

# The Determination of Moisture in the Total Particulate Matter of Cigarette Smoke

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## Introduction

This paper presents a rapid, routine, gas chromatographic, technique for the determination of moisture in total particulate matter of cigarette smoke. (T.P.M.) and results by this method are compared with those obtained by the two currently-used methods.

With some modifications, this method has been applied to the analysis of moisture in leaf and filler. The results of these analyses will be given in a subsequent presentation.

The delivery of total particulate matter (T.P.M.) for any cigarette is dependent on the method by which the cigarette is smoked. Not only does the amount of T.P.M. vary, but also the ratio of the components of the T.P.M. is altered by different smoking procedures. When using the smoking procedure of Cogbill, Wartman, and Harlow (1959) with a standard 80 mm. filtered cigarette, smoked to a 25 mm. butt length, it was found that approximately 9-12% of the T.P.M. was water.

Cogbill (1959) and Keth (1957) showed that the blend, the moisture in the cigarette, and other internal factors, as well as the external smoking conditions, have a distinct effect on the amount of moisture in the T.P.M. Their results also showed that, when a number of standard cigarettes were smoked under identical physical conditions and by the same method, the variation of water in T.P.M. between samples should be small.

At present there are two methods

for the determination of moisture in T.P.M.: the Karl Fischer analysis, as originally adapted by Morgareidge (1958) and modified by Holmes and Cridlin (1960), and the near-infrared spectrophotometric analysis for water, which was adapted to T.P.M. by Crowell (1961).

Gas chromatography was first used by Irby (1959) to substantiate data obtained on the moisture content of T.P.M. determined by other methods.

## Experimental

### Reagents:

Isopropyl alcohol certified

### Apparatus:

Perkin-Elmer Model 154D Vapor Fractometer

6 feet by  $\frac{1}{4}$ " polyethylene glycol/chromosorb column "W" obtained from Perkin-Elmer Co., Norwalk, Conn.

## Procedure

Four cigarettes per sample were smoked through a Cambridge filter on a smoking machine of the type described by O'Keeffe and Lieser (1958) in the manner presented by Wartman, Cogbill, and Harlow (1959). As soon as smoking was complete, the filter holders were weighed immediately for T.P.M. Each pad was then transferred into a 125 x 15 mm. test tube. Five ml. of isopropyl alcohol were pipetted into each tube. The test tubes were sealed with rubber serum bottle stoppers and shaken for fifteen minutes. Three blank pads conditioned at the same temperature

and relative humidity as those used in smoking, were extracted in the same manner. These extracts were used as blanks for determining the amount of moisture in the isopropyl alcohol and the T.P.M. pad before smoking. Use of this type of blank eliminated the necessity of oven drying the pads prior to analysis.

The standards were prepared by pipetting 5 ml. of isopropyl alcohol into four individual test tubes; the tubes were then capped. Three of the standards were loaded with 5, 10, and 20 mg. of water respectively. The water was introduced through the serum cap by using a micro syringe. The fourth standard was used as a reagent blank. The instrument was equilibrated at a temperature of 80°C. Helium was used as a carrier gas with a flow rate of 100 cc./min.

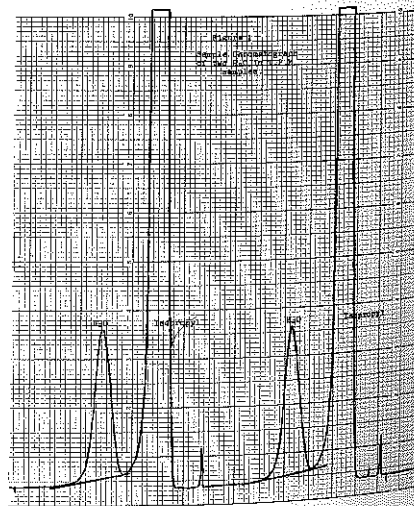


Figure 1. Chromatogram of sample.

The detector current was 250 ma. The injection port was heated to 100°C.

A sample aliquot of ten (10) microliters was chromatographed. Approximately ten minutes per sample was required. (Figure 1)

The responses of the standards were corrected by subtracting the response due to the reagent blank. The corrected response was then plotted against the corresponding concentration. A linear standard curve was obtained. A corrected response for the samples was found by subtracting the average response for the three blank pads from that of each sample. The corrected response was then converted to total mgs. of water per pad by a direct reading from the standard curve.

### Results and Discussion

It is important that the sample have limited exposure to the atmosphere throughout the entire analysis; therefore, the filter holders were capped immediately upon removal from the smoking machine. When the pads were placed in test tubes, they were immediately sealed with serum bottle caps. This permitted sampling from each tube with no further exposure to the atmosphere. When the standards and sample were treated in the same manner, it was possible to keep them for an indefinite length of time. Samples prepared and analyzed after two hours and again at twenty-six and fifty hours showed no increase or decrease in water content. (Table 1)

The minimum length of time necessary for extraction was found to be 20 minutes. (Figure 2)

The recovery level for the analysis was established by analyzing forty samples of known water concentration. Ten samples were each prepared with 5, 10, 20, and 30 mgs. of water. The average recovery for all forty samples was 101%. The 10-20 mg. range which is the level for moisture in T.P.M. exhibited a standard deviation of 3.4%. (Table 2)

*Comparison with Karl Fischer Analysis.* Table 3 shows a comparison of the gas chromatographic and Karl Fischer methods. Ten samples of four cigarettes each were smoked. Five samples were analyzed by the Karl Fischer method and the remainder by gas chromatography. The average of the two sets varied by 1.1% moisture. This variation points out a second advantage of the gas chromatographic method over the Karl Fischer. The gas chromatographic method separates the mois-

**Table 1.—Recovery of 10 mg. of water vs. time**

Sample	TIME OF STORAGE, HRS.		
	2	26	50
A	10.0 mg.	10.0 mg.	9.8 mg.
B	9.4	9.8	10.0
C	9.8	9.8	9.8
D	10.4	10.4	10.4
E	10.0	10.0	10.0

**Table 2.—Study of percent water recovery**

mg. H <sub>2</sub> O added to pad	5 mg.	10 mg.	20 mg.	30 mg.
	104%	100%	103%	101%
	100	94	103	100
% RECOVERY	94	98	105	101
	106	104	105	93
ON TEN	114	100	95	97
	106	106	100	100
REPLICATE	94	100	97	100
	114	98	97	99
	104	100	100	99
	106	97	102	104
avg.	104%	100%	101%	99%
S. D.	6.9	3.4	3.4	2.9

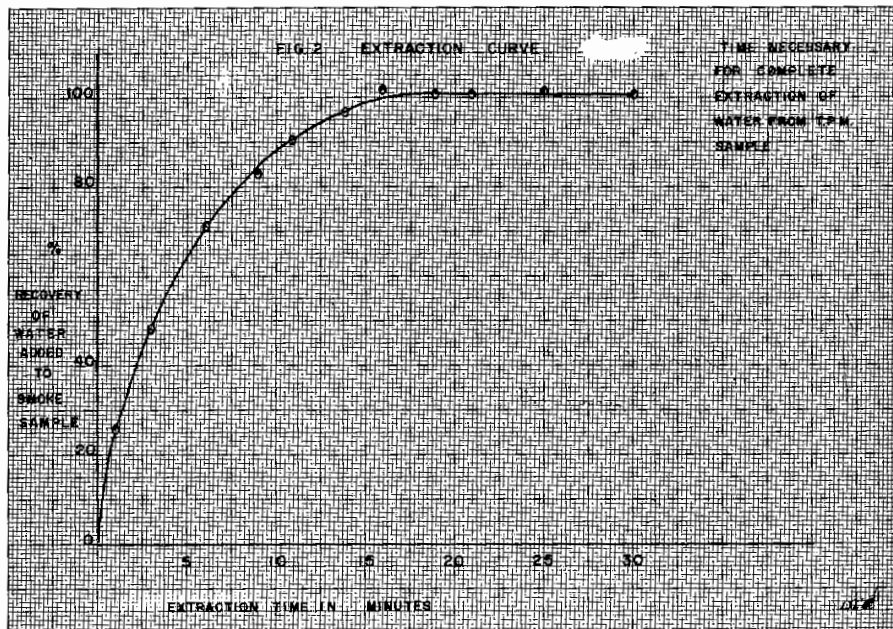


Figure 2. Extraction curve.

ture from all interfering substances and specifically measures the moisture. Results obtained by the gas chromatographic method are therefore more accurate than those obtained by the Karl Fischer method. The Karl Fischer method requires

immediate analysis of the sample and also requires that the entire sample be used for the moisture determination. The gas chromatographic method does not require immediate analysis of the sample. Furthermore, only a fraction of the

total sample is used per analysis; additional moisture determinations can be made on the sample when the gas chromatographic method is used. (Table 4)

*Comparison with Near-Infrared Analysis.* Table 5 shows a comparison of the gas chromatographic and near-infrared methods. Ten (10) samples of a different cigarette were smoked. Five (5) of the T.P.M. pads were submitted to gas chromatographic examination and the remaining five T.P.M. pads were analyzed by near-infrared. The samples examined by the near-infrared method required a considerable amount of time per sample for analysis. Since water is absorbed from the air if the samples are not analyzed immediately, only a few determinations can be made at one time. This limits the near-infrared as a routine method for a large number of samples. In contrast, the methods of handling and storing the samples for gas chromatographic analysis prevent delay in analysis from affecting the concentration of the samples. This is the reason a large number of samples can be submitted for analysis simultaneously. This gives the gas chromatographic method a tremendous advantage over the near-infrared method.

#### Summary

A technique which offers an easy and rapid method for moisture analysis of T.P.M. has been developed. The necessity for immediate analysis after smoking has been eliminated. The method also allows several moisture determinations on a single sample. Through the use of the gas chromatographic method, a large number of samples can be analyzed for moisture with a high degree of precision in a relatively short period of time.

**Table 3.—Comparison of gas chromatography and Karl Fischer methods**

GAS CHROMATOGRAPHY			KARL FISHER		
mg. H <sub>2</sub> O	mg. t.p.m.	% H <sub>2</sub> O	mg. H <sub>2</sub> O	mg. t.p.m.	% H <sub>2</sub> O
3.2	27.9	11.5	3.9	31.9	12.2
3.1	27.1	11.4	3.0	26.0	11.5
3.5	27.9	12.5	4.0	28.5	14.0
3.4	27.4	12.4	4.0	28.1	13.2
3.0	26.5	11.3	3.5	27.3	12.8
		avg. 11.8			avg. 12.7
		S.D. .57			S.D. 1.06

**Table 4.—Ten replicates of one sample**

mg. H <sub>2</sub> O	MG. T.P.M.	% H <sub>2</sub> O IN T.P.M.
2.6	27.6	9.42
2.6		9.42
2.5		9.06
2.6		9.42
2.7		9.78
2.6		9.42
2.6		9.42
2.7		9.78
2.7		9.78
2.5		9.06
		avg. 9.46
		S.D. .27

% H<sub>2</sub>O based on sample T.P.M. weight of 27.6 MG.

**Table 5.—Comparison of gas chromatography and near infrared methods**

GAS CHROMATOGRAPHY			NEAR-INFRARED		
mg. H <sub>2</sub> O	mg. t.p.m.	% H <sub>2</sub> O	mg. H <sub>2</sub> O	mg. t.p.m.	% H <sub>2</sub> O
2.4	27.2	8.7	3.48	30.8	11.3
2.6	25.9	9.9	2.70	26.7	10.1
2.8	26.3	10.6	2.57	26.8	9.6
2.5	25.8	9.6	2.25	25.6	8.8
2.3	26.3	8.8	3.00	26.3	11.4
		avg. 9.5			avg. 10.2
		S.D. .79			S.D. 1.1

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