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EVALUATION OF CAPILLARY GAS CHROMATOGRAPHY FOR THERMOLABILE PHENYLUREA HERBICIDES

COMPARISON OF DIFFERENT COLUMNS INCLUDING FUSED SILICA

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SUMMARY

The study reported was carried out first to define the possibilities and limitations of capillary gas chromatography (GC) for the analysis of phenylurea herbicides. Secondly, it was a useful means of studying the degradation of labile compounds on the column. Problems such as the detection of catalytic activity or the absence of a correlation of such activity with characteristics determined by known general testing procedures for assessing column quality are discussed. The analysis of intact phenylurea herbicides by capillary GC is possible for a restricted number of the more stable species. The compounds are degraded into the corresponding isocyanates upon thermal stress. Thin-film capillaries should be used to reduce the elution temperature as far as possible. Further improvment may be acchieved by using hydrogen as the carrier gas to minimize retention. The capillary column may promote the decay by catalytic activity. Barium carbonate columns and a Chrompack column caused moderately high degradation rates, but considerably less than a Carbowax deactivated fused silica column. Persilanized columns were found to be the most suitable. An optimized sampling technique using vapourising injection may cause relatively little degradation in the injector but, as this requires stream splitting, sensitivity is restricted. The precision and accuracy of this method are poor. Cold on-column sampling eliminates such problems.

INTRODUCTION

There are various methods for determining phenylurea herbicides. An early spectroscopic method measured the aniline obtained upon hydrolysis of the phenylurea[1]. More recently, high-performance liquid chromatography (HPLC) was applied to the analysis of intact phenylureas[2–5]. A number of techniques have been developed for gas chromatography (GC) with packed columns. Such methods had to overcome the problem that the phenylureas are thermolabile and readily decay during the analysis, partly in the hot injector and partly in the column. According to a well documented technique, the ureas are hydrolysed and the free or derivatized anilines

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are determined by GC (and if necessary also the amine of the non-aromatic fraction of the molecule)[6–8]. Other workers stabilized the phenylureas by replacing the N-hydrogen atom with a methyl group, forming the 3-N-methyl analogue[9,10]. Silylation of the ureas may have a similar effect[11]. For some of these herbicides it was proposed to pyrolyse the phenylurea in the injector and to quantitate the substituted phenylisocyanate generated[12].

Derivatization of compounds prior to the analysis suffers from well known disadvantages. If the analysis of the phenylureas is based on their anilines or isocyanates there is the additional drawback that several herbicides form the same derivative, resulting in a reduced specifity of the analysis. On the other hand, attempts in many laboratories to analyse the phenylureas directly have often produced doubtful results. Spengler and Hamroll[8] have demonstrated by GC–mass spectrometry that the pyrolysis product (the isocyanate) was analysed instead of the intact phenylurea as claimed[13,14]. As the degradation was seldom complete, the results were inconsistent. Spengler and Hamroll concluded that phenylureas should not be analysed directly. Nevertheless, other workers have made successful claims for the direct analysis of phenylurea herbicides[12,15,16].

It is tempting to use capillary GC for the direct analysis of phenylureas, hoping for lower degradation rates due to reduced elution temperatures and lower retentions. Experiments were carried out by Deleu and Copin[17,18] using two of the most difficult phenylureas. Unfortunately, it seems that they fell into the same trap as other workers more than 10 years earlier: instead of analysing metoxuron and neburon they determined the corresponding pyrolysis products, the isocyanates, as can be concluded from the retention times indicated. The injector temperature was between 250 and 300°C.

The work reported here was intended to optimize the conditions and to establish the limitations of capillary GC for difficult samples such as phenylurea herbicides. Capillary GC has some distinct advantages over HPLC or packed column GC for pesticide analysis. The high resolution requires less clean-up of the sample as the byproducts are more likely to be separated from the peaks of interest than by less efficient chromatographic methods. Capillary GC therefore allows rapid methods to be used with little risk of introducing artefacts or memory effects or of losing some of the sample during long clean-up procedures.

IMPORTANCE OF THE ELUTION TEMPERATURE

When using cold on-column sampling[19,20], the degradation of the phenylureas observed is due to the column exclusively. Before comparing different types of columns it should be noted that the degradation rates are extremely dependent on the thermal stress imposed on these compounds, *i.e.*, column temperature and retention time. In temperature-programmed runs the important parameters are the programming rate and the elution temperature. Fig. 1 shows the results obtained for diuron on a 30-m capillary coated with OV-73. The temperature programme used was constant. The carrier gas flow-rate was changed to elute diuron at different temperatures. When eluting at 150°C diuron degraded by 35%, but this increased to 80% at 165°C. Later this column was separated into halves. Using one of these 15-m columns the temperature programming rate was doubled, again varying the carrier gas flow-rate. The

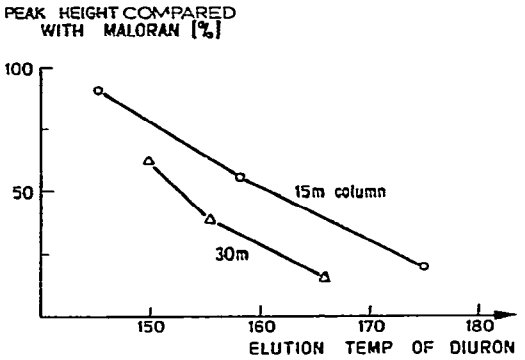


Fig. 1. Dependence of degradation of diuron on elution temperature and retention time △, 30 m × 0.30 mm column coated with 0.11-μm OV-73 temperature programming rate 2 5°C/min; carrier gas (hydrogen) flow-rate varied to shift the elution temperature; cold on-column injection. ○, Half of the above column temperature programming rate 5°C/min Peak heights of diuron are expressed as a percentage of the height of the similar, but more stable, maloran. Note the rapidly increasing losses of diuron with increasing elution temperatures. The halved column (*i.e.*, halved retention time) reduces the proportion of diuron degraded considerably

corresponding curve in Fig. 1 shows a considerably lower degradation owing to the halved retention time. The dependence of the degradation rate on the elution temperature remained the same.

As no column could be used without degradation of at least some phenylureas, an optimized analysis was required to reduce the thermal stress to the absolute minimum. For a given column this can be achieved by using a high carrier gas flow-rate, but this is limited by the decrease in column efficiency when using forced conditions. The most important parameter to select is the film thickness of the stationary phase. As shown previously[21], changing the film thickness by a factor of two results in a change in the elution temperature of 15°C, other conditions being equal. Fig. 1 may demonstrate the potential of this parameter. Retention (temperature programming rate) is strongly dependent on the carrier gas. When hydrogen is used chromatography for a given separation efficiency is twice as rapid as with helium and three times as rapid as with nitrogen. Finally, the column length should be reduced to the minimum (a 5-m capillary column is far more efficient than an average packed column

DETERMINATION OF THE DEGRADATION PRODUCT

Phenylureas were found to be degraded to their isocyanates, as occurs in hot injectors also[8]. This conclusion was drawn from the results of an experiment with two capillary columns, one being installed normally in a GC oven (producing the degradation products) and the other (coated with 0.6 μm of SE-52) hanging on the top of the instrument to serve as a trap for the materials eluted from the first column. The detector head was removed, the exit end section of the column in the oven pushed through the detector block and the two columns joined by means of shrinkable PTFE tubing. The joint was then pushed back into the hot detector block (175°C) to ensure complete transfer into the trapping column. Standards of individual phenylureas were injected by cold on-column injection and chromatographed by temperature

programming to the previously determined elution temperature. To identify the degradation product recovered in the trapping column, the isocyanate expected was injected into the trapping column before starting the temperature programming.

CHEMICAL ACTIVITY OF THE COLUMN

The decay of a sample component during GC analysis does not necessarily mean that this is due to the column. First, a compound may have already been degraded in a vapourizing injector. This is easily detected by the breakdown products forming sharp peaks (breakdown products generated in the injector start chromatography as sharp bands, which is usually not the case on emergence from the column). Cold on-column injection excludes such degradations. Secondly, if the decay does occur in the column, this chemical reaction may be primarily spontaneous, as was shown to be the case for triglycerides[22] on persilanized columns. At present we do not know of a simple way to detect chemical activity of the column, *i.e.*, to establish whether the column contributes to the decay of a compound or not.

For the phenylureas we found that the column exhibits some catalytic activity. Columns prepared by different procedures were tested using the phenylureas under comparable conditions. They showed considerable differences in degradation rates, and therefore in their chemical activities. However, this does not give any information on the absolute activity of these capillaries.

Little is known about column testing for chemical activity. On the other hand, tests on adsorptivity of capillaries are not only useful for the evaluation and comparison of columns, but are essential for the development of improved column preparation procedures. The extension of such tests to establish chemical activity is mainly hindered by the lack of knowledge about this kind of activity. Little is known about the mechanisms of the reactions (mostly degradation) taking place in the columns, such as reactions catalysed by basic or acidic sites, reactions initiated by an electron transfer, reactions with the silanol groups or transformations involving water. A meaningful study must include the investigation of different cases.

As a first step we related the degradation of the phenylurea herbicides to other column characteristics that can be determined by known procedures. For the determination of adsorption and acid–base effects we used the test described by Grob *et al.*[23] and we examined the stability of silylated fatty acids according to Donike[24] Chromatograms obtained in these tests are shown in Fig. 4.

COMPARISON OF COLUMNS

For the comparison of the chemical activities and other characteristics, the following four columns were tested:

(1) A "barium carbonate" column prepared according to Grob *et al.*[25] (leached soft glass, treated with barium hydroxide and carbon dioxide and deactivated with small amounts of Carbowax 1000 and Triton). It was coated with 0.15 μm of SE-52.

(2) A column obtained from Chrompack (Middelburg, The Netherlands), presumably deactivated with pyrolysed methylpolysiloxanes and coated with about 0.3 μm of a methylpolysilixane fluid.

(3) A fused silica column prepared by Hewlett-Packard (Avondale, PA, U.S.A.), deactivated with (large amounts) of Carbowax 20,000 and coated with about 0.2 μm of a methylpolysiloxane fluid (SP 2100).

(4) Persilylated columns[26,27] coated with OV-73 of different film thicknesses; a column with a film thickness of 0.15 μm was used for direct comparison with the other columns.

The conditions for the adsorption tests were standardized[23]. The results of the Donike test with the silylated fatty acids were little dependent of the chromatographic conditions. A carrier gas (hydrogen) flow-rate of 50 cm/sec and a temperature programming rate of 3.5°C/min for 20-m columns were used. Because of the too small inner diameter of the two commercial columns, the preferred on-column injection was excluded and all injections were made by stream splitting (about 1:50), using the "hot needle" technique[28] and an injector at 250°C. For the phenylureas the chromatographic conditions are very important, as shown above. The temperature programming rate was 4°C/min for all columns and the carrier gas flow-rate was adjusted to elute monuron/diuron at 170–175°C. Again a vapourizing injector had to be used. To avoid degradation in the injector its temperature was kept at 200°C, using stream splitting (about 1:50), the "hot needle" technique and an empty glass insert. A comparison of the results with those obtained by cold on-column injection did not show significant differences with respect to losses by degradation.

The results are summarized in Table I. The "barium carbonate" column was relatively inert regarding adsorption of polar solutes. It was not fully inert toward 2,6-dimethylphenol (DMP) and 2,6-dimethylaniline (DMA), indicating acidic and basic sites or adsorption of electron-rich compounds. Most of the dicyclohexylamine and all of the 2-ethylhexanoic acid were lost in the column. Of the four columns tested, the "barium carbonate" column had the highest acid–base activity. The degradation of the silyl esters was also relatively high. Further, it is known[29] that triglycerides degrade easily on this kind of support. Hence it was surprising that the losses of the phenylureas were only moderate.

The Chrompack column was adsorptive for polar compounds and showed a similar activity towards DMA and DMP as the "barium carbonate" column. It

TABLE I
RESULTS OF COMPARISON OF COLUMNS
ol = 1-Octanol; DMP = 2,6-dimethylphenol; DMA = 2,6-dimethylaniline; for other abbreviations, see legend to Fig. 2.

Column	*Adsorption*			*Donike test*				*Phenylureas*					
	ol	*DMP*	*DMA*	*14**	*18*	*22*	*26*	*Coto*	*Monu*	*Tolu*	*Butu*	*Diu*	*Metoxu*
"Barium carbonate" (22 m)	100	85	90	50	10	–	–	60	20	10	30	–	–
Chrompack (25 m)	60	90	80	75	70	50	15	80	30	5	25	–	–
Fused silica (24 m)	100	100	100	75	50	10	–	20	–	–	–	–	–
Persilanized (22 m)	100	100	100	100	100	100	75	100	100	90	100	20	40

* Chain length of silylated acids

eluted about 30% of the carboxylic acid and 50% of the amine. The silyl esters were degraded to a considerable extent, although less than on the "barium carbonate" column. The losses of the phenylureas were moderate.

The fused silica column showed surprising characteristics. Inertness towards 1-octanol, DMA and DMP was complete, comparable to that of a good persilanized column. On the other hand, the silyl esters were not stable and the phenylureas were degraded far more than on any other column. The elevated baseline in the front of the chromatogram (Fig. 2) is due to the degradation products of the labile ureas. As the retention of the isocyanates and the amines is relatively small, the elution temperature of this "hump" indicates that the decay occurred at low temperatures.

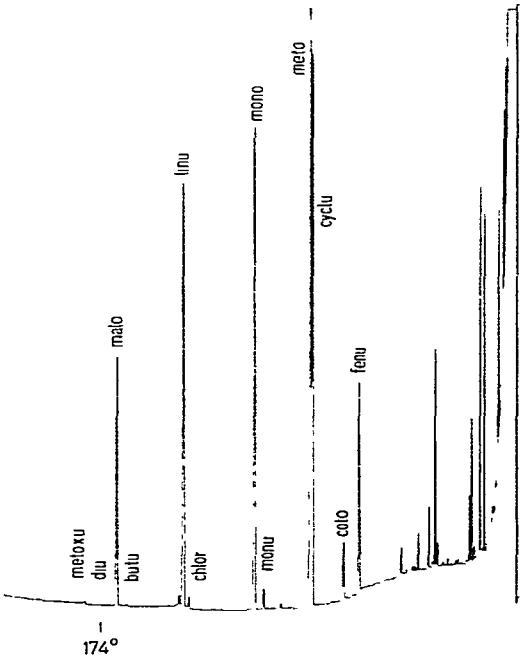


Fig 2 Chromatogram of phenylureas on fused silica column (24 m × 0 20 mm, SP 2100) Mixture of equal amounts of the ureas listed in Table II; fenu = fenuron; coto = cotoran; cyclu = cycluron; mono = monolinuron; monu = monuron; meto = metobromuron; chlor = chlortoluron; linu = linuron; butu = buturon; malo = maloran; diu = diuron; metoxu = metoxuron Neburon did not elute from any column (would be after metoxuron) Fenuron and cotoran eluted in small proportions; even moderately stable ureas were completely degraded The elevated baseline in the front part of the chromatogram is due to the degradation products of the lost ureas The retention of the "hump" indicates that the degradation occurs at low temperatures. The early sharp peaks are due to degradation products formed in the injector Split injection (1:40) of 1 μl of sample; "hot needle" injection; injector at 200°C; components diluted 1·15,000 in acetone

The persilanized column was generally inert, its adsorption characteristics being comparable to those of the fused silica column. However, the silylated fatty acids passed through the column with virtually no losses and the phenylureas eluted better from this column than from the others. A 2-year-old, heavily used SE-52 column with a film thickness of 0.6 μm (eluting the phenylureas more than 30°C

above the temperature used for the comparative study) still produced better results than the fused silica column (Fig. 3). The "hump" of the degradation products appeared at a temperature 40°C higher than on the fused silica column.

Adsorption of polar solutes may be strongly reduced by deactivating the support surfaces with Carbowaxes ("barium carbonate" and fused silica columns) or by persilylation. Although being similarly effective for the elution of polar compounds, there is little correlation with the catalytic activity for degradation of the phenylureas. In fact, the two columns with the lowest adsorptivity (the fused silica and the persilanised columns) represented opposite extremes concerning the stability of the phenylureas.

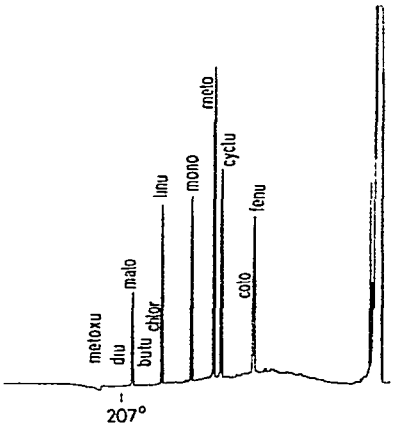


Fig 3. Phenylureas eluted from a thick-film (0.6 μm) SE-52 column on a persilanized support Although the elution temperatures were more than 30°C above those in Fig 2 (fused silica column), the results were better (see cotoran and fenuron). The "hump" due to the degradation products of the labile ureas eluted at around 175°C, indicating that the decay occurred at a temperature 40°C higher than on the fused silica column 20 m × 0.30 mm SE-52 column; 0 5 atm of hydrogen as carrier gas; temperature programmed at 4°C/min from 150 to 230°C.

Acid–base effects did not seem to be of importance with respect to the degradation of the phenylureas (although no very acidic or very basic columns were tested). The acid–base active "barium carbonate" column exhibited less catalytic activity than the much less active fused silica column.

The stability of silylated fatty acids depends on reactivity of the column, but not on catalytic activity as the losses of these esters are due to trans-silylation. On injecting silyl esters on to a column eluting carboxylic acids, peaks of free fatty acids may be observed, indicating that the silyl esters act as a silylating agent for active hydroxyl groups. Such hydroxyl groups may be present as silanols in the glass surface or in impurities in the silicone stationary phases. Terminal alcohol groups of polyglycols are also reactive. Columns coated with polyglycol stationary phases do not elute silyl esters. However, the traces of Carbowaxes used to deactive non-polar columns are probably sufficient to cause activity. In the "barium carbonate" columns the barium ions seem to complex the active silanols. The losses of the silyl esters on this type of columns are probably due mainly to the Carbowax and Triton used (in

small amounts) for deactivation purposes. The Chrompack column presumably contains silanols exclusively, some in the glass surface and some in the pyrolysed polysiloxane material. The fused silica should be almost free of silanols. However, deactivation with excess amounts of Carbowax (as recommended by many laboratories) creates a relatively high concentration of alcohol groups in the column. The excellent stability of the silyl esters on the persilanized columns is due to the fact that all accessible silanol groups are silylated such that (with the exception of impurities in the silicone phase) no further hydroxyl groups are left.

The stabilities of the silyl esters and the phenylureas are not directly related to each other. However, as the degradation of the phenylureas involves a proton transfer, it would be plausible to ascribe the activity to the same silanols that are active in cleaving the silyl esters. From the results in Table I, fair agreement might be deduced, although the "barium carbonate" column, being the most active for silyl esters, cannot be classified as such for the phenylureas. However, this agreement could not be confirmed when further columns were taken into consideration. On testing some very thin-film columns (0.04 μm), a capillary was found that was one of the best for phenylureas, but it gave very poor results in the other two tests (see Fig. 4). The column was adsorptive for all components tested and the silyl esters were degraded to an extent that was very unusual for persilylated columns. Although the phenylurea peaks showed tailing, they eluted in high proportions (the tailing cannot be related to the degradation). In fact, the preparation of this column differed from the standard procedure in that the dehydration was carried out under extremely mild conditions, possibly leaving some free silanols or adsorbed water that were active for adsorption and trans-silylation, but inactive for the kind of catalytic activity tested.

INJECTION TECHNIQUE

According to one technique[12], some phenylureas are routinely pyrolysed in vapourizing injectors to produce the more stable isocyanates. If intact phenylureas were to be analysed with vapourizing injection, this should be done with suitable precautions. The degradation of the ureas depended on the injector temperature, the exposure of the sample to hot surfaces and the time the sample remained in the injector. Splitless injections produced higher degradation rates than split injections, owing to the long transfer time to the column. Split injections (the pre-set ratio being about 1:40) into an injector at 250°C, equipped with an empty glass liner, caused about 15% of the diuron to degrade into its isocyanate. At 350°C this degradation reached 50%. A packing of silanized glass-wool in the injector insert degraded most of the diuron at 250°C. On passing through an empty glass liner, a considerable proportion of the sample was not evaporated, *i.e.*, not heated above the boiling point of the solvent (acetone) when it reached the column. The proportion of degraded material depended on some other parameters such as the column temperature during the injection, the length of the syringe needle (mainly determining the distance between the tip of the needle and the column entrance) and the width of the glass liner, generally tending to conditions that favour minimal evaporation in the injector[30]. The degradation affected less than 10% of the most sensitive phenylureas tested if the injector was kept at 225°C, a 7.5-cm long syringe needle and a narrow glass liner (2 mm) was used. The results were also improved when injecting into a cap-

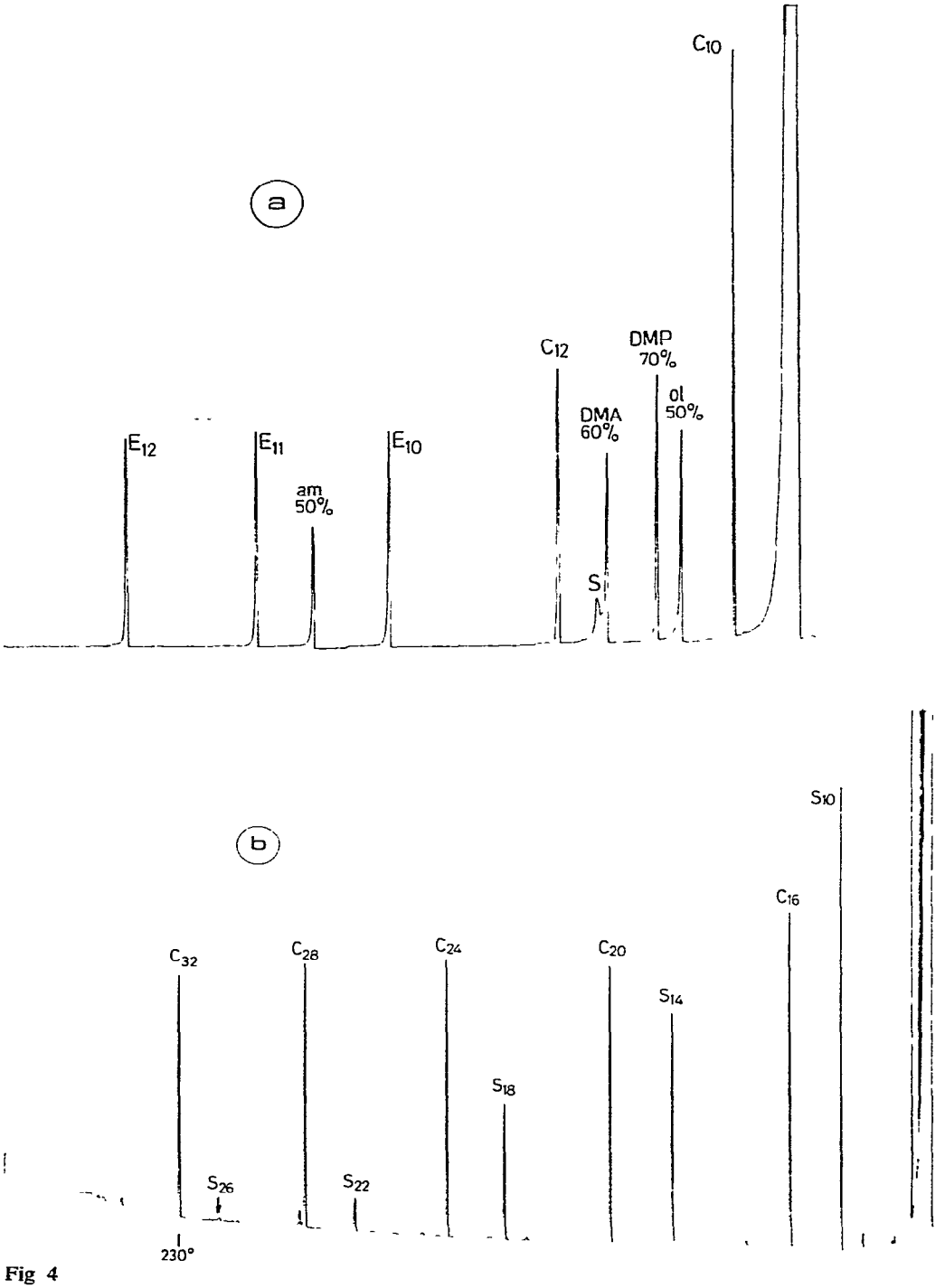


Fig 4

(Continued on p 226)

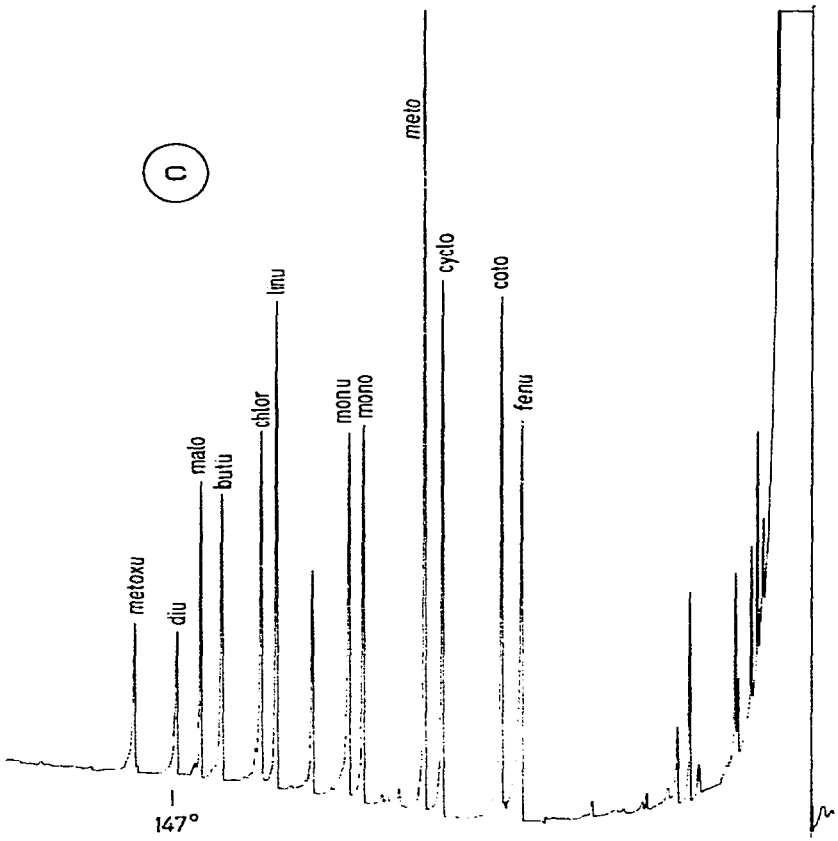


Fig. 4. Results obtained with a persilanized column (15 m × 0.3 mm) coated with 0.04-μm OV-73. (a) Test according to ref. 23. Peaks: alkanes (C_{10} and C_{12}); methyl esters of the C_{10}–C_{12} acids (E_{10}–E_{12}); 1-octanol (ol); 2,6-dimethylphenol (DMP); 2,6-dimethylanilin (DMA); 2-ethylhexanoic acid (S) (giving overloaded peaks on apolar phases); dicyclohexylamine (am). The column temperature was programmed according to standardized parameters. The quantitative composition of the mixture was such as to produce identical peak areas, so that well shaped peaks should be as high as indicated by the dotted line. The test shows the column to be adsorptive, and therefore of unusually poor quality for persilanized capillaries. (b) Test according to Donike[24] on the stability of the C_{10}–C_{26} silylated fatty acids (marked S_x). The peaks of the silyl esters should be compared with the neighbouring alkane (C_{16}–C_{32}). Reduced areas of the ester peaks compared with the alkanes indicate losses. Cold on-column injection; 0.4 atm of hydrogen as carrier gas; column temperature programmed at 5°C/min from 80 to 250°C. Again, the column shows poor characteristics, as a good persilylated column elutes the silyl esters nearly perfectly. (c) This "bad" column shows very good results for phenylureas. All "difficult" ureas (Table II; for peak identity see Fig. 2) elute without losses and even diuron and metoxuron are degraded by only about 50%. It is concluded that the two test chromatograms (a) and (b) do not allow a prediction of whether or not a column is suitable for urea herbicides. Terms such as "good" or "bad" for a column have to be specified. Furthermore, there remains an uncertainty as to whether the improvment of column preparation procedures [usually tested by mixtures such as those in chromatograms (a) and (b)] really improve chemical inertness.

illary kept at room temperature, as an accelerated transfer into the column is achieved. Unfortunately, these are conditions that result in large standard deviations (low injector temperature) and cause the true splitting ratios to deviate considerably from the pre-set value. Usually at least five times more sample enters the column than

is derived from the pre-set splitting ratio[31], a fact which may be useful for the trace analysis of phenylurea residues as splitless injection did not appear to be a possible alternative.

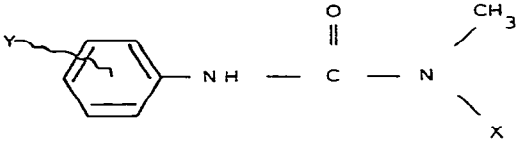
The method of choice for the sampling of phenylureas is cold on-column injection, which completely eliminates degradation due to the injection.

CONCLUSIONS CONCERNING THE ANALYSIS OF PHENYLUREAS

The GC analysis of intact phenylureas is restricted to the more stable species. In Table II we have attempted to classify these herbicides into "easy" to "impossible" with regard to routine quantitative analysis. It was easy to optimize a system to elute, *e.g.*, buturon without any losses. This compound is nevertheless classified as "difficult" because special care has to be taken and the column has to be checked periodically for increased activity due to "dirt" introduced into the column by injecting extracts (catalytically active impurities?). Similarly, it is possible to produce a reasonable peak for diuron. The peak is even surprisingly reproducible and a calibration graph did not deviate far from a straight line passing through the origin. However, it is considered to be almost impossible to elute diuron completely with the usual conditions and column length. Thin-film (0.04 μm) persilanized columns coated with OV-1, OV-73, SE-52 or similar materials eluted completely all compounds classified as "difficult". Diuron and metoxuron were 40–80% and 50–90% eluted, respectively. No peaks were detected for neburon and chloroxuron (tenoran).

Comparing the stability of the phenylureas during GC analysis with their structure (Table II), there appears to be a simple relationship. Compounds with a

TABLE II
CLASSIFICATION OF HERBICIDES WITH RESPECT TO EASE OF ANALYSIS



Ease of analysis	*Y*	*X*	*Herbicide*
Easy	*p*-Br	OCH_3	Metobromuron
	p-Cl	OCH_3	Monolinuron
	p-Cl, *m*-Cl	OCH_3	Linuron
	p-Cl, *m*-Cl	OCH_3	Maloran
Fairly easy	–	CH_3	Fenuron
	m-CF_3	CH_3	Cotoran
Difficult	*p*-Cl	CH_3	Monuron
	p-Cl	$CH(CN)CH_3$	Buturon
	p-CH_3, *m*-Cl	CH_3	Chlortoluron
Impossible	*p*-Cl, *m*-Cl	CH_3	Diuron
	p-Cl, *m*-Cl	C_4H_9	Neburon
	p-OCH_3, *m*-Cl	CH_3	Metoxuron

methoxy group on the nitrogen atom are relatively stable, independent of the substitution of the aromatic part of the molecule. Of the dialkylated herbicides, fenuron without any substitution of the phenyl ring is stable, whereas increasing substitution of the ring results in increasing losses in the column. At least part of this classification is related to the elution temperature of the compounds.

Most of the experiments were run with flame-ionization detectors (FID), injecting a few nanograms of an individual phenylurea. Tests on some good columns have shown, however, that the chromatograms did not change considerably when an alkali flame-ionization detector (AFID or NPD) was used, sampling only about 50 pg of the compounds. The degradation seems to occur with a fairly constant proportion of the labile phenylureas, *i.e.*, saturation of the active sites in the column could not be detected.

CONCLUSIONS CONCERNING CATALYTIC ACTIVITY

It was one of the aims of this work to emphasize the lack of understanding of catalytic activity in GC. No simple method is known for determining catalytic activity, either its presence or its intensity. Also, the ways in which the column may catalytically support chemical reactions are not known.

It is shown that the column activity promoting the decay of phenylureas does not correlate satisfactorily with adsorption, acid–base effects or the stability of the silyl esters as detected by the available column testing procedures. The lack of a suitable testing procedure for catalytic activities has some important consequences: (1) it is laborious to find the most suitable column for a labile compound to be analysed; (2) it is nearly impossible to compare the many column types known today sufficiently comprehensively to include catalytic activity; (3) when developing procedures for preparing capillary columns, this is inevitably done on the basis of deficient testing. The procedures are pragmatically optimized to produce the best test chromatogram. As long as the catalytic activity is not part of the testing, there is a high probability that this column quality will be neglected. For example, after experimenting with the phenylureas it seems to be doubtful that the deactivation procedure with Carbowax is as successful as has been believed for a long time. Similar conclusions may apply to other methods. An experimentally well founded testing procedure for catalytic activity is probably a prerequisite for developing better columns for the GC of labile compounds.

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