading is relatively high, so that V_s and V_i are approximately constant. Then eqn. 1 can be written as

$$V_N = V_l K_l + A \tag{3}$$

where $A = V_s K_s + V_i K_i =$ a constant. Differentiating eqn. 3 with respect to V_l gives:

$$\frac{\mathrm{d}V_N}{\mathrm{d}V_l} = K_l \tag{4}$$

The multiplication of differentials

$$\frac{\mathrm{d}V_N}{\mathrm{d}V_l} \cdot \frac{\mathrm{d}V_l}{\mathrm{d}V_{\mathrm{acc}}} = \frac{\mathrm{d}V_N}{\mathrm{d}V_{\mathrm{acc}}} \tag{5}$$

and eqns. 2 and 4 give:

$$V_l = V_l^{\mathrm{B}} + \frac{\mathrm{d}V_N}{\mathrm{d}V_{\mathrm{acc}}} \cdot \frac{1}{K_l} \cdot V_{\mathrm{acc}} \tag{6}$$

In eqn. 6, V_l is a linear function of the total accumulated carrier gas volume, V_{acc}, provided dV_N/dV_{acc} is constant. When V_l^B, dV_N/dV_{acc} and K_l for a solute have been determined for a given stationary phase at a certain temperature, a true value of V_l can be calculated at any accumulated carrier gas volume. V_l^B can be determined at the preparation of the column, and dV_N/dV_{acc} can be obtained as described in the Experimental section. Depending on whether or not adsorption occurs, K_l can be determined in two slightly different ways.

No adsorption occurs

Here $V_N = V_l K_l$. For the determination of K_l the volume of the stationary phase and the corresponding retention volume are needed. It is best to use the stationary phase volume V_l^B measured when the column is prepared because it is easy to determine. Thus, if V_N^B is the retention volume when V_{acc} is zero, then:

$$K_l = V_N^B / V_l^B \tag{7}$$

If the retention volume V_N^E at the end of the experiment and the corresponding stationary phase volume V_l^E are used:

$$K_l = V_N^E / V_l^E \tag{8}$$

Adsorption occurs

Here eqn. 3 is applicable. In this case we must know the stationary phase volumes and the corresponding retention volumes at two different occasions, preferably at the beginning and at the end of the experiment. Then eqn. 3 gives

$$V_N^B = V_l^B K_l + A$$

$$V_N^E = V_l^E K_l + A$$

leading to:

$$K_l = \frac{V_N^B - V_N^E}{V_l^B - V_l^E} \tag{9}$$

Thus eqn. 6 combined with 7 (no adsorption) or 9 (adsorption) can be used to calculate the volume of the stationary phase at any value of the accumulated flow. The slope dV_N/dV_{acc} is determined from retention-volume measurements as described in the Experimental section.

Simplified method

The slope in eqn. 6 can also be calculated from the saturation vapour pressure of the stationary phase, provided the carrier gas flow-rate is sufficiently low for the carrier gas to be saturated with the vapour of the stationary phase at the column outlet. Then

$$n = \frac{p \cdot V_{acc}}{RT} \tag{10}$$

where n is the number of moles of stationary phase that have evaporated, p is the saturation vapour pressure of the stationary phase at the temperature T and R is the gas constant. Differentiating n with respect to V_{acc} gives:

$$\frac{dn}{dV_{acc}} = \frac{p}{RT} \tag{11}$$

The change in the number of moles in the liquid stationary phase given by $(dV_l/dV_{acc})\cdot(\delta/M)$ is equal but of opposite sign to the change in the number of moles in the vapour phase given by dn/dV_{acc}. Thus

$$\frac{dV_l}{dV_{acc}} = -\frac{dn}{dV_{acc}}\cdot\frac{M}{\delta} \tag{12}$$

where M is the molecular weight and δ is the density of the stationary phase.

Eqns. 4, 5, 11 and 12 give:

$$\frac{dV_N}{dV_{acc}}\cdot\frac{1}{K_l} = -p\cdot\frac{M}{RT\delta} \tag{13}$$

If p and δ are known, $(dV_N/dV_{acc})\cdot(1/K_l)$ may be obtained from eqn. 13 and used in eqn. 6 to correct for column bleeding. Unfortunately, very few values of p are available for different stationary phases.

Calculation of stationary phase pressure

With $V_l^B = w_l^B/\delta$ where w_l^B is the weight of the stationary phase when the column is packed, eqns. 7 and 13 give:

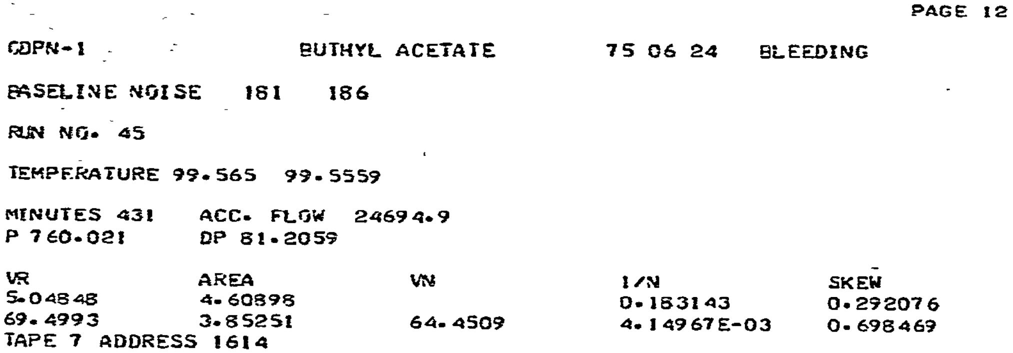
$$p = -\frac{dV_N}{dV_{acc}}\cdot\frac{w_l^B}{V_N^B}\cdot\frac{RT}{M} \tag{14}$$

Thus when dV_N/dV_{acc} is determined from retention-volume measurements, the stationary phase pressure can be calculated. Since there is a choice in selecting the solute, it is usually not difficult to find a solute for which adsorption effects can be neglected and to use eqn. 14 for the calculations of dV_N/dV_{acc} or p.

EXPERIMENTAL

All of the measurements were made by use of a high-precision gas chromatograph coupled on-line with an Alpha LSI-2 mini-computer, with 16 K of core memory. This system, developed by Jönsson and co-workers[6,7], is described elsewhere.

Two stationary phases, n-octadecane (n-C_{18}) and 3,3'-oxydipropionitrile (ODPN) were used in our investigation of column bleeding in GLC. Seven V-shaped columns (1000 × 4 mm I.D.) were used, containing *ca.* 4 g of packing loaded with *ca.* 20% w/w of stationary phase. Supasorb (40–60 mesh), acid washed and treated with hexamethyldisilazane (BDH, Poole, Great Britain), was used as the support. Hydrogen was the carrier gas and methane was used for the determination of the



```
                                                              PAGE 12

ODPN-1                BUTHYL ACETATE          75 06 24   BLEEDING

BASELINE NOISE    181    186

RUN NO. 45

TEMPERATURE 99.565  99.5559

MINUTES 431    ACC. FLOW  24694.9
P 760.021      DP 81.2059

VR             AREA              VN               1/N             SKEW
5.04848        4.60898                            0.183143        0.292076
69.4993        3.85251           64.4509          4.14967E-03     0.698469
TAPE 7 ADDRESS 1614
```

Fig. 1. Computer output for one run. The list shows the name of the column and sample, the date and type of experiment, values signifying the baseline noise, the temperature before and after the run, the time since the start of the experiment, the volume of carrier gas that has passed through the column and the outlet pressure (P) and the pressure drop (DP) along the column. The following table gives the retention volumes V_R and V_N, where V_N is corrected for the void volume, the area and the skew of the peaks and $1/N$ where N is the number of theoretical plates.

void volume. Vapour samples, mixtures of methane and other solutes, were automatically injected during each experiment. After each run, completed in 10–20 min, the computer registered a number of parameter values which were recorded on a cassette tape and printed on a teletypewriter. A typical list produced after a run can be seen in Fig. 1.

The retention volume was calculated by the computer using the method of statistical moments[8]. The volume of carrier gas that has passed through the column, corrected to 1 atm pressure and column temperature, is based on measurements of the flow-rate made each minute. A typical experiment required *ca.* 40 h. Other essential experimental conditions are given in Table I.

The amount of packing material and the percentage of the stationary phase was carefully measured at the preparation of the columns. For columns 1 and 5, the remaining percentage of stationary phase after completion of an experiment was also determined by means of a combustion procedure described elsewhere[9]. When an experiment had been completed, the computer was used to calculate the regression lines.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE BLEEDING EXPERIMENTS

a = *n*-heptane, b = benzene, c = *n*-nonane, d = butyl acetate.

Column	*Stationary phase*	*Solute*	*Temp. (°K)*	*Flow (ml/min)*	*Accumulated flow, V_{acc}^E (l)*	*No. of injections*
1	*n*-C_{18}	a, b	333.20	26.2	75.4	92
2	*n*-C_{18}	a, b	333.16	41.4	106.1	152
3	*n*-C_{18}	a, b	333.20	51.1	98.4	83
4	*n*-C_{18}	a, b	333.17	62.1	111.1	115
5	*n*-C_{18}	a, b	333.22	84.1	64.2	64
6	*n*-C_{18}	c	370.85	61.4	218.3	177
7	ODPN	d	372.68	58.0	157.3	289

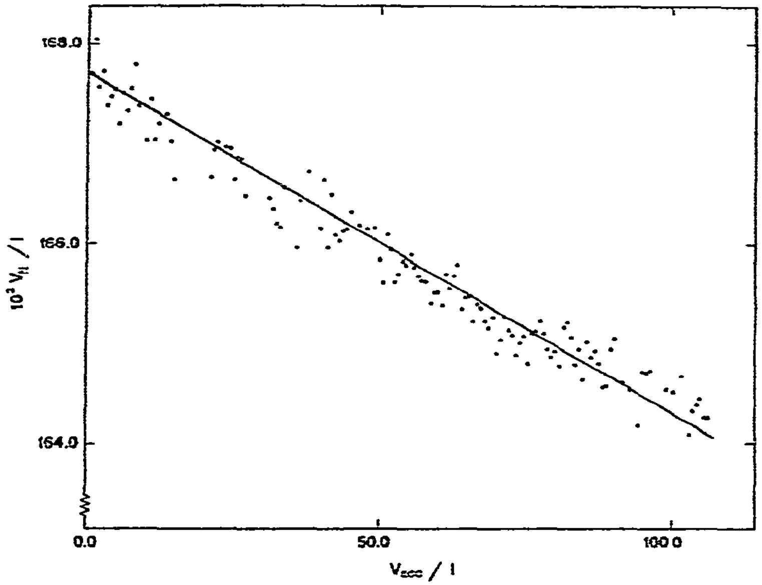


Fig. 2. Plot of the retention volume for benzene *versus* the total accumulated carrier-gas volume corrected to column temperature and 1 atm pressure for column 2.

RESULTS AND DISCUSSION

The retention volume for the solutes decreased linearly when plotted *versus* the total volume of carrier gas that had passed through the column (Fig. 2). Eqn. 6 can then be used to correct for the change in V_l on both the non-polar octadecane and the rather strongly polar ODPN columns. Thus the change in retention volume can be used to correct for changes in the volumes of the stationary phases independently of the polarity of the stationary phases.

The changes in solute retention volumes with accumulated carrier gas volumes for the different columns were calculated from the regression lines which were based on the number of experimental points given in Table I. The solute retention volumes at the beginning of the experiments were calculated from the regression lines by inserting $V_{acc} = 0$. Values of dV_N/dV_{acc} and V_N^B together with their 95% confidence intervals are given in Table II. A thermogravimetric investigation[10] has shown that a maximum systematic error of 0.1% can arise in the determination of phase loading due to the adsorption of water on the support. The resulting systematic error in the determination of phase bleeding or of stationary phase pressure is negligible and has not been taken into account. Densities used in the calculation of V_l for octadecane and ODPN were calculated from data in ref. 11 and refs. 12 and 13, respectively. The values used for octadecane were 0.7558 g/cm^3 at 333.2 °K and 0.7300 g/cm^3 at 370.9 °K, and for ODPN, 0.979 g/cm^3 at 372.7 °K.

K_l and p were calculated from eqns. 7 and 14 in which adsorption effects were not considered. The adsorption effects are negligible for solutes such as *n*-heptane and benzene on columns loaded with long-chain alkanes, as they are expected to dissolve easily in the stationary phase. This has been discussed in a previous paper[9]. In the

TABLE II

RESULTS

For a–d see Table I. Values are given with 95% confidence intervals.

Column	*Solute*	*Weight of stationary phase,* V_l^B *(g)*	*Retention volume,* V_N^B *(ml)*	*Change of retention volume,* $10^5 \cdot \frac{dV_N}{dV_{acc}}$	*Partition coefficient,* $K_l = \frac{V_N^B}{V_l^B}$	$10^7 \cdot \frac{dV_N}{dV_{acc}} \cdot \frac{1}{K_l}$	*Pressure,* *p (Pa)*
1	a	0.75592	332.5 ± 0.4	6.62 ± 0.80	332.4 ± 0.4	1.99 ± 0.24	1.44 ± 0.17
	b		177.8 ± 0.3	4.10 ± 0.46	177.8 ± 0.3	2.30 ± 0.26	1.67 ± 0.19
2	a	0.74030	313.7 ± 0.2	5.44 ± 0.30	320.3 ± 0.2	1.70 ± 0.09	1.23 ± 0.07
	b		167.9 ± 0.1	3.43 ± 0.18	171.4 ± 0.1	2.00 ± 0.11	1.45 ± 0.08
3	a	0.82810	364.0 ± 0.2	7.80 ± 0.36	332.2 ± 0.2	2.35 ± 0.11	1.70 ± 0.08
	b		194.6 ± 0.1	4.55 ± 0.12	177.6 ± 0.1	2.56 ± 0.07	1.86 ± 0.05
4	a	0.72464	306.2 ± 0.1	4.27 ± 0.27	319.4 ± 0.2	1.34 ± 0.08	0.97 ± 0.06
	b		163.6 ± 0.1	2.39 ± 0.11	170.7 ± 0.1	1.40 ± 0.06	1.02 ± 0.05
5	a	0.76296	328.0 ± 0.3	5.02 ± 0.79	324.9 ± 0.3	1.55 ± 0.24	1.12 ± 0.18
	b		175.3 ± 0.1	3.11 ± 0.30	173.6 ± 0.1	1.79 ± 0.17	1.30 ± 0.12
6	c	0.64785	188.9 ± 0.1	68.54 ± 0.08	212.8 ± 0.1	32.21 ± 0.04	32.92 ± 0.04
7	d	0.64648	67.87 ± 0.05	14.09 ± 0.08	102.8 ± 0.1	13.71 ± 0.07	26.4 ± 0.1

same way, a polar solute such as butyl acetate is expected to dissolve in the polar ODPN phase with negligible adsorption effects. The very small adsorption effects in these cases is further confirmed by the low skew measured on both of the octadecane and ODPN columns.

A comparison between values of p (Table II) for octadecane columns, run with different flow-rates (Table I), shows no marked dependence on flow-rate. Turkel'taub and Luskina[14] found, using a capillary column (1 m × 1 mm I.D.), that the pressure of n-$C_{13}H_{28}$ was not affected by the flow-rate of the carrier gas up to 150 ml/min and for temperatures between 343 and 393 °K.

For two columns (1 and 5), the amount of stationary phase remaining at the end of the experiment was determined by combustion. The difference between the combustion results and the V_l value at the end of the experiment calculated from eqn. 6 was +0.5% and −0.7%, respectively. This is well within the confidence interval for the determination of the loading by the combustion procedure. The factor $(dV_N/dV_{acc}) \cdot (1/K_l)$, which is a measure of the bleeding of the stationary phase, was slightly higher with benzene than with n-heptane as the solute. A possible explanation for this behavior is a small, continuously changing, side effect, caused by adsorbed water or the faster bleeding of a more polar substance such as octadecene present as an impurity in the stationary phase. This is also reflected in the different pressures obtained with the two solutes.

The means of the pressure determinations for octadecane were calculated to be 1.29 ± 0.36 and 1.46 ± 0.41 Pa with n-heptane and benzene, respectively, as solutes. (The intervals are for the 95% confidence level and the pressure values were treated as five independent observations with the same variance.) In Fig. 3 literature values for the logarithm of the vapour pressure of octadecane at 303–313 °K (ref. 15) and 393–454 °K (ref. 16) are plotted against reciprocal temperature. It can be seen that the pressures for octadecane at 333 and 371 °K determined with n-heptane and

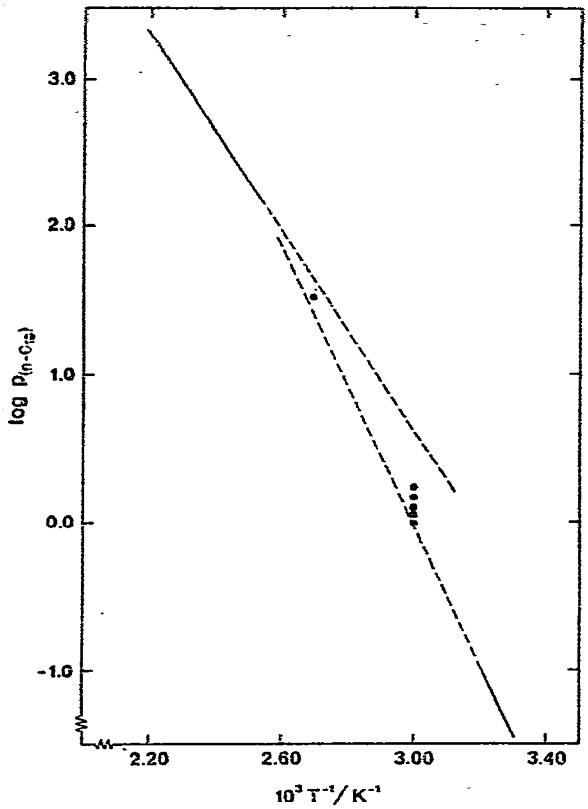


Fig. 3. Literature values for the logarithm of the vapour pressure for octadecane *versus* the reciprocal temperature[15,16]. ●, Experimental values using *n*-heptane and *n*-nonane as solutes (this work).

n-nonane as reference solutes and calculated from eqns. 7 and 14 agree well with the available literature vapour pressures extrapolated to our temperatures. *n*-Nonane was used at 371 °K since *n*-heptane gave too low a retention volume at this temperature.

For the ODPN column, the vapour concentration has been determined to be 10^{-6} g/ml at 376 °K by Dimitrov *et al.*[17] which corresponds to a vapour pressure of 25 Pa in good agreement with the value of 26.4 Pa and 373 °K determined in this investigation. The results show that the carrier gas has been saturated with the vapour of the stationary phase, and also demonstrate the very good stability of the equipment, since a small percentage decrease in V_l over several days can be adequately measured.

CONCLUSIONS

We have shown that solute retention volume can be used for correcting the change in phase volume, due to column bleeding, and for the determination of vapour pressure of polar and non-polar phases.

ACKNOWLEDGEMENTS

This work was performed with financial support from the Swedish Natural Science Research Council. The authors thank Dr. Paul Monk for correcting the English in the manuscript.

REFERENCES

1 R. A. Keller, R. Bate, B. Costa and P. Forman, *J. Chromatogr.*, 8 (1962) 157.
2 R. A. Keller and G. H. Stewart, *J. Chromatogr.*, 9 (1962) 1.
3 V. G. Berezkin, A. I. Parimskii and P. M. Petryakov, *Zavod. Lab.*, 40 (1974) 505.
4 J. R. Conder, D. G. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
5 Z. Suprynowicz, A. Waksmundzki and W. Rudziński, *J. Chromatogr.*, 72 (1972) 5.
6 J. Å. Jönsson and R. Jönsson, *J. Chromatogr.*, 111 (1975) 265.
7 J. Å. Jönsson, R. Jönsson and K. Malm, *J. Chromatogr.*, 115 (1975) 57.
8 E. Grushka, H. N. Myers, P. D. Schettler and J. C. Giddings, *Anal. Chem.*, 41 (1969) 889.
9 L. Mathiasson and R. Jönsson, *J. Chromatogr.*, 101 (1974) 339.
10 A.-M. Olsson, L. Mathiasson and J. Å. Jönsson, in preparation.
11 W. G. Cutler, R. H. McMickle, W. Webb and R. W. Schiessler, *J. Chem. Phys.*, 29 (1958) 727.
12 Beilstein, *Handbuch der Organischen Chemie*, Springer, Berlin, 4th ed., 1961, E III 3, p. 544.
13 D. L. Meen, F. Morris, J. H. Purnell and O. P. Srivastava, *J. Chem. Soc., Faraday Trans. I*, 69 (1973) 2080.
14 G. N. Turkel'taub and B. M. Luskina, *Zavod. Lab.*, 35 (1969) 1193.
15 R. S. Bradley and A. D. Shellard, *Proc. Roy. Soc., Ser. A*, 198 (1949) 241.
16 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, Ohio, 1972, D 170.
17 Khr. Dimitrov, N. Petsev, St. Nikolov and P. Petrova, *Chem. Abstr.*, 77 (1972) 96634y.