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Parameters Affecting the Selective Filtration of Certain Tobacco Smoke Components*

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INTRODUCTION

The filtration of the thousands of compounds in cigarette smoke, 1350 of which have been identified (1), depends on three fundamental phenomena:

1. Mechanical interaction, in which the solid or liquid particles are mechanically trapped by the filter material. The efficiency of mechanical filtration depends on the size of the aerosol particles, aerosol velocity, and physical form of the filter. The factors affecting mechanical filtration were described in detail by *Overton* (2), *Reynolds* (3), and *Keith* (4).
2. Elution of smoke components, in which certain compounds are trapped initially on the filter and subsequently are eluted from the filter by the aerosol stream. This phenomenon was studied by *Curran* and *Kiefer* (5).
3. Selective removal, in which there is some chemical or physical interaction between the filter material and certain smoke components at a molecular level. This selective filtration by cellulose acetate is probably limited to the "semivolatile" compounds (boiling point 100–300° C).

Although a large number of compounds are known to be selectively removed from smoke (6–9), very little is known about the factors which affect the selective filtration of these compounds. It is widely believed that one criterion for the selective removal of a given compound from cigarette smoke by filtration is that the compound be in liquid-vapor equilibrium. Therefore, selective removal of a compound will depend on its vapor pressure or perhaps on its rate of vaporization.

A second criterion for selective removal of a smoke compound by a filter is that the compound has an affinity for the filter material. A smoke compound which is in liquid-vapor equilibrium in the filter should dissolve in or react with the filter material. When this happens, the compound should be irreversibly removed from smoke.

The purpose of this work was to determine whether there is a correlation between the selective filtration of certain smoke components and certain physical measurements and properties of the compounds. Such a correlation would help in the prediction of which smoke compounds might be removed selectively by filters. In this study, a correlation was found between selective removal of smoke compounds and the equilibrium distribution of these compounds between cellulose acetate and air. A further correlation was found between the selective filtration of certain smoke components and their relative rates of vaporization and solubility parameters.

THEORY

The selectivity, S_x, of a filter for a given compound may be expressed by a number of dimensionless quantities (10–12). The expression

$$S_x = (1 - R_{TPM})/(1 - R_x) \qquad [1]$$

was developed by *Davis* and *George* (10) and was used in this work: R_{TPM} and R_x are the fractional retention of TPM (total particulate matter) and component x, respectively.

The equilibrium distribution coefficient, K_d, for filter material was calculated by the use of equation 2:

$$K_d = \frac{(\text{g compound x/g filter})}{(\text{g compound x/cm}^3 \text{ air})} \qquad [2]$$

The rate of vaporization of aromatic substances is of great interest in the perfume industry. Scientists in this field (13, 14) have found that the rate of vaporization, R_v, can be described by:

$$R_v = kPMD^{1/3} \quad , \qquad [3]$$

where k is a constant, P is the vapor pressure of the compound, M is the molecular weight of the compound, and D is the diffusion coefficient of the compound.

If the rates of vaporization of different compounds are compared under identical conditions, the relative rates of vaporization can be determined by the product $PMD^{1/3}$, known as the nominal coefficient of vaporization, (R'_v).

The vapor pressures of most organic compounds are listed in the literature; however, values for the diffusion

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coefficients are not usually available. The diffusion coefficient, D, in cm^2/s, is the net transport of a substance from one region to another within a single phase. The diffusion coefficient can be calculated from a number of empirical correlations, the most accurate of which was proposed by *Fuller, Schettler,* and *Giddings* (15). The equation is:

$$D = \frac{0.001\ T^{1.75}(1/M_1+1/M_2)^{1/2}}{P[(\Sigma v_1)^{1/3}+(\Sigma v_2)^{1/3}]^2} \quad , \qquad [4]$$

where T is temperature in °K, M_1 and M_2 are the molecular weights of the gas and organic molecules, respectively, and v_1 and v_2 are the atomic diffusion volumes of the gas and organic compounds, respectively. Empirical values for the atomic diffusion volumes for gases are given by *Fuller* et al. (15). The atomic volumes of an organic molecule may be calculated from the number and kinds of atoms in the molecule.

The solubility parameter, δ, of a compound is used to predict and interpret solubility in a semiquantitative manner (16). The solubility parameter is given by:

$$\delta = (-E/v_1)^{1/2} \quad , \qquad [5]$$

where −E is the cohesive energy of the liquid, and v_1 is the molal volume of the liquid.

The value $(\delta_A - \delta_B)^2$ is a measure of the energy of mixing for components A and B and is therefore a measure of the affinity of these two compounds. Estimated values of the solubility parameters for most compounds are obtained from their heat of vaporization, vapor pressure, and solubility data.

EXPERIMENTAL

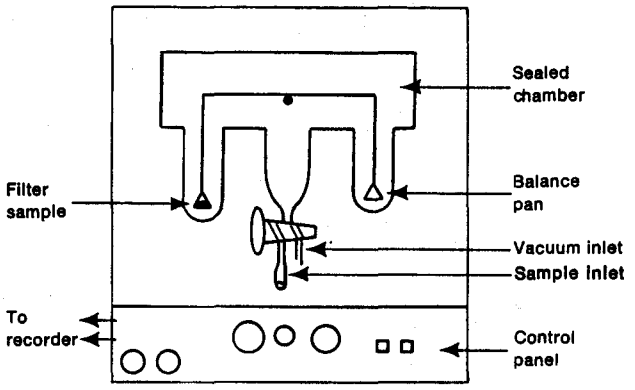
Determination of Selective Filtration

A determination of semivolatile smoke compounds which was described previously (6) was used to measure the filtration of some of the compounds in cigarette smoke. The method is based on the gas chromatographic separation of semivolatile smoke compounds on a 160 m glass capillary column. The details of the method are given in a previous publication. Other selectivity data were taken from publications of *Graham* (7) and *Waltz* and *Häusermann* (8). All of the filtration data for cellulose acetate filters containing triacetin were converted to selectivity coefficients using equation 1.

Determination of Distribution Coefficients

A 10 mm filter segment (50–60 mg) which had been previously dried was placed in a recording electrobalance (Cahn Instrument Co.) and the weight was recorded on a strip chart recorder (Figure 1). The balance chamber was evacuated to approximately 0.1 Torr. Vapor from the test compound was admitted into the sample inlet to attain a pressure of 0.2 to 20 Torr depending on the compound, and the pressure, P, was recorded. The system was closed to the vapor source, and dry air was admitted to bring the system to atmospheric

Figure 1. System for measuring distribution coefficients.



pressure. The weight of the filter was recorded as it absorbed the vapor until equilibrium was reached. The distribution coefficient, K_d, was calculated from the amount of vapor absorbed by the filter and its concentration in the air of the closed system. Ideal gas behavior was assumed at the very low vapor concentration (approximately 5×10^{-4} atm) so the total weight of compound in the chamber initially was calculated from the ideal gas law. The weight of compound in the vapor at equilibrium was calculated by difference:

$$g_x \text{ in air} = g_{total} - g_x \text{ in filter.} \qquad [6]$$

The equilibrium distribution coefficient, K_d, was then calculated by equation 2.

Rate of Vaporization

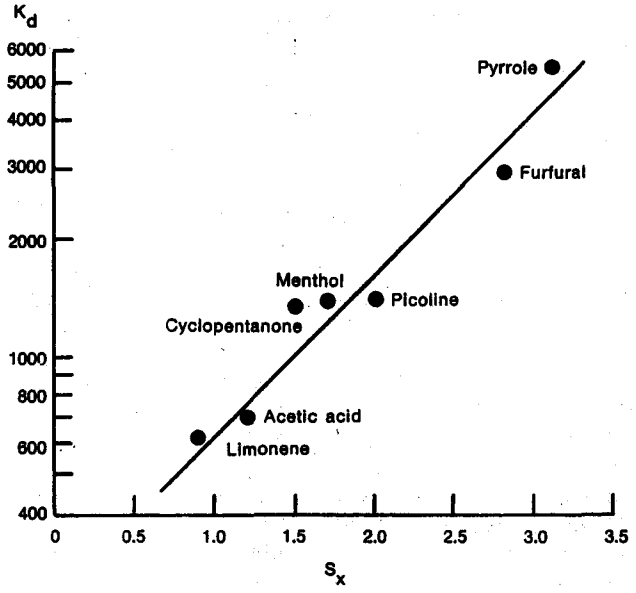
Values for the nominal coefficient of vaporization were calculated from the quantity $PMD^{1/2}$. The vapor pressure of the compounds was taken from the literature (17) or from a computer file maintained by the Design Data Research Laboratory at Tennessee Eastman Company. Diffusion coefficients were calculated from equation 4 with the aid of a computer program. The input to the program consisted of the name and molecular weight of the compound, and the types and numbers of atoms in the compound. A tabular output was obtained with the names of the compounds and their diffusion coefficients listed for 10° increments from 15 to 85° C. Values for solubility parameters were taken from the literature (18), or they were calculated from heat of vaporization data or solubility data.

RESULTS AND DISCUSSION

Correlation of Distribution Coefficient (K_d) with Selective Filtration

The data in Figure 2 indicate a correlation between selective removal of a smoke component with filters and the K_d values obtained for smoke components having a vapor pressure of 0.5 to 20 Torr at 25° C. The K_d values were obtained under ideal conditions; they may be significantly changed under actual smoking conditions. The deposits of TPM and moisture and the

Figure 2. Relationship between selectivity and distribution coefficients.

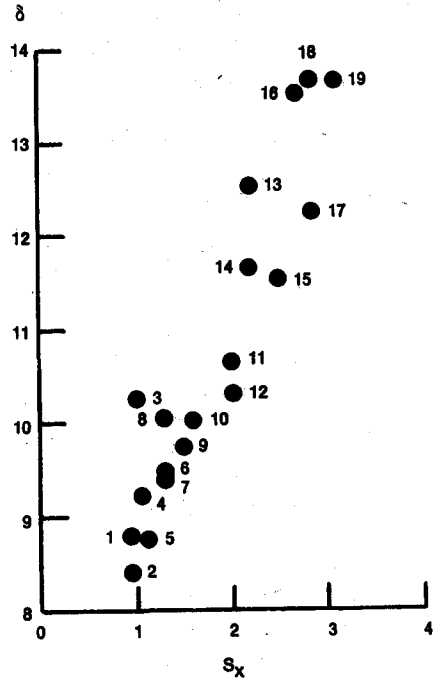


variation in the temperature of filter could influence the selective filtration of specific smoke components. This could account for some of the scatter in the data in Figure 2. This technique may be used to experimentally predict the removal of certain smoke components.

Correlation of Physical Parameters with Selective Filtration

For a compound to be selectively removed from cigarette smoke by a filter, a significant portion of the compound should be in a vapor state as it passes through the filter. Secondly, the compound should have some affinity for the filter medium. This work is an attempt to incorporate these two concepts into an approximate, empirical model. One term in the model is the relative rate of vaporization of smoke compounds, and the other is a measure of their polarity, the solubility parameter.

Figure 3. Relationship between selectivity and solubility parameter.



The relationship of solubility parameters of smoke compounds and their selective removal by cellulose acetate filters is shown in Figure 3. A general increase in the selective removal of compounds occurs with increasing solubility parameter. This trend is somewhat surprising considering that the total solubility parameters for cellulose acetate and triacetin are 11.1 and 10.7, respectively. Usually, a measure of the solubility or affinity of two components is given by $(\delta_A - \delta_B)^2$. Thus, one might expect compounds with a total solubility parameter of about 11 to have an optimum affinity for cellulose acetate filters. However, after one puff of smoke is taken on the cigarette, water and particulate matter from smoke are present on the filter. The presence of these substances, particularly water, must affect the subsequent removal of the polar smoke compounds. Thus, the very polar compounds such as pyrrole ($\delta = 13.6$) are removed to a greater extent than compounds of intermediate polarity ($\delta = 11$).

The relationship of the selective removal, S_x, as defined by equation 1 to the nominal coefficient of vaporization, R'_v, is shown by Figure 4. These data follow a general trend and pass through a maximum in the region $R'_v = 100{,}000$. The compounds included in this work as well as the numerical values of S_x and other parameters are given in Table 1. The data indicate that certain hydrocarbons have a sufficient vapor pressure or rate of vaporization to be selectively removed, but

Figure 4. Relationship between selectivity and rate of vaporization.

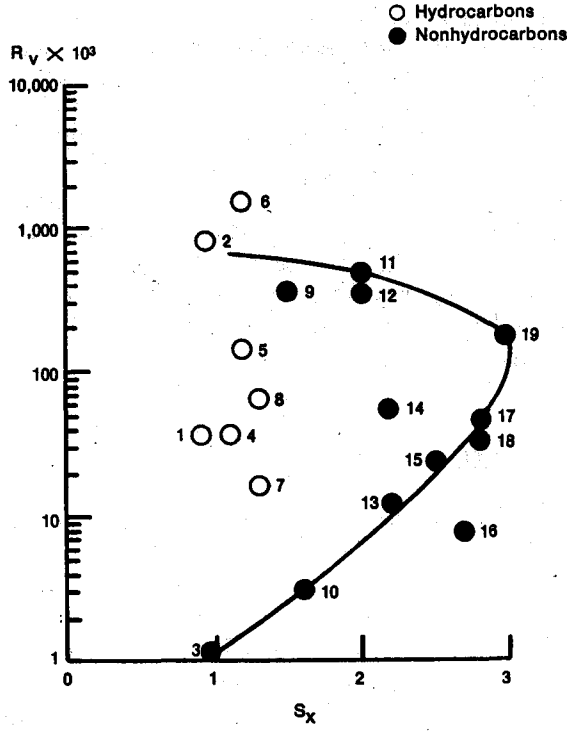


Table 1. Physical data on smoke compounds.

	Selectivity (S_x)	Vapor pressure (P)	Solubility parameter (δ)	Vaporization rate ($R_v \times 10^3$)
1. Limonene	0.9	1.0	8.78	36
2. Ethylcyclopentene	0.9	36	8.34	946
3. Eugenol	1.0	0.02	10.28	1.0
4. Methylindane	1.1	1.1	9.23	37
5. Cumene	1.2	4.6	8.60	146
6. 3-Heptyne	1.2	40	7.76	1052
7. Methylindene	1.3	0.5	9.48	16
8. Indene	1.3	1.7	10.07	68
9. 2-Cyclopentanone	1.5	11	9.72	350
10. Ethylphenol	1.6	0.1	10.01	2.8
11. Pyridine	2.0	20	10.62	490
12. 2-Picoline	2.0	10	10.30	360
13. o-Cresol	2.2	0.4	12.50	12
14. Acetylfuran	2.2	1.1	11.64	56
15. 5-Methylfurfural	2.5	0.5	11.52	24
16. Phenol	2.7	0.3	13.50	7.5
17. Furfural	2.8	1.6	12.19	47
18. Furfural alcohol	2.8	0.8	13.64	31
19. Pyrrole	3.1	8.2	13.61	180

they apparently do not have a sufficient affinity for the cellulose acetate.

To determine if a correlation exists between the vaporization rate, solubility parameter, and the selective filtration of smoke compounds by cellulose acetate, a nonlinear regression analysis was performed. The data were found to fit the following equation:

$$S_x = b_o + b_1\delta + b_2\delta\ (\ln R_v). \qquad [7]$$

The values for the constants b_o, b_1 and b_2 are -2.51, 0.28, and 0.01, respectively. Table 2 is a comparison of the actual selectivity data on the compounds investigated to the selectivity calculated from equation 7. The correlation coefficient for the observed and calculated values of S_x is 0.94; the average difference between these two values is 10%. The experimental selectivity values depend on both the accuracy of the TPM removal and the removal of component x. This work shows that it is possible to predict if a compound will be selectively removed from smoke by cellulose acetate filters. A compound having a nominal coefficient of vaporization of 10^2 and a high solubility parameter ($\delta = 13$) will be selectively removed from cigarette smoke by cellulose acetate filters containing triacetin.

SUMMARY

The purpose of this investigation was to attain a better understanding of the selective removal of certain compounds from cigarette smoke by filters. A gas chromatographic method for the determination of selected semivolatile smoke compounds was developed. The method, which utilizes a 160 m glass capillary column, was used to determine the efficiency of filters for the removal of these selected semivolatile compounds. A correlation was found between the selective filtration of these compounds from cigarette smoke and their distribution coefficients [K_d = (g compound/g filter)/(g compound/cm^3 air)] between air and various filter materials. In addition, a correlation was found between the physical and chemical nature of certain smoke compounds and their selective filtration. Previous work indicated that if a compound is to be selectively removed from tobacco smoke by a filter, [1] a significant portion of that compound should be in the vapor state as it passes through the filter and [2] the compound should have an affinity for the filter material. The relative rate of vaporization (R_v) was used as a measure of 1., and the total solubility parameter (δ) was taken as a measure of 2. Values for the vaporization rate were calculated from the product, vapor pressure (P), molecular weight (M), and diffusion coefficient (D), ($R_v = kPMD^{1/3}$). The correlation of R_v and δ with the selectivity (S_x) of cellulose acetate filters for smoke compounds is described by

$$S_x = b_o + b_1\delta + b_2\delta\ (\ln R_v),$$

where b_o, b_1, and b_2 are constants.

This equation may be used to predict the selective filtration of semivolatile compounds from cigarette smoke.

Table 2. Comparison of observed and calculated selectivities.

No. Compound	S_x observed	S_x calculated	Difference	Difference %
1. Limonene	0.90	0.97	0.07	8
2. Ethylcyclopentene	0.90	1.13	0.23	26
3. Eugenol	1.00	1.14	0.14	14
4. Methylindane	1.10	1.18	0.08	7
5. Cumene	1.20	1.07	0.13	11
6. 3-Heptyne	1.20	0.92	0.28	23
7. Methylindene	1.30	1.18	0.11	8
8. Indene	1.30	1.60	0.30	22
9. 2-Cyclopentanone	1.50	1.64	0.14	9
10. Ethylphenol	1.60	1.20	0.40	25
11. Pyridine	2.00	2.04	0.04	2
12. 2-Picoline	2.00	1.88	0.12	6
13. o-Cresol	2.20	2.33	0.13	6
14. Acetylfuran	2.20	2.20	0.00	0
15. 5-Methylfurfural	2.50	2.06	0.44	18
16. Phenol	2.70	2.64	0.05	2
17. Furfural	2.80	2.40	0.40	14
18. Furfural alcohol	2.80	2.92	0.12	4
19. Pyrrole	3.10	3.11	0.01	0
			Average	10.7

ZUSAMMENFASSUNG

Die hier beschriebenen Untersuchungen hatten ein besseres Verständnis der selektiven Retention bestimmter Rauchinhaltsstoffe durch Filter zum Ziel. Für die

Bestimmung ausgewählter halbflüchtiger Verbindungen des Rauches wurde ein gaschromatographisches Verfahren entwickelt. Die Methode, bei der eine Glaskapillarsäule von 160 m Länge benutzt wurde, wurde eingesetzt, um die Wirksamkeit von Filtern in der Entfernung dieser ausgewählten Verbindungen zu bestimmen. Es wurde eine Korrelation zwischen der selektiven Filtration der Verbindungen aus dem Cigarettenrauch und deren Verteilungskoeffizienten [K_d = (g Verbindung/g Filter) / (g Verbindung/cm³ Luft)] zwischen Luft und verschiedenen Filtermaterialien gefunden. Darüber hinaus wurde eine Korrelation zwischen der physikalischen und chemischen Beschaffenheit bestimmter Rauchinhaltsstoffe und deren selektiver Filtration beobachtet. Frühere Arbeiten hatten gezeigt, daß, wenn eine Verbindung aus dem Tabakrauch durch einen Filter selektiv entfernt werden soll, [1] die Verbindung sich bei der Passage durch den Filter zu einem signifikanten Anteil in dampfförmigem Zustand befinden und [2] eine Affinität von der Verbindung zum Filtermaterial bestehen sollte. Die relative Verdampfungsrate (R_v) diente als Maß für 1., und der Gesamtlöslichkeitsparameter (δ) als Maß für 2. Die Berechnung der Verdampfungsrate basierte auf dem Produkt, dem Dampfdruck (P), dem Molekulargewicht (M) und dem Diffusionskoeffizienten (D), ($R_v = kPMD^{1/3}$). Die Korrelation zwischen R_v und δ und der Selektivität (S_x) von Celluloseacetatfiltern gegenüber Rauchinhaltsstoffen wird mit der Gleichung

$$S_x = b_0 + b_1\delta + b_2\delta\ (\ln R_v)$$

beschrieben, in der b_0, b_1 und b_2 Konstanten sind.
Diese Gleichung kann für die Beurteilung der selektiven Filtration von halbflüchtigen Inhaltsstoffen des Cigarettenrauches benutzt werden.

RESUME

Le but de cette étude est une meilleure compréhension de l'élimination sélective, par des filtres, de certains composés de la fumée de cigarette. On a mis au point une méthode de chromatographie en phase gazeuse pour la détermination de certains composés semi-volatils de fumée. Dans cette technique, on se sert d'une colonne capillaire de verre de 160 m. On l'a utilisé pour déterminer l'efficacité de filtres à éliminer les composés semi-volatils sélectionnés. On a pu trouver une corrélation entre la filtration sélective de ces composants de fumée et leurs coefficients de distribution entre l'air et différents matériaux de filtre [K_d = (g composé / g filtre) / (g composé / cm³ air)]. En outre, on a trouvé une corrélation entre les caractéristiques physiques et chimiques de certains composants de fumée et leur filtration sélective. Des travaux précédents ont indiqué que pour qu'un composé soit sélectivement éliminé par un filtre, il faut [1] qu'une partie importante de ce composé soit en phase vapeur en passant par le filtre et [2] que ce composé doit avoir une affinité pour le matériau dont le filtre est fabriqué. On a pris le taux relatif d'évaporation (R_v) comme mesure du 1° et le paramètre de solubilité totale (δ) comme mesure du 2°. Les taux d'évaporation ont été calculés à partir du produit, de la tension de vapeur (P), du poids moléculaire (M) et du coefficient de diffusion (D). La formule utilisée est $R_v = kPMD^{1/3}$. La corrélation de R_v et δ avec la sélectivité (S_x) des filtres en acétate de cellulose pour les composants de fumée est décrite par la formule suivante:

$$S_x = b_0 + b_1\delta + b_2\delta\ (\ln R_v),$$

où b_0, b_1 et b_2 sont des constantes.
Cette équation peut être utilisée pour prédire la filtration sélective des composants semi-volatils de la fumée de cigarette.

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