

ONTARIO RESEARCH FOUNDATION

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Department of Chemistry

Report SI-596-58-153

July 21, 1958

Arsenic in Tobacco

Imperial Tobacco Company of Canada Limited,  
P.O. Box 6500  
Montreal 30, Quebec.

Attention: Mr. L. G. Laporte  
Director of Research  
and Development.

Introduction:

It was requested that a project be undertaken to determine the arsenic contents of the tobaccos from each of fifteen brands of cigarettes. The amount of sampling and testing required to associate definitely a given arsenic content with a given brand, even over a short period of time, would have been prohibitive. It was, therefore, decided to purchase a few packages of each brand from various locations (5) throughout Ontario and from Montreal, Quebec. It was decided to take a single cigarette from each package, for a given brand, and combine these for analysis as a single sample. Two such samples would be collected and analysed for each brand. It was realised that it would be impossible, on the basis of these results, to make direct statistical inferences about the arsenic contents of all of the tobaccos used in the manufacture of each of the brands. It was hoped, however, that this work would give a good general idea of the magnitude of the arsenic contents that might be expected. The fifteen brands have been designated A to O inclusive and may be identified by the attached code. One package of each brand was purchased from each of the following locations: Hamilton, Simcoe, London, Toronto, Ajax, (Ontario); and Montreal, Quebec.

Summary of Results:

None of the samples of tobacco analysed contained as much as 2 parts per million of arsenic, expressed as arsenic trioxide. Most samples appeared to have in the order of 1 part per million.

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Conclusions:

The arsenic content of the tobacco samples analysed has probably arisen from natural sources, since it is known that soils generally contain minute amounts of arsenic.<sup>2</sup> It is quite unlikely that the quantities of arsenic determined in the samples are the result of direct application of arsenical sprays as the arsenic content of tobacco leaves which have been sprayed with arsenic compounds would, undoubtedly, be much higher than the values obtained.

Discussion:

The method followed was the Official Method of Analysis, of the Association of Official Agricultural Chemists, for arsenic in tobacco, Section 24, Eighth Edition. The method involves the wet oxidation of the tobacco by digestion with concentrated nitric and sulphuric acids followed by evolution and detection of the arsenic present by the Gutzeit method. A special step was taken to remove interfering pyridine and nicotine compounds that are not always destroyed in the oxidation. It is recommended in this method that enough sample be taken to contain in the order of 0.05 to 0.15 mgm. of arsenic trioxide. This would have required a 50 to 100 gm. sample of tobacco. It was found by experience, however, that it was impossible to digest samples of such size in a reasonable length of time. It was, therefore, decided to use samples in the order of 5 to 6 gms. and operate below the recommended range suggested in the method. It has been pointed out that the Gutzeit method of arsenic determination has an inherent error of 5 to 10%<sup>3</sup>. Since we were operating outside the recommended range, it was felt that our coefficient of variation would be even larger. It was, therefore, decided that there should be two Gutzeit determinations on each digested sample of tobacco in order to minimize the random variations introduced into the results because of the Gutzeit step of the analysis.

In addition, the Hanford-Pratt Company, manufacturers of the special paper used in the test, point out that there is a certain amount of group uniformity to be expected in the results. Sensitized strips from the same sheet, sensitized at the same time and used at the same time, show better agreement than those from different sheets, sensitized at different times and used at different times.

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■ Firman E. Bear, Chemistry of the Soil, Reinhold Publishing Corp., 1955.  
 ■■ Cassil C.C., J. Assoc. Official Agr. Chem., 21, 199-200 (1938). It is assumed that by "inherent error", it is meant coefficient of variation.

In order, then, to increase the precision of our estimates it was decided to run the Gutzeit arsenic detection step in randomized complete blocks with sensitized strips from the same sensitized sheet used for each block.

Results:

The results have been tabulated in Table I found at the end of this report. The Analysis of Variance follows below.

<u>Analysis of Variance</u>			
<u>Source of Variation</u>	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
<u>Brands</u>			
Controls vs. Commercial	653.40	1	653.40 <sup>■</sup>
Commercial	177.33	14	12.67
Controls	555.17	2	277.59 <sup>■</sup>
<u>Runs</u>			
"Groups" X Brands	147.91	17	8.71 <sup>■■</sup>
"Runs within groups" X Brands	142.02	34	4.18
Total	1720.65	71	

■ Judged to be highly significant.

■■ "Groups" X Brands represents the error with which to assess the significance of the difference between brands. The difference between the commercial brands is not significant while the difference between the controls and commercial brand is. It is valid, therefore, to use the least significant difference only in comparing the commercial brands with the controls.

(5%) L.S.D. =  $t \cdot s^2 \left( \frac{1}{i} + \frac{1}{j} \right) = 2.11 \frac{8.71}{2} = 4.4$

(1%) L.S.D. =  $2.90 \frac{8.71}{2} = 6.1$

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By applying the least significant differences to the mean values given in Table I, it may be seen that the difference between control 2 and all the brands is significant even at the 1% level. There are no significant differences between the brands and control 1. Control 1 contained the equivalent of 0.0050 mgm. of arsenic trioxide on a digested sample. Since most samples contained 5 to 6 grams of tobacco, this would correspond to the equivalent of about 1 part per million arsenic trioxide. Control 2 contained the equivalent of 2 ppm arsenic trioxide. We are, therefore, able to conclude that in none of the brands was there as much as 2 ppm arsenic trioxide detected.

There was some suggestion that the step designed to remove unoxidized pyridine and nicotine might not prove completely effective. Some of the solution from a commercial brand was, therefore, added to one of the controls. It was found that the theoretical value calculated for the result was not significantly different from the result itself. These figures are as follows:

Calculated -

Control 2 +  $\frac{1}{2}$  brand A = 21.8 ma.

Measured -

Control = 24.3 ma.

The figures represent the means of four determinations. It was felt on the basis of the above results that there was no basis for assuming that the step taken to remove the unoxidized pyridine and nicotine was not completely effective.

#### Experimental Procedure:

The method of analysis followed was the official method of the A.O.A.C. for arsenic in tobacco. It involved the wet oxidation of the tobacco from six cigarettes, one from each package, with concentrated nitric and sulphuric acids. The digestions usually took four to seven hours for completion and required frequent additions of concentrated nitric acid as that reagent was consumed. The arsenate was then precipitated as the magnesium ammonium arsenate salt, filtered, washed and redissolved in dilute hydrochloric acid and diluted to 100 ml. in volumetric flasks. The same amount of acid was used for the dissolution in each case. Twenty ml. aliquots of the resultant solutions were placed in the Gutzeit generators along with 4 grams of granulated zinc and 5 c.c. of concentrated hydrochloric acid, as well as the usual reagents. All evolutions

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were carried out in a constant temperature bath kept at a temperature of  $24 \pm 1^{\circ}\text{C}$ .

A Fisher-Payne dip coater with a linear withdrawal rate of about one foot in three minutes was used to withdraw the sensitized paper from the mercuric bromide solutions. The papers for all of the work were sensitized in freshly made 5% alcoholic mercuric bromide solution 24 hours prior to the run in which they were used.

The scrubbing towers on the generators were filled with specially treated 20 - 30 mesh sand to remove hydrogen sulphide gas evolved. It was found that the sand, when treated with the lead acetate solution, had to be almost thoroughly dried; otherwise the excess moisture clogged the scrubber and was driven out the sensitized paper tube by the gas pressure.

All controls and blanks were subjected to the full digestion and precipitation steps as well as to the arsine evolution step.

Sgt: W.N.B. Armstrong  
for W.A. Petrie

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**TABLE I**  
**Results**

Brand	Group 1			Average Total Length of Stain in mm. Runs 1&2 Group 1	Group 2			Average Total Length of Stain in mm. Runs 1 & 2 Group 2	Average Total Length of Stains in mm. 2 Runs for each of 2 Groups.
	Weight of Tobacco in Grams	Total <sup>m</sup> Length of Stain in mm. Run 1 Group 1	Total <sup>m</sup> Length of Stain in mm. Run 2 Group 1		Weight of Tobacco in Grams	Total <sup>m</sup> Length of Stain in mm. Run 1 Group 2	Total <sup>m</sup> Length of Stain in mm. Run 2 Group 2		
A	6.15	8	7	7.5	6.19	6	9	7.5	7.5
B	5.04	8	7	7.5	5.00	5	7	6	6.8
C	5.77	9	11	10	5.56	8	10	9	9.5
D	6.28	7	13	10	6.41	9	7	8	9
E	6.14	5	5	5	6.25	6	8	7	6
F	6.31	12	6	9	6.20	9	9	9	9
G	5.32	2	7	4.5	5.11	7	9	8	6.3
H	5.20	14	13	13.5	5.15	7	9	8	10.8
I	5.90	10	11	10.5	5.83	9	9	9	9.8
J	5.75	18	14	16	5.51	7	5	6	11
K	5.16	10	10	10	4.90	8	7	7.5	8.8
L	6.39	12	8	10	6.17	9	8	8.5	9.3
M	5.26	7	5	6	5.28	5	7	6	6
N	5.82	15	8	12.5	5.72	9	13	10.5	11.5
O	6.06	6	8	7	5.96	7	11	9	8
Blank		0	0	0		0	0	0	0
Control 1		9	7	8		7	8	7.5	7.8
Control 2		21	15	18		18	18	18	18
Control 3		27	23	25		24	23	23.5	24.3

<sup>m</sup> Total Length of stain in mm. for both sides of paper, using 20 c.c. aliquot from 100 c.c. solution.

Control 1 contained 0.0010 mgm. arsenic trioxide in aliquot.

Control 2 contained 0.0020 mgm. arsenic trioxide in aliquot.

Control 3 contained 0.0020 mgm. arsenic trioxide in aliquot + 10 c.c. aliquot of Brand A solution.

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CODE

<u>Code Letter</u>	<u>Brand Name</u>
A	Sportsman
B	Matinee, Filter Tip
C	Rothmans, King Size, 4 pkgs. Filter Tip 2 pkgs. Plain
D	British Consols
E	Players
F	Export
G	Skyways, Long Size Filter Tip
H	Belvedere, Filter Tip
I	Winchester
J	Gaylon, King Size, Filter Tip
K	du Maurier, Filter Tip
L	Sweet Caporals
M	Mayfair, King Size, Filter Tip
N	Buckingham
O	Black Cat

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