Physical Test Methods Sub-Group

Technical Report

Tobacco Moisture, Water and Oven Volatiles

A status report of common moisture methods used within the tobacco industry

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Author:

Nils Rose
Borgwaldt KC GmbH, Germany

Sub-Group Coordinator:

Mario Mayr
delfortgroup AG, Austria

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1. Introduction

The determination of moisture is an important task in the tobacco industry because moisture has a great influence on tobacco and non-tobacco materials, their processing properties and finally on the finished product itself.

Therefore the CORESTA Sub-Group Physical Test Methods decided to collect and describe methods for moisture determination used within the tobacco industry in order to generate a status report. When referring to “moisture”, it is necessary to understand that there are widely varying and conflicting definitions and terminology in use within the industry. It is common for “moisture” or “moisture content” to be used to refer to water content of a material but in relation to the tobacco industry it is necessary to differentiate between “moisture” as water content and “moisture” as oven volatiles.

To conclude, the term “moisture” is not clearly defined. The remainder of this document will refer specifically to water content or oven-volatiles.

1.1 Terminology

Volatiles

Volatiles are defined as the percentage of volatile components contained in the total mass of a solid substance. This includes water and all other compounds as menthol or glycol for example. The relative loss of volatiles in relation to the total mass of the substance is given by

$$m_c[\%] = \frac{m - m_d}{m} \times 100$$

m_c Volatile content

m_d Dry mass

m Total mass

Water content

Water content is defined as the percentage of water contained in the total mass of a solid substance.

$$m_w[\%] = \frac{m_w}{m} \times 100$$

m_w Water content

m Total mass

Oven dry mass

Oven dry mass is the mass that remains after the volatile substances have been driven off by heating. It is expressed as a percentage of the total mass.

$$m_d[\%] = \frac{m_d}{m} \times 100$$

m_d Dry mass

m Total mass

m_c [%] = 100 - m_d [%]

2. General effects on material properties

The water and other volatile components of a material will have an effect on its properties, such as:

- Structure
- Texture
- Grading of Tobacco leafs
- Dark spots
- Viscosity
- Fluidity
- Plasticity / Elasticity (Filling Capacity)
- Density
- Refraction index
- Conductivity / Dielectric Constant
- Concentration
- Colour
- Weight
- Odour
- Flavour
- Purity
- Stability
- Taste
- And others

(Not ranked in a particular order)

3. Effects on Tobacco and Tobacco products

Important effects on material properties which depend on water and volatiles for correct processing of tobacco and non-tobacco-materials:

RAW Tobacco	PRIMARY Tobacco Preparation	SECONDARY Finished Products	NON TOBACCO MATERIALS
level of micro organisms	humidification (Direct Cylinder Conditioning Process) - final content at maximum elasticity	mass	paper: air permeability machine run-ability
lignification	homogenisation (box) - filling capacity	hardness	
seasonality of initial content	blending (leaf) - elasticity (fibre) affects smoking values	loose ends	
mass	refinement (Burley-Process)	circumference	filter rod: mass, pressure drop, circumference
price	Steam-Process	pressure drop	
	Diet-Process	filter ventilation	
		Spots on cigarette paper	
	Reconstitution - (blotting paper characteristics)	Smoke taste modification	

Based on the materials properties, all appropriate materials can be reliably checked by Quality Assurance to achieve:

- Compliance with technical requirements (production)
- Compliance with commercial agreements (contracts)
  - e.g. tobacco leaf purchase centres (Hearson oven for worldwide use)
  - e.g. non tobacco material target values (e.g. water content in pulps and papers)
- Compliance with testing standards (e.g. ISO, DIN)
- Compliance with legislation/regulation (e.g. Russian GHOST standard)

4. Measuring Methods

4.1 Historical Retrospect

The determination of water and volatiles in tobacco started with the development of methods such as the Hearson oven method and the Cyclohexane method.

Oven Volatiles Method	Water Method
Hearson Oven Method - 16 h at boiling point of water (depending on barometric pressure) - determination of oven volatiles	**Cyclohexane Distillation Method** - 3h distillation at 82,5 °C - former ISO 6488 - solvent distillation with high health risks - applicable for water content 12-14% - was in use only for cut tobacco - replaced by Karl Fischer method

Based on above mentioned, several methods have been established:

Oven Volatile Method	Water Method
Oven methods - Hearson oven method (~ 3 % higher results compared to Karl Fischer) - 3h / 82 °C - oven method with results comparable to Karl Fischer - 100 min / 103 °C - oven method with results comparable to Hearson oven method - 30 min / 106 °C - oven method with results in-between Karl Fischer and Hearson oven method - other oven methods (4.10 Applications)	**Karl Fischer method** - same results compared to Cyclohexane Distillation method - initial weight 5 g instead of 100 g (Cyclohexane Distillation method) - current ISO 6488, implemented in 2004 - volumetric titration - developed to reduce health risks - determination of any level of water content - chemical laboratory method

4.2 Classification

Over the years, various methods have been developed for different materials and applications. They can be classified into two main groups:

Direct methods	oven methods	oven infrared–oven NIR-oven heating chamber
	water content methods	gas chromatography Karl Fischer titration Distillation
Indirect methods	spectroscopic methods	micro wave nuclear magnetic resonance near infrared
	other methods	capacity methods conductivity

4.3 Weighing-Drying-Method with Oven and Balance

Principle:

- drying by using a convection oven / fan oven / air circulation oven or a heating chamber and a scale or a combination of both in one device (possibly in combination with a vacuum and defined time and temperature)
- calculation of the oven volatiles content by weighing before and after the drying process, expressed as percentage
- drying of the samples at defined temperature up to a stability of the mass or after a defined time
- temperature and time period influence the result

Advantages:

- simple method
- multiple sample measurement possible

Disadvantages:

- possible decomposition of the sample
- time consuming (Note: it depends on the point of views: *laboratory versus production*. It is a disadvantage for the labs where they usually dry several samples at the same time).

- risk of burns
- potential measuring fault by weighing (hygroscopic effects, mechanical losses...)
- re-moistening of the sample

Remark:

- content stands for a total mass loss
- no distinction to other volatile substances (ethanol, menthol, humectants, etheric oils...).
- limited applicability because of thermal disintegration of some material (dust), oxidation, thermal decomposition

4.4 Karl Fischer Titration Method

Volumetric determination:

- extraction of water by shaking the sample with dry methanol
- followed by an injection of an aliquot portion into the titration vessel
- titration with a pyridine-free Karl Fischer-reagent
- calculation of the water content (to the nearest 0,1%)

$$WT = \frac{\left(VT - \left(B \times Va\right)\right) \times E \times V \times 100}{M \times Va}$$

Wt = water content tobacco (%)

Vt = volume of reagent used for titration of the sample extract [ml]

B = blank value

Va = volume of the aliquote portion of the sample titrated [ml]

E = water equivalent [mgH2O/ml]

V = total volume of the sample extract prepared [ml]

M = mass of the test portion [mg]

Principle:

- oxidation of sulphur dioxide by iodine in a methanolic solution
- volumetric determination
- coulometric determination

Application:

- water specific determination
- no aqueous liquids, soluble solids
- solids containing extractable or bakeable water

Advantage:

- accepted method for water determination
- qualified for trace analysis

Disadvantage:

- work methodology must be adapted to every sample type

4.5 Spectroscopic Methods

Principle:

- relation between a measured spectroscopic value and the accordant value measured with a standard method

Application:

- wide range of application:
  Microwave Spectroscopy
  Infrared Spectroscopy
  Magnetic Resonance Spectroscopy

Advantage:

- non-destructive measurement
- real time measurement (fast and practicable)

Disadvantage:

- interdependence to different parameters
  (e.g. temperature, density, material, …)
  calibration against standard method

4.6 Microwave Spectroscopy

Principle:

- Microwaves = electromagnetic waves
- wave length 1 m – 1mm ; frequency range 0,3 – 300 GHz
- excitation of dipole- rotations of water molecules
- exposure of the sample to a field of microwaves and determination of the effects on the sample

Microwave methods:

Absorption:

- microwaves with a constant frequency, e.g. 2,45 GHz
- release of the absorbed energy as heat

Transmission / Reflection:

- change of wavelength and absorption

Resonance:

- excitation of a substance by microwaves within an electromagnetic resonator
- no heating of the sample (<10mW application of energy)
- 2 parameter measuring method, to separate the influence of water and density:
    - displacement of the resonance frequency
    - microwave absorption of water

Application:

- products and raw materials
- chemistry, pharmacy, building materials, foodstuff

Advantage:

- short testing time
- minimal sample preparation, non-destructive
- compensation of influences (temperature, density)
- determination of water content at the surface and within the core
- independent of colour- and surface-effects

Disadvantage:

- specific calibration to a standard method
- for linearity reasons the measurement of a water content over 25 % becomes critical

4.7 Nuclear Magnetic Resonance Spectroscopy

A research method that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms and molecules.

Principle:

- ^{1}H, placed in a magnetic field, absorb electromagnetic radiation at a frequency characteristic of the isotope
- Relaxation frequency, energy of the absorption, and the intensity of the signal are proportional to the strength of the magnetic field

Application:

- research technique in chemical and biochemical laboratories

Advantage:

- detailed information about the structure, dynamics, reaction state and chemical environment of molecules
- applicable to any kind of sample that contains ^{1}H nuclei possessing spin
- diversity of samples, including solutions and solids

Disadvantage:

- only applicable in research laboratories

4.8 Near Infrared Spectroscopy

Principle:

- NIR = electromagnetic spectrum
- wave length 0,75 – 2,5 µm
- molecular overtone and combination vibrations of water molecules
- water is a high absorber
- absorption line of water : 1,94 µm or 1,45 µm depending on content

Application:

- products and raw materials
- food industry, chemistry, pharmacy, medical diagnostics

Advantage:

- short testing time
- non-destructive testing
- minimal sample preparation
- widely used for online measurements

Disadvantage:

- only determination of water content at the surface
- sensitive to batch depth

4.9 Compare and Contrast

Comparison of the methods applied by the participants of the CORESTA Sub-Group Physical Test Methods – 6th meeting 2010:

Measuring Method			Measuring Principle	Advantages	Disadvantages	Measured Item
Thermal / gravi-metric methods	Drying Oven	Oven + Balance	heating by convection; weighing before and after drying	reference method, initial weight of multiple samples	possible decomposition, time consuming, not selective for water, elaborate operation, possible error sources, risk of burns (protection)	Oven volatiles
		Compact Device (Oven + Balance in 1 device)	heating by convection; weighing before and after drying	easy handling, automatic determination, reduced measuring fault, high operational capacity	possible decomposition, not selective for water, risk of burns (reduced)	Oven volatiles
Chemical methods	Karl Fischer titration	Volumetry	titration of water by iodine; determination of voltage	reference method (ISO 6488), high precision, compact	working technique must be adjusted for each material, laboratory method	Water
Spectros-copic methods	Spectro scopy	Micro-wave Spectr.	determination of absorption / reflexion of a MW radiation	quick determination, continuous measurement	Reference-specific calibration	Water and other dipole molecules
Micro-wave resonance method		Different resonator types for cigarettes, cut- and leaf tobacco	determination of resonance-frequency-shif t and absorption by molecule-rotation	independent of surface-effects, short processing time	Reference-specific calibration	Water and other dipole molecules

4.10 Applications

Current oven methods applied by the participants of the CORESTA Sub-Group Physical Test Methods – 6th meeting 2010:

Description	Temperature	Duration	Initial Weight
Oven + Separate Balance			
Factory Oven	104 - 116 °C	5 - 12 min.	100 - 200 g
Heraeus Oven T5060E	105 ± 2 °C	≥ 30 min.	ca. 20 g
Binder Oven	98 °C	30 min.	4 - 5 g
Binder Oven	103 °C	100 min.	10 g
Rotary Oven	100 ± 2 °C	1 h	1 - 5 g
Electric Air Blast Oven	100 ± 2 °C	2 h	
Mark III, IV,V Oven	110 °C	3 h	
Freas Oven	100 - 111 °C	3 - 3.25 h	
Precision Oven (1625 / 605)	108 - 110 °C	3.25 h	
Binder Oven	105 °C	4 h	4 - 5 g
Binder Oven (FED240)	105 °C	6 h	
Horo Oven	82 °C	3 h	6 - 16 g
Air Circulation Oven	80 °C	3 h	7 g
Hearson Oven	boiling point of water	16 h	5 g
Hearson Oven	boiling point of water	3h	5 – 7 g
Hearson Oven	94 - 100 °C	16 h	
Dietert Oven	103 °C	2,5 min	10 g
Hot air ventilated Oven	60 ± 0,5 °C	16 h	5 g
Compact Device			
SODIM Humidim Oven	50 - 150 °C	1 - 7 min.	8 - 15 g
Borgwaldt Oven F21	104 - 116 ± 0,3 °C (≤120 °C)	5 - 12 min. (≥1 min.)	100 - 200 g
Brabender Oven HAG	106 °C	30 min.	5 ± 0,005 g

5. Summary

By taking different physical principles and a broadly varied number of measuring instruments as a basis, the selection of the instrument and/or the procedure in order to determine the water and volatile content of a specific sample will lead to different results between instruments and laboratories. This report highlights:

- Possible reduction by fine-tuning (temperature, duration, sample preparation)
- Possible compensation by calculation of a bias correction factor:
  - substantiated comparative measurements
  - alignment to a reference method
  - experimental design
- Differences between direct and indirect methods
- Direct methods: essential
  - basis for all indirect methods
  - requires know-how (trained employees)
  - time-consuming
  - precise and reliable results
- Indirect methods: significant improvement during the recent years

6. Conclusion

At the time of writing of this report, there was no standardised method or protocol for water and oven volatile determination*.
Direct comparison of results was therefore not appropriate. There was no preferred method in use.
Water & Oven Volatiles measurements appear to have been developed in response mainly to internal or local specific needs and demands, and not to an international and global need. This explains the lack of standardisation within and between the companies.

** It must be noted that in the meantime, CORESTA was developing CRM N° 76 – Determination of Moisture Content (Oven Volatiles) of Smokeless Tobacco Products, which was published in February 2014.*

7. Bibliography

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