

A Review of the Uses of Nuclear Radiation in Tobacco and Smoke Research *

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SUMMARY

In summary, nuclear radiation has been widely used to elucidate many aspects of the mechanisms of tobacco being converted to smoke. In addition, the mechanisms of smoke transfer, tobacco inorganic chemistry and smoke filtration have been clarified by many authors worldwide. The newer techniques now being developed, using radiation detection coupled with the enhanced use of electronic-data reduction and interpretation, promise to continue the important role these techniques have played in understanding smoke-formation mechanisms.

ZUSAMMENFASSUNG

Zur Erforschung der einzelnen mit der Umwandlung des Tabaks zu Rauch verbundenen Prozesse machte man sich allgemein vielfach die radioaktive Strahlung zunutze. Auch wurde auf diese Weise in vielen Forschungsprojekten weltweit untersucht, unter welchen Bedingungen Inhaltsstoffe des Tabaks in den Rauch übergehen, welche anorganischen Verbindungen im Tabak enthalten sind und wie die Rauchfiltration vonstatten geht. Die jetzt in der Entwicklung befindlichen neueren Methoden bedienen sich der Strahlungsdetektion in zunehmendem Maße in Kombination mit rechnergestützten Analyse- und Auswertungsverfahren und zeigen, daß die Kernstrahlung auch in Zukunft bei der Erforschung der Rauchbildung eine wichtige Rolle spielen wird.

RESUME

Le rayonnement radioactif a fréquemment été utilisé pour étudier les différents mécanismes de la transformation du tabac en fumée. C'est également de cette manière que de nombreux travaux de recherche menés partout dans le monde ont étudié les conditions de passage dans la fumée de certains constituants du tabac, les composés non organiques contenus dans le tabac ainsi que le processus de filtration subi par la fumée. Les procédés récents en cours de développement utilisent de plus en plus la détection du rayonnement conjointement à des méthodes d'analyse et d'évaluation assistées par ordinateur. Ils montrent que les radiations nucléaires continueront à jouer à l'avenir un rôle important dans l'étude du mécanisme de formation de la fumée.

INTRODUCTION

Nuclear radiation in tobacco and smoke research is only thirty-five years old, whereas we are all aware that tobacco has been used and enjoyed for hundreds of years. How then could the usages of nuclear radiation in research have any major impact on the data base of knowledge in a product that has been used for so long? The answer to this question is the purpose of this paper. In any review, one cannot hope to cover every single experiment that utilized nuclear radiation in tobacco and smoke research. So the author has imposed limits on this review and intentionally will not cover literature citations that use radiation and radioisotopes simply as markers or internal standards in chemical isolation and/or recovery schemes, that use them for any aspect of biological testing, that are used for plant-physiology research to understand uptakes and tobacco

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chemical precursors prior to harvesting, or that are used routinely as industrial quality-control aids in tobacco processing. This is a literature review of published results through 1986.* The conclusions drawn from the individual papers are mainly those expressed by the original writers or those simple conclusions derived logically by the author of this review. In order to establish a format for this review, the following research areas are covered:

- A. Precursor-product studies,
- B. Cigarette construction and related effects on smoke,
- C. Individual cigarette-component contributions to smoke,
- D. Smoke composition vs. aerosol size,
- E. Tracer studies,
- F. Cigarette air volume,
- G. Radiation effects on tobacco,
- H. Instrumental neutron-activation analysis,
- I. Cigarette-rod density measurements,
- J. Neutron radiography.

A currently accepted model of smoke formation is reviewed emphasizing important observations made by the use of radiation and radioisotope techniques, and newer techniques are described which may lead to further experiments enabling a better understanding of how a cigarette burns.

A. Precursor-Product Studies

A review of carbon-14 precursor-product studies used to ascertain smoke products was given by this author at the 29th Tobacco Chemists' Research Conference in 1975 and was included in Volume 1 of the Recent Advances in Tobacco Science (1). It would be redundant to cover these papers again in the same degree of detail, therefore only the results that have a significant bearing on understanding the mechanisms that take place in the burning cigarette are summarized here, along with the research papers published since the earlier review was written.

Nicotine is the compound most studied in labelled precursor-product research. LARSON (2), JENKINS (1), HOUSEMAN (3) and THORNTON (4) all reported that the radioactivity transferred to mainstream-smoke total

particulate matter (TPM) from [^{14}C]nicotine was between 17.5% and 21.2% regardless of the variability in cigarette-tobacco fillers, papers, circumferences, weights and burn rates (Table 1). HOUSEMAN (3) showed that the mainstream transfer contained $\geq 95\%$ of the unchanged carbon-14 nicotine. This fact has been verified by many authors. In hindsight, it is easily understood today that nicotine distills essentially intact to mainstream smoke, but at the time this paper was published, many researchers felt that a portion of the nicotine in the cigarette may pyrolyze, giving rise to many of the nitrogen-containing compounds in mainstream smoke.

SCHMELTZ, WENGER, HOFFMANN and Tso (5) studied the thermal degradation of [^{14}C]nicotine in a pyrolysis tube. They found that by regulating the pyrolytic conditions, nicotine could be made to undergo extensive thermal degradation to produce a variety of pyridines, quinolines, aryl nitriles and aromatic hydrocarbons. They also studied the fate of [^{14}C]nicotine in a burning cigarette (5). They found that there was some minor degradation of nicotine in the mainstream smoke, but that the mainstream smoke contained essentially distilled nicotine. Their results reinforced earlier findings (6) that many pyrolysis experiments are of limited utility in predicting the fate of nicotine or other tobacco components in a burning cigarette and that each compound may behave differently.

The filtration by the unsmoked portion of a [^{14}C]nicotine cigarette (butt) has been studied by LARSON (2), THORNTON (4), JENKINS (1), HOUSEMAN (3) and CURRAN (7). These reports in general show that the physical construction parameters of a cigarette affect the amount of nicotine that is filtered in the butt. THORNTON (4) showed that the nicotine-transfer rate to mainstream smoke is decreased when large amounts of exogenous sugars are added to the tobacco filler. CURRAN (7) conducted experiments where [^{14}C]nicotine-labelled tobacco rods were smoked to deposit labelled nicotine onto cellulose-acetate filters. These filters were then attached to new non-radioactive tobacco rods and, upon smoking, the fresh smoke eluted the previously deposited [^{14}C]nicotine. Approximately 15% to 19% of the nicotine that had originally been deposited in the filter was subsequently eluted by successive puffs. These researchers have therefore provided much of our current understanding of filtration mechanisms. Not only is there a distribution between vapor and particulate phases, but also between the previously filtered material and the vapor phase from later puffs. This partition coefficient is also affected by the physical and chemical characteristics of the filter.

[^{14}C]Menthol studies have been conducted by NEWELL (8) and JENKINS (6). NEWELL (8) found that 96.4% of the carbon-14 transferred into mainstream-smoke total particulate matter was unchanged menthol. JENKINS et al. (6) found that of the radioactivity in the mainstream-smoke total particulate matter, 98.9% is unchanged menthol, while mainstream-smoke combustion

* Cited data were recomputed where appropriate to represent the percentage of radioactivity delivered into smoke from the amount of tobacco consumed. Hence any butt-filtration values reported had to be subtracted in order to give percentage distribution as shown in the tables.

Table 1.
Percentage distribution of nicotine radioactivity in smoke
(based on tobacco consumed*).

Smoke phase	Nicotine					
	LARSON (2)	THORNTON (4)	HOUSEMAN (3)	JENKINS (40)	JENKINS (34)	SCHMELTZ** (5)
Mainstream gas	3.0	n.r. ⁺	5.3	3.0	2.2	4.6
Mainstream total particulate matter	17.5	18.3	20.1	21.2	23.5	19.2
Sidestream gas	21.5	17.3	21.2	21.2	21.7	13.7
Sidestream total particulate matter	46.6	57.9	53.4	54.6	52.6	31.8
Butt	9.1	6.5	n.r.	n.r.	n.r.	3.1
Ash, paper	2.3		n.r.	n.r.	n.r.	0.2

* All data were recomputed to represent the percentage of radioactivity delivered into smoke from the amount consumed. Hence butt-filtration values had to be subtracted in order to give percentage distribution.

** Principally [¹⁴C]nicotine at about 73% of the total-alkaloid fraction.

+ n.r.: Data not reported or detected.

products accounted for 0.1%. Pyrolysis products (0.3%) were accounted for mostly as various methenes. These results laid to rest the many speculations concerning multitudes of compounds being formed from pyrolysis of menthol observed in tube-pyrolysis studies under "idealized" conditions.

Another tobacco constituent studied intensely was dotriacontane (Table 2). The fate of this high-boiling component of the waxy coating of tobacco was first investigated in cigarettes as a carbon-14 compound by

JENKINS (9). The major portion of this material transferred to the mainstream-smoke total particulate matter (95%), with 0.7% as combustion products and 4.2% as lower molecular-weight pyrolysis products. The lack of significant filtration by the unsmoked tobacco column led to the hypothesis that the filtration mechanisms of the direct removal of the non-volatile particulate phase by inertial impaction, direct impaction and diffusion play a minor role in smoke filtration compared to vapor-phase condensation as a filter mechanism.

Table 2.
Percentage distribution of dotriacontane radioactivity in smoke
(based on tobacco consumed*).

Smoke phase	Dotriacontane				
	JENKINS ^a (9)	JENKINS ^b (40)	JENKINS ^c (34)	DAVIS (11)	MADDOX ^d (10)
Mainstream gas	1.9	0.8	1.3	0.4	0.1
Mainstream total particulate matter	28.1	29.7	42.9	28.7	29.4
Sidestream gas	15.0	12.9	9.8	12.6	19.9 ^e
Sidestream total particulate matter	55.0	53.9	46.0	64.2	50.6
Butt	n.r. ⁺	2.7	n.r.	-5.9	6.9
Ash	n.r.	n.r.	n.r.	n.r.	0.1

* All data were recomputed to represent the percentage of radioactivity delivered into smoke from the amount consumed. Hence butt-filtration values had to be subtracted in order to give percentage distribution.

⁺: Not reported or detected.

a: Paper porosity: 41.0 cm³/(min cm² kPa), length: 70 mm.

b: Paper porosity: 13.2 cm³/(min cm² kPa), length: 70 mm.

c: Paper porosity: 10.5 cm³/(min cm² kPa), length: 85 mm.

d: Data recomputed assuming 23 mm butt and 85 mm cigarette.

e: 23 mm butt assumed.

Table 3.
Percentage distribution of radioactivity in smoke
(based on tobacco consumed*).

Smoke phase	Anthracene	Cholesterol ^a	β -Sitosterol ^a	L-Proline ^a	Phytosterols ^{a, b}
	THORNTON (19)	CHENG (21)	CHENG (21)	JENKINS (34)	SCHMELTZ (124)
Mainstream gas	0.2	n.r. ⁺	n.r.	11.4	1.6
Mainstream total particulate matter	33.6	16.3	13.1	9.9	19.0
Sidestream gas	2.0	n.r.	n.r.	63.0	25.7
Sidestream total particulate matter	55.9	n.r.	n.r.	7.2	17.2
Butt	8.3	4.0	3.1	8.5	6.7
Ash	n.r.	n.r.	n.r.	n.r.	1.2

* All data were recomputed to represent the percentage of radioactivity delivered into smoke from the amount consumed. Hence butt-filtration values had to be subtracted in order to give percentage distribution.

a: 85 mm cigarette.

b: 71.4% recovery.

+: Not reported or detected.

These [¹⁴C]dotriacontane findings were verified in other experiments by MADDOX (10) and DAVIS (11). At present, [¹⁴C]dotriacontane is used routinely by many laboratories worldwide as a marker of the amount of non-volatile total particulate matter deposited from smoke in various experimental studies (12 — 18).

Several other tobacco constituents were examined to determine their contribution to mainstream smoke. THORNTON and VALENTINE (19) studied [¹⁴C]anthracene and found it to transfer mainly intact to the mainstream-smoke total particulate matter (Table 3). Unusually high (8.3%) butt-filtration values led to the speculation that this may be indicative of compounds which sublime rather than distill. JENKINS et al. (20) studied a sublimable tobacco compound, [¹⁴C]L-proline, and indeed found similar results with an 8.5% butt-filtration value (Table 3). CHENG (21) studied the mainstream yield from cigarettes labelled with [¹⁴C]-cholesterol and β -[¹⁴C]sitosterol. He found transfer rates of 16.3% and 13.1%, respectively (Table 3). Mainstream-smoke total particulate matter analysis indicated that there was only a small decomposition of these compounds as they transfer to mainstream-smoke total particulate matter. The butt-filtration value for cholesterol again was higher than usually found for distillables, indicating a possible sublimation route into the smoke. SCHMELTZ et al. (5, 124) studied the fate of [¹⁴C]phytosterols in the burning cigarette and found 19% of the carbon-14 transferred to mainstream-smoke total particulate matter (Table 3). He speculated that the transferred material was most likely unaltered phytosterols, although this was not proven. His slightly higher values than those of CHENG (21) may be due to the low recovery (72%) of total radioactivity.

MARMOR and MINNEMEYER (122) conducted studies on the fate of [5-¹⁴C]3-phenyl-5-methyl-1,2,4-oxadiazole (PMO) added to 70 mm blended cigarettes. They showed that about 28% of the carbon-14 from the la-

belled PMO added to the cigarette transferred to the mainstream-smoke total particulate matter and about 22% to the sidestream-smoke total particulate matter. A reasonably large butt filtration was observed (37% with 29% already present on the unsmoked tobacco, for a net butt increase of 8%). The amount of [¹⁴C]PMO undergoing decomposition into the mainstream-smoke gas phase was less than one percent. Approximately 10% of the labelled PMO underwent decomposition during the static burn and was found in the sidestream-smoke gas phase. MARMOR et al. (122) did not report any chemical analyses on the mainstream-smoke particulate phase, but implied that most of the carbon-14 was unchanged PMO. The high butt values indicate that PMO acts more like a compound which undergoes sublimation rather than classical distillation.

Several authors have looked at the fate of [¹⁴C]sugars in cigarettes (2, 19, 20, 22). Most of the authors found that since sugars are not capable of distillation or sublimation, they undergo much more pyrolytic decomposition during smoking. Indeed, most found a much larger contribution to mainstream-smoke gas phase than to the total particulate matter. All the sugars show large butt-filtration values, but no substantial information on the chemical composition of the filtered material has been reported.

GAGER (22), when looking at cigarettes labelled with [¹⁴C]glucose or [¹⁴C]sucrose, found that a measurable amount of the radioactivity in the mainstream-smoke total particulate matter was composed of the original sugar. This information supports the theory that, during burning, the tobacco cells are exposed to a steep and fast-moving thermal gradient which causes rapid heating, during which many cells essentially explode, generating volatile gases, and physically entrain pieces of unpyrolyzed tobacco into the rearward moving gas stream. Those pieces of the proper aerodynamic diame-

ter might exit from the cigarette carrying traces of many compounds which were never exposed to temperatures high enough to cause pyrolytic degradation. The fate of added carbon-14 labelled carbohydrates was also investigated by NEWELL et al. (23). They added [^{14}C]starch, pectin and cellulose powders to tobacco filler and then measured their contribution to smoke. Starch exhibited the largest mainstream-smoke gas yield and a very low deposition in the butt. Pectin was lower in mainstream-smoke gas yield with a corresponding increase in sidestream smoke (again, a very low butt filtration). [^{14}C]cellulose delivered slightly more products to the particulate phase than either starch or pectin. All of the carbohydrates show a large mainstream-smoke gas contribution in comparison to mainstream-smoke total particulate matter (~ 2.8). This is the reverse of what was observed for the distillable compounds (0.04 to 0.2). The reported sidestream-smoke gas yields are very large for all carbohydrates. This is because of their inability to escape the approaching thermal gradient during a puff resulting in pyrolytic decomposition. The relatively low butt-removal values ($\sim 2\%$) along with a large gas-phase contribution show that, for the compounds studied, gaseous absorption, adsorption and possible chemical affinities are not large factors in tobacco-column filtration. This observation is reinforced when the results of NEWELL and BEST (24) on the fate of oxalic, malic and citric acids are studied. They found large gas-phase yields and low butt-removal values (0.2% to 0.8% of the total carbon-14 consumed). Especially with oxalic acid, one can reasonably expect a large CO_2 yield under thermolytic-decomposition conditions. Indeed they found 19% of the carbon-14 in the mainstream-smoke gas phase (24) and found only 0.2% in the tobacco column (butt), again supporting the lack of gaseous absorption or adsorption of CO_2 by the tobacco.

The final support for the lack of importance of CO_2 filtration is in the early work by MORRELL et al. (25) where the cigarette paper contained $\text{Ca}[^{14}\text{C}]\text{O}_3$. They found large gas yields (presumably CO_2) and little tobacco-column filtration. This paper by MORRELL et al. (25) also shows the importance of the air passage into the cigarette at the junction of the paper char line, as they reported 51% of the carbon from the $\text{Ca}[^{14}\text{C}]\text{O}_3$ added to the paper transferred to the mainstream-smoke gas phase, and not predominantly to the sidestream smoke as might have been expected.

B. Radioisotopically labelled Cigarette Construction and Associated Effects on Smoke Formation

Every analytical technique has its advantages and disadvantages. When radioisotopes are used to determine smoke-formation mechanisms and transfer pathways out of the cigarette, certain assumptions are usually made. Some of these are: [1] The radioisotopically la-

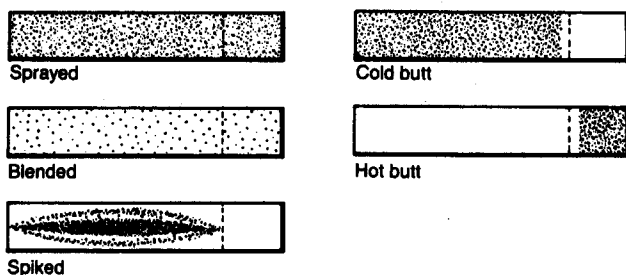
belled material that is added to the surface (exogenous) of the tobacco behaves in the same way as naturally occurring material (endogenous). [2] The added radio-tracer is uniformly applied to the entire cigarette rod. [3] Any variation in the concentration gradient caused by the method of radiochemical addition to the cigarette-tobacco filler is unimportant in the mechanisms of smoke formation and subsequent distribution into whole smoke.

Regarding exogenous vs. endogenous addition, this assumption was questioned by DAVIS et al. (26) who examined the transfer of exogenously applied and endogenous sterols and alkaloids into mainstream smoke. The authors concluded that although they could detect little difference in the transference of exogenously applied or endogenous nicotine, the exogenously applied sterols transferred at significantly lower rates than the same endogenous compounds. Cholesterol and β -sitosterol (applied by spraying onto the tobacco filler) had decreases of 20% and 26%, respectively, in their mass-transference rates. These reduced transference rates were essentially verified by CHENG (21) who studied cigarettes prepared by syringe spiking with [^{14}C]cholesterol and [^{14}C]sitosterol. The mass-loading levels for these sterols were not given, but transference-rate decreases for cholesterol of about 13% and 20% for sitosterol were reported. HOUSEMAN (3) studied the transference of [^{14}C]D-nicotine added to cigarettes by syringe spiking. He found that the specific radioactivity of the alkaloids transferred to the mainstream smoke was slightly higher than the calculated specific activity of the tobacco consumed by smoking. From these data, he concluded that the smoke-transfer characteristics of the exogenous D-nicotine and endogenous L-nicotine were similar. In a later report ARMITAGE et al. (27) studied the amount of nicotine absorption from smoke. In these experiments, the authors demonstrated that endogenous and exogenous nicotine transferred reproducibly, under a wide range of smoking conditions, with a slightly higher rate for the exogenous nicotine than that calculated for the endogenous material.

JENKINS and COMES (28) have also studied this question of nicotine transference, using [^{14}C]L-nicotine obtained biosynthetically from Bright tobacco. The ^{14}C -labelled nicotine was dissolved in ethanol and then added to the tobacco filler by spraying. Cigarettes were made and smoking was carried out on a piston-type machine. Their data show close agreement of the specific activities, with the exogenously applied nicotine, indicating about a 4% greater specific activity than the endogenous material in the unsmoked tobacco filler. Calculation from HOUSEMAN's data (3) also shows an increase of about 4% in the specific activity of the exogenous nicotine. The variation in specific activities found are within the error margin of the measurements and therefore the exogenous and endogenous values are not significantly different. This 4% difference is small when one considers the variation between the different cigarette deliveries.

It appears that the results of HOUSEMAN (3) and JEN-

Figure 1.
Axial renditions of various labelling methods (33).



KINS (28) substantiate that there is not a meaningful smoke-transfer difference for exogenously applied vs. endogenous nicotine. This may be the same for any compound that is distilled intact into smoke. This is not the case for tobacco sterols, as demonstrated by DAVIS et al. (26) and CHENG (21) and, therefore, each researcher must determine the exogenous and endogenous transfer rates of the individual tobacco distillables

Table 4.
Comparison of spiked vs. sprayed ^{14}C -labelled cigarettes (33).

Mode of addition	Axial radioactivity in tobacco (¹⁴ C / g tobacco)*	Radioactivity recovered from total smoke (¹⁴ C / total smoke per cigarette)*
	percentage standard deviation (σ = 1)	
[U-¹⁴C]Menthol		
spiked	± 3.7	± 2.9
[U-¹⁴C]Nicotine		
spiked	± 8.5	± 9.8
sprayed	± 4.4	± 4.2
[¹⁴C]Dotriacontane-16,17		
spiked	± 24.2	± 27.3
sprayed	± 1.8	± 1.4
[U-¹⁴C]Proline		
spiked	± 10.4	± 9.7
sprayed	± 6.9	± 8.1
15% ¹⁴ C sheet in 1R1 tobacco filler	± 9.9	± 9.6
20% ¹⁴ C sheet in 1R1 tobacco filler	± 9.7	± 9.5
¹⁴ C sheet random samples	± 4.2	—

* Sample size: 5 cigarettes.

being studied before making definitive analogies to the smoke precursor-product relationships in cigarettes.

The next question to be addressed is the assumption that the mode of radioisotopically labelled material addition has no influence on smoke composition and distribution. HOUSEMAN and HENEAGE (30), in 1973, published the first paper looking at the axial distribution of the ^{14}C activity in cigarettes that were spiked using a specially designed device. This device automatically dispersed the radiochemical from a syringe down the center of machine-made cigarettes.

RINGROSE, CRAWLEY and COGGINS (31) described a microprocessor-controlled device that will automatically syringe spike up to 100 cigarettes per minute. This instrument produced a uniform deposition pattern axially down the rod, but each cigarette end was somewhat depleted in material. This technique could be useful in cases where large volumes of labelled cigarettes are needed. Using an UV-absorbing compound, variable modes of addition of spiked materials were viewed and quantitative results were obtained on the deposition pattern (32). The syringe-injected materials were shown (Figure 1) to have a fusiform shape, depleted somewhat at each end as shown by RINGROSE et al. (31). Care had to be taken to regulate injection volumes. Too little leaves the non-volatile materials deposited down the center of the rod. Too much solvent causes wicking to the wrapper, a condition possibly resulting in different pyrolysis mechanisms.

JENKINS et al. (33) gave recommendations for the standardized preparation of labelled cigarettes. In this paper, cigarettes were labelled using syringe spiking, spraying onto the tobacco filler, and incorporation into blended sheet, depending on individual compound characteristics. The last two methods require either hand making or small-scale machine runs. Data were presented (Table 4) showing the resultant axial radioactivity distribution in the cigarette rod and the effects on smoke formation and delivery. They concluded that "the error generated in uniformly placing the radioactive label axially within the rod is also the degree of error reflected in the radioactivity recovery from total smoke. Although the spread of values may be larger from non-uniformly labelled cigarettes, the average total-smoke distribution values will agree when a sufficient quantity of cigarettes is smoked" (33).

When the added radiotracer is not uniformly distributed radially within the cigarette, the smoking of a large number of cigarettes might not overcome any bias imparted to the experimental results. JENKINS et al. (34) studied the effects that different radial placements of the labelled materials have on smoke composition. A series of cigarettes was prepared with carbon-14 labelled materials placed in different radial positions within the rods. These cigarettes were smoked and the total-smoke distribution of the radioactivity was measured. These data lead to the following conclusions: [1] The periphery plays a large contributing role (though not the sole role) in the formation of a) the mainstream-smoke particulate phase, b) sidestream-smoke

particulate phase (derived from non-distillable/non-sublimable materials), and c) mainstream-smoke gas phase (derived from non-distillable/non-sublimable materials). [2] The central portion of the cigarette rod plays a large contributing role in a) sidestream-smoke gas phase and b) sidestream-smoke particulate phase (derived from distillable/sublimable compounds). [3] The mainstream-smoke gas-phase yields from the distillable/sublimable compounds are due in large part to the pyrolysis/combustion products formed during the static-burn period. These products are carried into the mainstream smoke by the incoming air at the beginning of the puff and by diffusion due to the pressure gradient existing in the cigarette during the static-burn period.

These experiments have demonstrated the significant effects that the central portion of the cigarette rod has on sidestream-smoke formation and, conversely, the effects of the periphery on mainstream smoke. These conclusions of JENKINS et al. (34) were tested to some extent in 1984 by GREEN et al. (35) who described a radiochemical study on the use of ^{14}C -labelled vanillin. In this study, [^{14}C]vanillin was injected into the center of the cigarettes and also added to the cigarette paper. For the material added to the central core, it was shown that very little vanillin transferred intact to sidestream smoke whereas the material added to the paper transfers at a good rate. This study would indicate that perhaps the central core is mainly a contributor to the sidestream smoke for those spiked materials which cannot simply distill. One must bear in mind as cited earlier (34) that compounds capable of distillation tend to equilibrate throughout the rod when exposed to the warm edge of the approaching thermal gradient and therefore do not show the same mainstream/sidestream smoke preferences as non-volatile added materials.

C. Cigarette-Component Contributions to Smoke

In this review we have seen that the degree of volatility, thermal stability, affinity for the tobacco or filter, placement in the rod, etc. all play very important roles in determining whether a particular compound will distill or undergo pyrolysis, and of course this greatly affects the distribution of the compound within whole smoke. With this in mind, it is no surprise that a considerable amount of time has been spent trying to establish the contribution to smoke made by each type of tobacco, additive or paper. Most of these studies were conducted in 100% single blend-component cigarettes, resulting in cigarettes with greatly different burn characteristics. Usually cigarette construction had to be changed between blends. LARSON and HARLOW in 1958 (2) studied [^{14}C]Burley which had been intermixed with a cigarette blend. Their analytical techniques produced only a 78% recovery of their radioactivity, but this initial work led eventually to the fabrication of a variety

of total or whole-smoke collection machines, with each type having its own advantages. These various smoking machines were reviewed and their merits and disadvantages discussed by DUBE and GREEN (36). Most of these smoking techniques give essentially quantitative recoveries. Of course there are minor variations such as puff shape, free or restricted smoking, and sidestream-smoke collection techniques. Many of these machines were developed to fulfill specific needs regarding the subsequent chemical and radiochemical analysis. The major difference between radioactive-cigarette smoking and conventional techniques is the need to practice good radiological techniques. It is also imperative that every effort be made to prevent cross-contamination between smoking runs.

Another cigarette component investigated was the humectants. HOLMES (37) studied the distribution of humectants during smoking. This was followed by studies done by JENKINS and co-workers (9). As expected they found that distillation is the major mode of transfer for glycerol (1).

JENKINS et al. (1) reported on 70 mm blended cigarettes using [^{14}C]Burley, showing that the smoke distribution he obtained was markedly different from that obtained by LARSON et al. (2). LARSON (2) reported a mainstream/sidestream smoke gas value of 0.4 and a mainstream/sidestream smoke total particulate matter value of 1.2. This is in comparison to the values of 0.2 and 0.7, reported by JENKINS (1). The differences between the results obtained by these two authors may be due to the total recovery of the added radioactivity, 78% for LARSON and $\geq 95\%$ for JENKINS et al.

JENKINS, CHAVIS, BASS and OSDENE (38) conducted a series of studies using uniformly labelled cigarette components. They addressed the following basic questions: [1] What is the distribution of carbon in all of the portions of total cigarette smoke? [2] Is the assumption correct that each cigarette ingredient contributes its proportionate share of carbon to each phase of smoke? To answer these questions, carbon-14 labelled cigarettes were used. The Bright, Burley and Oriental tobaccos required were grown in a [^{14}C]O₂ chamber. These tobaccos were then cured and fabricated into laboratory duplicates of the 1R1 Kentucky reference cigarette. A series of cigarettes were made with one major ingredient labelled with carbon-14. The smoke distribution of the radioactivity from each of these cigarettes (Table 5) was multiplied by the actual weight amount of carbon consumed during burning, resulting in the carbon contribution of each cigarette-blend component to total smoke. This data is a measured contribution of total carbon to each smoke phase, from the ingredients in the 1R1-type cigarette. In many cases, the actual percentage contribution was greatly different from the theoretical contribution (Tables 6, 7, 8). The Bright lamina was found to be a larger carbon contributor to mainstream-smoke total particulate matter than expected and the Bright stem contributed considerably less. These results imply that Burley tobacco contributes more than the expected amounts of carbon to those

Table 5.
Percentage of carbon transferred to total smoke from each ¹⁴C component of the 1R1-type cigarette,
based on tobacco consumed* (38).

Smoke phase	Bright lamina	Bright stem	Burley	Oriental	Glycerol	Invert sugar	Paper (cellulose)
Mainstream gas	13.7	15.6	13.0	12.1	8.6	13.6	20.4
Mainstream total particulate matter	11.5	5.3	7.7	12.3	22.0	9.1	9.7
Sidestream gas	60.2	71.1	62.6	58.5	38.9	63.8	38.3
Sidestream total particulate matter	11.2	5.8	11.4	12.9	24.5	7.8	28.2
Butt	3.3	2.1	5.3	4.4	5.7	5.7	3.2

* All data were recomputed to represent the percentage of radioactivity delivered into smoke from the amount consumed. Hence butt-filtration values had to be subtracted in order to give percentage distribution.

Table 6.
Mainstream-smoke (carbon) contribution from 1R1-cig-
arette components in percent (38).

Cigarette component	Experimental		Theoretical
	Total particulate matter	Gas phase	Total particulate matter or gas phase
Bright lamina	46.8	40.9	40.9
stem	6.1	13.4	11.7
Burley	18.6	23.1	24.2
Oriental	13.4	9.7	11.0
Glycerol	6.1	1.0	2.8
Sugar	4.7	5.3	5.2
Paper	4.1	6.6	4.3

Table 7.
Tobacco-column (carbon) filtration from 1R1-cigarette
components in percent (38).

Cigarette component	Experimental	Theoretical
Bright lamina	34.2	40.9
stem	6.3	11.7
Burley	32.4	24.2
Oriental	11.7	11.0
Glycerol	4.5	2.8
Sugar	7.2	5.2
Paper	3.6	4.3

Table 8.
Sidestream-smoke (carbon) contribution from 1R1-cig-
arette components in percent (38).

Cigarette component	Experimental		Theoretical
	Total particulate matter	Gas phase	Total particulate matter or gas phase
Bright lamina	41.0	40.7	40.9
stem	6.1	13.7	11.7
Burley	24.7	25.0	24.2
Oriental	12.5	10.6	11.0
Glycerol	1.3	1.8	2.8
Sugar	3.5	6.6	5.2
Paper	10.9	2.7	4.3

smoke components which are more easily condensable, when compared with Bright tobacco, which contributes more than expected to the non-volatile particulate phase and less to the condensable phase. The cigarette paper was shown to contribute a disproportionate share of carbon to the sidestream-smoke total particulate matter. Glycerol was shown to contribute heavily to the mainstream-smoke total particulate matter, a result expected for distillable materials.

D. Smoke Composition vs. Aerosol Size

There has been a long ongoing interest in determining whether the various size ranges of the cigarette-smoke aerosol are identical in their chemical compositions. Early in the use of filtered cigarettes it was shown that the filters exhibited some selectivity in the removal of a few volatile smoke components. Most notable was the affinity of the triacetin plasticizer in the cellulose acetate for smoke phenol. Today, it is generally agreed that the major filtration mechanism taking place in the cigarette is vapor-phase condensation on the tobacco or filters. The selective removal of the non-volatile smoke particulate phase has been a dream of all filter-material suppliers for years. This is predicated on the assumption that various sizes of the smoke aerosol are composed of different chemical components.

JONES et al. (123) reported on a series of experiments where carbon-14 nicotine, dotriacontane, and hexadecane were investigated for their distribution among size-selected mainstream-smoke aerosols. The cigarettes were prepared by injecting the desired radiochemicals into 70 mm flue-cured Bright cigarettes. The mainstream-smoke aerosol was passed without dilution into a centrifugal size classifier. Upon removal of each particle-size range, data were expressed as the amount of carbon-14 and of the total condensate weight collected. Their results (Figures 2 a—c) showed the distribution of [^{14}C]nicotine to be essentially independent of particle size over the 0.1 μm to 1.3 μm size range. Dotriacontane was shown to be particle-size dependent with the larger particles enriched and the smaller particles depleted. Hexadecane was shown to be less particle-size dependent than dotriacontane. JONES et al. (123) concluded that there were some slight dependencies on particle size, but they felt that the differences were small enough to allow these compounds to be used as valid markers for the amount of total particulate matter.

JENKINS (39) later reviewed published results which showed some evidence that all smoke-aerosol particles are not chemically identical, but noted that many of these studies depended on the measurement of individual chemical components expressed as the percentage of weight of a size-selected portion of the smoke. The evaporative losses of water before and after smoke separation were of unknown magnitude. JENKINS et al. (39) also described a radiochemical method for measuring

the specific radioactivity of size-selected portions of the smoke aerosol produced from cigarettes with the major cigarette components individually carbon-14 labelled. The specific activity is the ratio of the amount of radiocarbon to total carbon present in the size-selected samples ($^{14}\text{C}/^{12}\text{C}$). This technique is chemically independent of the amount of water or the inorganic

Figure 2.
Relative concentration of added compound as a function of smoke-particle size (123).

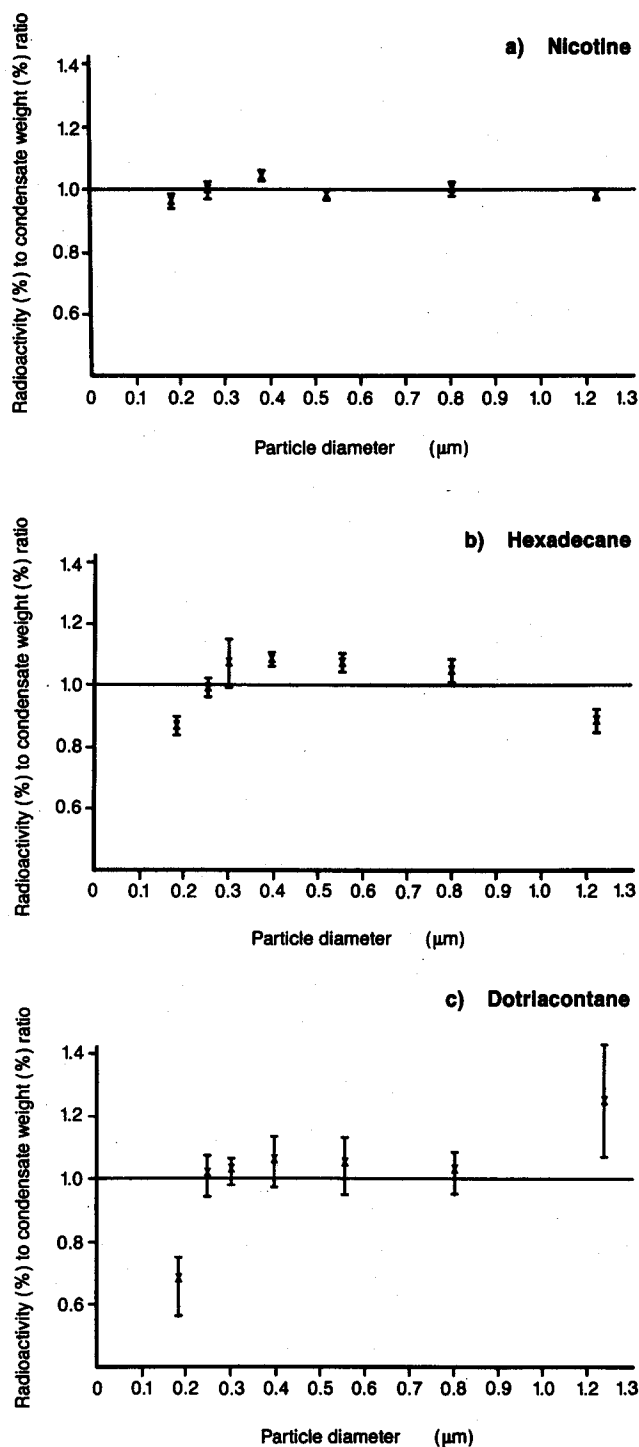
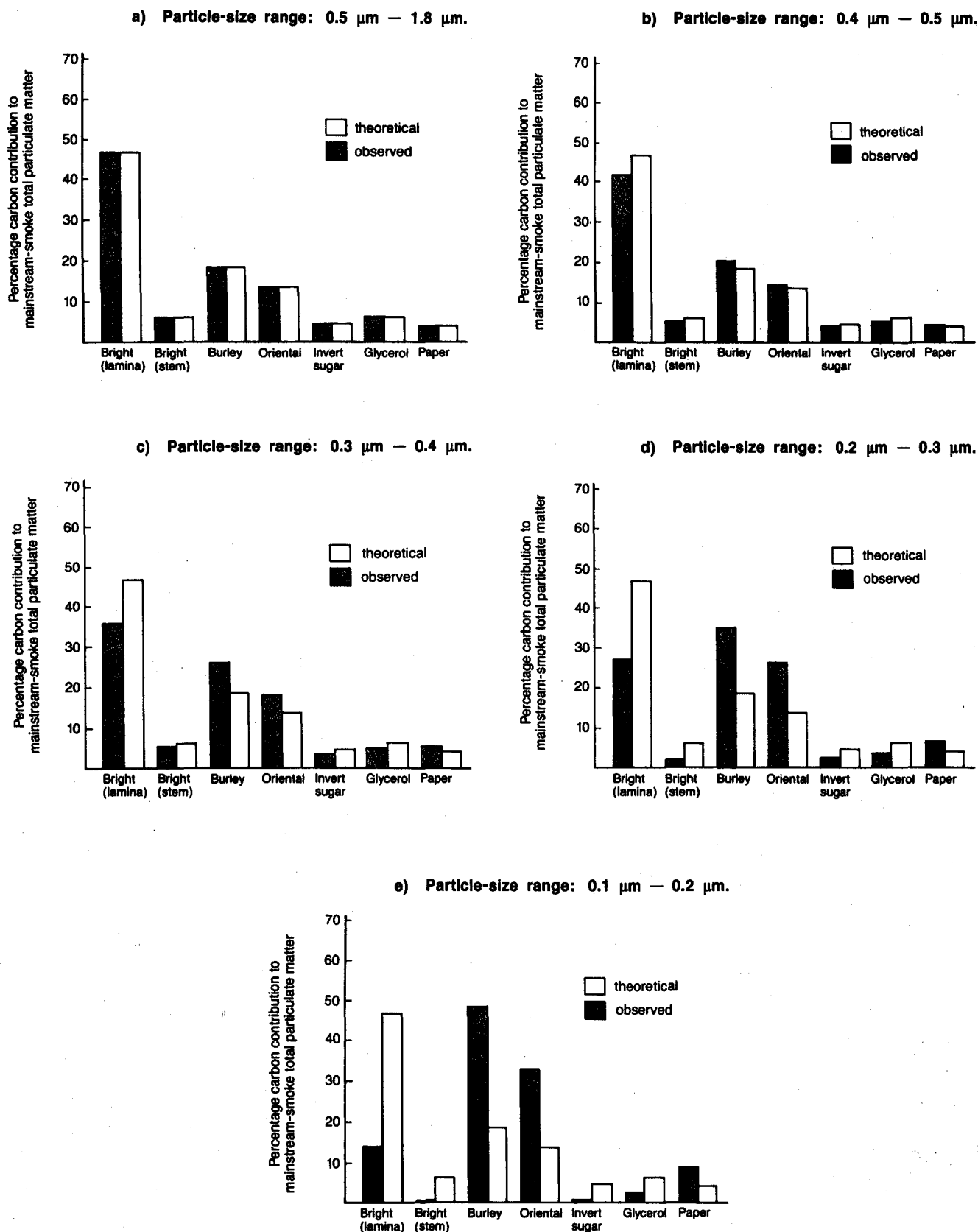


Figure 3.
Carbon contribution to mainstream-smoke total particulate matter from
individual 1R1-cigarette components (38).



composition of the particles. The non-volatiles were chosen for this study in order to minimize any chemical compositional changes due to evaporative losses. The cigarettes were made up individually of [^{14}C]Bright, [^{14}C]Burley and [^{14}C]Oriental tobaccos, [^{14}C]glycerol, [^{14}C]invert sugar, [^{14}C]Bright stems, [^{14}C]paper (cellulose) and [^{14}C]dotriacontane. With the exception of dotriacontane, the cigarettes were made according to the exact weight percentage of each cigarette component present in the 1R1 cigarette. The smoke was then generated by a conventional reverse-puffing technique (40). As soon as the smoke exited from the cigarette, diluent air (particle free) was simultaneously (during the 2 s puff) mixed with the smoke stream. The smoke was sampled on a copper strip inside a spinning spiral centrifuge. The copper strip was cut into particle-size ranges and each was pyrolyzed. The specific radioactivity ($^{14}\text{C}/^{12}\text{C}$) was measured by gas radiochromatography. The results were presented as relative specific radioactivity vs. particle size for each of the major cigarette components in the 1R1 cigarette and the tobacco constituent [^{14}C]dotriacontane.

In each case, the large-size smoke particles showed no differences in their specific activities. This was interpreted as evidence that coagulation had probably taken place, producing larger particles which would have lost the chemical individuality possessed by the smaller particles before they randomly combined during coagulation. The larger particle-size range (greater than $0.5\text{ }\mu\text{m}$) was assumed to represent the average overall specific activity.

The distillable compounds, [^{14}C]dotriacontane and [^{14}C]glycerol, were shown to be depleted relative to total carbon in the range of sizes below $0.5\text{ }\mu\text{m}$. [^{14}C]Invert sugar and [^{14}C]Bright tobacco also showed a considerable decrease in their proportional contribution to the small-size particles. However, paper, Burley and Oriental tobacco all show large relative contributions to the small-size particles. Since coagulation may have altered the results for the $0.5\text{ }\mu\text{m}$ and larger particles, there is some reason to speculate that the dramatic increases and decreases in contribution to the $0.1\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m}$ size ranges would have continued if coagulation had been prevented assuming primary particles of sizes above $0.5\text{ }\mu\text{m}$ were actually present. However, it remains unknown how much coagulation is actually responsible for the modification of the curves in the particle-size range of $0.5\text{ }\mu\text{m}$ and larger.

The data from the small-particle fractions show that individual cigarette components contribute differently to particular particle-size fractions in smoke. This is experimental evidence that different cigarette components produce smoke aerosols of different chemical composition in the non-volatile particulate phase.

In order to understand better the contribution of each 1R1-cigarette ingredient to each particle-size fraction in the $0.1\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m}$ range, the specific-activity data can be multiplied by the average contribution of each cigarette ingredient to the total particulate mass in the

mainstream smoke in terms of the carbon mass balance (JENKINS et al. (38)). This will result in the actual contribution (%) of each individual 1R1-cigarette component to each mainstream-smoke total-particulate-matter particle-size fraction. The data were then expressed as histograms for the various size fractions and are shown in Figures 3 a—e.

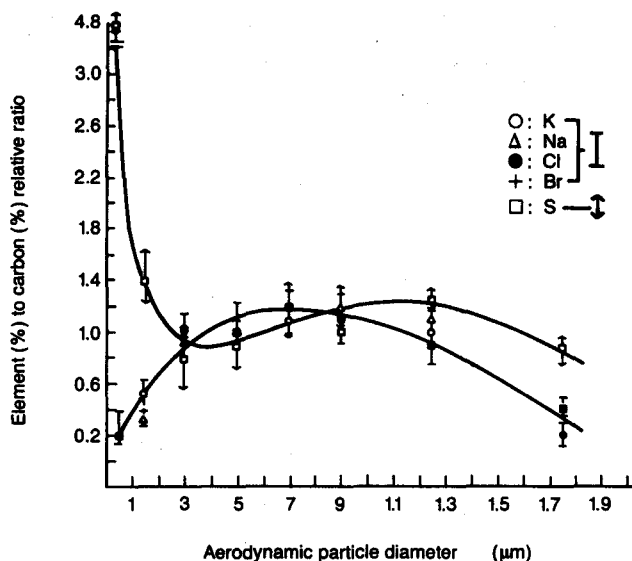
In summary, JENKINS et al. (39) drew the following conclusions:

1. Smoke particles are chemically different, varying with their aerodynamic sizes in the $0.1\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m}$ diameter range.
2. Particle analyses in the size range larger than $0.5\text{ }\mu\text{m}$ indicated, most probably, an influence of coagulation randomizing the chemical composition and, therefore, representing the overall average of mainstream-smoke total particulate matter.
3. In general, the distillables are "depleted" in the particles of sizes below $0.5\text{ }\mu\text{m}$ and there is an increase in distillables as the particle size increases.
4. The pyrolytic products appear "enriched" in the small particles below $0.5\text{ }\mu\text{m}$.
5. A mass balance of the contribution from each major ingredient in the 1R1 cigarettes has been established for all particle sizes in mainstream smoke from $0.1\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m}$ and the percentage contribution to the non-volatile portion of mainstream-smoke total particulate matter from each component in this cigarette has been calculated.

The variability of selected inorganics in mainstream smoke as a function of particle size was also studied by JENKINS and co-workers (41). University of Kentucky 1R1 reference cigarettes were activated with neutrons and these cigarettes were then smoked on a reverse-puff smoking machine. The mainstream smoke was immediately diluted with clean air. The diluted smoke was separated by particle size into fractions, based on aerodynamic particle diameter, in a spiral centrifuge. The size-selected fractions were subsequently counted on a Ge(Li)-detector system (gamma spectroscopy) mated to a dedicated computer. Data were presented showing the relative concentration ratios of K, Na, Cl, Br and Mn and S.

The neutron-activation analysis results showed that the relative ratio of Na, Cl, Br and Mn to K remains constant over the size range from $0.1\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m}$ of aerodynamic particle diameters. Sulfur shows a definite chemical variability compared to the other measured inorganics and is enriched in the smaller particle sizes below $0.3\text{ }\mu\text{m}$. Total carbon was also analyzed and data are shown in Figure 4 comparing the relative ratios of total carbon to Na, Cl, Br, S and K. Sulfur is enriched compared to carbon in the $0.3\text{ }\mu\text{m}$ and smaller particles. The K, Na, Cl, Br and Mn show depletions compared

Figure 4.
Relative ratio of elements to total carbon (41).



to carbon in both the small and large particles, but an enrichment in the 0.3 μm to 0.7 μm particles.

A comparison of the inorganic-compound ratios in cigarette inorganic residue and the ionic portions of the size-selected mainstream-smoke aerosol was also presented. A possible mechanism was formulated to explain how the major mass amounts of the inorganics studied were transferred to mainstream smoke. This mechanism involves mechanical "entrainment" of inorganic residue (ash) formed during the cigarette puff; these pieces then break off from the coal and are transferred into the smoke stream. The "entrained" residue is subsequently regulated in its maximum size by the normal filtration mechanisms that take place as smoke traverses the tobacco. These size-selected "entrained" inorganics then exit in the mainstream smoke. There are two ways that inorganics can transfer to smoke. One is by volatilization and coagulation into very small particles which serve as condensation nuclei for the formation of the aerosol. The other, as shown in this experiment, is the mechanical entrainment of "ash" particles several orders of magnitude larger in size than the condensation nuclei. Therefore, these larger entrained "ash" particles would account for the major portion of the chemical mass of the elements transferred to mainstream smoke.

E. Tobacco and Smoke Tracers

In Section A, the use of radioisotopically labelled compounds to ascertain precursor-product relationships in the cigarette was discussed. This area of research was aimed at understanding the major pyrolysis or distilla-

tion products. These studies were not directed at determining whether or not any measurable amount of a single compound was contributing to a specific chemical in smoke. In Section A, the experimental errors in obtaining mass balances of the radioactivity were large enough to prohibit measuring individual smoke components at less than a few percent of the original starting material. In tracer studies, the experiments are conducted using low-level counting techniques which allow measurements at dilutions of 10^{-6} routinely. Also, experiments which used radiation to monitor or measure any of the physical parameters involved in tobacco or cigarettes were not included. These techniques will be reviewed in this section.

RAYBURN, WARTMAN and PEDERSEN (42) were among the earliest workers to employ carbon-14 as a tracer. They grew tobacco in a $[^{14}\text{C}]\text{O}_2$ atmosphere, then extracted the $[^{14}\text{C}]$ paraffin fraction and added aliquots of this ^{14}C fraction back to cigarettes. They showed that less than 1/180 of the total polycyclic-hydrocarbon contribution to mainstream smoke came from the paraffins. In another study aimed also at the origin of the polycyclic hydrocarbon benzo[a]pyrene, JENKINS and co-workers (43) smoked $[^{14}\text{C}]$ dotriacontane-labelled cigarettes and conducted low-level counting of the benzo[a]pyrene fraction isolated. Their results showed that the naturally occurring dotriacontane could contribute only 1/1,500 of the total benzo[a]pyrene in mainstream smoke and 1/4,200 of the sidestream-smoke benzo[a]pyrene. These authors then concluded that the dotriacontane and perhaps the adjacent hydrocarbons naturally present in an average cigarette were not meaningful precursors to the smoke benzo[a]pyrene.

There have been several reports where $[^{14}\text{C}]$ dotriacontane has been used strictly as a tracer, marker, or to measure the amount of particulate matter delivered. Most reports using dotriacontane were cited earlier. PAGE et al. (15) and DONTENWILL et al. (44) have used $[^{14}\text{C}]$ hexadecane as a tracer for mainstream-smoke total particulate matter. Since the interpretation of these types of experiments is beyond the scope and purpose of this review, further analysis will be left to others.

SCHMELTZ et al. (124) syringe injected cigarettes with $[^{14}\text{C}]$ cholesterol and analyzed the mainstream-smoke tar fraction soluble in nitromethane, a procedure they have used to test for polynuclear aromatic hydrocarbons. They found that the nitromethane contained two percent of the initial activity of the added $[^{14}\text{C}]$ cholesterol. No data were reported on the exact chemical species in this fraction, but the authors state that this could represent a significant amount of the total polynuclear aromatic-hydrocarbon content of smoke and thus cholesterol may be a major precursor to this compound class.

There has been interest in the fate of agricultural chemicals in or on cured tobacco. Topping of tobacco has been shown to be advantageous to the farmer, but this practice leads to auxiliary bud growth, commonly

called "suckers". Certain chemicals are in use to inhibit the growth of these auxiliary suckers. Tso et al. (45 a and b) investigated the residue levels of some suckering agents on tobacco; lauryl alcohol, methyl laurate, Tween 20® surfactant and Tween 80® surfactant were prepared with a carbon-14 label. These materials were used as suckering agents for Maryland, Burley, and Bright tobaccos, and the carbon-14 residues determined. They found an average residue of 1.6 ppm of the fatty compounds and 1.0 ppm of the Tween surfactants. The quantities are far below the 7,000 ppm of similar naturally occurring fatty-type compounds found in tobacco. From this experiment, Tso et al. (45 a and b) concluded that the use of these suckering agents would have little effect on leaf quality or tobacco usability.

Methoprene or KABAT® is a juvenile-hormone mimic which has been developed for cigarette beetle and tobacco moth control (46). The fate of any residual tobacco methoprene was investigated by FRISCH et al. (47) who utilized [5-¹⁴C]methoprene added to 1R1 cigarettes. The distribution of the carbon-14 from the added methoprene was 38.2% in mainstream, 52.4% in sidestream smoke and 8.1% retained in the tobacco butt. Mainstream-smoke particulate-matter analysis showed that unchanged, distilled methoprene comprised 96.8% of the activity. Sidestream smoke showed only 81.5% unchanged material in the particulate phase. Only 1.3% of the [¹⁴C]methoprene activity that was in the tobacco consumed transferred to the mainstream-smoke gas phase and 86% was carbon dioxide and carbon monoxide. The remaining being present as other low molecular-weight pyrolysis products.

ATALLAH (48) reports a study where the ¹⁴C-labelled insecticides carbaryl, carbofuran, leptophos, DDT and Minex® were added to cigarettes which were then machine-smoked. Ten % to 20% of the carbon-14 from these labelled insecticides transferred to the mainstream smoke. Of this amount transferred, 72% remained as carbofuran, 42% as carbaryl, 43% as unchanged DDT, 70% as unchanged Minex®. ATALLAH states an important observation which comes from this work, that when taking the same total volume of mainstream smoke, but in 5 ml puff increments, considerably more pyrolysis takes place with all these compounds than when the same total volume was drawn at a single 35 ml puff. This observation indicates that before the start of the puff, much of the parent compound is "trapped" by the upward draft of the thermal gradient going to sidestream smoke and thermally breaks down. The rearward movement of the hot gases when the puff starts then effectively distills any parent compound still on the tobacco at a temperature low enough to minimize thermal degradation.

Looking at a common tobacco fumigant, UNDERWOOD (49) treated tobacco with ³²P-labelled phosphine and, after the fumigation was complete, determined that the residual phosphine present in the tobacco was less than 5 ppm. This value was quite variable, apparently depending on tobacco type, ventilation and moisture con-

tent. On smoking cigarettes that were made from this [³²P]phosphine-treated tobacco, he found ³²P present only in the ash and none present in the smoke. UNDERWOOD might have seen traces of ³²P in the smoke if that experiment had been run today with more sensitive equipment, but the important fact remains that he demonstrated that phosphine does not transfer meaningfully to smoke.

TSOUKATOS et al. (50) reported on a novel method of following the flow of cut tobacco during processing by labelling with ^{99m}Tc, which has a short half-life. He also studied the homogeneity of the addition of the top-flavoring agent sprayed on the tobacco filler as well as the percentage of tobacco loss during manufacturing. This appears to be a satisfactory tracer if the short half-life is not a problem to the user.

In perhaps the most unusual use as a tracer, PORSTENDORFER (51) described a method where ²²⁰Rn-decay products were allowed to attach themselves to fresh cigarette smoke. This smoke was diluted, separated and trapped on a copper strip in a spiral centrifuge. The distribution of radioactivity was measured by counting along the strip and, by referencing to standard latex spheres, the size distribution of the smoke was measured. He found that for mainstream smoke diluted by about 3×10^3 with air, the mean particle diameter was 0.21 μ m to 0.24 μ m. This is in general agreement with the values published, using non-radioactive techniques, and serves to complement data already generated (52).

One agricultural chemical added to help prevent a root-knot nematode problem in tobacco was Diamidafos® (phosphorodiamidic acid, *N,N'*-dimethyl-, phenyl ester). MEIKLE (53) used [¹⁴C]Diamidafos in transplant water at a rate of 0.33 lb./acre. He followed the fate of this material into cured leaves and found 1.29 ppm of the parent Diamidafos®. Upon making cigarettes and smoking, 4% of the available radioactivity went to the mainstream smoke. He found 32% of the activity in the filter. This high filter value immediately seems out of line until one examines the data MEIKLE reports for mainstream-radioactivity composition. In the mainstream-smoke particulate matter the largest component was phenol (2%) followed by phenyl- β -D-glucopyranoside (1.3%). In the filter, 27.8% of the activity exposed to smoking was present as phenol. This data then reinforces those earlier findings about the selective removal of phenols by cellulose-acetate filters. None of the Diamidafos® was found intact in mainstream smoke. The author concluded that the maximum amount of any residual Diamidafos® present in the tobacco could raise the total-phenol level of smoke by no more than 1/3 and therefore he believed it to be acceptable for use in commercial products.

In a novel experiment where cigarette beetles were allowed to be exposed to carbon-14 Bright tobacco, MINOR (54) showed by measuring the radioactivity in the beetle excreta that adult beetles do indeed feed on tobacco, but the actual amount of material is very small.

Knowledge of the amount of air entering into the cigarette, the amount diffusing out, the intra and inter-cellular air quantities and the air-flow patterns within a cigarette are all extremely important in understanding the mechanisms of cigarette-smoke formation. This area of research seems a natural place to use radioisotopes. WILLIAMSON *et al.* (55), FRISCH *et al.* (56) and JENKINS *et al.* (57) have all discussed the use of argon-41 to measure the amount of air in the cigarette. In the first studies (55, 56), the total air (which is composed of free air between the tobacco shreds and the intercellular air in the shreds) was measured. The cigarette was flushed with room air (0.9% argon) which had been irradiated with neutrons to produce air containing ^{41}Ar , and then the amount of ^{41}Ar present between the strands was measured. The intercellular air was determined by neutron-activation treatment of the cigarette and counting the radiation from the entire cigarette. The diffusion in and out of the shreds was shown to be relatively slow compared to the necessary counting times. By difference, the amount of intercellular air was estimated. They found that the 1R1 cigarette had a total air fraction of 74% and the free air volume to be 73%. The intracellular volume by difference was approximately 1%. A 100% expanded Bright-tobacco cigarette was found to have a total air fraction of 87% and an intracellular air volume of 15%. In a later report JENKINS *et al.* (57) reported a more precise method of determining the intercellular air of the cigarette by neutron activation, purging the free air, and then heating the cigarette in a closed-loop system. The exchange of ^{41}Ar in the cigarette with the ^{40}Ar in the carrier gas is reasonably slow until the tobacco temperature approaches 100 °C. At this temperature, vaporization of the internal water ruptures the cells and the ^{41}Ar is released and then counted. These studies showed that the 2R1 cigarette had a value of 1.7% of the cigarette volume as intercellular air. One important observation made in these ^{41}Ar studies was the establishment of a linear relationship between tobacco moisture and free-air volume. As the tobacco absorbed water, there was less free air space due to the swelling of the tobacco shreds. This supports BAKER's (58) theory that the swelling of the tobacco behind the cigarette coal is a factor of some unknown but significant importance in increasing the resistance to draw of a cigarette when it is first lit.

SHEAHAN (59) described a method where the incoming air into a chamber holding a smoking cigarette was labelled with krypton-81m. This labelling technique had the advantage in that $^{81\text{m}}\text{Kr}$ is a gamma emitter ($E_\gamma = 190 \text{ keV}$) and can therefore be monitored at greater distances between the sample and the detector as may be necessary in some experiments. The half-life of $^{81\text{m}}\text{Kr}$ is 13 seconds which for most scientists is a disadvantage so great as to offer no advantages over the use of ^{41}Ar -labelled air. Results were obtained as gamma radiographs which make quantitative measurements difficult.

When organic matter is irradiated, many poorly understood reactions, including oxidation, decarboxylation, depolymerization and decomposition, occur. BOENIG (60, 61) was the first to examine effects on tobacco and smoke of cigarettes made from gamma-irradiated tobacco. SEVERSON *et al.* (62) followed up on this work. They found essentially the same results, namely a slight reduction in the yields of condensate, nicotine and total free radicals. SEVERSON (62) reported that when 1R1 cigarettes had been gamma irradiated at 30 Mrad and 60 Mrad dose levels and their smoke compared to unirradiated control 1R1 cigarettes, there was no major difference in smoke composition. He particularly noted that there was no meaningful difference in the composition of the refined polycyclic aromatic-hydrocarbon (PAH) fractions. CASEY *et al.* (63) continued this type of study, but with one major difference. The difference was that the tobaccos were irradiated with high-energy electrons. The beta dosages were 25 Mrad and 50 Mrad. CASEY (63) noted that the irradiation produced tobacco that was discolored and extremely fragile. In fact, he reported that the stem material readily turned to dust when subjected to any mechanical action. He also reported that the irradiation expanded the cured tobacco, the results being somewhat comparable to a Freon[®]-expanded tobacco. He conducted photomicrographic analyses and concluded that the Freon-11[®]-expanded tobacco showed evidence of cellular expansion and rupture outside of the tobacco xylem. In contrast, the irradiated expanded tobacco showed cellular expansion outside of the xylem but with little rupture of the cell walls. Chemical analysis of the irradiated tobacco showed a 60% reduction in the cellulose crude-fiber concentration at the 50 Mrad dose. Pectin was also reduced, but somewhat less. The dextrin and lignin contents were increased. Little change was found in nicotine content, but the tannins were significantly reduced. Since the irradiated tobacco was so fragile, reconstituted sheet was made from it and from the control tobacco, followed by cigarette making. Studies on the smoke from these cigarettes showed no major effect of irradiation on the compounds in the mainstream-smoke gas phase and only minor effects (reduction) on the particulate phase.

The knowledge gained from the results of these irradiation studies is very interesting. It is generally accepted that since the structural materials in the tobacco cannot escape the increasingly higher temperatures in the approaching coal, they must undergo pyrolysis, producing a large portion of the smoke. Pyrolysis studies carried out in laboratory apparatus show that, depending on the exact heating rates, the total mass of sample, and the nature of the carrier gas, drastic changes in the chemical composition of the pyrolysis products can be made. These irradiation experiments of CASEY (63) have demonstrated that in the matrix of the burning cigarette, things may be more tolerant. The mechanisms of

pyrolytic degradations are of multi-step nature and pass through many intermediates of unknown thermal half-lives. These irradiation studies indicate that the initial pyrolysis-degradation steps are not as important in forming different final products as are the later degradation stages. The radiation appears to initiate depolymerization, chain breaking, etc. which destroys the structural integrity of these materials, but only serves to advance the overall decomposition scheme partially. The approaching high-temperature gradient from the coal just completes the degradation process to give essentially the same smoke composition as the unirradiated tobacco. These irradiation studies would seem to suggest why few significant differences appear in the smoke composition when the burn rate of a cigarette is deliberately changed. It thus can be argued that it is the final stages of the thermal-degradation mechanism that are the important ones to smoke composition and that relatively slow changes in the speed of the movement of the thermal gradient only affect the rate of the beginning decomposition mechanisms.

For years, irradiation has been used commercially for insect control in wheat, grains and many foods. It is therefore no surprise that the control of the cigarette beetle by irradiation has been the subject of a recent presentation by BENEZET (64). In this presentation he showed a 42% decrease in beetle population at a dose of 0.1 Mrad. This technique appears to hold promise technically but better economics and public acceptance are necessary before this becomes a viable alternative to chemical fumigation.

H. Instrumental Neutron-Activation Analysis (INAA)

Instrumental neutron-activation analysis is an analytical method for the qualitative and quantitative determination of many inorganic elements in tobacco. The use of INAA for tobacco analysis has been accepted worldwide (65 - 107). Tobacco is ideally suited for INAA. It has a large abundance of inorganic components, is an easy-to-handle solid, produces little gas during irradiation, is readily available and is rapidly assayed by INAA. The literature on the use of instrumental neutron-activation analysis in tobacco is so large as to prohibit an in-depth review element by element or by tobacco and/or cigarette type. Tobacco, because of its easy-handling characteristics, has always been a favorite choice as a material for non-tobacco-oriented reactor facilities to use as a model system for INAA. Therefore, important descriptions on tobacco types, curing routines, etc. are often missing. This lack of descriptive experimental information by the various authors on the exact data of the tobaccos or cigarettes used has been a major drawback to any meaningful intercomparison of the INAA results published in the literature. Many laboratories studied only tobaccos native to, or sold in, their own country. Therefore, rather than review each tobacco or cigarette type, the literature will be divided

up into the countries where the tobacco was grown, or sold and assayed by instrumental neutron-activation analysis. These countries are listed below.

1. *United States:*
Nadkarni, R. A., et al. (65 - 76),
Jenkins, R. W., et al. (77 - 81),
Kim, C. K., et al. (82),
Komiya, K., et al. (83),
Lee, B. K., et al. (84),
Maruyama, Y., et al. (85, 86),
Chun, S. Y., et al. (87),
Ganchev, L., et al. (88),
Yang, M., et al. (89),
Pung, T. C., et al. (90),
Day, J. M., et al. (91),
Slegers, G., et al. (92).
2. *Belgium:*
Slegers, G., et al. (92).
3. *Bulgaria:*
Marinov, V. M., et al. (93, 94),
Naidenov, M., et al. (95).
4. *China:*
Wey, M. T., et al. (96),
Pung, T. C., et al. (90),
Yang, M., et al. (89).
5. *Egypt:*
Iskander, F. Y., (126).
6. *Europe (undefined countries):*
Ganchev, L., et al. (88).
7. *France:*
Ganchev, L., et al. (88).
8. *Great Britain:*
Maruyama, Y., et al. (85, 86).
9. *Germany:*
Maruyama, Y., et al. (85, 86).
10. *Greece:*
Slegers, G., et al. (92).
11. *India:*
Purkayastha, B. C., et al. (97),
Slegers, G., et al. (92),
Mishra, U. C., et al. (98, 99).
12. *Japan:*
Komiya, K., et al. (83),
Maruyama, Y., et al. (85, 86),
Chun, S. Y., et al. (87).
13. *Korea:*
Chun, S. Y., et al. (87),
Yang, M., et al. (89).

Table 9.
Elemental transference from 2R1 cigarette to smoke
in micrograms per cigarette (107).

	Tobacco	Paper	Cigarette	Ash	Condensate
Weight (g)	1.1	0.05	1.15	0.17	0.033
Na	587 ± 51	11 ± 1	598 ± 52	546 ± 36	2.2 ± 0.2
Mg	5500 ± 1600	24 ± 2	5520 ± 1600	5800 ± 500	n.d.
Al	554 ± 170	2.4 ± 0.4	556 ± 170	570 ± 70	0.06 ± 0.015
Cl	7420 ± 2200	190 ± 15	7610 ± 2200	5840 ± 120	82 ± 3
K	38100 ± 5000	190 ± 23	38300 ± 5000	30300 ± 1200	130 ± 9
Ca	22100 ± 2900	1020 ± 50	25000 ± 2900	32100 ± 2000	n.d.
Sc	0.10 ± 0.03	0.002 ± 0.0005	0.10 ± 0.03	0.16 ± 0.03	0.000027 ± 0.000008
Mn	139 ± 35	0.4 ± 0.05	139 ± 35	160 ± 43	0.006 ± 0.002
Fe	360 ± 50	9.5 ± 2.3	370 ± 50	390 ± 50	n.d.
Co	0.77 ± 0.07	0.028 ± 0.003	0.80 ± 0.07	0.80 ± 0.40	0.011 ± 0.005
Br	124 ± 22	2.0 ± 0.2	126 ± 22	99 ± 8	1.4 ± 0.04
Rb	14 ± 4	n.d.*	14 ± 4	16 ± 1	0.08 ± 0.01
La	2.0 ± 0.3	0.011 ± 0.003	2.0 ± 0.3	1.7 ± 0.4	n.d.
Ce	2.0 ± 0.6	n.d.	2.0 ± 0.6	2.2 ± 0.6	n.d.
Sm	0.19 ± 0.03	0.003 ± 0.0002	0.19 ± 0.03	0.16 ± 0.03	n.d.

* not detected.

Table 10.
Percentage elemental delivery to mainstream-smoke condensate,
based on 33 mg of dry condensate per cigarette and 73% of the cigarette consumed during smoking (107).

Element	2R1 cigarette		1R1 cigarette	
	cold trap	Cambridge pad	cold trap	Cambridge pad
Cl	1.5	1.3	1.2	1.4
Br	1.5	0.89	1.5	1.2
Co	1.9	—	—	—
Rb	0.78	—	0.18	—
Na	0.50	0.31	0.25	0.29
K	0.46	0.33	0.20	0.38
Al	0.014	—	0.009	—
Sc	0.037	—	0.018	—
Mn	0.006	0.006	0.004	0.003

14. *Indonesia:*
Slegers, G., et al. (92).
15. *Iran:*
Abedinzadeh, Z., et al. (100-102).
16. *Malawi:*
Slegers, G., et al. (92).
17. *The Netherlands:*
Faanhof, A., et al. (103, 104).
18. *Pakistan:*
Ahmad, S., et al. (105).
19. *Rhodesia:*
Slegers, G., et al. (92).
20. *Turkey:*
Yang, M., et al. (89),
Slegers, G., et al. (92).
21. *Switzerland:*
Wyttenbach, A., et al. (106).

KINS et al. (107) and AHMAD (105). ABEDINZADEH et al. (102) determined 20 elements in the paper of an Iranian cigarette and they noted only a small, if any, contribution of these elements to the total-mass concentration in the smoke.

Some laboratories, in an attempt to correlate the transfer rate of inorganic components to smoke, have analyzed the cigarette ash. Normally, unless specified, this has meant the ash which drops off the cigarette while undergoing machine smoking. This analysis is very sensitive to precise weighings of an extremely fluffy material, coupled with enriched concentrations per unit weight. Slight errors in measurement are therefore magnified in the total-ash value. AHMAD et al. (105) reported that they had measured elemental concentrations in ash, but did not present any analytical results other than the approximate percentage of elements remaining in ash. Just how these data were determined is not clear, a very typical response from non-tobacco-oriented research groups. NADKARNI, EHMANN and BURDICK (72) report data on ash from the 1R1 cigarette as do JENKINS et al. (78). CHUN (87) measured bromine (5.8 ppm) and selenium (1.3 ppm) in the ash from Korean cigarettes. The importance of the ash to the inorganic mass in smoke was discussed earlier in this review.

There are a limited number of researchers who have been using instrumental neutron-activation analysis to elucidate smoke delivery and/or mechanisms. In mainstream smoke, various collection techniques have been used, ranging from impaction and/or cold traps to filtration devices. JENKINS and co-workers (78) smoked 1R1 reference cigarettes and collected the smoke condensate by impingement of the smoke through a capillary tube directly into a polyethylene irradiation vial. NADKARNI and EHMANN (71) have smoked 1R1 reference cigarettes and have trapped the whole-smoke condensate using Cambridge filter pads. They also compared this trapping method to the use of cold glass traps and found very little difference in the level of elements as a function of the trapping techniques. The use of standard smoking conditions and the 1R1 reference cigarette allows a comparison of data generated by JENKINS et al. (78) and NADKARNI et al. (71). In general, agreement is within the experimental variability experienced by all investigators due to the non-homogeneity of blended cigarettes and the small sample sizes used for instrumental neutron-activation analysis.

JENKINS et al. (107) have published whole-smoke condensate data collected using standard smoking conditions for the University of Kentucky 2R1 reference cigarette. There appears to be no significant differences between the elemental concentrations in the whole-smoke condensate from the 1R1 and 2R1 reference cigarettes (Table 10).

ABEDINZADEH et al. (102) have measured the whole-smoke condensate produced by a brand of commercial Iranian cigarettes. The condensate was washed in solvent, reduced in volume, and irradiated. The potential for contamination from the solvents is very real. This

There are so many differences in the geographic origin, available nutrients, genetic inheritances, stalk position, curing practices, etc. that any direct comparison of these results is very difficult. Some authors did utilize the University of Kentucky's reference cigarettes and these data generally show good agreement on the macroelements, but a wide difference is noted in the minor elements. This may be due in part to variances in either the equilibrium-moisture level or a failure to properly assay the amount of water present in the tobacco. Since most analyses were expressed on a ppm basis, any variation in weight caused by variable moisture levels would be reflected in the final numbers.

There is only one report (Table 9) on elemental determinations in the 2R1 reference cigarette. JENKINS et al. (107) showed no major differences in the 1R1 and 2R1 cigarettes when expressed on a ppm basis.

Cigarette paper has received less attention because it does not offer as many exciting elemental differences among paper types as seen in different tobaccos. NADKARNI et al. (72) have determined nine elements in cigarette paper for 12 brands of cigarettes. Some differences were noted from brand to brand in zinc concentration (in the range from below detection limit up to 46 ppm). Unless this variability can be related to some effect of transfer to smoke, its importance is diminished. The contribution of the cigarette-paper elements to smoke is extremely difficult to evaluate because the elements found to be present in the paper all exist in higher concentrations in the tobacco, and the contribution of the paper cannot be tested directly by instrumental neutron-activation analysis. Calcium is one element in cigarette paper (usually as a whitening agent) whose contribution to smoke has been studied by JEN-

Table 11.
Total-smoke distribution of halogens from 1R1 cigarette (81).

Smoke phase	Chlorine		Bromine	
	µg	percentage of total recovered	µg	percentage of total recovered
Butt	1880	24.6	37	22.5
Char-attached coal	750	9.8	15	9.1
Ash, dropped	4460	58.3	103	62.6
Mainstream total particulate matter	78	1.0	1.5	0.9
Mainstream gas phase	95	1.2	1.6	0.9
Sidestream total particulate matter	66	0.9	1.4	0.9
Sidestream gas phase	328	4.3	4.9	3.0
Total recovered	7657		164.4	
Neutron-activation analysis of total cigarette	7520		174	
Average recovered (10 runs)	101.8%		94.5%	

was pointed out by NADKARNI, EHMANN and BURDICK (72) who stated that they had observed high Zn contents in their blanks due to the metal containers used for solvent storage. MISHRA et al. (99) compared values for three brands of cigarettes sold in India with several published reports on different tobaccos and cigarettes and found agreement within the large variations present in his particulate-matter deliveries.

Most often the authors analyzing smoke condensate by INAA try to calculate the percentage transference of the elements from the cigarette. Each laboratory calculates this transference rate in a slightly different manner, and these values are highly dependent on the exact moisture level of the tobacco, the smoking environment and conditions, and the exact water content of the whole-smoke condensate. Most often this information is lacking in the papers reviewed, and therefore transference percentages are deliberately omitted because they would add confusion to an already unclear area of science.

The effects that cellulose-acetate filters have on the removal of inorganic components from whole-smoke condensate have been briefly studied by NADKARNI, EHMANN and BURDICK (72). They concluded that "filtered cigarettes are more effective than the non-filtered cigarettes in preventing the transfer from cigarettes into smoke condensate of 13 trace elements studied here" (72). This is to be expected since the purpose of adding filters to cigarettes has always been to reduce the total amount of smoke delivered. The real question that needs addressing is: do filters selectively remove more inorganics from smoke than expected based on total particulate matter removed? Upon examination of the data of NADKARNI et al. (72), it appears that instead of a selective reduction of inorganics from the whole-smoke condensate, the opposite effect of a relative enrichment appears to take place. One possible explana-

tion is that the bulk of the inorganic-chemical mass may not be totally associated within the organic components / water smoke-aerosol particles, but may exist to a large degree as small pieces of entrained inorganic residue as described by JENKINS et al. (107). These pieces of inorganic residue thus may exhibit entirely different filtration-removal rates and mechanisms by the tobacco column and by the cellulose-acetate filters. There could be a less effective removal of these inorganic particles than for the organic components / water portion of smoke and hence an observed enrichment in the inorganic-chemical concentration in smoke.

There has been little information published on smoking irradiated cigarettes. WEHNER et al. (108) irradiated cigarettes with neutrons and looked at Br, Na, and K in smoke. No gas-phase measurements were performed. Unfortunately values were presented which showed several smoke phases all added together, and, therefore, this data is of little utility in establishing anything but a total-mass balance.

JOHNSON et al. (109) studied labelled NaCl added to cigarettes which were then smoked. They verified these NaCl results using neutron-irradiated tobacco. They found that methyl chloride is formed by the conversion of ionic chloride, and that methyl chloride shows a strong preference for mainstream-smoke gas phase. A material balance for the total Cl was not obtained. In a later paper, JENKINS et al. (81) have presented mass balances for Na, K, Mn, Cl and Br in smoke from neutron-irradiated 1R1 cigarettes (Table 11). They studied the organohalogen composition of the gas phases and found them qualitatively identical, but quantitatively different. A significant conclusion of JENKINS et al. (81) was that, since both gas phases were qualitatively identical, the smoke-formation mechanisms taking place for the conversion of ionic to covalent bonds for the halo-

gens have threshold energies below the minimum temperatures that take place during puffing or in the static-burn mode.

There are only a few reports on the use of instrumental neutron-activation analysis as an analytical research tool to study reaction mechanisms. The works of JOHNSON and SMITH (109) and JENKINS, NEWMAN, LESTER, FRISCH and WILLIAMSON (81) on the formation of the organohalogens have already been discussed. These studies have demonstrated significant conversion of ionic halogens to organohalogens. The ionic and organohalogen content of the mainstream-smoke total particulate matter has also been investigated by JENKINS et al. (81).

A method for studying the inorganic-chemical composition of various fractions of mainstream smoke separated according to particle size has been described by JENKINS (41) and was reviewed earlier in this paper.

JENKINS et al. (107) have continued these types of INAA smoke-formation studies to determine filtration of selected inorganics by the tobacco rod and by cellulose-acetate filters. These data were used to construct filtration curves for each 5 mm section behind the cigarette coal. Na, K, Br, and Cl appear to be removed by direct impaction, interception, or diffusion of entrained inorganic-residue particles coming from the cigarette coal. Vapor condensation of the inorganic components studied is not considered a major filtration mechanism because a uniform filtration is observed at distances far enough behind the coal, past the point where condensation would be important.

JENKINS et al. (125) have used instrumental neutron-activation analysis to map the distributions of selected elements within the tobacco leaf at a single stalk position. These data show that not all elements are evenly distributed through the leaf.

I. Cigarette-Rod Density Measurements

Some of the more important research to be published on cigarette-smoke formation mechanisms and smoke delivery has evolved around the measurement of the various temperature profiles in the cigarette (109 - 112). EGERTON, GUGAN and WEINBERG (111) described in a classic paper a variety of methods which examined the mechanism of cigarette smouldering. They used X rays to detect the melting of different metal alloys which have definitive melting points. From this, they reconstructed the events taking place in and behind the coal. They observed an abrupt change in the cigarette density just behind the coal and attributed this to the condensation of volatile products. BAKER (113) determined temperature and gas compositions in the burning cigarette. In general BAKER's work complimented and extended the results of EGERTON et al. (111), resulting in a computer re-creation of the gaseous and temperature profiles and their associated changes as the cigarette is smoked. Another density-measurement experiment em-

ploying a beta-ray attenuation method with a modified ^{32}P -beta thickness gauge was described by JENKINS et al. (114). In this study, a beam of collimated beta particles was projected through the side of a cigarette towards a fixed detector as the cigarette burned past. A density profile of the burning cigarette was established for both the puffing and static-burn modes. The data were reduced using a mathematical model derived by WILLIAMSON (115). The profiles produced by this technique compared well to the temperature profiles established by BAKER (110) as shown in Figures 5 and 6. Studies in the static-burn mode revealed that the observed decline in the rod density starts about 2 mm inside (behind) the visual char line indicating that the distillables and pyrolytic products move away before the visual char line arrives. This is in agreement with BAKER (110) who reports a high-temperature region 5-6 mm inside the char line. In the normal puffing mode, agreement was again obtained with BAKER (110), in that tobacco density is lost because of distillation, pyrolysis and combustion over a longer region consistent with the rearward movement of the hot gases, predominately on the cigarette periphery. These studies were continued, with puff-by-puff density measurements being made. The changes due to the condensation of smoke volatiles behind the coal were measured as well as the subsequent reevaporation of these condensables during the static-burn period between puffs. The reevaporation of condensables was attributed to either an increase in tobacco temperature or a change in the relative humidity of the atmosphere over the tobacco by the diffusion of water from the rod. Resolving a single puff and its condensation of volatiles, JENKINS et al. (114) concluded that it appeared that water was uniformly distributed within the 35 ml puff volume.

J. Neutron Radiography

One of the newest nuclear techniques in tobacco and cigarette-density studies is that of neutron radiography. Since many investigators in smoke-formation research may be unfamiliar with the details of this technique, a brief description is appropriate. Neutron radiography is in many ways conceptually similar to X-ray radiography. When a beam of thermal neutrons (with energies less than 0.3 eV) passes through an object, some neutrons are absorbed or scattered from the beam. The transmitted neutrons can then be used to create an image of the object. Whereas X rays are strongly absorbed by the higher atomic-weight elements, thermal neutrons are efficiently attenuated by relatively few elements. For example, isotopes of boron and gadolinium are good attenuators as a result of their large neutron-capture cross sections; however, in the case of hydrogen, neutrons are attenuated primarily as a result of a large scattering cross section. One result of this is that although organic materials and water are nearly transparent to X rays, they are visible in neutron radio-

Figure 5.
Cigarette-rod density vs. static-burn char-line distance (114).

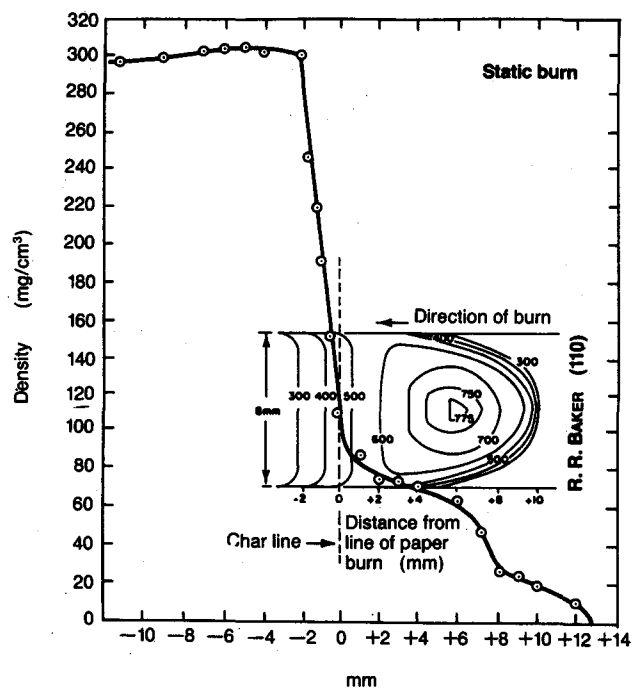


Figure 6.
Cigarette-rod density vs. puffing-burn char-line distance (114).

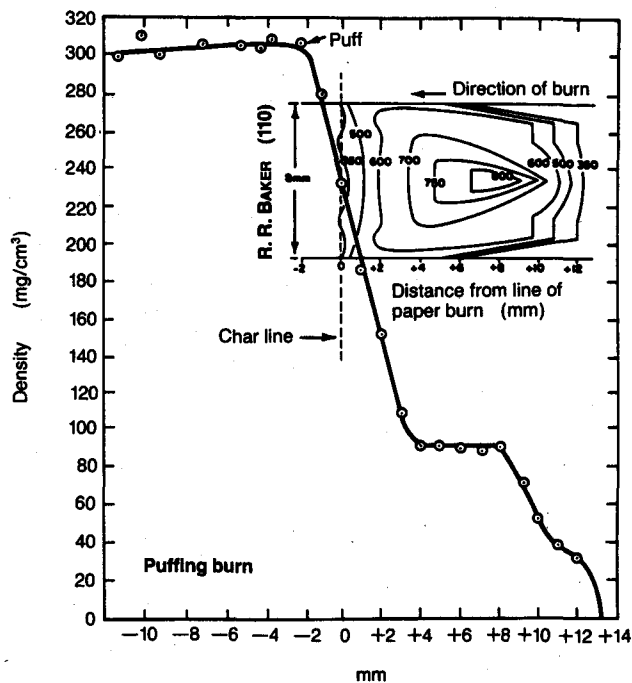
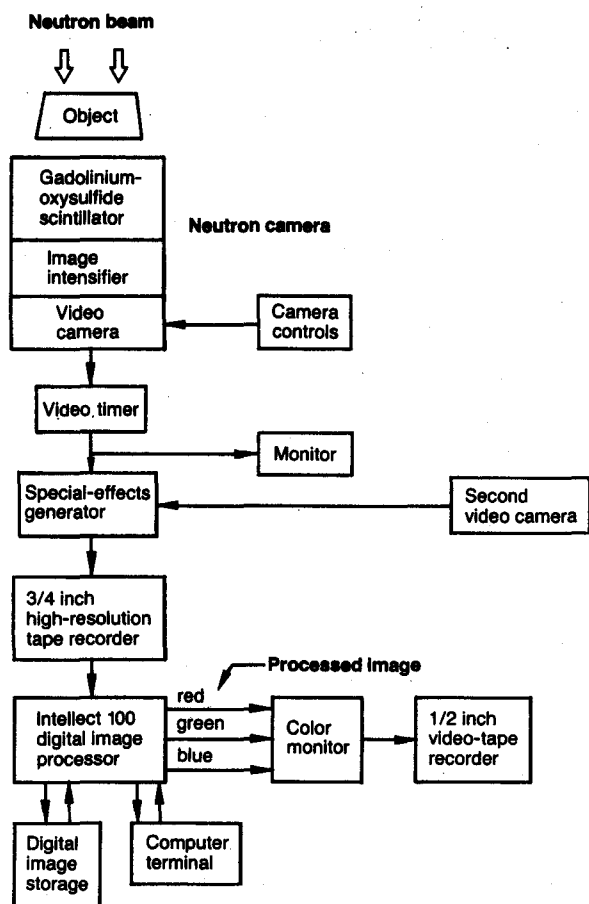


Figure 7.
Video-image handling system for real-time neutron radiography (120).

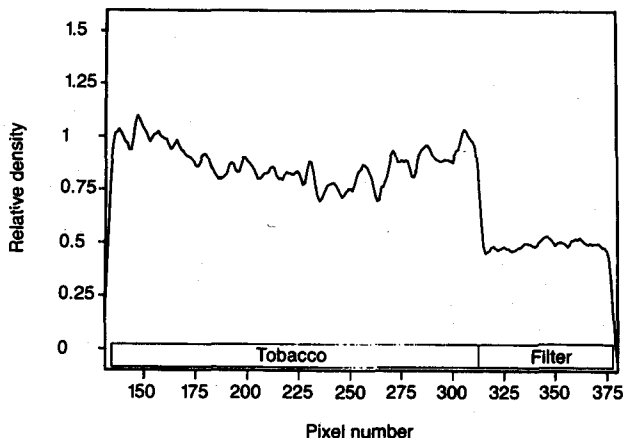


graphs as a consequence of their high hydrogen content. Neutron and X-ray radiography are therefore complementary, since neutrons can be used to produce an image of hydrogen, organic materials and strong neutron-absorbing isotopes present in an inorganic matrix, whereas X rays can produce an image of metallic objects contained in an organic matrix. McRAE et al. (116) have described the use of this system to observe the real-time deposition of a neutron-absorbing aerosol in a filter. An aqueous solution of $GdCl_3$ was nebulized, dried and neutralized to form the aerosol. The filters used for these experiments were standard cellulose-acetate cigarette filters. From the observations, the depositions were analyzed both as a function of time and penetration into the filter. These observations were made on a video system (Figure 7) designed specifically for neutron radiography by BRENIZER et al. (117). This system includes a neutron-sensitive image intensifier with a modified high-resolution video camera. The system also contains a video timer, special-effects generator, time-base corrector, video recorders and a digital image processor. A series of temperature-contrast agents was developed by BRENIZER et al. (118) to at-

tempt to measure exact thermal regions in a burning cigarette. Unfortunately these agents were water sensitive and not well suited for the environment of the burning cigarette. Gadolinium salts have been shown to be excellent markers or tracers for individual tobacco-strand visualization.

As discussed earlier, density measurements have been made in a burning cigarette and changes in the density behind the coal were observed and these density changes correlated with the temperature gradients in the cigarette (114). GOLDRING (119) used X-ray radiography to examine cigarette rods where visible variations in density of the tobacco were observed. BRENIZER et al. (120) used neutron radiography to also view density variations in cigarettes. By averaging center-line density scans for several cigarettes and using an image processor, large-scale variations in the density of the cigarette

Figure 8.
Average relative density calculated from the center-line data of ten experimental cigarettes (120).



rods were measured as shown in Figure 8. These measurements correlated well with actual-weight measurements, thereby allowing real-time observations of cigarette dense ends. McRAE (121) has refined both the hardware and processing software to provide a system which can quantitatively determine density variations that are not visible to the eye as were those in the earlier studies. At present, it would appear that much more information will be obtained on the condensation and reevaporation of smoke condensables in the tobacco column by neutron radiography than by using the beta-ray techniques. The main advantage is that data are collected at the television rate of 30 frames per second compared to 1 to 2 seconds per data point for the beta devices. The digital output of the neutron-radiography system is readily compatible with image processing, thereby providing the researcher with greater data-reduction capabilities.

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