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The Selective Retention of Phenol by Cigarette Filter Materials

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The physiological effects of phenols have been investigated by *Wynder* and *Hoffmann* (8). Tobacco smoke contains considerable amounts of various phenols and means for their removal are being investigated in several centra. It has been found that cellulose acetate filters, which are widely used, retain phenols selectively. However, work on more selective filters is in progress. Higher selectivity could be achieved by using other materials, or through the use of suitable additives.

The purpose of this investigation was to find a screening method not involving elaborate smoking experiments, according to which different structural materials for filters, their plasticizers and possible additives, could be compared with regard to their abilities to retain phenol. The method described here is based on gas chromatography. The materials to be tested were used as adsorbents or stationary phases in gas chromatographic columns and the retention time of phenol was measured for each column. The attention was limited to phenol because it is the most abundant component of the phenolic fraction of tobacco smoke (3, 7). It was also hoped that the results would cast some light on the mechanism of phenol retention. A study in this direction, also making use of gas chromatography, has been undertaken by *de Vries* (1).

When using the method described here differences in physical properties, e. g. weight and fibre denier, often found in cigarette filters are eliminated, whereby differences in chemical structure become more apparent. It should be pointed out, however, that several new variables are introduced during the various stages of the procedure, i. e. applying the material to the solid column support, packing the column and injecting a phenol sample. The reproducibility of each step had to be determined. The influence of variations in certain easily controllable factors, e. g. the size of the injected sample, was also investigated.

The method was used to compare the phenol retaining abilities of different cellulose acetates, and the effects of various plasticizers and additives on these abilities. Additives were chosen on the basis of expected interaction with phenol through hydrogen bonding. They were not necessarily compounds that could be used in cigarette filters. Hydrogen bond association of phenol to a large number of substances has been studied (2, 5).

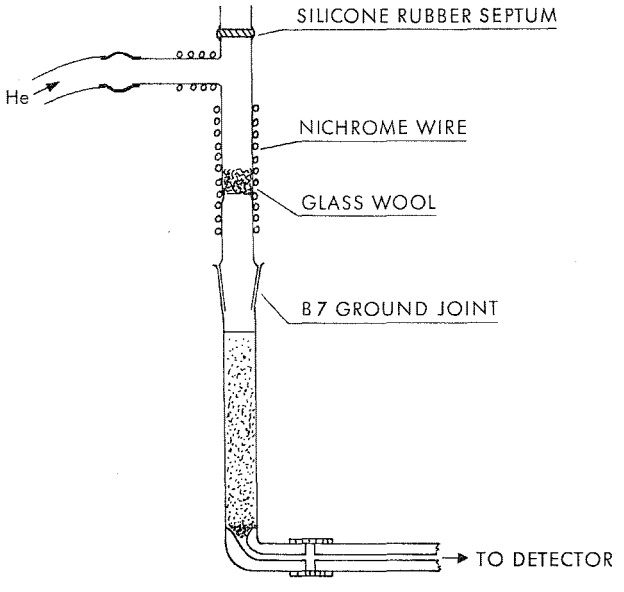
The solid support used was 60—100 mesh Embacel, acid washed and treated with dimethyldichlorosilane. Filter materials used were fully acetylated or "primary" cellulose acetate (PCA) and partially acetylated or "secondary" cellulose acetate (SCA) (6). Secondary acetates from two different sources were used, denoted by SCA I and II. The following plasticizers were employed: glyceryl triacetate (triacetin), glycerol and Flexol EPO and JPO, both of which are epoxy plasticizers manufactured by Union Carbide Corporation. However, it should be pointed out that, for practical purposes, the only plasticizing action is obtained in the case of triacetin and SCA.

The SCA was washed with ether and applied to the support by dissolving it in acetone, mixing the solution with the right proportion of support and evaporating the solvent in a rotary evaporator. Methylene chloride was used as solvent in the case of PCA. In the same manner the plasticizers and additives were applied to the support already coated with cellulose acetate, using a solvent that did not dissolve the acetate. Ethanol was used for all the plasticizers and the majority of additives, water for glucose, gelatine and sodium chloride, and 20% ethanol in water for glutamic acid. Embacel coated with SCA I in the ratio 100:1 served as the basic material to which the additives were added. Triacetin was added together with each additive, in the ratio of 1:10 for triacetin : SCA (or 9.1% on the total weight of SCA and triacetin), because it is usually present in SCA filters.

A Perkin-Elmer Model 154D Vapor Fractometer with a thermistor detector was employed, using helium as carrier gas. Columns were packed in a short glass tube of 5 mm. inner diameter, which was connected to the inlet system by means of a B7 ground glass joint (see Fig. 1). The latter consisted of a 5 mm. glass tube provided with a side arm, a silicone rubber septum and a 10 ohm heating coil of nichrome wire. Columns were packed by alternate pouring and tapping, using a weighed quantity of material. The tapping was continued until no further contraction occured. Both column and inlet system were mounted outside the oven of the gas chromatograph, so that the detector could be maintained at a much higher temperature than the column in order to prevent condensation. The carrier gas was fed from the detector block through a 1/4 inch copper tube to the side tube of the inlet system. The column inlet was connected to the detector block by means of a 1 mm. inner diameter glass capillary.

A 10 microliter syringe with a Chaney adaption was used for injection of samples. The sample solution consisted of 20% phenol in ethanol. The temperature of the inlet heater was regulated by means of a variable transformer.

FIGURE 1 **The apparatus**



The following values for the experimental parameters were used:

Column length	3 cm.
Weight of column packing	0.17 g.
Column temperature	26° ± 2° C
Detector temperature	150° C
Sample size	1 µl.
Carrier gas flow rate	100 ml./min.

The column temperature was of the order of that of a cigarette filter during smoking. The other values were chosen so as to provide the most desirable peak shape and size, as well as con-

venient retention times. The solvent being eluted immediately upon injection, its peak could be identified with the air peak. Therefore retention times were determined by measuring the distance between the maxima of the solvent and phenol peaks.

RESULTS

The Reliability of the Method

The coating of Embacel with SCA II in the ratio 100:1 was repeated seven times. Every time a column was packed and the retention time (t_R) of phenol measured. A mean value of 2.2 minutes was obtained, with a standard deviation of 0.1 min.

The reproducibility of packing the column was determined by packing it four times with Embacel coated with SCA II, taken from the same batch, and four times with PCA. At the same time the reproducibility of injecting phenol samples was determined by injecting six samples into each column packing, every time measuring t_R. The results are represented in Table 1. The standard deviation for successive injections varied between 0.05 and 0.15. The standard deviation among column packings was 0.1 for SCA and 0.15 for PCA.

Thus the coefficient of variation in retention time for the whole procedure was 5% for both acetates.

The variation in peak height was also determined for successive injections, and for different modes of injection. With fast injection and removal of the needle a variation of 3% was obtained, whereas with slower injection it was only 1%.

TABLE 1

The reproducibility of packing columns and injecting samples

Material	$\bar{t}_R$ (min.)	Standard deviation
PCA	2.95	0.05
	2.65	0.05
	2.60	0.10
	2.95	0.15
	2.80	
SCA II	2.30	0.05
	2.30	0.10
	2.10	0.10
	2.10	0.10
	2.20	

$\bar{t}_R$ = mean retention time for 6 injected samples

The effect of the solvent used in the preparation of the column packing was determined. Acetone was replaced with formic acid as solvent for SCA and then with methylene chloride, to which some acetone was added, until solution occurred. The retention time remained virtually unchanged.

The effect of the amount of SCA applied to the support on retention time can be seen in Table 2. Its effect on peak height was striking. A rapid decrease in peak height with increasing concentration was observed. This was much more marked than the normal decrease due to increasing retention time and the width did not change appreciably. At a ratio of 1:20 no phenol peak was observed.

The influence of the period of conditioning of the column was investigated, because it was feared that this might have led to irreproducible results. However, no difference in retention time outside the limits of experimental error was found after different conditioning periods, ranging from 15 minutes to 4 1/2 hours.

The effect of sample size on retention time can be seen in Figure 2. A column with SCA I was used. It is evident that care should be taken in sampling. A sample size of 1 microliter was chosen, although the curve is less steep at 0.5 microliter, because reproducibility of peak height was also desired, as will be seen later.

TABLE 2

The effect of the amount of SCA in the column (SCA I)

SCA : Support ratio	t_R (min.)
1 : 200	1.4
1 : 100	1.9
1 : 50	3.2

The Retention of Phenol by Cellulose Acetates

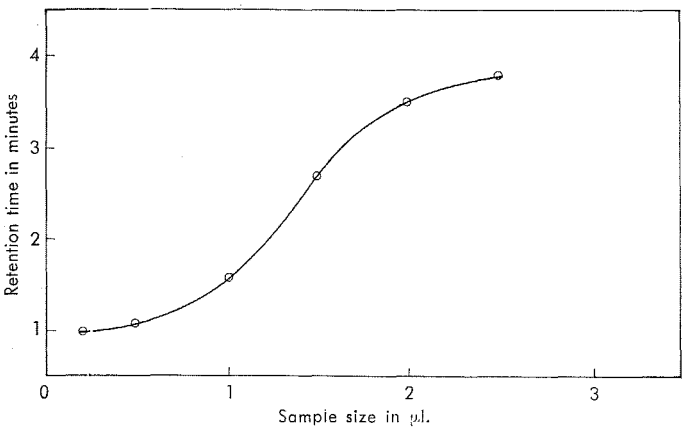
The retention times of phenol on SCA and PCA (both 1:100) are given in Table 3. There is a significant difference in t_R, indicating stronger adsorption of phenol on PCA than on SCA.

When the peak heights for a series of samples injected into the same column were compared an interesting

phenomenon was observed. There was a marked difference between the height of the first peak and that of all the subsequent peaks. The difference was 17% in the case of SCA and 23% in the case of PCA, the first peak always being smaller. This effect will be referred to as the "first peak anomally". It probably indicates that a portion of the phenol is held back after elution of that portion represented by the peak.

FIGURE 2

The influence of sample size on retention time

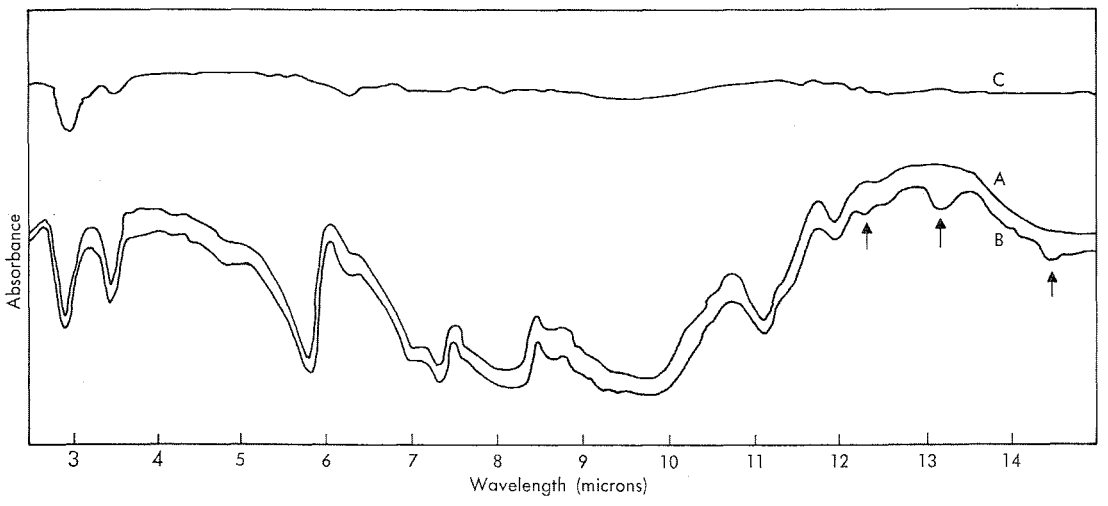


To test this hypothesis several experiments were carried out. SCA was cut into short fibres and ground with anhydrous potassium bromide. The mixture, which contained 2% of SCA, was dried at 60° C in a vacuum oven over P_2O_5 for 5 hours. Two samples of 0.25 g. each were taken, one of which was pressed into a disc. The other was packed into the glass tube used for the other experiments. The tube was connected to the gas chromatograph and a 1 microliter sample of 20% phenol solution in ethanol was injected and eluted. Solvent and phenol peaks appeared as before and elution was continued until the recorder pen had returned to the base line. The column packing was then also pressed into a disc.

The infra-red spectra of both discs were obtained. The spectrum of the second disc had three adsorption bands that were absent in that of the first, i. e. at 12.3, 13.2 and 14.5 microns. These bands could be assigned to phenol. The other bands of phenol lie in regions obscured by strong bands of SCA. An attempt was made to find evidence of hydrogen bonding of phenol to SCA, but no information could be obtained from the region of the OH stretching vibration, two bands of SCA lying in this region. The spectra are given in Figure 3.

FIGURE 3

The infra-red spectra of: (A) SCA in KBr, (B) SCA in KBr, phenol passed through, (C) KBr, phenol passed through Spectrum A has been shifted upwards



To determine whether phenol was not held back by the potassium bromide, a phenol sample was injected into a column packed with this salt. A disc was pressed and no phenol bands were present in its spectrum.

The effect of heat on the residual phenol was investigated. Two phenol samples were injected into a column containing SCA on Embacel. The difference in peak height was observed.

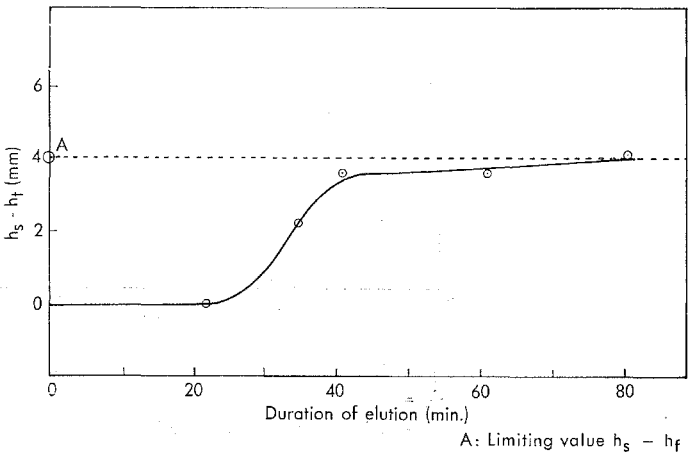
The column packing was then heated for an hour at 100° C, again packed into a column and two more samples were injected. The difference in peak height was the same as for the first set, i. e. before heating.

According to this result it should be possible to remove the residual phenol by prolonged elution. Henceforth the phenol retained by cellulose acetate after the portion giving rise to the peak has been eluted will be referred to as "residual" phenol in order to make a clear distinction. Let h_f represent the height of the first peak of a series, h_s that of the second (and third, etc.) and h_t that of a peak obtained after elution for a time t. Then $(h_s - h_t)$ can be regarded as a measure of the restored capacity of the column to retain phenol (i. e. in the manner in which the "residual" phenol is retained). It is therefore a measure of the amount of "residual" phenol eluted during the time interval t. When $h_t = h_f$ the original capacity has been restored, i. e. all the "residual" phenol has been eluted. A plot of $(h_s - h_t)$ vs. t can thus be regarded as an integral elution curve. Such a curve has been obtained (see Figure 4). The values of h_f and h_s were 12.1 and 16.2 mm. respectively. It is possible to conceive the existence of a point of maximum elution rate at about 33 minutes, indicating an elution peak. The experiment was repeated, giving the same result.

A phenol sample was then injected into a newly packed column of SCA and elution continued for longer than 40 minutes. However, no verdict could be given as to the presence of a second elution peak, even after the experiment had been repeated several times, the base line being rather irregular.

FIGURE 4

Elution of the residual phenol



A comparison was made between the retention volume corresponding to the hypothetical second peak and the retention volumes of phenol on SCA at different temperatures, reported by *de Vries* (1). As *de Vries* used a column length of 50 cm., an SCA content of 10% and a flow rate of 135 ml./min., compared to 3 cm., 1% and 100 ml./min. in this investigation, corrections had to be made for all these factors.

The correction for SCA content was made by first extrapolating the retention time values in Table 2 to 10% SCA in order to obtain the ratio t_R (10% SCA) : t_R (1% SCA). This ratio was assumed to hold for the hypothetical second peak as well and was used along with correction factors for column length and flow rate to calculate the retention volume. It should be noted that *de Vries* made corrections for temperature and pressure drop over the column. However, in the experiments described here it was unnecessary, the column being at room temperature and the pressure drop being negligible.

A value of 33 min. was adopted for the retention time of the "second peak", giving a corrected retention volume of 3.62×10^5 ml. A corrected retention volume was also calculated for the observed phenol peak and these values were arranged, together with those given by *de Vries*, in a logarithmic plot against the reciprocal of the absolute temperature of the column. The resulting plot can be seen in Fig. 5.

In order to eliminate effects due to possible hydrogen bonding of the solvent, ethanol, it was replaced with carbon tetrachloride. Some of the experiments were repeated and the same effects were observed.

The effect of water on the retention of phenol by SCA was also investigated. Phenol sample solution was mixed with an equal volume of water and 2 microliter samples were injected into an SCA column. No difference in retention time was found between the samples with and without water.

FIGURE 5 **The influence of temperature on the retention volume**

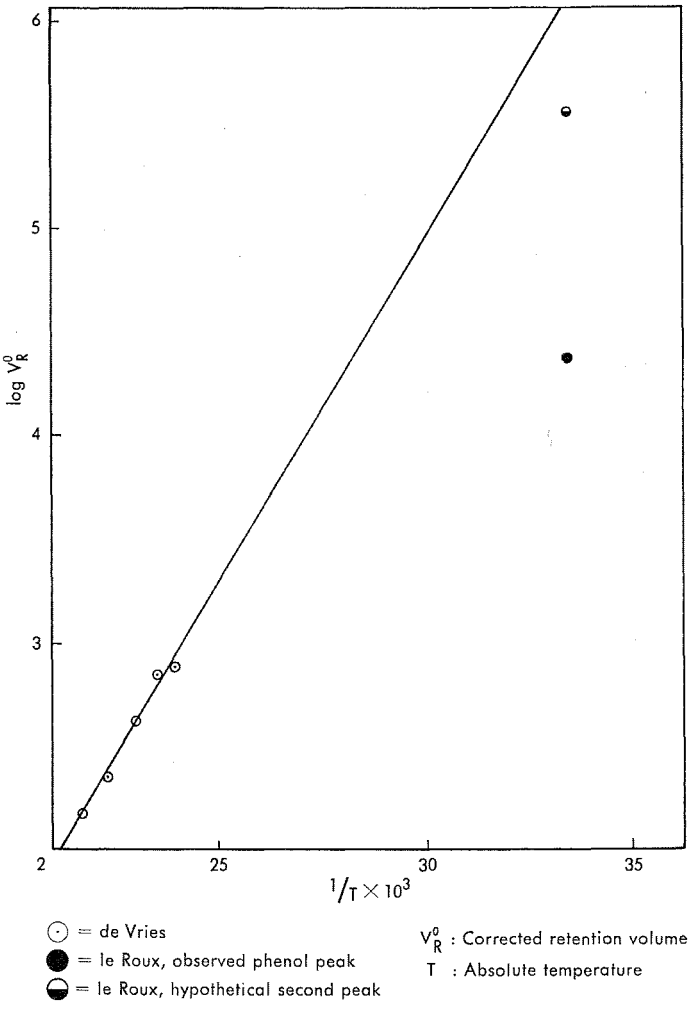
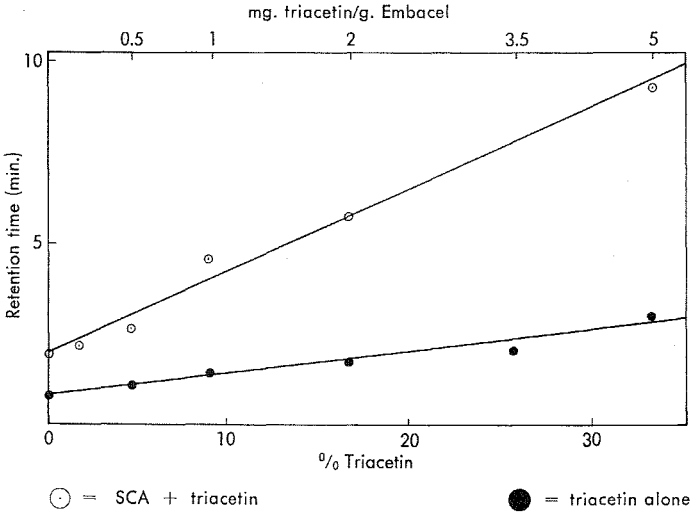


FIGURE 6 **The effect of triacetin content**



The phenol retention times for SCA I and PCA with triacetin are given in Table 3. Retention times were measured for different values of triacetin content in the case of SCA. SCA I was used, applied to the support in the ratio 1:100. Control experiments were also carried out with equivalent amounts of triacetin on the solid support alone. The results are represented graphically in Fig. 6. Straight lines were drawn through the two sets of points by means of the method of least squares.

TABLE 3

The retention of phenol by the support and cellulose acetates, with and without plasticizer

Material	t_R (min.)
Uncoated support	0.85
SCA I	1.9
SCA II	2.2
PCA	2.8
SCA I + 9.1 % triacetin	4.0
PCA + 9.1 % triacetin	3.5

TABLE 4

A comparison between various plasticizers*

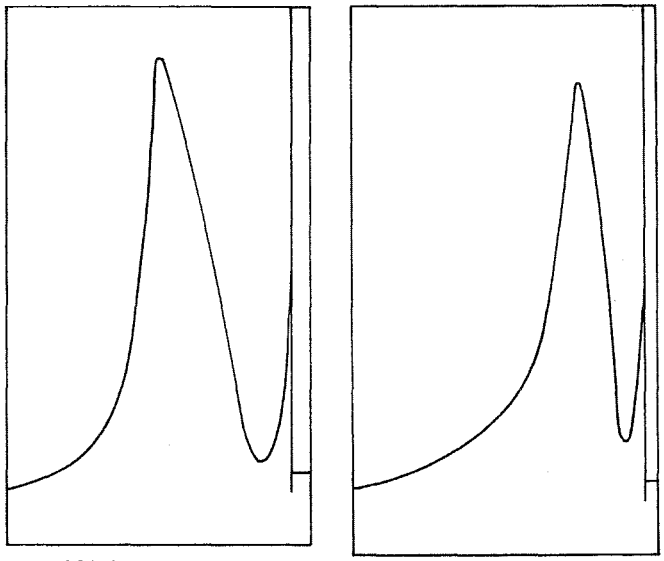
Plasticizer	Percentage added	t_R (min.)
Triacetin	15.0	5.3
Flexol EPO	16.1	3.0
Flexol JPO	14.5	3.4
Flexol EPO + triacetin (1:7)	16.7	3.1
Glycerol	20.0	3.6

* Added to SCA I (1:100)

Results obtained when other plasticizers were added to SCA I are given in Table 4. Plasticizer content is given as weight percentage based on the weight of cellulose acetate plus plasticizer.

Two interesting observations were made with regard to peak height and shape. In the first place the peak anomally was only noticed in the case of SCA with 2 % of triacetin. In the case of 4.8 % triacetin on SCA no difference was observed for five consecutive samples, also when the sample size was increased to 5 microliters, overloading the column. Secondly, peak tailing was greatly reduced when any of the plasticizers was added to the cellulose acetates, as is shown in Fig. 7.

FIGURE 7 **The influence of triacetin on peak shape**



The retention times for columns containing SCA with triacetin and additives added to it are given in Table 5. The amounts of additives applied are given as weight percentages, based on the total weight of SCA, triacetin and additive (triacetin was added to SCA in the ratio 1:10).

The retention time of phenol on the uncoated support, which was long enough to effect separation between phenol and the solvent, was also determined and is given in Table 3.

DISCUSSION

It has been found that the retention time of phenol can be measured with an error limit of 5 %. Differences that would be of practical significance would be much larger than this, making such a precision sufficient.

There are, however, some limitations to the method. It is only applicable to structural materials

TABLE 5

The influence of additives*

* Added to SCA I (1:100) with 9.1 % triacétin

Additive	Percentage added	t_R (min.)
Urea	15.4	9.3
Nicotinamide	14.7	8.1
Polyethylene glycol	15.4	6.9
Triphenyl phosphine oxide	16.7	5.9
Coumarin	16.0	5.1
Sodium chloride	16.7	4.6
N,N'-Dimethylurea	15.1	4.5
Glutamic Acid	17.8	4.2
Glucose	15.9	3.9
Gelatine	13.4	3.4

for which solvents can be found. Furthermore, when plasticizers and additives are tested solvents have to be found that dissolve them but not the structural material to which they are added. The ideal is to deposit them on to a layer of the latter, but it would be difficult to decide whether this is achieved. A complication also arises through the first peak anomally, as will be discussed later.

The method can be used as a rapid screening method, facilitating the classification of series of possible plasticizers or additives according to their abilities to retain phenol. The better ones among them can then be subjected to smoking tests, determining phenol retention (3, 7), before the final choice is made.

Cellulose Acetates

Before a comparison is made between the retaining properties of SCA and PCA the anomally in the height of the first peak should be discussed. The results indicate that portions of the phenol are eluted at two different rates, probably because they are retained through two different mechanisms, say mechanism I, giving fast elution, and mechanism II, giving slow elution.

Support for this hypothesis also comes from the fact that the height of the phenol peak observed, representing the phenol held by mechanism I, decreases with increasing amounts of cellulose acetate in the column. This may be due to an increasing amount of phenol being held back by mechanism II. It has been shown that for an SCA to support ratio of 1:100 the first phenol peak is about 20% smaller than the others, whereas for a ratio of 1:20 it disappears altogether. Further proof can be obtained from the results of the experiment where use was made of infra-red spectra.

Evidence that hydrogen bonding takes place between phenols and cellulose acetates has been given by *de Vries* (1). It is probable that mechanism II is hydrogen bonding. Mechanism I, on the other hand, gives rise to an elution rate comparable to, though significantly slower than that obtained for phenol on the solid support alone (see Table 3). This seems to indicate that mechanism I is adsorption, due to *van der Waals* type of forces, on the cellulose acetate, on exposed parts of the support and on phenol molecules already adsorbed.

According to the proposed model a trail of phenol, held by mechanism II, will be left behind the zone of adsorbed phenol as it moves along the column. It is therefore not likely that a recognizable peak will be formed due to elution of the residual phenol. This probably explains why no second phenol peak could be observed, although its existence was predicted from the integral elution curve (Fig. 4). Moreover, the shape of this curve indicates a very broad "peak".

From Fig. 5 it is quite evident that the retention volume calculated for the maximum of the hypothetical second peak shows a much closer correspondence to the values given by *de Vries* than does that obtained for the observed phenol peak. It is probable that, at the high temperatures used by *de Vries* (145 to 188°), adsorption due to *van der Waals* type of forces did not play a significant role, so that he obtained peaks due to hydrogen-bonded phenol. It is therefore likely that, if a second phenol peak is obtained at room temperature, it represents a portion of the phenol which is retained through hydrogen bonding. More experimental evidence is needed, however, before the existence of a second peak can be established beyond any doubt.

The fact that there is an increase in retention time with increasing phenol sample size (see Fig. 2) is significant, because it is quite contrary to what is to be expected, as well as to what

was found by *de Vries* (1). For adsorption according to the *Langmuir* isotherm, efficiency decreases with increasing amount of adsorbate. This means that a bigger sample will move faster through the column than a smaller one.

A possible explanation why the opposite was found in the experiment described here is that phenol might be adsorbed more strongly on a layer of its own molecules than on SCA (except, of course, for the portion of the phenol which is held by hydrogen bonding). Thus, with a bigger sample the SCA surface is more completely covered with phenol molecules, so that further amounts of phenol are adsorbed on a more efficient substrate.

Support for this explanation can be obtained from an examination of peak shapes. The increase in retention time with sample size is accompanied by a change in peak shape, a transition from tailing to leading taking place between 1.0 and 1.5 microliters. This means that, with bigger samples the more concentrated part of the zone of adsorbate lags behind.

As has been stated before, the phenol peak obtained at high temperatures can be attributed to hydrogen bonding. For this mechanism a limited number of active sites exist, so that the efficiency of retention will decrease with increasing amount of adsorbate. In this case a decrease in retention time with sample size is to be expected, and it has indeed been found (1). This may serve as a further indication that the phenol peak observed at high temperatures (145 to 188 °) represents a mechanism which differs from that related to the peak observed at room temperature.

When the phenol retention times for the two cellulose acetates, as well as the deviations in peak height are compared, it is evident that phenol is held somewhat stronger by PCA than by SCA, considering both mechanisms. The difference in the retention times of SCA I and SCA II might be due to a difference in acetyl content.

Other investigators have found that the presence of water enhances the retention of phenol by cellulose acetates. This effect, however, was not reflected in the retention times measured in the experiment described here.

Plasticizers and Additives

The effect of triacetin on the retention time of phenol on SCA is striking, as can be seen from Fig. 6. There is a linear increase with triacetin content, and when the slope of the line obtained is compared to that for triacetin alone, it is clear that this enhancement is due, not to the effect of the plasticizer on its own, but to the combination of SCA and plasticizer.

In the case of PCA the effect of triacetin is less marked (Table 3). It should be kept in mind that triacetin is not a true plasticizer for PCA. Comparison of glycerol and the Flexols with triacetin (Table 4) also shows that plasticizing action helps on phenol retention. This can be explained if one bears in mind that the plasticizer serves to push the polymer chains apart, thus increasing the effective surface area.

On the other hand, evidence that solution of phenol in the plasticizer plays an important role can be obtained from a comparison of peak shapes (see Fig. 7). When unplasticized SCA is used there is considerable peak tailing, which is typical of adsorption on a solid surface (phenol represented by the tail should not be confused with phenol held by mechanism II). In presence of triacetin, however, tailing is greatly reduced, giving the type of peak encountered in partition chromatography. This may mean that the more active adsorption sites of the SCA surface are covered, or that solution of phenol in the plasticizer takes the place of adsorption on SCA. Tailing is also reduced in the case of glycerol and the Flexols.

The first peak anomally was not observed in the case of cellulose acetates to which 4.8 % or more triacetin or other liquids were added. It should not be concluded at this stage, however, that an unplasticized filter would be a more selective filter for phenol than a plasticized one, because hydrogen bonding of phenol to cellulose acetate is impaired by the presence of triacetin. Experiments with actual cigarette filters have shown the contrary to be true (4).

It is possible that hydrogen bonding still takes place, but that distinction can no longer be made between portions of phenol held through different mechanisms. Retention of phenol is

now governed by a single partition coefficient, the size of which depends on the equilibria:

Phenol in moving phase $\rightleftharpoons$ phenol in solution (unbonded)

Phenol in solution $\rightleftharpoons$ phenol H-bonded to triacetin

Phenol in solution $\rightleftharpoons$ phenol H-bonded to cellulose acetate

This view is supported by the fact that an increase in retention time is brought about by the addition of substances capable of hydrogen bonding to phenol (Table 5), rather than a difference in the height of successive peaks. It may also explain the finding that triacetin on SCA gives a longer retention time than the equivalent amount of triacetin on the relatively inert surface of the support (Fig. 6).

As far as the additives are concerned, a substantial increase in phenol retention is brought about by urea and nicotinamide (Table 5). In the case of polyethylene glycol, however, the increase is about the same as that effected by an equivalent amount of triacetin, as can be read off from the graph (Fig. 6).

Triphenyl phosphine oxide came out quite low in the series, in spite of the extremely high association constant of its complex with phenol (2). It should be kept in mind, however, that it has a high molecular weight, comparisons being made on a basis of equal weight in this investigation.

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SUMMARY

A method is described for the study of the abilities of different substances to remove phenol from a gas stream, with application to the selective filtration of tobacco smoke in mind. Use was made of gas chromatography, measuring the retention time of phenol on columns containing different materials. Differences in the mechanism through which phenol is retained by pure and plasticized cellulose acetates became apparent. A number of substances expected to give hydrogen bonding with phenol were added to the usual cigarette filter materials. Considerable increase in phenol retention was only found in the cases of urea and nicotinamide.

ZUSAMMENFASSUNG

Im Hinblick auf selektive Filtrierung des Tabakrauches wird eine Methode beschrieben, die es ermöglicht, die Eignung verschiedener Stoffe zur Entfernung von Phenol aus einem Gasstrom zu untersuchen. Durch Anwendung der Gaschromatographie wurde die Retentionszeit des Phenols auf verschiedene Substanzen enthaltenden Kolonnen gemessen. Es zeigten sich Unterschiede in den Mechanismen, durch die Phenol durch reine und mit einem Weichmacher versetzte Celluloseacetate zurückgehalten wird. Eine Anzahl von Verbindungen, von denen Wasserstoffbindungen mit Phenol zu erwarten waren, wurden dem üblichen Material der Cigarettenfilter zugesetzt. Eine bedeutende Zunahme in der Phenolretention wurde nur bei Zusatz von Harnstoff und von Nikotinamid festgestellt.

RÉSUMÉ

En vue de la filtration sélective de la fumée de tabac une méthode est décrite par laquelle l'aptitude de diverses substances à éliminer le phénol d'un courant de gaz peut être examinée. Moyennant la chromatographie gazeuse la durée de la rétention de phénol est mesurée sur des colonnes contenant des substances différentes. Les mécanismes par lesquelles l'acétate de cellulose pure et l'acétate de cellulose mélangé avec un émollient retiennent le phénol se montraient être différents. Les matériaux dont les filtres se composent ordinairement étaient mélangés avec

plusieurs substances avec lesquelles se combine, en général, le phénol par liaison hydrogénique. La rétention de phénol n'augmentait d'une manière importante qu'en présence de l'urée et de la nicotinamide.

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