



# **Tobacco, Cigarettes and Cigarette Smoke**

*An Overview*

Otmar Geiss, Dimitrios Kotzias

Institute for Health and Consumer Protection  
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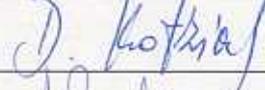
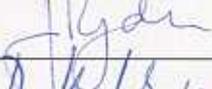
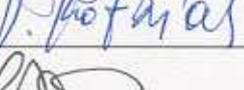
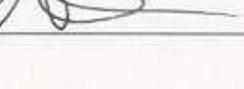
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## **Preface**

DG JRC's Institute for Health and Consumer Protection (IHCP) is acting upon DG SANCO's request to serve as reference point for issues related to the implementation of the Tobacco Directive. The field of activities covers the characterization of ingredients in cigarette brands, the study of diverse smoking regimes and collaboration with other international organizations to establish technical guidelines for the measurement of emissions during the burning of tobacco products, as well as the evaluation of data lists on tobacco ingredients that national authorities transmit to DG SANCO within the frame of the Tobacco Directive's requirements.

JRC-IHCP is hosting the Network of Government Laboratories for Tobacco and Tobacco Products (GoToLab) with the aim to establish a close collaboration between relevant Member State authorities and the JRC on tobacco control to develop validated measurement methods and techniques.

JRC-IHCP has also provided substantial support to Commission Services for the preparation of the Green Paper on Environmental Tobacco Smoke (ETS), particularly on the impact of various air change rates on the levels of ETS components.

This technical note provides an overview of the origin and mode of treatment of tobacco, tobacco ingredients and pesticide residues found in tobacco leaves. This note also reports on experiments carried out at the JRC-IHCP related to the chemistry of tobacco constituents and it gives information on analytical methodologies used for measuring tar, nicotine and carbon monoxide.

Dimitrios Kotzias

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## General information about the Tobacco plant

Family : *Solanaceae* ( Nightshade family, the same as Potato and Tomato )  
Genus : *Nicotiana Tabacum* ( 1 Year Plant )  
*Nicotiana Rustica* ( 1 Year Plant)

There are about 67 species, which are mainly found in America. *Nicotiana africana* is the only indigenous species in southern Africa, endemic to Namibia. In addition, there are 3 naturalised species in southern Africa.



Native Americans used tobacco before Europeans arrived in North and South America; early European settlers learned to smoke and brought the practice back to Europe, where it became hugely popular. At extremely high doses, tobacco becomes hallucinogenic; accordingly, Native Americans generally did not use the drug recreationally, rather, it was often consumed in extraordinarily high quantities and used as an entheogen by experienced shamans or medicine men. In addition to being smoked, uncured tobacco was often eaten, drunk as tobacco juice, or used in enemas. Early missionaries often reported on the state caused by tobacco, but as it spread into the west, it was no longer used in such large quantities or for entheogenic purposes. Religious use of tobacco is still common among many indigenous peoples, particularly those of South America.

With the arrival of Europeans, tobacco became one of the primary products fueling the colonization of the future American South, long before the creation of the United States. The initial colonial expansion, fueled by the desire to increase tobacco production, was one cause of the first colonial conflicts with Native Americans and became a driving factor for the use of African slave labour.

The importation of tobacco into Europe was not without resistance and controversy in the 17th century. King James I of England (James VI of Scotland) wrote a famous polemic entitled *A Counterblaste to Tobacco* in 1604 (published in 1672). In his essay, the king denounced tobacco use as "custome lothsome to the eye, hatefull to the Nose, harmefull to the braine, dangerous to the Lungs, and in the blacke stinking fume thereof, nearest resembling the horrible Stigian smoke of the pit that is bottomelesse." In that same year, an English statute was enacted that placed a heavy protective tariff on every pound of tobacco brought into England.

## **Types of Tobacco**

Many kinds of tobacco are grown in the world, with a variety of uses. The types of tobacco vary according to tobacco classes in various countries and elements such as manipulation of nitrogen fertilization, plant density, time and height of topping, harvesting and curing are added to favourably influence the usability of the cured leaves for specific products. Some of the most common types are listed below.

**Virginia** (40 % of world tobacco production)

Virginia is high in sugar and low in oils. The colour of the leaves ranges from bright lemon yellow to medium brown; the lighter colours being spicier in flavour and the darker coloured leaves having a more deeper and complex taste.

Virginia is used almost entirely in cigarette blends. Some of the heavier leaves may be used in mixtures for pipe smoking. Some English cigarettes are entirely composed of Virginia tobacco.

Major producers in the world are China, U.S.A., Brazil, India and Zimbabwe.

**Burley** (11 % of world production)

It is high in oil, low in sugar and has a nutty type of flavour.

Burley is usually light air-cured, derived from the White Burley which arose as a mutant on a farm in Ohio in 1864. Burley is used primarily in cigarette blends. Some of the heavier leaves are used in pipe blends and also for chewing.

Cured burley leaf is characterised by low sugar content and a very low sugar to nitrogen ratio (high nicotine). This is enhanced by high amounts of nitrogen-fertilisers, harvesting at an early stage of senescence, and the air curing process allows for oxidation of any sugar which may have occurred.

Main producers: U.S.A., Italy, Korea, Brazil, Mexico

**Maryland** (small total world production)

It is a neutral type of tobacco with a mild flavour.

Maryland is another usually light air-cured type. It is used in some American blended cigarettes and to a greater extent in certain Swiss cigarette blends.

Maryland tobacco is extremely fluffy, has good burning properties, low nicotine and a neutral aroma.

Production countries : U.S.A. and Italy

**Oriental** (16% of total production)

Oriental tobacco is mild with a very characteristic aroma. Resins, waxes and gum exuded by glandular hairs (trichomes) supply the aroma. Nicotine is low, averaging around 1,0%. The tobacco is usually sun-cured.

Main producers : Russia, Turkey, Bulgaria, Greece, Serbia, Romania, Italy

**Rustica**

When the first settlers reached Jamestown, Virginia (in what is now the USA), they found the Native Americans smoking *Nicotiana rustica* which contains about 10% nicotine. Over the following 300 years, *rustica* lost a lot of ground to *nicotiana tabacum*. Nowadays *rustica* is grown and used in India, Pakistan, Bangladesh, Russia, Indonesia, Afghanistan, Burma, Iran, Iraq, Algeria, parts of Africa and parts of South America.

*Nicotiana rustica* is smoked primarily in water pipes but is occasionally smoked in cigarettes or chewed.

## **Composition of commercial cigarettes**

### **Tobacco Blends**

A cigarette seldom contains only one type of tobacco. Most cigarettes contain a mixture, or blend, of several types of tobacco from a variety of sources. The main types that can be used are brown, Virginia, Burley and Oriental tobacco. Brown tobacco blends sometimes also include Oriental tobacco. English blends mainly comprise Virginia tobacco, while blends for American consumers contain Virginia, Burley and Oriental tobacco. Casing and flavouring ingredients may be used in the blends, in varying quantities, depending on the style of blend.

Most of the blend will be flue cured Virginia. About 1/3 will be burley and about 10% oriental or Maryland. The oriental and Maryland are a little bitter tasting and are used sparingly.

These are the main types of blended cigarettes, which are made with a mixture of tobacco varieties:

#### **American-blend cigarettes**

The most popular of the blended cigarettes, made with a mixture of flue-cured, burley and oriental tobacco. The specific percentage of each type varies from brand to brand, but generally contain 50% Virginia and 37% air cured burley, while oriental is the smallest percentage of the blend at around 13%.

#### **English-blend cigarettes**

English-blend cigarettes are made almost entirely of flue-cured tobacco. Also known as Virginia cigarettes.

#### **German-blend cigarettes**

Similar to American-blend cigarettes, but more oriental tobacco is used in the blend. Also, these cigarettes have a milder taste because the tobacco is not as heavily cased and flavoured as American-blend cigarettes.

#### **Oriental-blend cigarettes**

As their name suggests, Oriental-blend cigarettes are made almost exclusively of oriental tobacco.

#### **Virginia cigarettes**

Virginia cigarettes are made almost entirely of flue-cured tobacco. Also known as English cigarettes.

## Reconstituted Tobacco

The processing of Reconstituted Tobacco (RT) provided the opportunity to utilize the fines, ribs, and stems of the tobacco leaf in the production of cigarettes. In the past, most of these “tobacco by-products” were wasted. Using RT was also attractive because laboratory studies had shown that cigarettes made exclusively from RT delivered lower smoke yields of “tar” and volatile phenols.

RT is composed of tobacco dust, fines, particles, and the ribs and stems . Various additives may be incorporated.

There are four ways of making RT; two relate to the paper process, one involves a slurry, and the fourth is based on the preparation of a tobacco paste with rollers using water or low boiling solvents. For the paper process, a mixture of fines, midribs and sometimes tobacco stems is broken up and extracted with water. The extract is concentrated by evaporation. The insoluble residue is further macerated and the resulting material is formed into a paper-like web on a paper-making machine. The web (paper roll) is dried, impregnated with the concentrated extract, and further dried and cut. The shredded material is added to the tobacco blend.

Since the aqueous extracts of the tobacco contain nicotine (and nitrate) and this extract is added to the tobacco web as a concentrate, this process has been considered a “nicotine-enriching process”. Not adding the aqueous extract to the insoluble part would lead to RT that is low in nicotine and nitrate.

RT is used in tobacco production to allow cigarette manufacturers to make the most efficient use of their tobacco by utilizing the scrap and stems instead of discarding them. The resulting paper-like sheets of reconstituted tobacco are then cut into strips and used in cigarettes.

## Puffed, Expanded and Freeze-dried Tobaccos

These modified tobaccos have up to twice the filling power, thus requiring less tobacco per cigarette. The principle applied here is to expand the tobacco cell walls by quick evaporation of water and other agents that readily volatilize, including those added to tobacco (e.g. Trichlorofluoromethane).

	<b>100% expanded cigarette</b>	<b>Non-expanded cigarette</b>
Tobacco per cigarette	363 mg	667 mg
Tar per cigarette	12.4 mg	21.7 mg

## **Tobacco Curing**

Harvesting and curing tobacco are the final jobs of tobacco field production. Both practices have changed more than any other phase of tobacco production.

Curing is the process that brings about the rapid destruction of chlorophyll, giving leaves their yellow appearance, converting starch into sugar and removing moisture. Curing brings out the aroma and flavour of each variety of tobacco.

Before tobacco is cured, the leaves contain 80-85% water. After the curing cycle, essentially no water is left.

Many factors affect the curing schedule, including the soil, the position of the leaf on the stalk and the weather.

### **Stages of Curing**

Curing involves three essential steps: yellowing, leaf drying and stem drying. The curing environment can be manipulated by controlling heat, humidity and air movement.

The *Yellow Stage* is a continuation of the ripening process and is thought to be the most important part of the curing process. The leaf is still alive during the yellowing phase, which allows it to carry on certain biological processes needed to convert starch to sugar and break down chlorophyll.

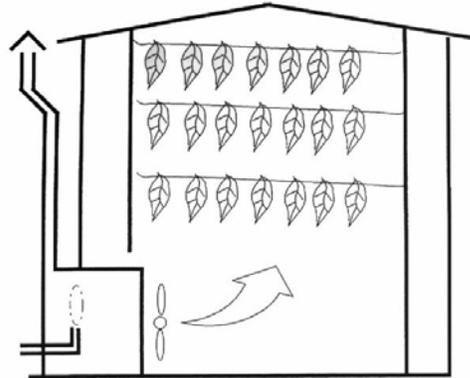
The *Leaf Drying Stage* is where the leaf tissue is dried to a particular moisture level.

The *Stem Drying Stage* is referred to as the “killing out stage” because all moisture is removed from the stem and leaf, killing them.

Each type of tobacco responds best to a certain curing method.

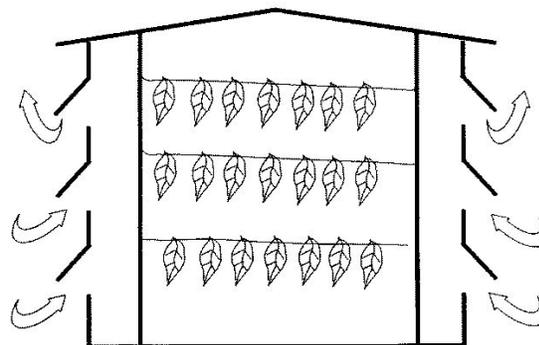
### **Flue – Cured**

Flue-cured tobacco is dried in a closed building with furnace-driven heat from flues or pipes that extend from a furnace into the barn. The temperature is gradually raised until the leaves and stems are completely dried. As the heat and humidity are controlled, moisture is removed, resulting in dried yellow leaves and stems.



### **Air – Cured (Burley)**

Burley tobacco is air-cured. Air curing barns require an open framework where sticks of tied leaves or the whole stalk is hung and protected from the wind and sun. Barns are equipped with ventilators that can be opened or closed to control temperature and humidity.



### **Fire – Cured**

Fire-cured tobacco is dried with low-burning wood fires on the floors of closed curing barns. The smoke is what gives fire-cured tobacco its smoky aroma and flavour. These leaves have a low sugar content but high nicotine content.

### **Bulk – Curing**

Bulk-curing requires fewer workers and uses less fuel than other methods. Racks of harvested tobacco are placed in bulk barns either by machine or by hand. Tobacco is pressed into containers or hung evenly throughout the metal barn where heat and ventilation are controlled while air is forced through the leaves.



### **Post-cure processing**

After the tobacco has been cured, it is moved from the curing barn into a storage area for processing. If whole plants were cut, the leaves are removed from the tobacco stalks in a process called stripping. For both cut and pulled tobacco, the leaves are then sorted into different grades. In colonial times, the tobacco was then "prized" into hogsheads for transportation. In bright tobacco regions, prizing was replaced by stacking wrapped "hands" into loose piles to be sold at auction. Today, most cured tobacco is baled before sales are made under pre-sold contracts.

## Summary

- Harvesting of tobacco leaves
- Drying of picked leaves (4-8 weeks)
  - water reduction (20-25 %)

Fermentation occurs during the drying process. Processes during the fermentation:

- Degradation of Proteins in Amino acids, NH<sub>3</sub>, Amides and Carbonic Acids → pH<7
- Degradation of Carbohydrates (in Dextrines and Monosaccharides)
- Degradation of Nicotine (10-90 % degradation due to microbiological activity)
- Formation of Polyphenolic substances (brown colour)

The process of fermentation can be driven by controlling humidity and temperature. Good fermentation needs a slow rise of temperature during the heating period.

Temperature-Maximum : 60 C  
Humidity Minimum : 10 % (below that, no fermentation is possible)  
10-27 % enzymatic reactions  
> 27 % enzymatic and microbiologic reactions

Natural Curing : Air Curing and Sun-Curing  
(30-90 days)

Artificial Curing : Flue-Curing, Bulk-Curing and Fire-Curing  
(3-5 days)

## **Tobacco Additives**

### **Definition of Additives:**

"Additive" means any substance, chemical or compound, other than tobacco, water or reconstituted tobacco sheet, that is introduced by a manufacturer into the tobacco, paper or filter of a cigarette or into cigarette tobacco during the processing, manufacturing or packing of the cigarette or cigarette tobacco.

### **Casings**

Before the the leaves are cut, a “sauce” is added to the tobacco. This sauce contains a variety of ingredients, such as sugars, humectants (2.5-3.5%) and aromatic substances. The addition of sugars to tobacco (4-6%) results in acidic smoke (pH 5.2-6.2) by neutralizing the alkalinity of the nitrogenous compounds

Tobacco additives have been used in cigarettes throughout the history of cigarette manufacturing. The majority of these ingredients (such as cocoa and sugars) are used to enhance aroma and flavour. Others are used to enhance sensory aspects, including taste, associated with the smoke (such as menthol), to facilitate tobacco processing and cigarette manufacturing (such as carbon dioxide and water), and to preserve moisture levels in the finished cigarette (such as water and glycerine).

### **Aims of Additives**

- Humectants are added to keep the tobacco and smoke moist.
- Flavours are added to create a special brand flavour.
- Menthol, sweeteners and other additives are included to make the smoke easier to inhale.
- Some additives are designed to reduce objections to second-hand smoke.
- Various additives are used to enhance the appeal of cigarettes to young people.
- (Pharmacologically active additives are added to increase the speed and size of the nicotine "hit" and improve the chances of addicting a smoker).

## **Examples of Additives**

### **Ammonia and Ammonia-like compounds [12]**

The base ammonia, as well as ammonia-forming compounds such as diammonium phosphate (DAP) and urea, is thought to be routinely added to the tobacco used in cigarettes. Though denied by major American tobacco companies, the U.S. Food and Drug Administration (FDA) has argued that one intent of this use of ammonia is to increase and control the delivery of the alkaloid nicotine to the respiratory tract of the smoker.

No real evidence has yet been found to demonstrate that ammonium-salts are deliberately added with the aim to increase the portion of free-base nicotine.

Therefore, space is given below to both *pro* and *contra* of this argumentation (in no way does the following reflect the attitude of the JRC, although a variety of investigations have been performed over the last years<sub>[18]</sub>).

#### **a) Arguments supporting the deliberate adding of Ammonium-salts theory**

When added to a tobacco blend, ammonia reacts with the indigenous nicotine salts and liberates free [base] nicotine.

#### **Why are nicotine-enhancing compounds added to tobacco?**

In the past, legislators felt that if tar levels were reduced, the health problems associated with smoking would decline. Cigarette manufacturers responded in the sixties by developing low-tar or light cigarettes.

Manufacturers designed “Light” Cigarettes with filters and filter ventilation holes at the top of the cigarettes. The holes in the filter allowed pure air to be drawn into the smoker’s mouth which diluted the smoke, thus reducing the amount of nicotine and tar.

Tobacco companies were concerned that these ventilation holes would result in a weaker taste because smoke would be diluted with air. Tobacco manufacturers introduced additives as taste enhancers so smokers would not have this weakened taste.

Tobacco manufacturers can control nicotine delivery by various design and manufacturing techniques. One of these techniques is referred to as additive technology. Additives are used by many tobacco manufacturing companies to influence the pharmacological effects of nicotine, mask the discomfort of inhaling smoke, and create an appealing taste.

#### **What has been done to increase Nicotine Delivery ?**

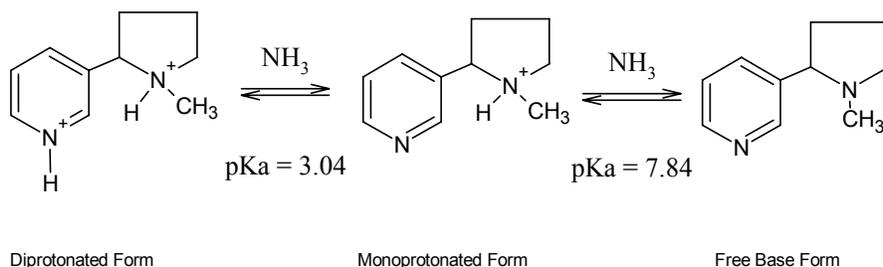
- Using high-nicotine tobaccos and also higher nicotine-containing parts (i.e. stems) of the tobacco leaf to raise the nicotine concentration in low tar cigarettes
- Adding completely extraneous nicotine
- Using Ammonia compounds to increase the delivery of free nicotine to smokers

- Genetically engineering tobacco plants so as to increase their nicotine content
- Developing analogs that will have the same dependency-causing effect

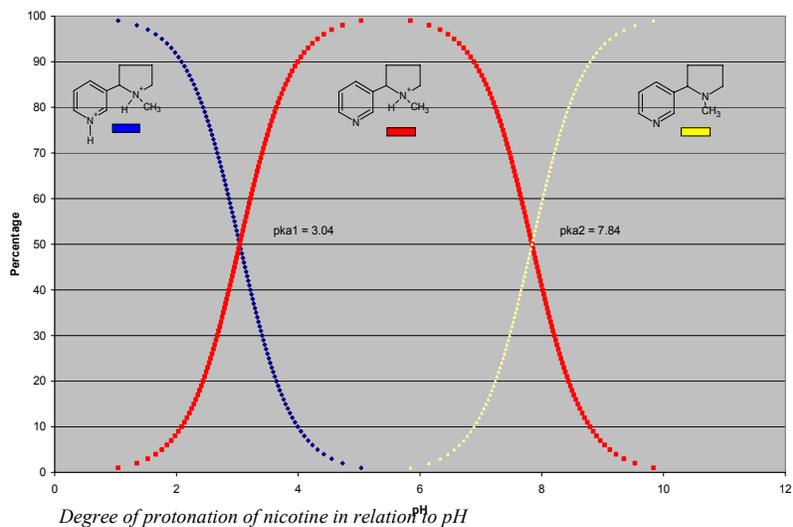
Why is Ammonia added and what happens in the cigarette smoke ?

When used as an additive in tobacco, ammonia causes nicotine to change its form. This change results in more nicotine being delivered to the smoker.

Ammonia extracts free nicotine from tobacco blends through an acid-base interaction. Ammonia increases the pH allowing the liberation of free nicotine.



Once nicotine is free, it is absorbed into the smoker's bloodstream at a faster rate. Nicotine in basic tobacco smoke (pH 8.0) is absorbed much more readily through the mucous membrane of the mouth than nicotine in acid tobacco smoke (pH 5.6) because of higher concentrations of unprotonated nicotine in basic smoke.



The pH of smoke from non-diluted filters ranges from 5.0-6.0. The kind of tobacco used as the filler for cigarettes has a decisive influence on the physico-chemical nature of the smoke. The pH of cigarette smoke made only with flue-cured tobaccos or with American blends ranges between 5.7 and 6.2 – that is, it is slightly acidic – whereas the smoke pH of

cigarettes made with air-cured tobaccos lies in the range of 6.5-7.8 (Brunnemann & Hoffmann, 1974; Sensabaugh & Cundiff, 1967).

Ammonia-generating substances: Ammonia Gas, Ammonium Bicarbonate, Ammonium Carbonate, Ammonium Hydroxide, Urea

Reasons for the use of ammonia:

- Ammonia is a slightly stronger base than nicotine for freeing nicotine from its salts
- Ammonia is present in untreated tobacco and tobacco smoke
- The price is economical

Negative aspects of ammonia-addition

- Ammonia and nicotine react with sugars present in tobacco
- A high amount of ammonia results in a lower burning-quality of tobacco

How does Ammonia Technology fool the FTC and ISO Smoking Machines?

Cigarette companies use additive technologies to register low tar readings on the smoking machines while administering higher levels of nicotine to the smoker. The smoking machine measures levels of liquid and solid nicotine. It is not able to register the concentration in the vapour phase where free nicotine is found.

→ Changing the state of nicotine from liquid or solid phase to gas evades the standard measuring process.

### **b) Arguments NOT supporting the deliberate adding of Ammonium-salts theory<sup>[19]</sup>**

Ammonia and ammonia-releasing compounds are natural constituents in tobacco. Because the tobaccos used in cigarettes are naturally acidic, ammonia is protonated in tobacco, i.e., it exists as ammonium salts of natural tobacco carboxylic acids, otherwise the ammonia would be lost by evaporation. The typical concentration of ammonia in commercial American cigarette tobacco blends is ca. 0.1-0.4 %.

Ammonia is present in both the gas and particulate phases of tobacco smoke. In today's commercial cigarettes, ammonia is found in mainstream smoke (MS) in amounts up to 35 µg per cigarette. A far greater amount of ammonia is found in sidestream smoke (SS). The SS/MS (mass) ratio is ca. 40-170:1.

Ammonia compounds are used in manufacturing some types of cigarettes for two reasons:

Firstly, tobacco-identical ammonia compounds such as ammoniumhydroxide (i.e. an aqueous solution of ammonium) and diammonium phosphate are added as processing agents in the production of some types of tobacco sheet.

Secondly, ammonia compounds serve as flavourings and also as flavour precursors. They can react during tobacco processing and smoking with oxygen-containing compounds,

including sugars, to form flavourings. This is analogous to the formation of important flavours during the cooking of food.

The addition of ammonia compounds to tobacco can increase the ammonia content of mainstream smoke. Other tobacco blend constituents such as amino acids, proteins and inorganic nitrates can form ammonia during the smoking process and hence influence the ammonia content of mainstream smoke. A recent study of ten commercial American cigarettes revealed a correlation between mainstream smoke ammonia yield and “tar” yield. Cigarettes with comparable “tar” yields had approximately equal amounts of ammonia in mainstream smoke while differing in their ammonia content in tobacco by a factor of three. This suggests that ammonia deliveries in commercial cigarettes, which appear to be correlated to total smoke delivery, are affected by cigarette design and blend characteristics rather than by tobacco additives.

A number of reports have discussed the potential effect of ammonia, or other bases, on the transfer of nicotine to smoke. It is well known that nicotine can exist in its nonprotonated free base form or as mono- or diprotonated salts. While the free base is a high boiling point liquid (247 °C) that measurably evaporates only with heating, the protonated forms must first dissociate, decompose or disproportionate to the free base form before nicotine can be transferred to smoke. In principle, adding ammonia or ammonia-releasing substances to tobacco could convert protonated nicotine to non-protonated nicotine. However, the thermal energy provided by the burning cigarette is more than sufficient to convert the protonated forms to the free-base form, irrespective of the presence of ammonia.

Some attention has been placed on using the measured values of pH of tobacco and pH of smoke chemistry. For example, studies have been reported using pH to quantify the percentages of nicotine in its three forms. While a knowledge of the pKa values of the compounds of interest and the pH of the aqueous solution accurately predicts the position of acid-base equilibria of components in a dilute aqueous solution at equilibrium, this theory cannot be applied to tobacco or smoke directly. Neither tobacco nor smoke is a dilute aqueous solution and neither one is at equilibrium.

Two recent studies, one based on ten American commercial brands and one based on reference cigarettes containing varying levels of ammonia-producing compounds as additives, demonstrated that the pH of smoke was not significantly affected by ammonia content in the tobacco. These two studies also demonstrated that ammonia content in smoke did not significantly affect the pH of smoke as measured.

**Further Examples of Tobacco Additives**

<b>Substance</b>	<b>Place of use</b>	<b>Function</b>
Glycerol Triacetate	Filter	Filter bonding Agent
Ink	Paper	Monograms
Cellulose Acetate	Filter	Filter Material
Titanium Dioxide	Filter	Whitening Agent
Calcium Carbonate	Paper	
Sodium-Potassium Citrate	Paper	
Guar Gum	Paper	Binder
Polyvinyl Acetate	Paper	Adhesive
Sugar	Paper	
Phenolic Resin	Paper	
Glycerol	Tobacco	Humectant
Hexanal	Tobacco	Flavour
Lemon Oil	Tobacco	Flavour
Linalool	Tobacco	Flavour
Potassium Sorbate	Tobacco	Preservative
Propyl-PHB	Tobacco	Preservative
Sugars – Invert Sugar	Tobacco	Humectant, Flavour
BHT	Paper	Antioxidant
Cocoa and Theobromine	Tobacco	Encourages expansion of airways and facilitates increased smoke and nicotine intake
Glycyrrhizin	Tobacco	Ingredient of liquorice. Acts as bronchodilator

## **How can the behaviour of additives in burning cigarettes be studied?**

In order to understand the behaviour of tobacco additives in the burning cigarette, it is important to know whether they transfer intact to the smoke or whether there is any decomposition during smoking.

Some practical problems arise when comparing the chemical analysis of whole smoke from cigarettes with and without additives. Changes to the smoke chemistry may be insignificant in analytical terms and therefore missed from a general scan.

The targeted analysis of key components potentially overcomes this concern. Pyrolysis-GC-MS is an attractive solution in that it potentially enables the effects of combustion of a single material to be studied in isolation. However, it is not entirely valid to base an assessment of a material on a pyrolysis experiment alone, unless the results can be demonstrably related to the cigarette smoke chemistry.

*The variables that affect the outcome of combustion are:*

- Temperature
- Rate of change of temperature
- Oxygen concentration
- Chemical environment (Matrix and gas phase)

The key to a work done in 1999 <sup>(17)</sup> lies in performing pyrolysis experiments under a range of different conditions and relating the experimental conditions to those within the burning zone of the cigarette to give a prediction of smoke chemistry.

## Pesticides in Tobacco

Tobacco is a sensitive plant prone to many diseases. It therefore requires high chemical inputs: up to sixteen applications of pesticide are recommended during one three-month growing period. Some of the chemicals are absorbed by the plant and residues remain in the final tobacco product. Residues of some pesticides used to grow tobacco remain on the tobacco leaf and can be present in cigarettes. Other pesticides that have not been used for years, such as DDT, may be found in tobacco due to the persistence of these chemicals in the soil where tobacco is grown.

Although the food chain has been recognised as a major source of human exposure to pesticides, tobacco and tobacco smoke are also considered as sources of exposure.

### Examples of Pesticides used in Tobacco Cultivation

Pesticide	Brand Name	Toxicity to Mammals	Family	Employment
Acephate	Orthene	L	OP	Insecticide
Aldicarb	Temik	H	Carbamate	Insecticide
Azinphos-Methyl		H	OP	Insecticide
Bacillus Thuringensis	Dipel, Agree, Javelin, Xentari			
Butralin	Butralin	L		Herbicide
Carbaryl	Sevin	L	Carbamates	Acaricide, Insec.
Carbofuran	Furadan	H	Carbamates	Acar., Insec.
Chloropicrin	Chlor-O-Pic 100	L	OCC	Fungicide, Insec.
Chlorpyrifos	Lorsban	L	OP	Insecticide
Clomazone	Command	L	unclassified	Herbicide
Diazinon	Diazinon	M	OP	Insecticide
Dichloropropen	Telone, C-17	L	Fumigants	
Disulfoton	Di-Syston	H	OP	Insecticide
Endosulfan	Iodan	H	OCC	Insecticide
Ethephon	Ethrel	L	OP	Growth Regulator
Ethoprop	Mocap	M	OP	Insecticide
Fenamiphos	Nemacur	H	OP	Insecticide
Ferbam	Carbamate	L	Carbamates	Fungicide
Flumetralin	Prime+	L		Growth Regulator
Fonofos	Dyfonate	H	OP	Insecticide
Imidacloprid	Admire	L		Insecticide
Isopropalin	Paarlan	L	Dinitroaniline	Herbicide
Malathion		L	Organophosphate	Insecticide
Maleic Hydrazide	Several	L		Growth Inhibitor
Mefenoxam	Ridomil Gold	L		
Metalaxyl	Ridomil		Xylylalanine	Fungicide
Metam Sodium	Busan 1020		Carbamate	Fumigants, Herb.
Methidathion	Supracide	M	OP	Insecticides
Methomyl	Lannate	H	Carbamates	Insecticides
Methyl Bromide	Terr-O-Gas			Fumigants, Ins.
Napropamide	Devrinol	L	Carbamates	Herbicide

Oxamyl	Vydate	H	Oxim-Carbamate	Insecticide
Parathion (Ethyl)	Parathion	H	Organophosphate	Insecticide
Parathion (Methyl)	Pennacp-M	H	Organophosphate	Insecticide
Pebulate	Tillam	L	Carbamate	Herbicide
Pendimethalin	Prowl	L	Dinitroaniline	Herbicide
Sethoxydim	Poast		Cyclohexen Oxim	Herbicide
Sulfentrazone	Spartan	L	Tricazolon	Herbicide

*H = LD50 less than 30mg/kg M = LD50 30mg/kg-100mg/kg L = LD50 greater than 100 mg/kg*

OP = Organophosphorus Pesticides    OCC = Organochlorinated Pesticides

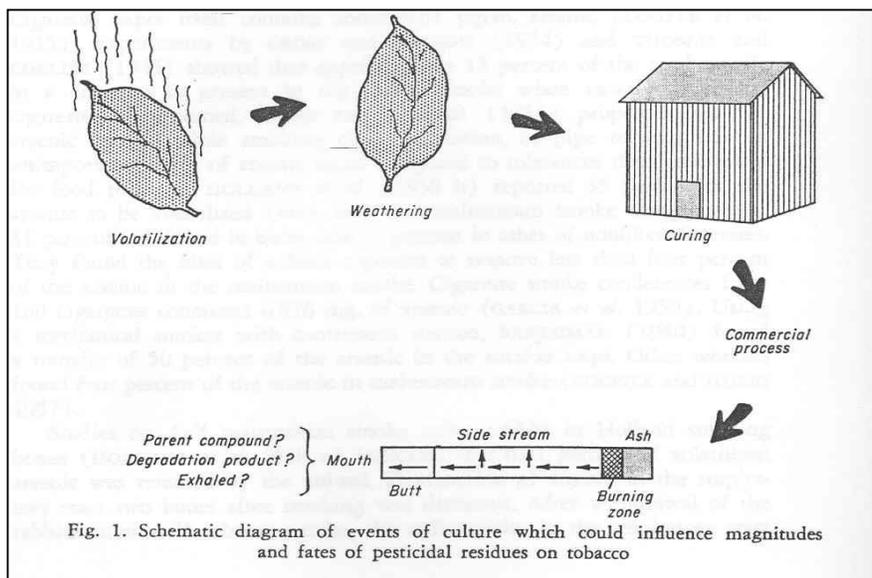
## Events which might affect pesticide residues

### *Loss during Curing* [2,9]

The flue-curing process causes up to 40 percent loss (vaporisation) in residues of chlorinated hydrocarbon pesticides and 80 percent, or greater, loss of the phosphate and carbamate insecticides. Some of this loss might be caused by conversion of the pesticides to other products.

### *Loss during Commercial Processing* [2]

Although the duration of tobacco storage varies considerably, a two-year aging period is considered normal. The residue content of tobacco samples treated at purposefully high rates of organ chlorine compounds does not significantly alter during a two-year aging period nor during subsequent steps to prepare the processed tobacco into cigarettes.



Guthrie, F.E.; Bowery, T.G.; Pesticide residues on tobacco [2]

### ***Loss during smoking*** [3]

It is important to know whether tobacco additives transfer intact to the smoke or whether there is any decomposition during smoking. Some of the decomposed substances may be less harmful.

### ***Effect of Filters*** [6]

Different types of filters reduce pesticide presence in smoke by up to 50%, but very little selectivity is demonstrated by any filter.

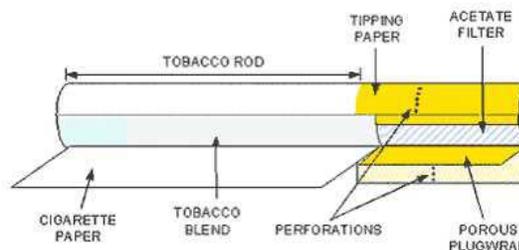
In 2003, the European Commission's DG Joint Research Centre (JRC) in Ispra, Italy, [18] investigated the content of organo chlorine pesticides in a selection of commercially available cigarette brands :

<b>Brand</b>	<b><i>Pesticides</i></b>	
	Organ chlorine Pesticides [ $\mu\text{g}/\text{kg}$ dry tobacco]	
Marlboro Red	$\alpha$ -Endosulfan	22
	$\beta$ -Endosulfan	21
	Heptachlor-Epoxide	47
	4,4-DDE	17
Philip Morris Ultra Lights	$\alpha$ -Endosulfan	32
	$\beta$ -Endosulfan	101
	Endosulfan-Sulfat	25
	Heptachlor-Epoxide	91
Gauloises Legeres	$\alpha$ -Endosulfan	55
	$\beta$ -Endosulfan	16
	Heptachlor-Epoxide	22
	4,4-DDE	31
MS Filtro	$\alpha$ -Endosulfan	33
	$\beta$ -Endosulfan	39
	Heptachlor-Epoxide	86
Karelia Superior Lights	$\alpha$ -Endosulfan	4
	$\beta$ -Endosulfan	7
	Heptachlor-Epoxide	12
BF Ultra One	$\alpha$ -Endosulfan	19
	$\beta$ -Endosulfan	30
	4,4-DDE	21
Ernte 23	$\alpha$ -Endosulfan	13
	$\beta$ -Endosulfan	3
	Heptachlor-Epoxide	77
	4,4-DDE	3
Rot Haendle	$\alpha$ -Endosulfan	4
	$\beta$ -Endosulfan	6
	Endosulfan-Sulfat	4
	4,4-DDE	4
Imperial	$\alpha$ -Endosulfan	14
	$\beta$ -Endosulfan	9
	Heptachlor-Epoxide	5
	4,4-DDE	5
Krong Thip 90	$\alpha$ -Endosulfan	97
	$\beta$ -Endosulfan	97
	4,4-DDE	31

## Non-Tobacco Components of a Cigarette

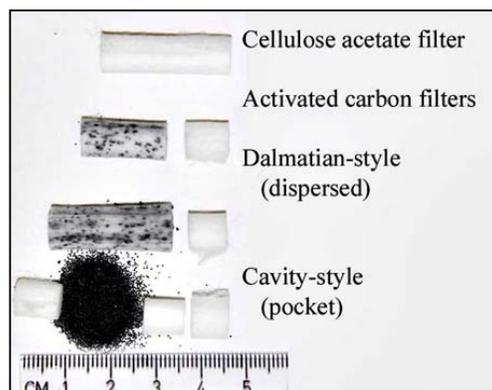
### Cigarette Paper

Cigarette paper is made of pure cellulose pulp from textile fibres such as flax or hemp, or from wood. It may be porous to varying degrees, i.e. capable of letting through a stream of air that regulates how the tobacco burns. Smoke from a burning cigarette will therefore depend to a large extent on the paper characteristics. Industry claims that cigarette paper can influence overall product performance more than any other non-tobacco component.



### Filter

Cigarette filters are usually made of tow or cellulose acetate. They are designed to trap nicotine and tar, to varying degrees, as measured by the ISO standard smoking test method. Filters often provide ventilation that also reduces the nicotine and tar yield of cigarettes. The ventilation depends on the capacity of the tipping paper, which secures the filter to the tobacco rod, to let in air through holes whose size and number control its intensity. Air that passes through the tipping paper during a cigarette puff (together with the air that flows through the cigarette paper) dilutes the smoke and thus lowers nicotine, tar and carbon monoxide yields. Cellulose filters remove some of the particulate phase of smoke (depending on particle size), particularly volatile nitrosamines and up to 80% of semi volatile phenols. Charcoal filters selectively remove a range of vapour phase components.



Studies in the 1950s established that the smokers' lung cancer risk is clearly linked to the exposure to "tar". This observation has led to a gradual increase in the percentage of cigarettes with filter tips, which brought about declining smoke yields of cigarettes as measured in standardized machine smoking in laboratory procedures.

Over the past 50 years, many materials have been patented for use as cigarette filter tips. These include natural and synthetic foams and sponges, synthetic resins, paper in various forms, cotton, other natural fibres (e.g. silk, flax, corn silk), synthetic fibres (especially cellulose esters and ethers), absorbents (such as granules and powders of carbon), aluminium oxides and salicylates, and fine-cut tobacco. Several other filter materials such as silicates, or filter additives have also been suggested but have never been used in commercial cigarettes.

Paper, charcoal and especially cellulose acetate have generally been and continue to be the major materials used in cigarette filter tips.

Even though the average contact time of cigarette smoke passing through a 20-mm filter tip is below 0.1s, some volatile components are selectively removed from cigarette smoke by charcoal filter tips (Kirk & Othmer, 1951, Norman et al., 1968; Tiggelbeck, 1967, 1976).

#### **Sideseam adhesive**

A sideseam adhesive is used in small amounts to secure the cigarette paper around the tobacco rod.

#### **Monogram Ink**

A small brand identifying mark (monogram) is often printed either on the cigarette paper towards the filter end of the cigarette or on the tipping paper. The monogram is printed on the paper using a minute amount of ink which may contain, e.g., black, blue, red and/or yellow pigments.

#### **Filter Adhesives**

Filter adhesives are used both to secure the plug wrap to the filter and to secure the filter to the tobacco rod. Like sideseam adhesives, filter adhesives are used in very small amounts.

### **Examples of non-tobacco components used for cigarette manufacturing (taken from Philip-Morris Web-Page)**

#### **CIGARETTE PAPERS** (*Selection*)

CELLULOSE  
CALCIUM CARBONATE  
MONOPOTASSIUM PHOSPHATE  
POTASSIUM CITRATE  
SODIUM CITRATE

#### **SIDESEAM ADHESIVES** (*Selection*)

ETHYLENE/VINYL ACETATE, COPOLYMER EMULSION IN WATER  
POLYVINYL ACETATE  
STARCHES and/or MODIFIED STARCHES  
VINYL ALCOHOL-VINYL ACETATE COPOLYMER  
POLYVINYL ALCOHOL

#### **MONOGRAM INKS** (*Selection*)

IRON OXIDE BLACK  
LINSEED VARNISH  
PIGMENT YELLOW 14  
CARBON BLACK  
PIGMENT BLUE 15  
PIGMENT BLUE 27

**FILTRATION MATERIALS** *(Selection)*

CELLULOSE ACETATE  
CELLULOSE  
CARBON  
TRIACETIN  
POLYETHYLENE GLYCOL 200

**FILTER PAPERS (including PLUG WRAPS, TIPPING PAPERS, and TIPPING PAPER INKS)** *(Selection)*

CELLULOSE  
CALCIUM CARBONATE  
TITANIUM DIOXIDE  
ALUMINUM FOIL  
STARCHES and/or MODIFIED

**FILTER ADHESIVES** *(Selection)*

ETHYLENE/VINYL ACETATE, COPOLYMER EMULSION IN WATER  
ALPHA METHYL STYRENE POLYMER  
DIETHYLENE GLYCOL, DIBENZOATE  
DIPROPYLENE GLYCOL DIBENZOATE  
MICROCRYSTALLINE WAX

## **Tobacco Regulation** <sup>[32]</sup>

### **Historical Development of Products**

Prior to 1955, probably no cigarettes had a tar content below 35 mg. Since then, the extension of research concerning tobacco plants and their cultivation, as well as the introduction of new technologies for cigarette manufacturing (for filters, paper, ventilation, and reconstituted and expanded tobacco), have led to gradual, spectacular declines in tar content. Nicotine and carbon monoxide content levels have fallen in roughly the same proportions as tar content.

Leading manufacturers have gradually introduced products, covering all market segments, with tar contents ranging from 0.5 to 12 mg, in order to provide consumers with a choice.

Since the sixties, many countries have issued numerous recommendations to reduce nicotine and tar content. Laws introduced in France in 1977 and in Spain in 1982 to inform consumers of nicotine and tar content and, in 1992, to prohibit products with tar contents beyond a certain limit, have confirmed these recommendations.

The new European Tobacco Directive 2001/37/EC of 5 June 2001 calls for the elimination of all information on cigarette packs that might suggest that a particular product is less harmful than another.

### **EU – Directive**

#### ***Directive 2001/37/EC (5<sup>th</sup> June 2001)***<sup>[27,32]</sup>

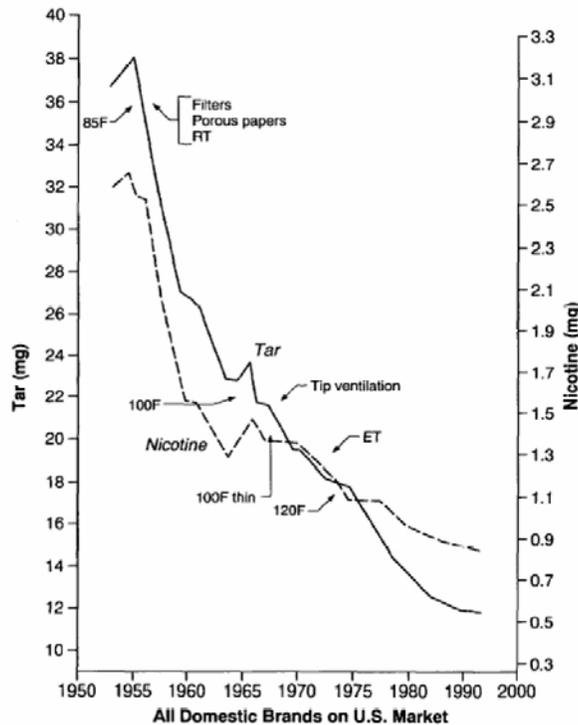
On 5<sup>th</sup> June 2001, the European Parliament and the Council adopted Directive 2001/37/EC with the aim to consolidate and update existing legislation covering the manufacturing, presentation and sale of tobacco products. This new text contains provisions designed to reduce the tar content, set limit values for nicotine and carbon monoxide, place warnings on cigarette packets and prohibit misleading descriptors.

Directive 2001/37/EC includes the following provisions: <sup>[32]</sup>

**Article 3:** sets maximum yield of nicotine (1mg/cigarette) and carbon monoxide (10mg/cigarette) and a further reduction in maximum tar yields to 10 mg/cigarette as from 1<sup>st</sup> January 2004.

The reduction in machine-smoked tar yields of cigarettes was the key strategy for reducing harmfulness during the last century. No limits or reductions were set for nicotine yields until the most recent directive (which set an upper limit of 1mg/cigarette by 1<sup>st</sup> January 2004). Nevertheless, as the machine based tar yields declined, so, to a large extent, did the machine based nicotine yields. Techniques such as increasing the ventilation of the filter affected nicotine readings on the cigarette testing machines in a similar way to the tar yields.

The main problem with the reduction in tar yields strategy is that the tar yields are measured using cigarette smoking machines which do not measure what consumers ingest from their cigarettes, because people do not smoke like machines.



Key: RT = reconstituted tobacco; F = filter; ET = expanded tobacco.  
Source: Hoffmann and Hoffmann, 1994a.

Manufacturers achieved the reduction in machine measured tar yields by using several techniques:

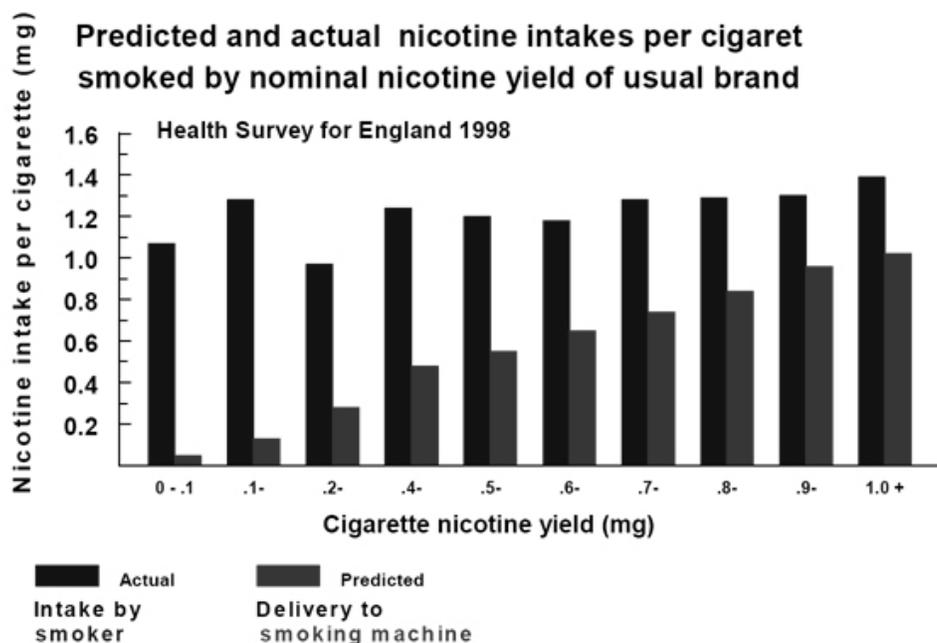
- Increasing the ventilation of the filter
- Increasing burn rate
- Decreasing tobacco density
- Increasing the porosity of the wrapping paper
- Changes in tobacco blending
- Changes in filter efficiency, e.g. pressure drop alterations

However, as most smokers regulate their nicotine intake to maintain a relatively constant intake of nicotine each day, they alter the way they smoke to achieve their preferred nicotine level (a process referred to as *compensation*). Cigarettes with reduced tar and nicotine yields are smoked more intensively by, for example, taking more and deeper puffs and/or blocking the ventilation holes in cigarettes, to achieve a satisfactory dose of nicotine.

The ventilation holes are positioned in the filter where smokers place their fingers, and are therefore easy to block unintentionally. Cigarette testing machines cannot take account of

this relationship between nicotine intake and behaviour as the machine puffing patterns are standardised and the ventilation holes cannot be covered.

Machine delivered measurements differ greatly from smoke intake measures from smokers [28]



From: Jarvis et al 2001

Nicotine intake per cigarette smoked, as estimated from salivary cotinine level, did not correspond with machine-smoked yields at any level of nicotine yield.

The second problem with the reduction in tar yield approach concerns the concept of “tar”. There are more than 2000 chemical constituents in tobacco and about twice that number when tobacco is burned during smoking. Tar has different compositions across different products and across different countries. Hence the concept of tar as a single homogeneous toxic substance is very misleading.

Hoffmann has demonstrated how trends in the concentrations of different carcinogens within tobacco smoke change differently and independently of tar over time<sup>[29,30]</sup>, for example, NNK did not correlate at all with tar yields and increased between the late 70s and early 90s.

The concept of “tar” is therefore outdated and needs to be replaced with a more sophisticated understanding of the different constituents of tobacco and/or smoke.

It is now broadly recognised that the ISO/FTC standard measurement methodology is inappropriate as a basis for regulating the harm caused by cigarettes. Reductions in machine-smoked tar yields can be achieved relatively easily by cosmetic changes to the

cigarette, and, together with compensatory changes in smoking behaviour, they do not result in differences in exposure to the smoker.

*Intense Smoking Regimes*

Some countries have introduced more intense standards for machine cigarette testing. Health Canada adopted the modified ISO test method in their federal tobacco reporting regulation and required both standard and modified measurements to be provided to consumers on packets in the form of a range.

	Standard ISO	Modified ISO (Canadian)	Massachusetts
Puff Volume [ml]	35	55	45
Puff Interval [s]	60	30	30
Puff Duration [s]	2	2	2
Ventilation Holes	Not blocked	Fully blocked	50% blocked

The philosophy of the Massachusetts Department of Health was not to obtain a maximum yield (differing from the Canadian regime) but a more realistic estimate of the yield to an average smoker. The modified (Canadian) smoking regime is informative as it should theoretically provide figures on a maximum amount of smoke which could be delivered to the smoker.

*Tar/Nicotine ratios*

An alternative adaptation of the ISO tests was proposed by Professor Michael Russell in 1976. He suggested that cigarette smoking could be made less hazardous by reducing tar and other toxins relative to nicotine<sub>[31]</sub>. This was based on the fact that smokers tend to regulate their nicotine intake, so it would be favourable to reduce the quantity of toxins for a given dose of nicotine over time.

**Article 4:** stipulates that the yield should be measured on standard smoking machines to ISO specifications making reference to the ISO standards 4387, 10315 and 8454 for tar, nicotine and carbon monoxide respectively, as well as ISO standard 8243 concerning the tar and nicotine indications on packets.

**Article 5:** stipulates that the machine measured yields of nicotine, CO and tar must be displayed on cigarette packets. This article also establishes new bolder, larger, black and white health warnings and traceable markings on tobacco packets enabling the place and time of manufacture to be determined.

The directive requires the printing of tar, nicotine and CO yields of cigarettes on the packets. The provision has been strongly criticised as the tar and nicotine yields are based on ISO measurements and do not provide meaningful information for consumers, as discussed above.

In Canada, a range of yields (from the lowest possible to the highest possible) is published on cigarette packets. Providing a low and high range for emission levels of toxic chemicals is reflective of how people smoke differently and provides a more accurate indication of the real health risks to individuals exposed to tobacco smoke.

Another way to inform smokers could be through the use of packet inserts.

**Article 6:** stipulates that a list of all ingredients and their quantities used in manufacturing tobacco products by brand name and type should be supplied by 31<sup>st</sup> December 2002 and annually thereafter. The list had to be accompanied by a statement setting out reasons for inclusion of the ingredients, indicating function and category and available toxicological data regarding the ingredients in burnt or unburnt form, referring in particular to health and addictive effects.

The Directive defines ingredient as : “Any substance or any constituent except for tobacco leaf and other natural or unprocessed tobacco plant parts used in the manufacture or preparation of a tobacco product and still present in the finished product, even if in altered form, including paper, filter, inks and adhesives”

Ammonia is not mentioned in the list of ingredients provided by Philip Morris to the Member States. The claim that PM does not add ammonia as an ingredient does not mean that ammonia is not present in the product. The tests could not indicate whether ammonia was added during the agricultural or manufacturing process.

**Article 7:** misleading descriptors and the use of other signs (texts, names, trade marks and figurative or other signs) suggesting that some tobacco products were less harmful than others, are banned by 30<sup>th</sup> September 2003.

**Article 9:** stresses the need to adapt to scientific and technical process in measurement methods (in particular those given under Article 4), health warnings and identification markings.

**Article 11:** outlines that by 31<sup>st</sup> December 2004 and every year thereafter the EC would submit a report on the application of the directive to the European Parliament, the Council and the Economic and Social Committee, with the assistance of scientific and technical experts. A number of areas are listed for attention in the report:

*Methodologies for more realistic assessing and regulating toxic exposure and harm*

- Subsequent reduction of the maximum yields laid down in Article 3
- Possible links between these yields
- Methodologies for more realistically assessing and regulating toxic exposure and harm
- Development of standardised testing methods to measure the yields of constituents in cigarette smoke other than tar, nicotine and CO.

### Ingredients

- Evaluation of the addictive affects of the ingredients which encourage addiction
- Toxicological data to be required from manufacturers on ingredients and the manner in which they should be tested in order to allow public health authorities to assess their use

### **Which constituents should be regulated?** [32]

From over 4000 smoke constituents, 69 have been considered as possible or proven carcinogens. The following table shows a selection of these compounds:

<i>Compound Name</i>	<i>IARC Group</i>	<i>Compound Name</i>	<i>IARC Group</i>
<i>Benzo[a]pyrene</i>	<i>1</i>	<i>NNAL</i>	<i>2 B</i>
<i>4-Aminobiphenyl</i>	<i>1</i>	<i>1,3 – Butadiene</i>	<i>2 A</i>
<i>2-Naphthylamine</i>	<i>1</i>	<i>Acetaldehyde</i>	<i>2 B</i>
<i>Formaldehyde</i>	<i>1</i>	<i>Isoprene</i>	<i>2 B</i>
<i>Benzene</i>	<i>1</i>	<i>Styrene</i>	<i>2 B</i>
<i>Ethylene Oxide</i>	<i>1</i>	<i>Catechol</i>	<i>2 B</i>
<i>Cadmium</i>	<i>1</i>	<i>Nickel</i>	<i>2 B</i>
<i>NNK</i>	<i>1</i>	<i>Cobalt</i>	<i>2 B</i>
<i>NNN</i>	<i>1</i>	<i>Lead</i>	<i>2 B</i>

IARC Group I : Carcinogenic to humans  
IARC Group II: Probably carcinogenic to humans  
IARC Group III: Possibly carcinogenic to humans

The above compounds are mainly formed during combustion processes (exceptions are the metals and N-nitrosamines, the latter formed during fermentation of tobacco leaves), therefore it is rather difficult to regulate these compounds . Technological modifications of the cigarette design influence the amount formed of each of the above listed compounds.

A second important group of compounds which can potentially be regulated are the additives. Additives can reach and be entirely or partially part of the vapor phase of smoke through micro-distillation processes. This makes regulation necessary for those additives, which are directly or indirectly harmful to health.

Additives are indirectly harmful to health when added to make smoke easier to inhale (giving an incentive to smoke), to enhance the appeal of cigarettes to young people, or when active additives are added to increase the speed and size of the nicotine “hit”, increasing the chance of addicting a smoker. Moreover, additives may contribute to an increase of tar and CO formation during the burning process.

## Environmental Tobacco Smoke

The aim of occupational health and safety legislation is to provide a safe work environment.

Working in an environment where smoking is permitted, as well as encouraging active smoking, can lead to high levels of exposure to environmental tobacco smoke (ETS) deriving from employee smokers and general public smokers visiting such workplaces. This is particularly a problem in the entertainment industry, e.g. pubs and nightclubs, where large numbers of patrons smoke.

### Environmental Tobacco Smoke Constituents

ETS comprises exhaled mainstream smoke, sidestream smoke emitted from smouldering tobacco, contaminants emitted during the puffs and contaminants that diffuse through the cigarette paper and the mouth end of cigarettes between puffs.

Emissions contain both particle phase and vapour phase contaminants. Sidestream smoke is the major component of ETS, contributing over half of the particulate matter and nearly all of the vapour phase.

Every time someone lights up a cigarette, cigar or pipe, tobacco smoke enters the air from two sources. The first is *mainstream smoke*, which the smoker pulls through the mouthpiece when inhaling or puffing. Non-smokers are also exposed to mainstream smoke after it is exhaled. The second, and even more dangerous source, is *sidestream smoke*, which goes directly into the air from the burning tobacco.



There are substantial similarities as well as differences between the mainstream smoke and sidestream smoke components of ETS. The main differences are due to the differences between the tobacco combustion temperature, pH and the degree of dilution with air. This dilution is accompanied by a corresponding rapid decrease in temperature.

Mainstream smoke is generated at a higher temperature than sidestream smoke.

Mainstream Smoke	:	800-900 °C
Sidestream Smoke	:	600 °C

Mainstream Smoke has a lower pH than sidestream smoke.

Mainstream Smoke	:	6.0 – 6.7
Sidestream Smoke	:	6.7 – 7.5

Differences in mainstream smoke and sidestream smoke are also ascribable to differences in the oxygen content.

Mainstream Smoke	:	16 %
Sidestream Smoke	:	2 %

Because sidestream smoke is produced at lower temperatures and under more reducing conditions than mainstream smoke, many carcinogens and other toxicants are generated in greater amounts in sidestream smoke than in mainstream smoke.

After its production, sidestream smoke is rapidly diluted in the air. This results in the sidestream smoke particle size distribution being smaller than in mainstream smoke. For example, nicotine is predominantly present in the particle phase in mainstream smoke but it is found mainly in the gas phase in sidestream smoke. This shift to the gas phase is due to the rapid dilution in sidestream smoke. The particle size range for sidestream smoke is typically 0.01-1.0  $\mu\text{m}$  while the mainstream smoke particle size is typically 0.1-1.0  $\mu\text{m}$ . These differences in size distributions for sidestream smoke and mainstream smoke particles, as well as the different breathing patterns of smokers and non-smokers, have implications for the deposition patterns of the particles in the various regions of the human respiratory tract.

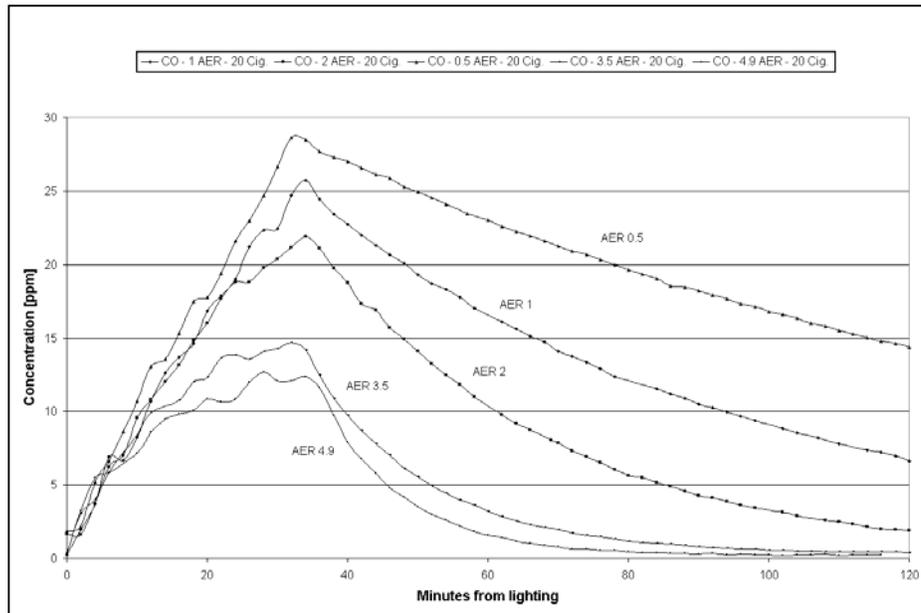
In addition to the production of vapours and particulates, tobacco smoking causes significant emissions of carbon monoxide. Environmental tobacco smoke in dwellings, offices, vehicles and restaurants can raise the 8-hour average CO concentration by up to 23-46  $\text{mg}/\text{m}^3$  (2-40 ppm).

### **Removal of ETS by increasing the ventilation rate<sub>[25]</sub>**

Restaurant and bar owners argued that increasing the ventilation rate would lower the ETS-pollution level to an extent that staying in these location would no longer present a health risk.

Experiments conducted at the European Commission's DG Joint Research Centre disprove this argument.

Twenty cigarettes were smoked inside a 30 $\text{m}^3$  walk-in environmental chamber. A selection of VOC and inorganic gases were measured, varying the air exchange rate (AER). The experiments have shown that achievable ventilation rates inside a restaurant or pub, do not lower ETS-pollution to such a level not to cause any health risk.



*Measurements of carbon monoxide levels at various air-exchange rates (20 cigarettes smoked)*

### **Measurements of indoor air concentrations of ETS constituents<sup>[23,24]</sup>**

Many factors are involved in the selection of atmospheric tracers of environmental tobacco smoke. Since many environmental tobacco smoke compounds can exist in the vapour and/or in the particulate phase, the measurement of one particular component will not necessarily reflect exposure to other components.

Furthermore, it can be expected that gas-phase compounds in environmental tobacco smoke will be removed at different rates in indoor environments. The relationship of various gas-phase components to each other and to the particulate phase of ETS will be dependent on their relative removal rates. It is therefore important to determine the gas-particle distribution of key environmental tobacco smoke constituents and select appropriate markers for each phase of environmental tobacco smoke.

It may also be important to select both a reactive and a non-reactive marker, because the lifetime of the latter depends only on the ventilation rate in an indoor environment, while the removal of the reactive species will be dominant by reactions with other chemical compounds and surfaces.

A good tracer should have the following characteristics:

- unique to ETS. This is to ensure minimal contribution from other sources.
- easily detectable at low concentrations
- have similar emission rates among various tobacco products
- have consistent proportions to other ETS compounds for different environments and tobacco products

The most widely used marker compounds for assessing the presence and concentration of ETS in indoor air are:

#### **Vapour-phase nicotine**

Nicotine is present in the particulate phase in mainstream smoke (MS), but it is diluted in sidestream smoke (SS); nicotine volatilises and is mainly present in the gas phase in ETS. Nicotine is used as a tracer because it is unique to tobacco smoke, it is easily measurable at realistic concentrations indoors and the ratio of nicotine to particulate matter does not appear to vary among different brands of cigarettes.

#### **Points against the use of vapour phase nicotine as a ETS tracer**

- As vapour phase nicotine is mainly present in the vapour phase, its use as particulate-phase tracer has been questioned.
- Nicotine deposited on surfaces can be re-emitted to the gas phase.
- Nicotine readily sorbs onto surfaces, so it is not an ideal marker for the more volatile components of ETS which have significantly lower deposition rates.

Concentration levels up to 50 to 75 micrograms per cubic metre have been measured in public bars.

#### **Respirable suspended particle mass**

The reasons for using RSP as an ETS tracer are : a) most of the most toxic compounds (including carcinogens) are found in the particulate matter phase of ETS, b) RSP concentrations can be correlated with number of cigarettes smoked in indoor environments, c) RSP is easily measurable above background levels indoors as long as there is no other major source of particles.

#### **Points against the use of RSP as a ETS tracer**

- RSP is not unique to ETS and it is not an adequate measure of environmental tobacco smoke exposure in the presence of other sources of RSP
- Exposure to tobacco smoke RSP will not necessarily represent exposure to vapour-phase constituents of ETS.

### 3-Ethenylpyridine

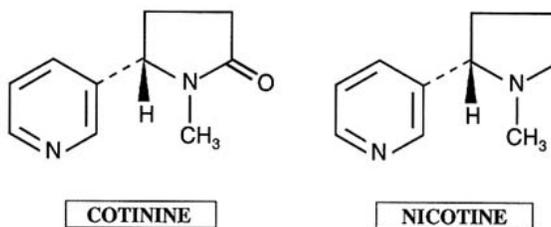
When tobacco is burned, 3-Ethenylpyridine (3-EP), a compound more volatile than nicotine, is formed by the pyrolysis of nicotine. 3-EP is probably unique to tobacco smoke in indoor environments and is less reactive than nicotine.

3-EP is the most suitable tracer for the volatile components of ETS.

### **Biological Markers of Exposure**

Exposure to ETS can be measured directly by the analysis of physiological fluids such as blood, urine or saliva for tobacco smoke constituents or their metabolites known as biomarkers.

The most widely used biomarker of ETS is Cotinine. Cotinine is a major metabolite of nicotine. Saliva levels correlate well with blood levels.

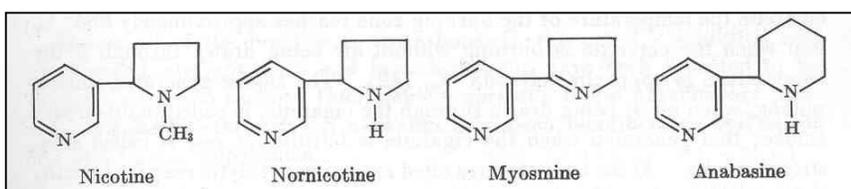


## Chemistry of Tobacco

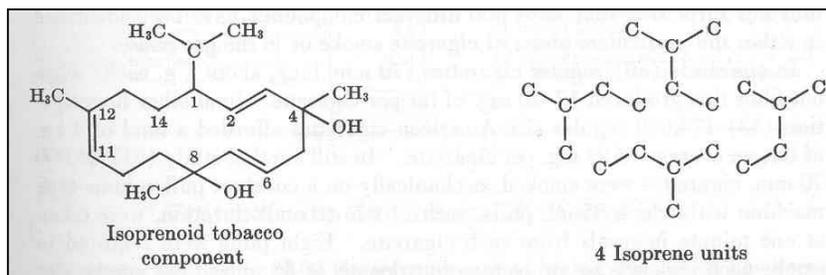
A tobacco leaf contains a complex mixture of chemical components: cellulose products, starches, proteins, sugars, alkaloids, pectic substances, hydrocarbons, phenols, fatty acids, isoprenoids, sterols and inorganic minerals.

Two groups are specific to tobacco:

The alkaloid nicotine and the related companion substances nornicotine, myosmine and anabasine. These nitrogen-containing substances are all basic and hence extractable with acid.



Seven members of a second group of compounds fairly distinctive to tobacco have been isolated and characterised. They are described as isoprenoids.



## Composition of smoke-ready Tobacco

Water 12-14 %

### In dried tobacco

Cellulose	7-16 %	Starch	2-7 %
Sugar	0-22 %	Ashes (most Ca/K)	9-25 %
Triglycerides	1 %	Organic Acids	7-25 %
Proteins	3.5-20 %	Waxes	2.5-8 %
Nicotine	0.6-5.5 %		
Pectinic Substances, Polyphenoles, Flavones, Carotinoides, etheric Oils, Paraffinans			
Sterines : 7-12 %			

## Composition of tobacco smoke

Tobacco smoke components are distributed between the particulate phase and the vapour (or gas) phase of the smoke aerosol. The following definitions of particulate phase and vapour phase mention a Cambridge filter pad. Cambridge filters are used in smoke analytical procedures. They are glass fibre filters stabilised by an organic binder, manufactured by the Cambridge Filter Corporation, Syracuse, New York.

The filter is 99.9% efficient in trapping aerosol particles larger than 0.1 $\mu$ m in diameter. In general, substances with a molecular weight below about 60 g/mol tend to be predominantly present in the vapour phase and substances with a molecular weight above 200 g/mol tend to be wholly present in the particulate phase.

### a) Particulate phase and condensable substances

Definition Particulate Phase

The portion of smoke which is retained on a Cambridge filter pad at room temperature.  
Substances with MW > 200 g/mol

Cigarette smoke is a heterogeneous mixture of gases, uncondensed vapours and liquid particulate matter.

As it enters the mouth, the smoke is a concentrated aerosol with millions of particles per cubic centimetre. The median size of the particles is about 0.5 micron.

For the purposes of investigating chemical composition and biological properties, smoke is separated into a particulate phase and a gas phase; the gas phase is frequently subdivided into materials which condense at liquid-air temperature and those which do not.

An important factor determining the composition of cigarette smoke is the temperature in the burning zone. While air is being drawn through the cigarette, the temperature of the burning zone reaches approximately 884 °C; when the cigarette is burning without air being drawn through it, the temperature is approximately 835 °C.

Extensive pyrolytic reactions occur at the cited temperatures. Some of the constituents of tobacco are stable enough to distil unchanged, but many others suffer extensive reactions involving oxidation, dehydrogenation, cracking, rearrangement and condensation.

The large number and variety of compounds in tobacco smoke tar recalls the composition of the tar formed by carbonisation of coal, which in many cases is conducted at temperatures lower than those of a burning cigarette.

Compound	µg/Cig.	Compound	µg/Cig.
Nicotine	100-3000	Scopoletin	15-30
Nornicotine	5-150	Other Polyphenols	
Anatabine	5-15	Cyclotenes	40-70
Anabasine	5-12	Quinones	0.5
Other tobacco alkaloids		Solanesol	600-1000
Bipyridils	10-30	Neophytadienes	200-350
n-Hentriacontane	100	Limonene	30-60
Total non-volatile HC	300-400	Other Terpenes	
Naphthalene	2-4	Palmitic Acid	100-150
Naphthalenes	3-6	Stearic Acid	50-75
Phenanthrene	0.2-0.4	Oleic Acid	40-110
Anthracenes	0.05-0.1	Linoleic Acid	150-250
Fluorenes	0.6-1.0	Linolenic Acid	150-250
Pyrenes	0.3-0.5	Lactic Acid	60-80
Fluoranthenes	0.3-0.45	Indole	10-15
Carcinogen PAH	0.1-0.25	Skatole	12-16
Phenol	80-160	Other Indoles	
Other Phenols	60-180	Quinolines	2-4
Catechol	200-400	Other aza-arenes	
Other Catechols	100-200	Benzofuranes	200-300
Other Dihydroxybenzenes	200-400		

*Major constituents of the particulate matter of the mainstream smoke of non filtered cigarettes (other than higher Polycyclics)*

#### Carcinogenic Hydrocarbons and Heterocyclics in Particulate Phase

Benzo[a]pyrene is one of the most potent of all known carcinogens.

Most of the carcinogenic compounds identified in cigarette smoke are not present in the native tobacco leaf but are formed by pyrolysis at the high burning temperature of cigarettes. It appears that the pyrolysis of many organic materials can lead to the formation of components which are carcinogenic to mice. Cigarette paper consists essentially of cellulose. Pyrolysis of cellulose has been shown to produce benzo[a]pyrene.

<i>PAHs</i>	<i>N-Nitrosamines</i>
Benz[a]anthracene	N-Nitrosodimethylamine
Benzo[b]fluoranthene	N-Nitrosoethylmethylamine
Benzo[j]fluoranthene	N-Nitrosodiethylamine
Benzo[k]fluoranthene	N-Nitrosopyrrolidine
Benzo[a]pyrene	N-Nitrosodiethanolamine
Dibenz[a,h]anthracene	N-Nitrosoarcosine
Dibenzo[a,i]pyrene	N-Nitrosornicotine
Dibenzo[a,l]pyrene	4-(Methylnitrosamino)-3-(pyridyl)-1-butanone
Indeno[1,2,3-cd]pyrene	N <sup>7</sup> -Nitrosoanabasine
5-Methylchrysene	N <sup>7</sup> -Nitrosamorpholine
<i>Aza-arenes</i>	<i>Aromatic Amines</i>
Quinoline	2-Toluidine
Dibenz[a,h]acridine	2-Naphthylamine
Dibenz[a,j]acridine	4-Aminobiphenyl
7H-Dibenzo[c,g]-carbazole	

**b) The Gaseous Phase (not condensable)**

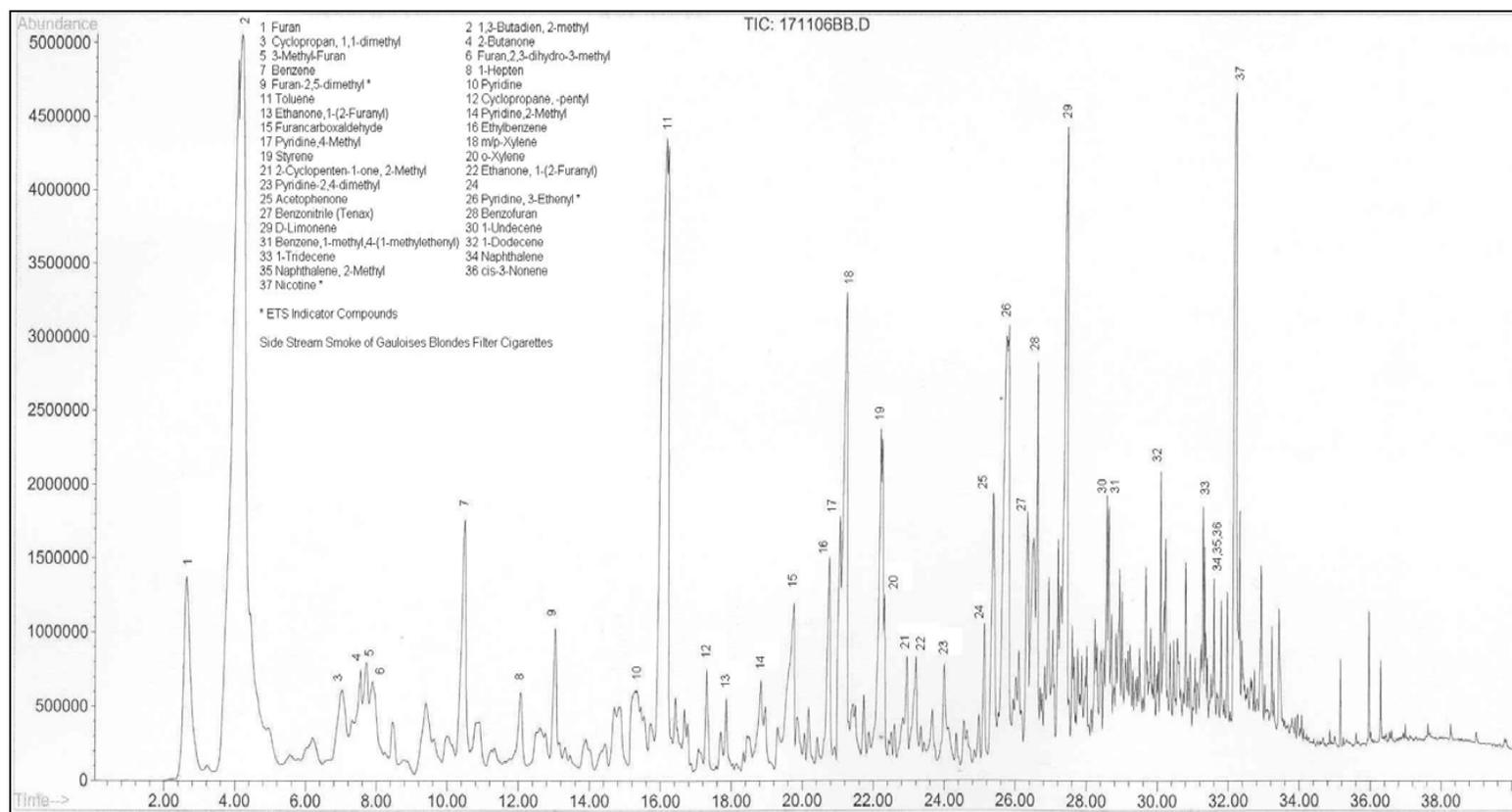
Definition gaseous phase

For the purposes of a generally accepted definition, the portion of smoke that passes through a Cambridge filter pad at room temperature is called the vapour phase. Substances with MW < 60 g/mol

*The gas phase accounts for 60 percent of total cigarette smoke.*

Compound	Concentration/Cigarette (% of total effluent)	Compound	Concentration/Cigarette (% of total effluent)
Nitrogen	280-120 mg (56-64 %)	Methyl- formate	20-30 µg
Oxygen	50-70 mg (11-14 %)	Other volatile Acids	5-10 µg
Carbon Dioxide	45-65 mg (9-13 %)	Formaldehyde	20-100 µg
Carbon Monoxide	14-23 mg (2-5 %)	Acetaldehyde	400-1400 µg
Water	7-12 mg (1.5–2.5 %)	Acrolein	60-140 µg
Argon	5 mg (1 %)	Other Volatile Aldheydes	80-140 µg
Hydrogen	0.5-1.0 mg	Acetone	100-650 µg
Ammonia	10-130 µg	Other volatile Ketones	50-100 µg
Nitrogen Oxides NOx	100-680 µg	Methanol	80-100 µg
Hydrogen Cyanide	400-500 µg	Other Volatile Alcohols	10-30 µg
Hydrogen Sulfide	20-90 µg	Acetonitrile	100-150 µg
Methane	1.0-2.0 mg	Other Volatile Nitriles	50-80 µg
Other volatile Alkanes	1.0-1.6 mg	Furan	20-40 µg
Volatile Alkenes	0.4-0.5 mg	Other Volatile Furanes	45-125 µg
Isoprene	0.2-0.4 mg	Pyridine	20-200 µg
Butadiene	25-40 µg	Picolines	15-80 µg
Acetylene	20-35 µg	3-Vinylpyridine	7-30 µg
Benzene	6-70 µg	Other volatile Pyridines	20-60 µg
Toluene	5-90 µg	Pyrrole	0.1-10 µg
Styrene	10 µg	Pyrrolidine	10-18 µg
Other aromatic hydrocarbons	15-35 µg	N- Methylpyrrolidine	2.0-3.0 µg
Formic Acid	200-600 µg	Volatile Pyrazines	3.0-8.0 µg
Acetic Acid	300-1700 µg	Methylamine	4-10 µg
Propionic Acid	100-300 µg	Other aliphatic Amines	3-10 µg

*Major constituents of the vapour phase of the mainstream smoke of nonfiltered cigarettes*



*Gaseous phase of side stream smoke sampled on Tenax TA*

## Chemical composition of tobacco-smoke and its related health risks

A considerable amount of epidemiological research over the past 50 years has shown tobacco smoking to be the cause of a variety of serious diseases such as lung cancer, emphysema, chronic bronchitis and heart disease.

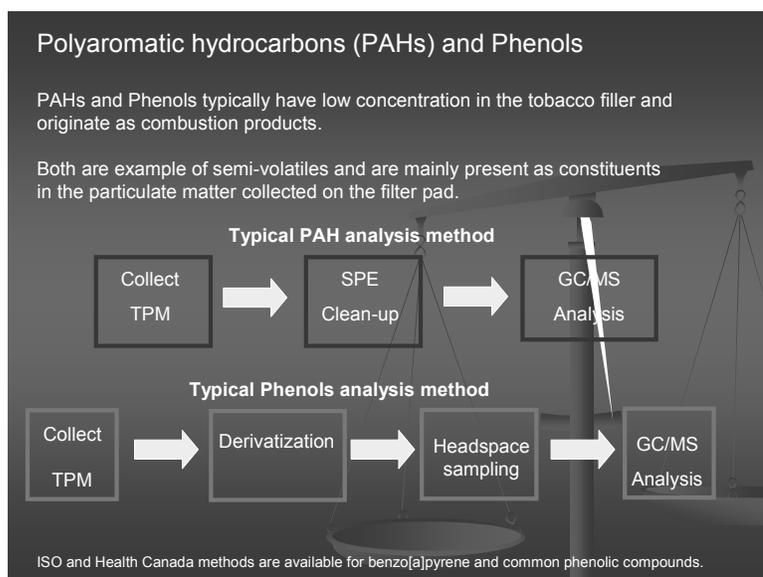
Since the 1950s, the tobacco industry has collaborated with public health bodies to modify cigarettes with the aim to reduce the risks. One crucial element of this work has been the development of a greater understanding of smoke chemistry.

Since Doll and Hill's paper in 1950<sup>[20]</sup> there have been many attempts to isolate the substances in smoke that may be responsible for the adverse health risks associated with smoking. The earliest substances identified were benzo[a]pyrene (BaP) and other polynuclear aromatic hydrocarbons, which were known to produce tumours in animal experiments.



PAHs are formed by pyrolysis and pyrosynthetic reactions of long-chained hydrocarbons, terpenes, phytosterols such as stigmasterol, paraffins, sugars, amino acids, celluloses and reactions involving primary hydrocarbon radicals. Cigarette paper consists essentially of cellulose. Pyrolysis of cellulose has been shown to produce benzo[a]pyrene.

In the 1950s and 1960s the tobacco industry undertook a considerable amount of work to reduce or eliminate BaP and PAHs in smoke by filtration and various cigarette design modifications, but no method was found to reduce BaP selectively from “tar”.



*PAHs Analytics*

O'Conner, R., Watson, C., Product Testing and Monitoring [26]

Moreover, as analytical techniques advanced, other classes of carcinogens were discovered in smoke. In particular, in the 1960s the presence of nitrosamines in cigarettes came to be regarded by some as a more significant set of carcinogens than BaP and the PAHs.

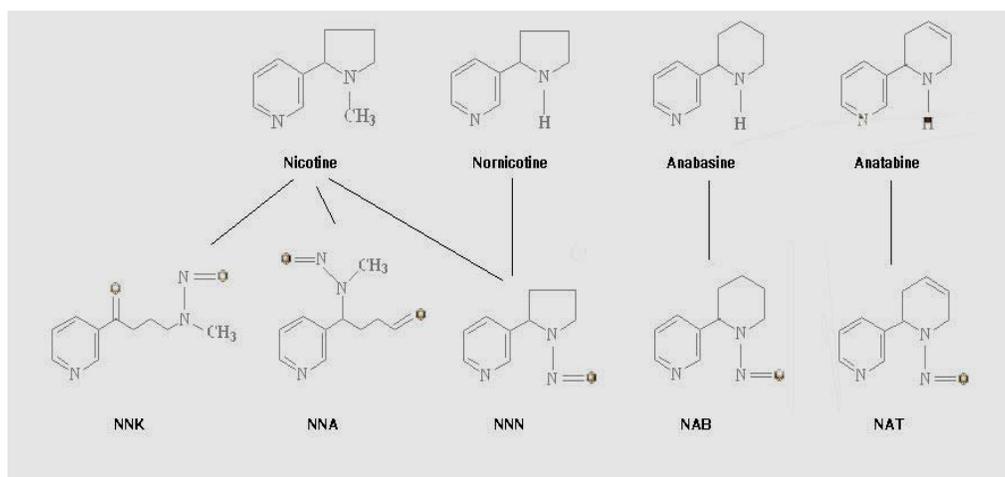
Tobacco specific nitrosamines (TSNA) are only found in tobacco products<sup>[21]</sup> and they are highly carcinogenic. There is no safe level of exposure to the most potent of the TSNA carcinogens. Besides the TSNA, non-tobacco specific nitrosamines are also formed during the smoking process.

Nitrosamines contain the organic functional group N-N=O, and are formed by the nitrosation (addition of an N=O group) of secondary and tertiary amines. The nitrosating agent is nitrite, derived from tobacco nitrate by the action of bacteria and tobacco enzymes during curing. In tobacco, these amines are nicotine, nornicotine, anabasine, and anatabine (alkaloids).

When tobacco burns during cigarette smoking, the tobacco specific nitrosamines can transfer to smoke and decompose thermally; additional nitrosamines can form pyrosynthetically.

TSNA are created during fermentation, curing and burning of the tobacco leaf.

*Chemical formation of TSNA : Nitrosation of tobacco alkaloids to form tobacco specific nitrosamines*



*Tobacco specific nitrosamines and their carcinogenic rating*

Name	Acronym	Carcinogenicity
N-nitrosornicotine	NNN	Group 1 IARC
4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone	NNK	Group 1 IARC
4-(methylnitrosamino)-1-(3-pyridyl)-1-butanol	NNAL	
N'-nitrosoanatabine	NAT	Group 3 IARC
N'-nitrosoanabasine	NAB	Group 3 IARC
4-(methylnitrosamino)-4-(3-pyridyl)-1-butanol	NNA	Group 3 IARC
4-(methylbitrosamino)-4-(3-pyridyl)-1-butanol	iso-NNAL	
4-(methylnitrosamino)-4-(3-pyridyl)butyric acid	iso_NNAC	

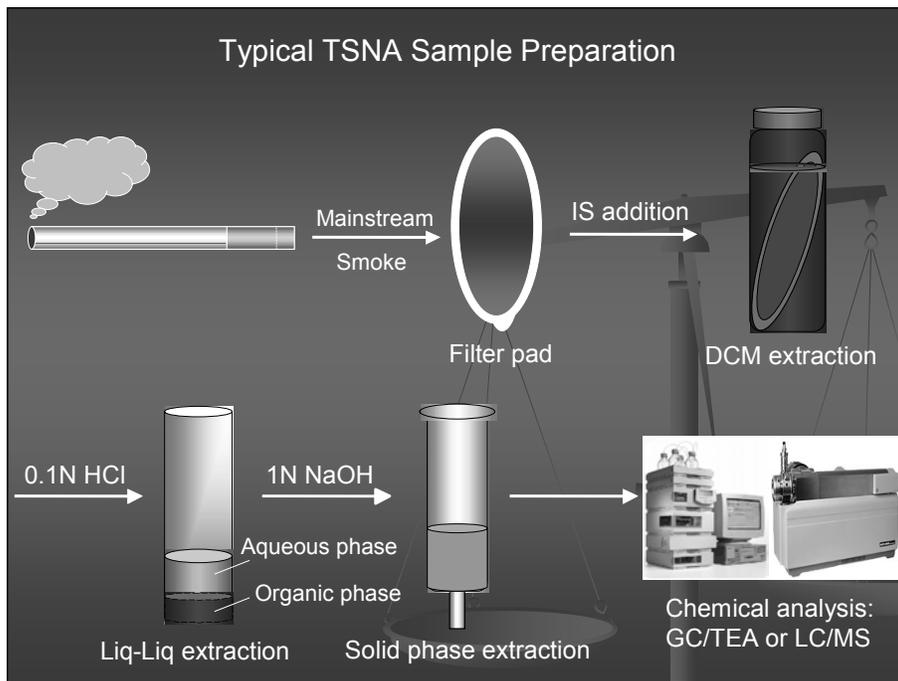
The most comprehensive lists of tobacco smoke constituents relevant to smoking related diseases have been drawn up by Dietrich Hoffmann and co-workers of the American Health Foundation in New York [22]:

Constituent class and examples	Amount/cigarette	Phase	Type of toxicity
<i>PAHs</i>			
Benzo[a]pyrene	ng	P	C
<i>Aza-arenes</i>			
Quinoline	ng	P	C
<i>Heterocyclic compounds</i>			
Nicotine	mg	P	T
Pyridine	µg	P	T
<i>Aromatic Amines</i>			
2-Naphthylamine, 4-aminobiphenyl	ng	P	C
<i>N-heterocyclic amines</i>			
Amino pyridoindoles and imidazoles	ng	P	C
<i>N-Nitrosamines</i>			
NNK	ng	P	C
Volatile nitrosamines	ng	V	C
<i>Aldehydes</i>			
Formaldehyde	µg	V	C
Acetaldehyde	µg	V	C
Acrolein	µg	V/P	T
Crotonaldehyde	µg	V/P	T
<i>Volatile Hydrocarbons</i>			
1,3-Butadiene	µg	V	C
Isoprene	µg	V	C
Benzene	µg	V/P	C
Styrene	µg	P	SC
<i>Miscellaneous Organic</i>			

<i>Compounds</i>			
Ethylene Oxide	µg	V	C
Methanol	µg	V	T
Phenol, Catechol	µg	P	TP
Acetamid, Maleic Hydrazide	µg	P	SC
<i>Inorganic Compounds</i>			
CO	mg	V	T
NOx, CS2, HCN, H2S	µg	V	T
Metals (Ni, Cd, Co, Cr, Pb)	ng	P	C

P = Particulate Phase V = Vapour Phase V/P = between Vapour and particulate Phases  
 C = Carcinogen SC = Suspected Carcinogen T = Toxic TP = Tumour Promotor

### TSNA – Analytics



O'Conner, R., Watson, C., Product Testing and Monitoring [26]

## Burning Questions

A burning cigarette is a complex system in which many types of chemical reactions and physical processes occur in parallel.

There are two main regions inside the cigarette burning zone:

**a combustion zone** and **a Pyrolysis/distillation zone**

In the combustion zone, oxygen reacts with carbonised tobacco, producing simple gases such as carbon dioxide and carbon monoxide. Temperatures between 700 and 950 °C are generated during a puff.

Immediately downstream of the combustion zone is the pyrolysis/distillation zone, where temperatures are in the range of 200 to 600 °C and oxygen levels are relatively low. About a third of the smoke constituents, including nicotine, distil out of tobacco in this region.

What results is a super saturated vapour, which cools to near ambient temperatures in a few milliseconds and condenses into the aerosol particles that make up the smoke.

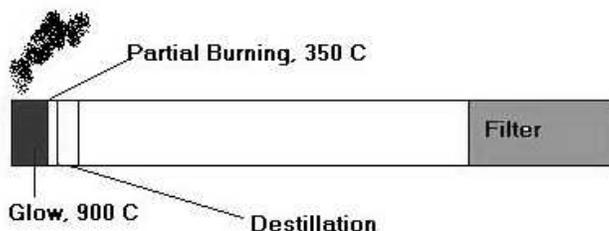
Low molecular weight hydrocarbons are generated in the pyrolysis/distillation region of the burning zone and reside largely in the vapour phase of the smoke.

Long chain n-alkanes and alkenes are generated at temperatures up to about 700 °C and reside in the particulate phase of smoke.

At temperatures above about 500 °C, in the cigarette burning region, benzene and alkylbenzenes form.

More than 75 monocyclic aromatic hydrocarbons such as benzene and toluene are formed by the pyrolysis of amino acids, fatty acids, cinnamic acid, sugars and paraffins, precursors with an aromatic or cyclohexane ring, and pyrosynthesis from primary hydrocarbon radicals.

At temperatures above about 700 °C naphthalenes are formed. At least 80 naphthalenes are present in smoke.



## Tar

### Definition

Tar (NFDPM = Nicotine Free Dry Particulate Matter) is defined as total particulate matter (TPM) minus water minus nicotine, collected on the Cambridge filter pad in smoking machines from mainstream smoke. The relationship between tar per cigarette levels and health risk is not clear. It has not been substantiated that lower tar cigarettes present less of a health risk.

Burning tobacco generates tar, like all burning plant matter. Although cigarette smoke contains tar, this compound is not well-defined because it is actually a composite of thousands of different substances. Its composition therefore varies, depending on certain variables associated with the cigarette.

The tar content of a cigarette is measured by the ISO standard smoking test method and it is indicated on the cigarette packet. Health authorities have long considered that lung cancer risks due to cigarette smoke exposure were related to the presence of tar.

Since the mid-fifties, manufacturers have taken initiatives to reduce tar content using new technologies. As a result, since 1955, the average tar content in cigarettes has dropped from 35 mg to the present 10 mg .

The European Union limited tar content to 15 mg in 1993, then lowered this limit to 12 mg in 1998. The new directive 2001/37/EC of 5<sup>th</sup> June 2001 lowers tar content to 10 mg as from 1<sup>st</sup> January 2004.

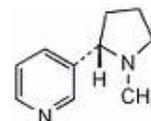
## Nicotine

### Distribution of Nicotine

Nicotine is present in the particulate phase in mainstream smoke (MS) but it is diluted as sidestream smoke (SS); nicotine volatilises and is mainly present in the gas phase in ETS.

Nicotine is a natural compound found in tobacco plants. When a cigarette burns, a small portion of the nicotine in the tobacco enters and becomes a component of the smoke. Nicotine contained in the smoke is measured using the ISO standard smoking test method and this content is listed on the cigarette packet.

Nicotine belongs to a family of natural compounds called alkaloids - along with caffeine in coffee, theobromine in cocoa and other substances which can affect the nervous system. It is often considered responsible for cigarette smoker addiction. In this area, however, much remains uncertain concerning the exact effects of nicotine, since addiction also stems from other factors, including social behavior.



*Nicotine*

The decline in tar content since the mid-fifties has led to reductions in nicotine content in roughly the same proportions. Accordingly, the average nicotine content has declined from 3 mg per cigarette in the fifties to 0.4 mg today.

The new directive 2001/37/EC of 5<sup>th</sup> June 2001 limits nicotine content to a maximum of 1 mg per cigarette starting from 1<sup>st</sup> January 2004.

## **Carbon Monoxide**

Carbon monoxide is a gas that forms when any material, such as wood, coal or heating oil is burned. When a cigarette burns, it therefore forms carbon monoxide as a component of the gaseous fraction of the smoke.

The presence of carbon monoxide has sometimes been linked to the risks of cardiovascular disease in cigarette smokers because it fixes in the haemoglobin and consequently reduces the capacity for taking oxygen into the blood. Over a period of 30 years, the technological innovations used to reduce tar content have also halved the carbon monoxide content.

The new directive 2001/37/EC of 5<sup>th</sup> June 2001 lowers the carbon monoxide content in cigarettes to 10 mg as from 30<sup>th</sup> September 2002. The quantity of carbon monoxide measured by the ISO standard smoking test method is indicated on cigarette packets.

## **Physical parameters of cigarettes and their influence on tar/nicotine, BaP and CO yields**

At least four physical parameters have a decisive influence on smoke yields:

### Cigarette Length

As the length of a cigarette increases, there is more opportunity for air to enter through the paper and for certain gaseous components, such as CO and NO, to diffuse through the paper into the environment.

### Circumference

With the packing density remaining constant, a decrease in circumference of a cigarette reduces the amount of tobacco available for burning. As a result, “tar” and nicotine yields in the smokestream are reduced.

### Tobacco Cut

When the width of shredded tobacco is modified from a fine to a coarse cut, the number of puffs per cigarette increases. In general, cigarettes that are filled with a more coarsely cut tobacco burn less efficiently than those made with fine cut shreds.

### Packing Density

Increasing the mass of tobacco in a cigarette means increasing the packing density, and it is expected that yields of “tar” and nicotine in the smoke will rise accordingly. However, packing more than 1.0 g tobacco into an 85mm cigarette causes the yield of “tar” and nicotine in the smoke to decrease, most likely because the tobacco acts as a filter for the smoke and retains more of it.

Parameter	“Tar”	Nicotine	CO	BaP
Cigarette Length	↑	↑	↑	↑
Circumference	↑	↑	↑	
Tobacco Cut	↑	↑	↑	↑
Packing Density	↑	↑	↑	↑
Paper Porosity	↓	↓	↓	↓
Reconstituted tobacco	↓	↓	↑↓	↑↓
Expanded Tobacco	↓	↓	↓	↓

*Effects of physical parameters of cigarettes on smoke yield*

Smoke Compound	Filter	Perforated Filter	Cigarette Paper	Reconstituted Tobacco	Expanded Tobacco	Bright Tobacco	Burley Tobacco
“Tar”	+	++	+	+	+	↑	+
Nicotine	+	++	+/-	+	+	+/-	+/-
pH	NC	NC	NC	NC	NC	↓	↑
CO	+/-	+	NC	+	+	↑	↓
HCN	NC	+	NC	+	+	+/-	+/-
Vol Aldehydes	NC	+	NC	+	+	↑	+
Vol. Nitrosamines	++	++	NC	+	+	++	↑
Phenol	++	++	NC	+	+	↑	+
PAH	+	++	NC	+	+	↑	+
TSNA	+	++	NC	?	?	++	↑

*Changes in cigarette design and composition: Effects on smoke yields of selected toxic agents*

+/- Can increase, can decrease  
 + Significant decrease  
 ? unknown  
 ↓ trend for decrease

NC no significant change  
 ++ more than 50% decrease  
 ↑ trend for increase

## “Light” Cigarette Products

Why do some smokers choose “low tar” and “light” cigarettes ? Because they think these cigarettes may be less harmful to their health than regular cigarettes.

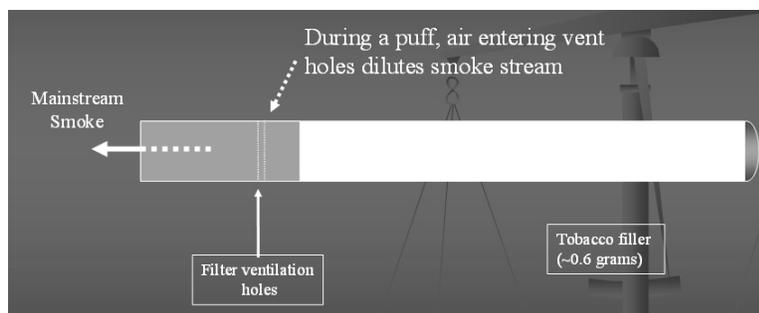
The American Federal Trade Commission (FTC) states that cigarette tar and nicotine ratings cannot predict the amount of tar and nicotine the smoker inhales from any particular cigarette, because how a cigarette is smoked can significantly affect the amount of tar, nicotine and carbon monoxide inhaled.

Research indicates that many smokers of “low tar” or “light” cigarettes compensate by taking deeper, longer, or more frequent puffs from their cigarettes. The amount of tar and nicotine a smoker actually inhales can also increase if the smoker unintentionally blocks tiny ventilation holes in cigarette filters that are designed to dilute smoke with air. In fact, studies have shown that blocking filter vents in low-tar cigarette brands increased smokers’ carbon monoxide exposure by 44 to 239 percent, and there is no difference in carbon monoxide concentrations in expired air between smokers of “light” brands and smokers of regular brands [16].

	<b>Marlboro Lights</b>	
	<b>Tar</b>	<b>Nicotine</b>
Displayed on the pack	6 mg	0.5 mg
No blocking	6.3 mg	0.54 mg
Half blocked	7.6 mg	0.62 mg
Fully blocked	10.5 mg	0.77 mg

### What is done technologically to obtain “light” cigarettes ?

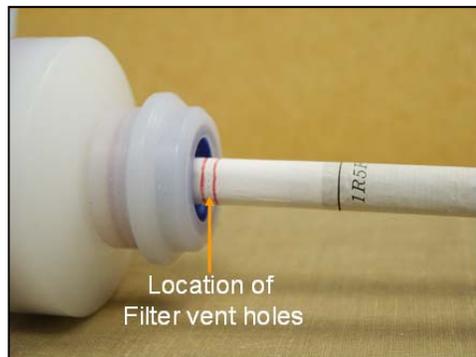
Many low tar cigarettes have filters with very small vent holes in the sides that allow air to dilute the smoke in each puff. The quantity and the quality of tobacco in a low tar cigarette is very similar or identical to that in conventional



cigarettes. Low tar cigarettes do not rely on “low tar tobacco” because there is no such thing. The difference is almost completely in the filter and the way this performs when tested in a smoking machine.

The filter works in two ways: it retains tar and nicotine as smoke is drawn through the filter and, importantly, it can have ventilation holes that allow air to be drawn in to mix with the smoke. In some cases the fresh air accounts for over 70% of the puff. This mixing

of air with the smoke reduces the apparent tar and nicotine content of the smoke. Cigarette filter ventilation is one way that tar yields (as measured by the machine test method) are reduced. The ventilation holes utilized on some brands permit the controlled introduction of diluting air into the smoke stream during puffing by the consumer. As noted in the diagram, the holes are placed approximately 12 mm from the end of the filter; brands that utilize more than one row of holes place additional rows further from the end.



*Air dilution through filter vent holes reduces machine smoked mainstream delivery*  
*Pictures taken from [26]*



*Finger or lip blockage increases mainstream smoke deliveries*

Other ways are being followed to create “light” cigarettes: the cultivation of tobacco plants that yield lower tar amounts, and fewer, or different, kinds of fertilisation used in cultivations, as lower amounts of nitrate yield a lower amount of tar and nicotine.

## **Innovative cigarette products**

### **The ECLIPSE Cigarette**

A cigarette which aims to be less harmful to health is being sold to American smokers. The Eclipse cigarette is being marketed to a selected set of people in Texas, and over the internet.

It is lit in the normal way, but instead of burning fully, the tobacco in the cigarette is primarily heated instead of burned, so 90 percent less second-hand smoke filters into the air and 75 percent fewer cancer-causing agents enter the body.

The advertising campaign for the Eclipse cigarette will say that while the best choice for smokers concerned about their health is to quit, the next best choice is to smoke "safer" cigarettes.

RJ Reynolds, the company behind Eclipse, marketed a no-smoke cigarette called Premier several years ago, but consumers rejected it because they did not like the taste. While

Eclipse is based on the same principle as Premier, its design is essentially different. For example, Premier contained an aluminum capsule that held and released glycerin and flavourings, while Eclipse does not.

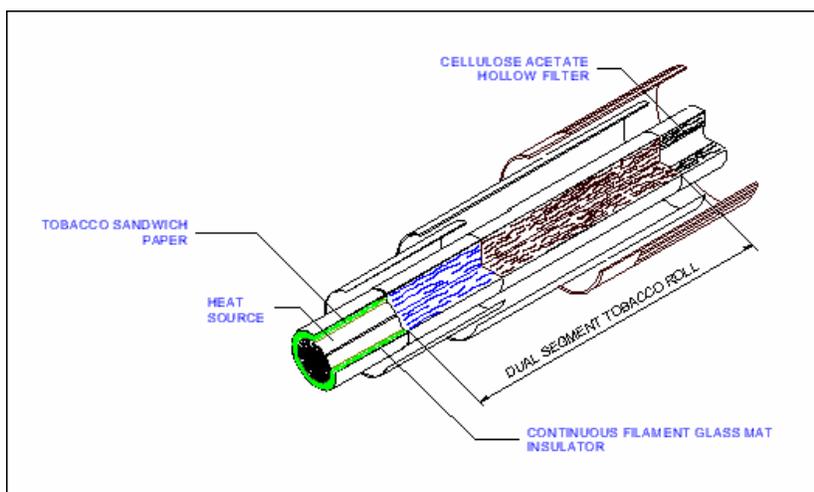
In addition, Premier burned no tobacco whatsoever, while Eclipse does burn a small amount. Although the Eclipse cigarette burns a small amount of tobacco, its smoke chemistry is much simpler than that of current, tobacco-burning cigarettes. In addition, the company says that the biological activity of the smoke is greatly reduced, as assessed by a battery of toxicological assays.

### How Eclipse Works

Eclipse looks like, and is smoked, much the same way as any other cigarette. The smoker lights the tip of the cigarette and puffs on the mouth-end to draw smoke through the cigarette rod and filter into the mouth.

But because Eclipse primarily heats, rather than burns, tobacco, some significant design differences distinguish it from other cigarettes (Figure 1).

FIGURE 1. Eclipse Cigarette



At the tip of Eclipse is a heat source made primarily of high purity carbon. The heat source also contains binders and a small amount of tobacco. The heat source is surrounded by a specially designed continuous-filament glass-mat insulator that reduces heat loss to the surrounding air. The glass-mat insulator is made from continuous-filament glass with an average diameter of 8.5 microns (ranging from 5.5 microns to 14 microns) and a length of 9500 microns. The type and size of these filaments were specifically engineered to be non-respirable.<sup>1</sup> A thin layer of tobacco paper is sandwiched between two layers of the glass insulator. The tobacco paper and the tobacco in the heat source burn when Eclipse is lit to provide tobacco taste when the cigarette is first lit and while it is being smoked.

Immediately behind the heat source is a tobacco roll that contains two segments. The first segment is a roll of processed cut tobacco impregnated with glycerin<sub>2</sub> (a common food ingredient which is found in most cigarettes). The second segment of the tobacco roll contains another processed tobacco blend. At the mouth-end of the cigarette is a cigarette filter made from cellulose acetate (the filter material used in most cigarettes). Holding the cigarette together are cigarette papers and laminates of cigarette paper and food-grade aluminum foil. The foil helps to retain the heat and conduct it through the cigarette.

The smoker lights an Eclipse by puffing on the filter while the heat source is exposed to a flame. As the smoker puffs on an Eclipse, heated air flows through the dual segment tobacco roll and the filter. As the heated air passes through the cigarette, it produces smoke by vaporizing the glycerin and by releasing flavorants, aroma, taste and flavour components (including nicotine) from the tobacco. After about 6 or 7 minutes, the heat source self-extinguishes and the cigarette stops producing smoke. The carbon heat source and a few other components of the heat source assembly are the only parts of the cigarette that burn. Therefore, an Eclipse is the same size when it is finished as it was before it was lit.

As a simple analogy for purposes of illustration, the process Eclipse uses to produce smoke can be thought of as similar to the process used to make drip coffee. In the coffee maker, water is heated and then passed through coffee grounds to release the aroma, taste and flavor components. In the Eclipse, air is heated and then passed through tobacco to release components that produce smoke, taste and flavor, including nicotine.

### *ACCORD Cigarette*

Philip Morris is testing a high-tech cigarette called the Accord. The kit includes a battery charger, a puff-activated lighter that holds the cigarette, and a carton of special cigarettes. When a smoker sucks on the little box (which could pass for a kazoo), a microchip ignites the cigarette. The process gives the smoker one drag and releases no ashes or smoke. Accord appears to reduce the risk of secondhand smoke, but a study published late last year reported that Accord smokers took bigger and longer puffs than with conventional cigarettes. The researchers concluded that the Accord is unlikely to reduce the smoker's risk.



## **Other types of tobacco use (*other than cigarettes*)**

### ***Bidis***

Bidis (pronounced “bee-dees”) are small, thin hand-rolled cigarettes imported to the United States primarily from India and other Southeast Asian countries. They consist of tobacco wrapped in a tendu or temburni leaf (plants native to Asia), and may be secured with a colorful string at one or both ends. Bidis can be flavoured (e.g., chocolate, cherry, and mango) or unflavoured.

They have higher concentrations of nicotine, tar, and carbon monoxide than conventional cigarettes sold in the United States.



### ***Kreteks***

Kreteks (pronounced “cree-techs”) are sometimes referred to as clove cigarettes. Imported from Indonesia, kreteks typically contain a mixture consisting of tobacco, cloves, and other additives. As with bidis, standardized machine-smoking analyses indicate that kreteks deliver more nicotine, carbon monoxide and tar than conventional cigarettes. There is no evidence to indicate that bidis or kreteks are safe alternatives to conventional cigarettes.



### ***Pipes***

The smoking pipe typically consists of a small chamber (the bowl) for the combustion of the tobacco to be smoked and a thin stem (shank) that ends in a mouthpiece (also called a bit). Pipe smoke, like cigar smoke, is not usually inhaled. It is merely brought into the mouth and then released.

### ***Cigars***

A cigar is a tightly rolled bundle of dried and fermented tobacco, one end of which is ignited so that its smoke may be drawn into the smoker's mouth through the other end. Cigar tobacco is grown in significant quantities in such nations as Brazil, Cameroon, Cuba, Dominican Republic, Honduras, Indonesia, Mexico, Nicaragua and the United States of America. Cigars manufactured in Cuba are widely considered to be without peer, although many experts believe that the best offerings from Honduras and Nicaragua rival those from Cuba.

### ***Chewing Tobacco***

Chewing tobacco is a smokeless tobacco product. Chewing is one of the oldest ways of consuming tobacco leaves. Native Americans in both North and South America chewed the leaves of the plant, frequently mixed with lime.

***Snuff (Dip)***

Dip is commonly confused with chewing tobacco. Instead of literally chewing on tobacco, a small clump of dip is 'pinched' out of the tin, and placed between the lower or upper lip and gums. The dip rests on the inside lining of the mouth where saliva carries nicotine to the inferior or superior labial arteries, usually for 20-30 minutes or possibly an hour. It can cause irritation to the esophagus and nausea. Smokeless tobacco is sometimes used in the workplace by employees, especially if the employer does not provide many cigarette breaks or the employee is constantly using both hands during work (which doesn't provide opportunities for cigarette smoking).

## Tobacco and Smoke Analytics

### Smoke–Analytics and Smoking Machines

For the purposes of investigating chemical composition and biological properties, smoke is separated into a *particulate phase* and a *gas phase*; the gas phase is frequently subdivided into materials which condense at liquid-air temperature and those which do not.

The chemical analysis of cigarette-smoke generally involves a three-step process:

- Collection
- Extraction
- Quantification

#### Collection

Cigarette smoke is collected by a “smoking machine”. The filtered end of the cigarette is placed into a port, and “puffed” by the suction of a pump.

There are two types of smoking machines: rotary and linear.

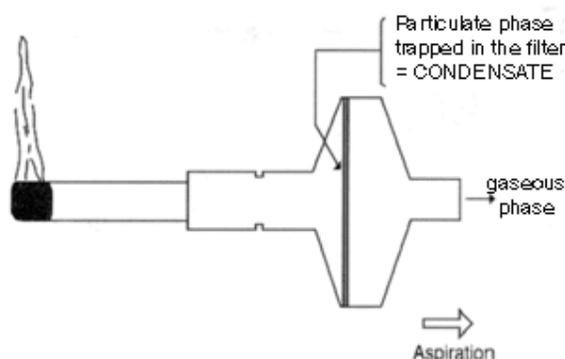
*Rotary smoking machines* collect a cumulative sample from several cigarettes per run, with each cigarette being puffed in turn by the one pump. This is the best method for collecting chemicals that are present in tobacco in very small quantities.



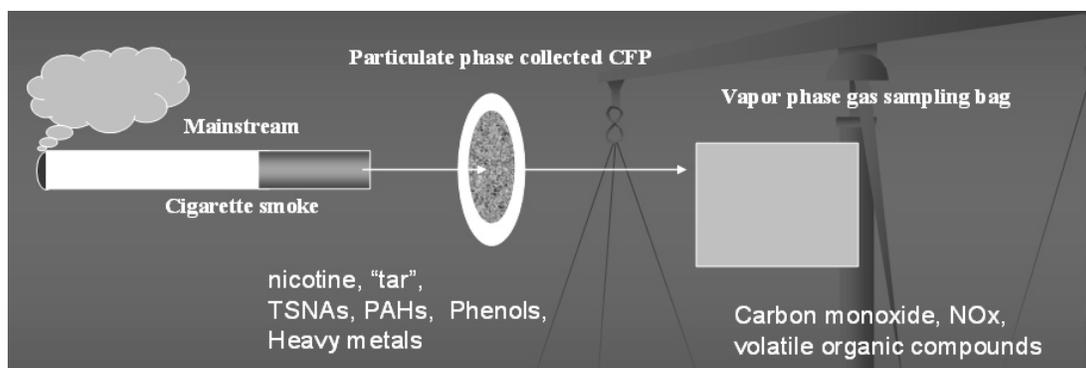
*Linear smoking machines* operate with one cigarette port per pump, thus each cigarette is puffed with each intake of the pumps, and samples are collected individually per port. This method is used for collecting larger quantities of chemicals, such as tar and nicotine samples.



The **particulate matter** (Tar) is collected on filter pads. Mainstream smoke particulate is collected on filter pads located behind the cigarette port. Tar is defined as the cigarette smoke condensate or total particulate matter (TPM) minus nicotine and water, collected on the Cambridge filter pad in smoking machines from **mainstream smoke** (defined as that drawn through the filter by the smoker, as opposed to sidestream smoke which rises from the lit end of the cigarette). Particles in the smoke that are larger than 1  $\mu\text{m}$  are trapped with 99% efficiency.

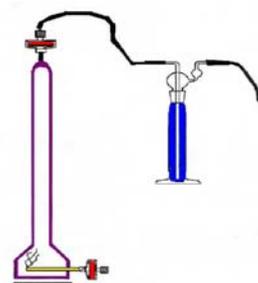


The **gaseous phase** or vapour phase of the smoke passes mostly through the filter.



O'Conner, R., Watson, C., Product Testing and Monitoring [26]

**Sidestream smoke** is collected with the use of BAT "fishtail" devices, which allow smoke to travel up the glass enclosure to a filter pad located at the top. Any of the desired chemicals that travel through the filter are later trapped by "impingers".



Apparatus for Sidestream Smoke Collection

### ***Extraction***

Filter pads are weighed before and after a “smoking” run to determine the *Total Particulate Matter (TPM)*.

The filter pads are then placed either into the impinger solution or another solvent and the mixture is shaken or in some other way extracted in order to release the chemicals from the filter pads into the solution.

### ***Quantification***

The method to be used depends on the substance to analyse (GC-FID, GC-MS, IC, HPLC, HPLC-MS, IR etc).

### ***Analytics of the vapour phase***

As the gaseous compounds of smoke mostly pass through the filter, the gas phase has to be collected after the Cambridge filter pad. These techniques can be applied:

- trapping in cold trap (Tenax, activated charcoal or other trapping phases)
- trapping in (cold) solvent
- trapping in Tedlar bags



*Tedlar Bag*

## **Measuring Nicotine, Tar and Carbon Monoxide Content**

### **The ISO Standard**

The interest of scientists in cigarette smoke has led them to design equipment that produces smoke mechanically. The first smoking machines were designed early in the 20th century and it was soon recognized that such variables as volume, duration and frequency of puffs affected test results. The basic variables were proposed in the thirties and frequently used in smoke research conducted in the fifties. They were officially recognized for the first time in the United States by the Federal Trade Commission (FTC) in 1967 and adopted by the International Organization for Standardization (ISO) in 1976.

ISO, whose members include AFNOR in France, DIN in Germany and AENOR in Spain, published a series of international standards for measuring nicotine, tar and carbon monoxide content in smoke between 1978 and 1986. The standards were revised in 1992

and 2000 to allow for advances in measuring and analytical techniques. They include procedures to be conducted using a smoking machine that takes 35 millilitre puffs for duration of two seconds each minute. Particulates in the smoke are collected in a special fibre-glass filter and the gas fraction is collected in a leak tight bag. Total particulates are measured by weighing, while the water, nicotine and carbon monoxide are measured by chemical analysis. The tar content is then calculated by subtracting the quantity of water and nicotine from the total particulate matter.

These methods are recognized in most countries around the world, including the European Union, which officially adopted the ISO smoking method in 1990 for testing maximum tar content and indicating nicotine and tar contents on cigarette packets. Each European Union member state is responsible for monitoring compliance with these regulations at the domestic level. In France, the National Testing Laboratory (LNE) conducts smoking tests five times a year on products sold on the French market, and the test findings are published in the Official Bulletin of the Health Ministry. The LNE also issues yearly certificates of compliance for each product, which are required in order to keep products on the market. In Spain, the Finance Ministry's Central Laboratory certifies products when they are first introduced and the laboratories of the Health Ministries of the Autonomous Communities are in charge of periodically verifying that labelling is compliant.

The use of these standards provides a reliable classification of cigarettes on the basis of nicotine, tar and carbon monoxide content in the smoke obtained under stringently controlled laboratory conditions. They cannot, however, indicate the quantity of nicotine, tar and carbon monoxide produced by a particular smoker because personal smoking habits vary considerably. Since smokers may smoke a product in different ways depending on circumstances, no standard smoking method can claim to represent the entire spectrum of smoker habits. Only the ISO smoking test methods have received validation at international level. In certain countries, specifically Canada and the United States, other smoking variables have recently been proposed as more representative of the way people actually smoke.

Parameters for the standard ISO test

Puff Volume	:	35 ml
Puff Interval	:	1 per minute
Puff duration	:	2 seconds
Butt length	:	23mm for nonfiltered and 3mm above filter overlap for filter tipped cigarettes

A variety of problems arise in applying this ISO standard for cigarette smoking. They are described in Article 3 of the European Directive on page 23.

## **Green Leaf, Cured Tobacco and Processed Tobacco Analytics**

The analytics can be divided into three main sections:

- **Extraction**

Extraction can be done by Soxhlet, SFE, ASE, MWAE or any other extraction technique

The extracts of cured and cigarette tobacco carry high level of wax. Waxes create problems with the GC-columns and therefore have to be separated from the pesticides:

- **Clean-up of Extract**

The clean-up procedures separate the analyte from any of the matrix-compounds, e.g. waxes, fats or pigments. Solid Phase Extraction is used for this purpose. One of the most commonly used cartridge materials is Florisil.

The activity of the Florisil must retain the impurities and let the pesticides pass quantitatively. The recovery must be better than 95%.

- **Analysis of cleaned extract**

HPLC, GC etc.

*Analytical Methods for Tobacco (not burned-Tobacco)*

Substance Class	Method
Nicotine Alkaloids	DIN 10 241
Mono-and Disaccharide's (Glucose, Fructose, Mannose, Sucrose, Lactose, Maltose, Sorbitol, Xylose)	DC, Enzymatic, HPLC, IC
N-Nitrosamine	
Toxic Trace Metals (Pb,Cd,Hg,Ni,Se,Cr,As)	AAS, IC
Pesticides (Residues)	LC-MS, GC-ECD/FID/MS
Formaldehyde	
Ammonia	IC
pH	
Humectants (Propylene Glycol, Glycerol, Triethylene Glycol)	DC, Enzymatic
Glycyrrhizine Acid (Licorice)	HPLC
Theobromine/Caffeine (Cocoa)	HPLC
Organic Acids (Citric, Lactic, Tartric, Acetic, Propionic, Butyric)	DC, IC
Antioxidants (PG, BHA, BHT, TBHQ, THBO)	DC, HPLC
Amino Acids	Amino Acid Analysator
Common Ions (Na <sup>+</sup> ,K <sup>+</sup> ,Ca <sup>2+</sup> ,Mg <sup>2+</sup> ,P,Cl <sup>-</sup> ,PO <sub>4</sub> <sup>3-</sup> )	IC
Silica	
Ash	LMBG §35
Nitrate	IC, Photometric
Head Space Analysis	GC
Beta and alpha – Carotene	
TVB, Total Volatile Bases	
Total Nitrogen	Kjeldahl
Water	Karl – Fischer
Vanillin, Ethylvanillin, Cumarin	
Benzioc Acid, Sorbic Acid	
Lipids	Soxhlett, Weibull-Stoldt

## Pesticide Analytics

### *Organochlorine Pesticide Analytics*

Most of the organochlorine pesticides are metabolised after their application on different substrates, for example the tobacco plant. The parent insecticide may transform or degrade to a compound which may or may not be toxic.

The quantification of total pesticide residues involves the estimation of the parent pesticide and its toxic metabolites, such as total DDT, p,p and o,p isomers of DDT, p,p and o,p isomers of DDE and p,p and p,e isomers of TDE.

Similarly, alpha, beta gamma and delta-HCH need to be determined for HCH. Alpha-endosulfan, beta-endosulfan and endosulfan-sulfate give the total picture for endosulfan. Endosulfan lactone, diol and ether are not toxic and therefore may not be quantified.

The basic units of pesticide residue analysis are:

1. Sampling
2. Extraction of pesticide from the sample
3. Clean-up/derivatisation of residues from the sample
4. Identification and quantitative determination of the pesticide residue.

### Extraction

Sample material with a low fat and wax content can be extracted directly, separated and analysed by GC.

Tobacco contains large amounts of waxes and pigments which result in low response and may even damage the column packing.

Extraction techniques are Solid Phase Extraction (SPE), Soxhlet, Solid Phase Micro Extraction (SPME) and Supercritical Fluid Extraction (SFE) .

### Clean-up

A large number of clean-up methods are available for the organochlorine insecticides.

Commonly used methods for clean-up of raw extracts of samples are chromatographic columns filled with adsorbent such as Florisil, alumina, Silica gel or SEP-PAK cartridges filled with the same materials.

Florisil has gained the greatest attention of all the sorbents used in residue analysis. As Florisil retains some lipids preferentially (25g Florisil with 3% water retains 1g of fat), it is particularly well suited for the clean-up of fatty matrixes.

When a Florisil column is eluted with solvent mixtures of low polarity, non-polar residues are recovered almost quantitatively. The eluates are very clean for GC-ECD analysis. However, A major disadvantage is that activity may vary from one batch to another.

## **ISO Reference Methods for Pesticide Determination**

***ISO 6466-1983*** : Tobacco and tobacco products – Determination of dithiocarbamate pesticide residues – Molecular absorption spectrometric method

***ISO 4876-1980*** : Tobacco and tobacco products – Determination of maleic hydrazide residues

***ISO 4389-2000*** : Tobacco and tobacco products – Determination of organochlorine pesticide residues – Gas chromatographic method.



## References

- 1) Baker, R.R.; The Development and Significance of Standards for Smoking-Machine Methodology; *Beitraege zur Tabakforschung International*, Volume 20, No.1, February 2002
- 2) Guthrie, F.E.; Bowery, T.G.; Pesticide residues on tobacco; *Residue Reviews*; Volume 19; Pages 31ff; 1967
- 3) Djordjevic, M.V.; Fan, J.; Hoffmann, D.; Assessment of chlorinated pesticide residues in cigarette tobacco based on supercritical fluid extraction and GC-ECD; *Carcinogenesis*, Vol. 16; No.11; pp.2627-2632; 1995
- 4) Lawson, F.R.; Corley, C.; Schechter, M.S.; Insecticide Residues on Tobacco during 1962; *Tobacco Science*. Vol. 8; pp110; 1964
- 5) Ladisch, H.; Ueber das Vorkommen chlororganischer Insektizide in Tabak und Tabakrauch; *Zeitschrift fuer die gesamte Hygiene*; pp579, 1973
- 6) Atallah, Y.H.; Dorough, H.W.; Insecticide Residues in Cigarette Smoke. Transfer and Fate in Rats; *J.Agr.Food,Chem.*; Vol.23; No.1, 1975
- 7) Entomology Faculty; Insecticide Residues as a Source of Off-Flavor in Tobacco; *Tobacco Science*
- 8) Thurm, V.; Untersuchung ueber Pestizidruueckstaende auf Tabakwaren. Uebergang von DDT und Dieldrin aus Tabakwaren in den Rauch; *Mitt.Nahrung*; 16; 353; 1972
- 9) Bowery, T.G.; Evans, W.R.; Guthrie, F.E.; Rabb, R.L.; Insecticide Residues on Tobacco; *Agricultural and Food Chemistry*; Vol.7; No.10; 1959
- 10) Hengy, H.; Thirion, J.; The Determination of Malathion Residues in Tobacco and Tobacco Smoke Condensate; *Beitraege zur Tabakforschung*; Band 5, Heft 4, 1970
- 11) Mussalo-Rauhamaa, H.; Salmela, S.S.; Cigarettes as a source of some trace and heavy metals and pesticides in man; *Archives of Environmental Health*; Vol.41, No.1; 1986
- 12) James F. Pankow, Brian T. Mader, Lorne M. Isabelle, Wentai Luo, Andrea Pavlick, and Cikui Liang; Conversion of Nicotine in Tobacco Smoke to its Volatile and Available Free-Base Form through the Action of Gaseous Ammonia; *Environ.Sci.Technol*; Vol. 31, 1997, 2428-2433
- 13) Mirjana V. Djordjevic, Jingrun Fan, Saul Ferguson, Dietrich Hoffmann; Self-regulation of smoking intensity. Smoke yields of the low-nicotine, low-“tar” cigarettes; *Carcinogenesis*; Vol. 16; No. 9; pp 2015-2021; 1995
- 14) Hans-Jochen Eberhardt and Gerhard Scherer; Human Smoking Behaviour in Comparison with Machine Smoking Methods: A Summary of the Five Papers Presented at the 1995 Meeting of the Coresta Smoke and Technology Groups in Vienna; *Beitraege zur Tabakforschung International*; Vol. 16; No.4; 1995
- 15) Commission of the European Communities; Information on Agriculture; Pesticide residues in tobacco and tobacco products; No.14, July 1976
- 16) Sweeney, C.T. et al.; Effect of Filter Vent Blocking on Carbon Monoxide Exposure from Selected low tar cigarette brands; *Pharmacology and Behaviour*; 63(1); 167-173, 1999
- 17) Stotesbury, Steve; Digard, Helena; Willoughby, Louise; Couch, Andy; The Pyrolysis of Tobacco Additives as a Means of predicting their behaviour in aburning cigarette; *Beitraege zur Tabakforschung International*; Volume 18, No. 4, 1999

- 18) Geiss, O., Kotzias, D. – Determination of Ammonium, Urea and Pesticide Residues in Cigarette Tobacco. *Fresenius Environmental Bulletin (FEB)*, No. 12 (2003), 1562 – 1565
- 19) Dixon, M., Lambing, K., Seeman, J., Mini Review: On the Transfer of Nicotine from Tobacco to the Smoker. A brief Review of Ammonia and “pH” factors, *Beitraege zur Tabakforschung International (Contributions to Tobacco Research)*, Volume 19, No.2, (2000)
- 20) Doll, R., Hill A.B., *Br.Med. J.*, 1950, 739
- 21) Hecht, S.S., Hoffmann, D., Tobacco specific nitrosamines, an important group of carcinogens in tobacco and tobacco smoke. *Commentary, American Health Foundation*, pages 875-884
- 22) Hoffmann, D., Hoffmann, I, *J.Toxicol. Environ. Health*, 1997, 50, 307
- 23) Benner C.L. et al., Chemical Composition of Environmental Tobacco Smoke. 2. Particulate Matter Phase Compounds, *Environ.Sci.Technol.*, 1989, 23, 688-699
- 24) Hodgson, A.T. et al., Use of volatile tracers to determine the contribution of environmental tobacco smoke to concentrations of volatile organic compounds in smoking environments, *Environment International*, Vol. 22, No. 3, pp 295-307, 1996
- 25) Kotzias, D., Geiss, O., Leva, P., Bellintani, A., Arvanitis, A., Kephelopoulos, S., Impact of various air exchange rates on the levels of environmental tobacco smoke (ETS) components, *Fresenius Environmental Bulletin (FEB)*, Vol. 13, No. 12b, 1536-1549, (2004)
- 26) O’Conner, R., Watson, C., Product Testing and Monitoring, Slide Presentation at Tobacco Free Initiative, WHO, Geneva, Switzerland
- 27) McNeill, A., Joossens, L., Jarvis, M., Review of the implementation of the Tobacco Product Regulation Directive 2001/37/EC, Commissioned by ASH London, March 2004
- 28) Jarvis, MJ, Boreham, R, Primatesta, P., Feyerabend, C, Bryant, A, Nicotine yield from machine-smoked cigarettes and nicotine intakes in smokers: evidence from a representative population survey. *J Natl Cancer Inst.*, 93: 134-8
- 29) Hoffmann, D, Hoffmann, I, El-Bayoumy, K., The less harmful cigarette: a controversial issue. A tribute to Ernst L.Wynder, *Chemical Research in Toxicology*, 14, 767-790, (2001)
- 30) Hoffmann, D., Hoffmann, I., The changing cigarette: chemical studies and bioassays. In Anonymous: Risks associated with smoking cigarettes with low machine-measured yields or tar and nicotine. Bethesda, MD, US Department of Health and Human Services, National Institutes of Health<sup>1</sup>, National Cancer Institute: 159-91
- 31) Russell MAH. Low Tar medium nicotine cigarette: A new approach to safer smoking. *British Medical Journal*, 1, 1430-3, (1976)
- 32) McNeill, A., Joossens, L., Jarvis, M., Review of the implementation of the Tobacco Product Regulation Directive 2001/37/EC; Commissioned by ASH London, March 2004

## Internet:

- A very good website with all the information on single pesticides and pesticide groups can be found at: [www.hclrss.demon.co.uk](http://www.hclrss.demon.co.uk)
- [www.g-nitschke.de](http://www.g-nitschke.de)
- [www.altadis.com](http://www.altadis.com)
- [www.pmintl.com](http://www.pmintl.com) (Philip Morris International)
- [www.philipmorrisusa.com](http://www.philipmorrisusa.com) (Philip Morris USA)
- [www.nicnet.org](http://www.nicnet.org)
- [http://www.erowid.org/plants/tobacco/tobacco\\_inf2.shtml](http://www.erowid.org/plants/tobacco/tobacco_inf2.shtml) (Contents of tar, nicotine, CO in commercial brands)
- [www.uky.edu](http://www.uky.edu) (University of Kentucky → Reference Cigarettes)
- <http://www.rjrt.com> (R.J. Reynolds)
- <http://www.tobaccojournal.com> (Many useful web-addresses)
- <http://www.ash.org.uk/html/regulation/pdfs/review200137ec.pdf> (Review of the implementation of the Tobacco Product Regulation Directive 2001/37/EC)
- <http://www.iarc.fr/cgi-bin/htsearch> (IARC Webpage)

## Tobacco Relevant ISO – Norms

### Tobacco and Tobacco Products

ISO 2817:1999	Determination of silicated residues insoluble in hydrochloric acid
ISO 2881:1992	Determination of alkaloid content – Spectrometric method
ISO 3402:1999	Atmosphere for conditioning and testing
ISO 4389:2000	Determination of organochlorine pesticide residues – GC Method
ISO 4876:1980	Determination of maleic hydrazide residues
ISO 6466:1983	Determination of dithiocarbamate pesticide residues – Molecular absorption spectrometric method
ISO 6488:2004	Determination of water content – Karl Fischer Method
ISO 6565:2002	Draw resistance of cigarettes and pressure drop of filter rods Standard conditions and measurement
ISO 10185:2004	Vocabulary
ISO 13276:1997	Determination of nicotine purity – Gravimetric method using tungstosilicic acid
ISO 16632:2003	Determination of water content – GC method

### Cigarettes

ISO 3550-1:1997	Determination of loss of tobacco from the ends – Part1: Method using a rotating cylindrical cage
ISO 3550-2:1997	Determination of loss of tobacco from the ends – part 2: Method using a rotating cubic box (sismelatophore)

ISO 4387:2000	Determination of total and nicotine-free dry particulate matter using a routine analytical smoking machine
ISO10315:2000	Determination of nicotine in smoke condensate – GC Method
ISO 20773:2007	Determination of nicotine-free dry particulate matter and nicotine in sidestream smoke – Method using a routine analytical linear smoking machine equipped with fishtail chimney

Tobacco

ISO 4874:2000	Sampling of batches of raw material – General principles
ISO 15152:2003	Determination of the content of total alkaloids as nicotine Continuous-flow analysis method
ISO 15153:2003	Determination of the content of reducing substances – Continuous flow analysis method
ISO 15154:2003	Determination of the content of reducing carbohydrates Continuous-flow analysis method
ISO 15517:2003	Determination of nitrate content – Continuous-flow analysis method

Environmental Tobacco Smoke

ISO 15593:2001	Environmental tobacco smoke – Estimation of its contribution to respirable suspended particles – Determination of particulate matter by uv absorbance and by fluorescence
ISO 18144:2003	Environmental tobacco smoke – Estimation of its contribution to respirable suspended particles – Method based on Solanesol
ISO 18145:2003	Determination of vapour phase nicotine and 3-ethenylpyridine in air – GC Method

Other

ISO 12194:1995	Leaf tobacco – Determination of strip particle size
ISO 12195:1995	Treshed tobacco – Determination of residual stem content

## Appendix I

### Tobacco – Glossary

**Air-cured tobaccos** - Are dried naturally, sheltered from sunlight. This drying is carried out on the whole plant or as individual leaves reach maturity. There are generally five crops in a season. Sugar produced by the plants is degraded during the three months treatment.

**American blends** - These blends have the following components: Virginia, Burley and Oriental in variable proportions to which a "sauce" consisting of humidifying and sugar elements is added. These blends are finally sprayed with aromatic flavours.

**Aromatics** - Additives used to flavour tobacco, including cherry, apple, orange, chocolate, coffee, and whisky flavours.

**Band** - The ring of paper with the name of the cigar brand, wrapped near the closed head of the cigar and usually held on with a vegetable based glue.

**Binder** - The portion of a tobacco leaf that is rolled around the filler to hold it together.

**Blend** - A mixture of tobacco varieties. The purpose of creating a blend is to produce a type of tobacco that meets a customer's specifications of quality, flavour and aroma.

**Blended cigarettes** - Most of the cigarettes smoked today are blended, which means they are made with a mixture of tobacco varieties. The main types are American-blend, Oriental-blend, German-blend, English-blend (or Virginia), Maryland and dark cigarettes.

**Blending** - Mixing different varieties and grades of tobacco in order to produce a predetermined, uniform blend that meets a customer's specifications of quality, flavour and aroma. The tobaccos are blended according to specific formulas or recipes that dictate the percentage of each type and grade to be used.

**Bloom** - A fine white powder that forms on the wrapper of the cigar caused by the oils that exude from the tobacco. It can be gently brushed off with a small camel hair brush, though there is no need to do so. Bloom indicates that the cigar is alive, maturing as it should inside a well maintained humidor. Bloom should not be confused with mold. Mold is bluish-green and stains the wrapper. Mold usually indicates that a humidor is too warm or has excessive levels of humidity.

**Blue mold** - Blue mold is a damaging fungus that forms on the tobacco leaf and can ruin the crop. It is a considerable problem where there is a lot of humidity or rain.

**British Flake and Ready Rubbed** - The tobacco leaves are compacted under great pressure and heat is applied for some days. The tobacco cakes are then removed from the press and cut into thin slices on a guillotine. The pipe smoker breaks the flakes up in the palm of the hand to the texture that suits the pipe and style of smoking. This type of tobacco produces a cool slow burning smoke.

**Bunch** - The mix of filler and binder leaves before they are rolled into a wrapper.

**Burley** - Highly developed plants, the culture of which has recently expanded. This type of tobacco does not ferment like the "Dark", but generally "matures". Burley, though not very aromatic, is very useful in blending.

**Curing** - Immediately after harvesting, tobacco is cured to remove all the natural sap from the leaves so that it can be further processed. There are four primary curing methods: air-curing, flue-curing, fire-curing, and sun-curing; but all of them focus on regulating the rate at which moisture is removed from the tobacco.

**Dark blends** - Consisting of dark tobaccos from various origins (France, South America, Africa and Asia) and Oriental. Generally, they do not contain additives or "sauce".

**Dark tobaccos** - Are generally quite developed plants which, initially, were the most widely spread in the world. When used for cigar making, the leaf is subjected to a second treatment-fermentation.

**Fermentation** - There are primarily two types of fermentation, natural and forced fermentation. The duration of the process ranges from two days to two months or more. Natural fermentation, sometimes known as aging, is a chemical reaction caused by moisture and warm temperatures; it occurs when tobacco is packaged in bales or hogsheads. Natural fermentation generally gives tobacco a more uniform colour and a milder taste. Forced fermentation involves placing tobacco in huge stacks so that the chemical reaction caused by the moisture and warm temperatures is intensified by the pressure the tobacco is under. Forced fermentation generally gives tobacco a more uniform colour, as well as a smoother aroma and taste.

**Filler** - Tobacco used as the main body or core of a cigar that provides the significant portion of the taste.

**Fire-cured** - Is a type akin to Dark; its natural drying is completed by a wood-fired fumigation (oak is used by the traditionalists).

**Flake, Plug and Bar tobaccos**-- After the tobacco leaves have been prepared, they are put into moulding presses under great pressure, usually by means of hydraulics, and pressed into cakes. The cakes are then placed into retaining presses and cooled or heated. The amount of pressure and heat will determine the final tobacco colour. Flake tobaccos can be sold in slices, or as ready rubbed flake and partly broken flake.

**Flue-cured** - Represented by the majority of warm-air dried Virginia. The cultivation is expanding rapidly. The plant is average in size and six crops are produced yearly. Each crop is taken to a bulk curing barn where it is dried by warm air for seven days. The leaves become yellow as a result of a rapid rise of temperature. Among the Virginia are the aromatics and the fillers, the latter used as a major ingredient to balance the mixture. The blends and the taste-lines: Each industrial blend is the result of the scientific compositions of several grades from the same tobacco and from different types (from 20 to 40 in commercial products).

**Latakia** - a product of the eastern Mediterranean used in certain mixtures to give a distinctive flavour.

**Leaf** - These leaves grow just below the tips of the tobacco plant and are characterised by their relative length; they are firm and heavy-bodied. Nicotine content can range from 3% to over 3.5%, while the sugar level is around 15%.

**Lugs** - Lugs are the leaves around the bottom part of the stalk. They are characterised by their small size, thinness and brightness. They make up 13% of the plant's total weight. The nicotine content is around 2.5%, and the sugar level varies from 12-20%.

**Mixtures** - their unique character comes from careful blending of many different exotic tobaccos and plain natural Virginia and Shags. Some of the more exotic tobaccos in these mixtures have been previously pressed and darkened and may include rich flavourings to enhance the aroma and taste.

**Mould** - The wooden form used by cigar rollers to give shape to a finished bunch of cigar tobacco. Some moulds have two parts which are then placed in a press.

**Oriental** - Grown largely in the Balkans and eastern Mediterranean; distinctively aromatic.

**Perique** - Grown largely around New Orleans; subject to a curing process known to just one family, perique is used as a seasoner for other pipe tobaccos, providing a distinctive taste and aroma

**Priming (Sandleaves)** - These are the leaves at the bottom of the stalk. They are the first leaves to ripen and the first to be harvested. They make up about 12% of the plant's weight. Primings contain only 1.5 to 2% nicotine and 5 to 10% sugar.

**Smoking leaf** - "Smoking leaves" grow just above the middle of the stalk. They make up around 7.5% of the plant's total weight. These leaves ripen to a bright orange colour and contain about 3% nicotine. The sugar content is about the same as in the lugs.

**Sun-cured** - Represent almost the totality of Oriental tobaccos. Their cultivation is confined to Greece, Turkey, Bulgaria and to a lesser degree to adjoining countries. The essential characteristics of oriental tobaccos are their aromatic qualities and a high sugar content (10 to 15%). The smoke is generally mild and this characteristic brings a binding and homogeneous effect used in most mixtures.

**Tips** - The tips are the leaves growing at the top of the tobacco plant. They are relatively narrow and pointed, but are usually heavier-bodied than leaves lower down the plant. Tips represent around 18% of the plant's total weight, and contain a nicotine level of about 3.5%.

**Tobacco Plant** - One of the most common plants is Virginia tobacco. It is often used in US and European 'blended' cigarettes, and in particular in the so-called 'English' Virginian-type cigarettes. The heavier grades are used in various kinds of mixtures for pipe smoking. Flue-cured tobacco is grown in more than seventy countries. The major exporting

countries are China, the USA, Brazil, India and Zimbabwe. Around 40% of the world's tobacco is currently of a Virginian type plant. A well-grown plant reaches a total height of 160-190 cm, and will carry 18-22 harvestable leaves.

**Twist and Spun Cut** - Full bodied, powerful and rich, they are made in the traditional style developed by sailors, spun to form a rope. Usually only stocked by specialist tobacconists.

**Virginia blends** - This taste is the oldest known. It is characterised by the pure Virginia blends, originally without additives.

**Wrapper** - A tobacco leaf of varying quality that is wrapped around the finished bunch and binder to complete the cigar. Leaves with elasticity are used to restrain the filler within the cigar. Good wrappers usually have no visible veins. Colours vary according to the maturing process.

## Appendix II

### The Reference Cigarettes

Reference cigarettes are used to check the performance of smoking-machines. But they are NOT used for calibrating the smoking machines.

1R4F and 1R5F cigarettes are supplied by the University of Kentucky as highly consistent reference cigarettes very similar to commercially available low and ultra low tar cigarettes.

The stock of 1R4F is now depleted; however, a second run has been performed with 2R4F.

	1R3F	2R4F	1R5F
Tar	15.0 mg	9.9 mg	1.7 mg
Nicotine	1.16 mg	0.81 mg	0.16 mg

- 1R3F : Similar to a full flavour commercially available cigarette.  
2R4F : approx. 30% air dilution  
1R5F : approx. 90 % air dilution

The monitor test piece most used in Europe is called CORESTA MONITOR followed by a progressive number, which is currently number 4 (2006), but will be soon replaced by number 5.

This monitor test piece is manufactured according to provisions given in the International Standard, ISO/FDIS 16055. The monitor test piece was analysed in a study organised by the CORESTA “Routine Analytical Chemistry Sub-Group” by laboratories each equipped to analyse according to ISO 3308, 3402, 4387, 8243, 8454, 10315 and 10362.

Advice on the general use of the CORESTA monitor test piece can be found in ISO/FDIS 16055.

## Appendix III

### Tobacco Wholesalers:

#### *A1 (Alliance One)*

<http://www.aointl.com/>

#### *Tribac*

<http://www.tribac.com/>



European Commission

**EUR 22783 EN – DG Joint Research Centre, Institute for Health and Consumer Protection**

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**Abstract**

This technical note provides an overview of the origin and mode of treatment of tobacco, tobacco ingredients and pesticide residues found in tobacco leaves. This note also reports on experiments carried out at the JRC-IHCP related to the chemistry of tobacco constituents and it gives information on analytical methodologies used for measuring tar, nicotine and carbon monoxide.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.