

Vapor Phase Analysis of Tobacco Smoke

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Tobacco
Methanol
Formaldehyde

Introduction

The smoke stream issuing from burning tobacco products contains, in addition to the billions of visible smoke particles, a highly complex mixture of atmospheric gases and volatile combustion products. In the case of cigarette smoke this gaseous mixture represents 90 to 95 per cent of the mass of the effluent stream and contains a large number of components of widely differing volatilities which are present in widely differing concentrations. Over 95 per cent of the mixture comprises seven major components, nitrogen, oxygen, carbon dioxide and monoxide, hydrogen, argon, and methane and has been extensively studied both as to overall quantity and variations in quantity within a burning cigarette (15, 17, 19, 20). A considerable array of components makes up the balance of the mixture, and many of these have been identified and estimated (7, 19, 20, 21, 22).

The complexity of the vaporous mixture, and the extremely minute concentrations of the minor components when combined with the rapidly changing character of the mixture due to chemical and physical inter-action of it with the condensed smoke particles make its analysis

rather difficult. Previous studies have generally involved the low temperature condensation of smoke vapors from a number of cigarettes and the extensive fractionation of the condensate. Such techniques in addition to being time consuming generally permit the partial loss of some components through imperfect collection, volatilization during fractionation, or through chemical interaction of the condensed vapors. Also the results obtained by such methods are quite dependent on the collection system employed, as this frequently alters the partition of the less volatile components between the vapor and the particulate phases.

The recent increase of interest in the gas phase of cigarette smoke has made it desirable to develop a rapid and quantitative analytical system for its minor gaseous components. Many of these materials have long been known to be of physiological significance in concentrations far in excess of their reported levels in tobacco smoke, and have variously been classified as irritating, anaesthetic, or toxic vapors. In their minute concentrations in tobacco smoke, their chief contribution has been towards imparting the indefinite physiological sensations of "bite" and "sting" to the taste of the smoke. Recently Kensler and Battista (13) demon-

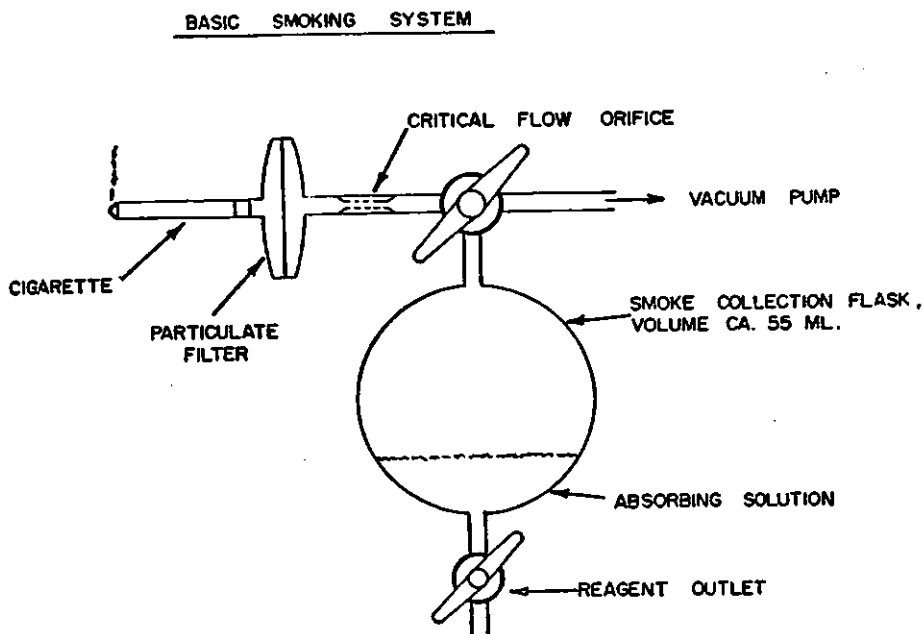


Figure 1. Basic Smoking System

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strated a more specific effect in their finding that the vapor phase of cigarette smoke can inhibit the action of mammalian ciliated tissue, and thereby interfere with the ability of the lung and trachea to eliminate foreign matter (6). They also have found that gaseous smoke constituents such as hydrogen cyanide, ammonia, acrolein, and formaldehyde inhibit ciliary motion at concentrations approaching those found in ordinary cigarette smoke. A companion development has been the introduction of a considerable variety of adsorbent bearing filters which serve to selectively reduce the levels of a number of the components of the gas phase.

To fulfill this need for a suitable gas phase analytical system, this paper describes a system for quantitatively collecting smoke samples, and applying a variety of colorimetric, electrometric, and chromatographic techniques to the unfractionated sample. As an illustration of the utility of the system, comparative data on eighty gaseous components

issuing from three different types of cigarettes are presented. It is thought that these techniques would also be of use in studies of other complex vapor systems.

Experimental

1. Smoking and Sample Collection System.

A simple smoking system which allows the quantitative collection and subsequent rapid analysis of the gaseous phase of a single puff of smoke is illustrated in Figure 1. The components are the cigarette under study, a particulate smoke filter, a flow limiting orifice, and an evacuated flask which provides the source of suction to withdraw the puff and also wholly contain the vapor sample. In the modification illustrated in Figure 1, the flask contains 10 ml of an absorbing solution appropriate to the component under study. In operation the flask is evacuated by an external pump, and the puff is taken by turning the three-way stopcock to connect the orifice, filter, and the previ-

ously lighted cigarette to the flask. Following the puff the sample of smoke vapors in the flask are transferred to the absorbing solution by manual shaking. The puff characteristics are controlled by the free volume of the flask (ca. 45 ml with 10 ml of absorbing solution), the vacuum drawn on the flask (27 in Hg), and the hole diameter of the orifice (0.508 mm). These parameters are found to provide a normal human puff volume of 40 ml with an appropriate velocity distribution during the two second duration of the puff.

The particulate filter (Cambridge CM-113 glass fiber filter) provides a crude separation of the particulate and vaporous smoke, and can be discarded if a total smoke sample is desired. Since the division of materials effected by such filters is generally becoming empirically defined as the division between particulate and gaseous tobacco smoke, and since the vaporous components of pharmacological interest pass through such filters, they have been used throughout these experiments.

Table 1. Flame response data, compared to n-hexane
 1×10^{-7} moles n-hexane—5415 integrator counts.

| Compound | No. of C atoms in molecule | Functional group | Change in response, No. of C atoms | Effective No. of C atoms in molecule Exp. | Literature (3) |
|-----------------------------------|----------------------------|---|------------------------------------|---|-------------------|
| Ethane | 2 | ... | +0.03 | 2.03 | 1.98 |
| Propene | 3 | ... | -0.07 | 2.93 | 2.88 |
| Butane | 4 | ... | -0.09 | 3.91 | |
| Isoprene (2-methyl-1,3-butadiene) | 5 | ... | 0.00 | 5.00 | |
| Benzene | 6 | ... | +0.12 | 6.12 | 6.00 |
| Acetonitrile | 2 | C≡N | ... | ... | 1.35 |
| Acrylonitrile | 3 | C≡N | -0.73 | 2.47 | |
| Propionitrile | 3 | C≡N | -0.64 | 2.36 | |
| Isobutyronitrile | 4 | C≡N | -0.64 | 3.36 | |
| Furan | 4 cycl. ether, C-O- | | -0.99 | 3.01 | 2.97 ^a |
| Methylfuran | 5 cycl. ether, C-O- | | -1.12 | 3.88 | 2.9 ^a |
| Methylacetate | 3 | $\begin{array}{c} \text{O} \\ // \\ \text{C}-\text{O}-\text{C} \end{array}$ | -1.27 | 1.73 | |
| Ethyl acetate | 4 | $\begin{array}{c} \text{O} \\ // \\ \text{C}-\text{O}-\text{C} \end{array}$ | -1.28 | 2.72 | 2.49 |
| Acetone | 3 | C-O | -0.85 | 2.15 | 2.00, 1.8 |
| 2-Butanone | 4 | C-O | -0.91 | 3.09 | 3.16 |
| 2-Pentanone | 5 | C-O | -1.02 | 3.98 | |
| 2,3-Butanedione | 4 | Two, C-O | -1.87 | 2.13 | |
| Acetaldehyde | 2 | C-O | -1.07 | 0.93 | |
| Propionaldehyde | 3 | C-O | -1.2 | 1.88 | |
| Isobutyraldehyde | 4 | C-O | -1.22 | 2.78 | 2.83 |
| Methanol | 1 | C-OH | -0.26 | 0.74 | 0.75 |

^a Diethyl ether

per cent *N,N*-dimethyl-*p*-phenylene diamine chloride in 1:1 HCl and 0.5 ml of 0.2 *M* aqueous FeCl₃, are added to the absorbing solution. After complete color development within 2 hours the solution is transferred and made up to 25 ml volume and its absorbance determined at 665 m μ against a reagent blank. Comparison of these with known sulfide solutions yielded the level of H₂S in smoke gases in micrograms per puff. Possible interfering materials, including heavy metals, oxidizing substances and other sulfide reactants present in smoke gases, were investigated and found to be present in insufficient quantities in smoke to seriously interfere with the measurement of H₂S.

Alternatively, the second modification of the basic smoking system can be used for estimating the H₂S coming from a whole cigarette rather than from individual puffs. In such experiments, the volumes of the various reagents are increased fivefold.

c. Nitrogen Oxides

The Saltzman (23) procedure utilizing Griess-Ilosvay reagent was found to be satisfactory for estimating the nitric oxide and nitrogen dioxide in cigarette smoke. 10 ml of an aqueous absorbing solution containing 20 mg of *N*-(1-naphthyl)-ethylene diamine dihydrochloride, five g of sulfanilic acid, and 140 ml of glacial acetic acid per liter was contacted with individual puffs of smoke vapors in the collection flasks. After one hour for oxidation of NO to NO₂ and for complete color development, the NO and NO₂ concentrations were estimated by the amounts of pink azo dye formed, as measured by the optical density of the reaction mixture at 550 m μ . Other experiments (14, 18) have shown that the mixture of nitrogen oxides in fresh tobacco smoke is in fact almost exclusively nitric oxide and that nitrogen dioxide is only detected if there is an appreciably long wait between generation and collection of the gaseous mixture, this arising through oxidation of the initial NO to NO₂. Because of this finding, all data are computed and reported herein in terms of μ g per puff of NO.

Saltzman (23) has investigated possible interference in the NO determination from other atmospheric pollutants. For the most part, the most active materials, such as ozone, sulfur dioxide, chlorine have not been reported to be present in tobacco smoke and the method appears to be well suited for smoke gas anal-

Table 2. Effect of cigarette filters on the yield of vaporized components. 85 mm blended cigarettes, components in order of increasing boiling point for each class.

| Material | No Filter | Yield in micrograms per 40 ml puff Acetate Filter | Yield in micrograms per 40 ml puff Combined Acetate Adsorbent Filter |
|---|-----------|--|---|
| Hydrocarbons: | | | |
| methane | 97 | 117 | 108 |
| ethylene | 22 | 21 | 20 |
| ethane | 51 | 67 | 61 |
| acetylene | 2.7 | 3.3 | 2.6 |
| propene | 25 | 27 | 24 |
| propane | 23 | 26 | 22 |
| propadiene | 0.5 | 0.5 | 0.3 |
| propyne | 0.7 | 0.9 | 0.9 |
| 2-methylpropane | 2.3 | 2.8 | 1.7 |
| 2-methylpropene | 6.6 | 7.7 | 4.4 |
| 1-butene | 6.2 | 7.6 | 4.6 |
| 1,3-butadiene | 4.3 | 5.4 | 2.8 |
| butane | 7.0 | 8.4 | 4.5 |
| <i>cis</i> -2-butene | 4.1 | 4.4 | 2.8 |
| <i>trans</i> -2-butene | 2.9 | 3.6 | 2.1 |
| 1,2-butadiene | 0.2 | 0.2 | 0.1 |
| 3-methyl-1-butene | 1.6 | 1.9 | 0.9 |
| 2-methylbutane | 1.9 | 2.1 | 1.2 |
| 1-pentene | 1.9 | 2.3 | 1.1 |
| 2-methyl-1-butene | 2.4 | 2.5 | 1.1 |
| isoprene (2-methyl-1,3-butadiene) | 47 | 47 | 18 |
| pentane | 2.3 | 2.5 | 1.0 |
| <i>trans</i> -2-pentene | 1.5 | 1.5 | 0.8 |
| <i>cis</i> -2-pentene | 1.0 | 1.1 | 0.5 |
| 2-methyl-2-butene | 6.8 | 8.5 | 3.2 |
| <i>cis</i> -1,3-pentadiene | 1.9 | 1.9 | 0.8 |
| <i>trans</i> -1,3-pentadiene | 1.2 | 1.2 | 0.5 |
| cyclopentene | 0.7 | 0.7 | 0.3 |
| 1,4-pentadiene | 0.2 | 0.2 | 0.1 |
| cyclopentane | 0.2 | 0.2 | 0.1 |
| 4-methyl-1-pentene | 0.4 | 0.4 | 0.2 |
| 4-methyl-2-pentene (<i>cis</i> + <i>trans</i>) | 0.4 | 0.4 | 0.2 |
| 2-methylpentane | 0.6 | 0.6 | 0.3 |
| 3-methylpentane | 0.2 | 0.2 | 0.1 |
| hexane | 1.0 | 1.2 | 0.5 |
| methyl cyclopentane | 0.2 | 0.2 | 0.1 |
| benzene | 6.1 | 5.9 | 1.9 |
| toluene | 9.7 | 8.7 | 2.9 |
| Alcohols: | | | |
| methanol | 13 | 10 | 1.8 |
| Aldehydes: | | | |
| formaldehyde | 4.1 | 3.6 | 3.5 |
| acetaldehyde | 81 | 82 | 48 |
| propionaldehyde | 6.9 | 6.7 | 2.4 |
| acrolein | 8.2 | 7.9 | 2.9 |
| isobutyraldehyde | 3.6 | 3.3 | 1.0 |
| methacrolein | 0.9 | 0.9 | 0.2 |
| glyoxaldehyde | trace | trace | 0.0 |
| butyraldehyde | 0.8 | 0.8 | 0.2 |
| isovaleraldehyde | 3.3 | 3.3 | 0.5 |
| valeraldehyde | 0.1 | 0.1 | trace |
| acetonaldehyde | 1.6 | 1.6 | 0.3 |
| 2-methylvaleraldehyde | 1.3 | 1.1 | 0.2 |

Table 2. (Continued)

| Material | Yield in micrograms per 40 ml puff | | |
|-----------------------|------------------------------------|----------------|-----------------------------------|
| | No Filter | Acetate Filter | Combined Acetate Adsorbent Filter |
| Ketones: | | | |
| acetone | 42 | 39 | 13 |
| 2-butanone | 10 | 9.4 | 2.3 |
| butenone | 3.7 | 3.5 | 0.9 |
| 2,3-butanedione | 15 | 15 | 3.9 |
| 3-methyl-2-butanone | 1.0 | 1.0 | 0.2 |
| 2-pentanone | 2.3 | 1.9 | 0.5 |
| 3-pentanone | 0.5 | 0.5 | 0.2 |
| Esters: | | | |
| methyl formate | 3.6 | 3.5 | 1.2 |
| ethyl formate | 0.5 | 0.5 | 0.2 |
| methyl acetate | 1.7 | 1.6 | 0.5 |
| isopropyl formate | 0.6 | 0.5 | 0.1 |
| vinyl acetate | 0.5 | 0.5 | 0.2 |
| ethyl acetate | 1.0 | 1.0 | 0.3 |
| Cyclic Ethers: | | | |
| furan | 4.6 | 4.3 | 1.7 |
| 2-methylfuran | 5.8 | 5.4 | 1.5 |
| tetrahydrofuran | trace | trace | 0.0 |
| 2,5-dimethylfuran | 4.9 | 4.5 | 1.0 |
| Nitriles: | | | |
| hydrogen cyanide | 32 | 29 | 11 |
| acrylonitrile | 1.5 | 1.3 | 0.4 |
| acetonitrile | 18 | 15 | 5.8 |
| methacrylonitrile | 0.4 | 0.4 | 0.1 |
| propionitrile | 2.8 | 2.5 | 0.7 |
| isobutyronitrile | 1.0 | 0.9 | 0.2 |
| crotonitrile | 0.4 | 0.4 | 0.1 |
| Miscellaneous: | | | |
| nitric oxide | 30 | 35 | 41 |
| methyl chloride | 19 | 24 | 22 |
| hydrogen sulfide | 3.4 | 3.1 | 1.3 |
| ammonia ^a | 12 | 13 | 7.6 |
| thiophene | 0.1 | 0.1 | trace |

^a Total of ammoniacal compounds determinable by the Nessler procedure, expressed as the equivalent micrograms of ammonia.

ysis.

d. Ammoniacal Compounds

Compounds in tobacco smoke that yield the ammonium ion in an acidic solution can be conveniently estimated by the colorimetric Nessler method (3, 11, 24) applied to smoke gas samples trapped in 0.02 N H₂SO₄. The basic smoking system containing 10 ml of acid solution per puffing flask was utilized. The H₂SO₄ trapping solutions from each flask were subsequently heated for 1 hour at 90-100° to expel interfering acidic gases and acetone. After cooling to 25°, addition of Nessler's reagent, and dilution to 25 ml, the optical density at 450 mμ was measured. Comparison of these observed absorbances with those of known (NH₄)₂SO₄ solutions provided a

measure of the ammoniacal compound content of smoke. This method does not differentiate between ammonium compounds and free ammonia.

Hydrogen sulfide and acetone are found to interfere with the determination of the ammonium ion through formation of colloidal products with Nessler's reagent. The extensive heating step is found to eliminate these materials from the absorbing solution, and thus avoid their interference.

e. Formaldehyde

Formaldehyde in cigarette smoke can most conveniently be estimated by the chromotropic acid method (1, 25) and alternately and less conveniently by Schryver's method (12). Utilizing the basic puffing flasks,

five ml of 0.1 per cent aqueous chromotropic acid solution (1,8-dihydroxynaphthalene-3,6-disulfonic acid) is utilized as an absorbing solution. After smoking and absorption of the smoke gases the solution is transferred to a 50 ml volumetric flask and 43 ml of concentrated H₂SO₄ is added. Color development is essentially immediate due to the heat of reaction of sulfuric acid and water. Subsequently on cooling the solution is made up to 50 ml with water and the optical density measured at 580, 500 and 600 mμ, the short and long wavelength values being for the purpose of providing a base line correction for the formaldehyde-chromotropic acid peak, thus eliminating acrolein interference. The amount of formaldehyde is calculated by comparison of the absorbance of smoke solutions with that of known formaldehyde solutions.

A variety of known smoke components including unsaturated and aromatic hydrocarbons, nitric oxide, aldehydes, ketones, phenols and alcohols were tested for possible interference with the formaldehyde reaction. In general, unsaturated hydrocarbons and acrolein were found to interfere, but the utilization of the aqueous collection system and the base line correction essentially eliminated these effects. It was found that the particulate smoke collected on Cambridge filter pads adsorbed appreciable quantities of formaldehyde, so that it was necessary to use a fresh pad for each individual puff.

Because of the possible lack of specificity of the chromotropic acid method for formaldehyde, additional estimations were made by Schryver's method (12) which involves the formation of an intense magenta coloration by the reaction of formaldehyde phenylhydrazone with potassium ferricyanide. Smoke gases were collected in 10 ml of 1 per cent aqueous phenylhydrazine hydrochloride solution. Subsequently this solution was diluted with water to 50 ml and a 10 ml aliquot of this was combined with one ml of freshly prepared 5 per cent K₃Fe(CN)₆ in water and four ml of 31.5 per cent HCl in water. The reaction mixture was diluted to 25 ml and its absorbance determined at 525 mμ within 10 minutes. Comparable results were obtained with both methods.

3. Chromatographic Techniques

Most of organic materials in cigarette smoke vapors are most conveniently estimated by gas-liquid chromatographic techniques. While

tive, and are based on the retention times of the individual materials on different column packings and on a comparison of this work with that of others. For the hydrocarbons listed in Table 2, Osborne *et al.* (19) and Philippe *et al.* (20, 21, 22), have provided sufficient evidence of the presence of most of these materials in cigarette smoke. Since our hydrocarbon column (column I) was essentially that used subsequently by Philippe (21) with the same elution order of hydrocarbons, the identity of these materials is fairly well established. For the oxygenated components analyzed with columns II and III, the considerable alteration of elution times between these packings and the comparison of these data with those of Irby and Harlow (9) and Grob (7) allows a tentative assignment of these materials. Figures 3 and 4 show the chromatographic tracings obtained with columns I, II, and III with and without the additional mercuric perchlorate and boric acid columns. These illustrate the degree of separation achieved. In Figure 3, the thorough scavenging effect of the mercuric perchlorate for unsaturated hydrocarbons is clearly shown, which allows the resolution of all but one of the overlapping peaks.

Considerably greater mixing of components is apparent in Figure 4, where eight to 10 overlapping peaks are evident in the two chromatograms. The considerably different polarities of these two columns resulted in a pronounced change in retention times for a number of components, thus allowing an interchange of partners in the mixed peaks. It was thus possible to resolve each mixture by means of difference calculations.

Calibration data using individual components and mixtures thereof were obtained for estimation of the amounts of each material. As has been reported previously (4), each class of compound was found to exhibit a linearly increasing flame ionization detector response with increasing numbers of carbon atoms in the molecule. The difference between classes of compounds which are primarily dependent on the nature of the functional groups present can be expressed in terms of an effective number of carbon atoms (N_c). For hydrocarbons N_c is essentially equal to the number of carbon atoms, while for materials containing carbon-oxygen bonds, the effective number is generally one unit less than the actual number. Table 1 summarizes some of our calibra-

tion data in terms of this quantity, which is measured relative to *n*-hexane, and compares these with values reported in the literature (4).

The general agreement between N_c values computed from our calibration data and those reported in the literature is useful in that it provides a check on our calibration procedures. Although calibration data were obtained for most of the compounds reported herein, the linearity of the flame response for homologous series was occasionally used to estimate minor members of such a series and provided a further check on the individual calibrations.

2. Analysis of Cigarette Smoke.

To demonstrate the utility of these methods, comparative data on three different types of cigarettes were obtained. These were chosen to demonstrate the effect of cigarette filters on this array of minor gaseous smoke components. All three cigarettes had the same tobacco column, which consisted of a commercial blend of the major types of cigarette tobaccos. The first sample, labelled "no filter," is representative of an 85mm unfiltered cigarette. The second, labelled "acetate filter," is also 85 mm long and is equipped with a 15 mm cellulose acetate filter, and is found to be quite similar to most ordinary commercial filter cigarettes in its smoke and gas filtration properties. The third 85 mm cigarette, labelled "combined acetate adsorbent filter,"

is equipped with a 20 mm combination filter consisting of two outer sections of cellulose acetate surrounding a five to six mm cavity filled with 100 to 120 milligrams of a specially impregnated granulated charcoal adsorbent.

The yields of minor gaseous components obtained from these cigarettes are given in Table 2. As is apparent from this table tobacco smoke contains a highly complex mixture of gaseous materials. As noted by Philippe *et al.* (21) the array of hydrocarbons approximates that of thermally cracked gasoline. The composition of the whole mixture suggests a combination of a randomized series of pyrolytic reactions which would form a large number of individual components and some destructive and non-destructive distillations which would generate the greater than expected amounts of such materials and 2,3-butanedione.

A striking feature of these data is the capacity of the adsorbent bearing filter to remove appreciable quantities of the less volatile gaseous constituents of tobacco smoke. Materials boiling above -30° to -10° are appreciably extracted from the smoke stream by the adsorbent and removals of up to 85 per cent are achieved for some of the less volatile materials. Although the contact time between the flowing smoke stream and the charcoal is only of

Table 3. Variation of the delivery of hydrogen cyanide and formaldehyde during the smoking process.

Combined acetate-adsorbent filtered cigarettes

1. Hydrogen cyanide ($\mu\text{g}/40$ ml puff) Cigarette/puff No.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Average(2-8) |
|---------|------|-----|------|------|------|------|------|------|--------------|
| 1 | 6.5 | 4.8 | 7.7 | 9.9 | 9.5 | 7.9 | 10.7 | 12.5 | 9.0 |
| 2 | 10.3 | 7.6 | 12.0 | 8.7 | 10.2 | 15.0 | 12.3 | 14.2 | 11.4 |
| 3 | 3.0 | 4.2 | 6.7 | 7.5 | 9.2 | 6.2 | 13.0 | 14.0 | 8.6 |
| 4 | 3.4 | 7.0 | 9.7 | 13.2 | 8.4 | 12.4 | 20.6 | 17.6 | 12.7 |
| 5 | 6.4 | 4.8 | 10.7 | 10.6 | 8.7 | 8.3 | 16.2 | 18.5 | 11.1 |
| AVERAGE | 5.9 | 5.7 | 9.2 | 10.0 | 9.2 | 10.0 | 14.6 | 15.4 | 10.6 |
| S.D. | 2.9 | 1.5 | 2.4 | 2.2 | 0.7 | 3.6 | 3.9 | 2.6 | 1.7 |

2. Formaldehyde ($\mu\text{g}/40$ ml puff) Cigarette/puff No.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Average(2-8) |
|---------|------|-----|-----|-----|-----|-----|-----|-----|--------------|
| 1 | 7.0 | 2.9 | 1.1 | 1.7 | 1.2 | 1.5 | 1.2 | 2.2 | 1.7 |
| 2 | 5.9 | 3.5 | 1.3 | 2.5 | 2.0 | 1.3 | 1.9 | 1.5 | 2.0 |
| 3 | 10.4 | 4.1 | 2.8 | 3.3 | 4.3 | 3.4 | 4.5 | 3.6 | 3.7 |
| 4 | 5.9 | 2.0 | 2.0 | 2.2 | 2.0 | 1.0 | 2.1 | 2.7 | 2.0 |
| 5 | 8.2 | 3.2 | 3.0 | 2.8 | 2.7 | 2.6 | 3.9 | 4.7 | 3.3 |
| AVERAGE | 7.5 | 3.1 | 2.0 | 2.5 | 2.4 | 2.0 | 2.7 | 2.9 | 2.5 |
| S.D. | 1.9 | 0.8 | 0.9 | 0.2 | 1.1 | 1.0 | 1.4 | 1.2 | 0.9 |