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THE ASCORBIC ACID CONTENT OF APPLE VARIETIES AND PRODUCTS
AVAILABLE TO THE WESTERN MONTANA CONSUMER
DURING THE WINTER MONTHS

by

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B.S. Montana State University, 1958

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for the degree of

Master of Science

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1959

Approved by:


Chairman, Board of Examiners


Dean, Graduate School

Date

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INTRODUCTION

Numerous determinations of the ascorbic acid content of apples have been made. Very few, however, have dealt with the ascorbic acid content of apples as the consumer might purchase them during the winter months. Jessie E. Richardson and Helen L. Mayfield of the Montana Agricultural Experimental Station determined the ascorbic acid content of raw and cooked apples in the winter but they dealt only with Winesap apples. (1) Other investigators have found the effect of storage at various temperatures upon the ascorbic acid content of apples and this information can give an approximation of the ascorbic acid content of winter apples by ascertaining the length of time they have been stored and the temperature at which they were stored. (2) (3) (4) The present study is designed to determine the ascorbic acid content of apples in the forms in which the Western Montana consumer might purchase and utilize them. These forms include raw apples, sauce prepared from the raw apples, evaporated apples and commercially canned apples.

Apples are generally considered a poor source of ascorbic acid. Studies have shown a wide variation in the ascorbic acid content of various apple varieties. (3) A few varieties have a very high content but these are the exception rather than the rule. The Sturmer apple has been found to contain approximately 35 mg. of ascorbic acid per 100 grams and a variety has been reported from Geneva, New York which

is nearly as rich as the orange in ascorbic acid. (5) The average apple, however, is considered, by the United States Department of Agriculture, to contain 5 mg. ascorbic acid per 100 grams. (6) The ascorbic acid content of apples is highest when the fruit is freshly picked. (4) (7) The loss thereafter is very rapid the first two weeks and the most loss occurs during the first two months of storage. Loss after that time is extremely slow. The ascorbic acid loss in apples occurs mainly from the skin of the apple by oxidation. (4)

Storage temperature has been found to affect ascorbic acid loss in apples. Cold storage, 32°F., preserves the ascorbic acid most effectively while common storage, 45°F., permits more rapid loss of the vitamin from the apples. (2) (3) (7) Batchelder reports that Washington Delicious apples held in storage at 32°F. for 6 months lost no ascorbic acid while apples stored at 45°F. lost one-sixth of their ascorbic acid content the first 3 months and up to one-fourth during storage for 6 months. (2)

The loss of ascorbic acid in apples during cooking is very great. Curran, Tressler and King report a loss of 25% in unstrained apple sauce made from peeled Northern Spy apples and a loss of 32% in strained apple sauce made from peeled apples. Losses up to 88% were reported during the baking of apples. They found, in the course of their studies, that the greatest loss occurred during the first 4 minutes of

cooking and that some additional loss occurred if the apple product was stored where air could reach it. (8) Studies on other apple varieties have shown from considerable to complete loss of ascorbic acid during cooking. It is believed that the apple peel contains from one-fourth to one-half the ascorbic acid found in the whole apple. (3) (9) This would then account for the great loss in apple sauce since the apples are ordinarily peeled before cooking. Curran, Tressler and King found, though, that careful peel removal seemed to have very little effect on the ascorbic acid loss in cooked apples. (8)

Apples, therefore, already a poor source of ascorbic acid would, by winter, have suffered their greatest ascorbic acid loss since it might be assumed that they would have been stored at unknown temperatures for at least two months. They usually suffer further loss upon cooking so at best the ascorbic acid available from apples during the winter months is slight. This study deals with the apples available to the Western Montana consumer in the winter months. These include Delicious, Golden Delicious, McIntosh, Rome Beauty and Winesap in the raw state; evaporated apple sauce and apple slices; and commercially canned, sweetened sauce and pie slices.

PROCEDURE

The apple varieties and products available in Missoula markets during the winter months were determined by inquiry at the various markets. A representative sample of these was then obtained. The apple varieties included Delicious, Golden Delicious, McIntosh, Rome Beauty and Winesap. The McIntosh apples were grown locally in the Bitterroot Valley while the other varieties came from Washington. Apple products found on the market were evaporated apple sauce, evaporated apple rings, commercially canned apple sauce and commercially canned apple pie slices. The evaporated apple rings came from California apples and the evaporated apple sauce had been prepared from California Gravenstein apples. The commercially canned apple sauce came from apples grown between Spokane and Coeur D'Alene. This sauce was sweetened. The commercially canned apple pie slices were from "northern" apples. No variety was listed on the label. These slices were unsweetened. The comparative prices of the apple varieties and products can be seen on the chart on page 5.

The raw apple varieties, sauces made from these apples, the evaporated products and the canned products were analyzed to determine their ascorbic acid content.

A photometric method was chosen for the ascorbic acid analysis. Biological assay methods and titrimetric methods are also available but the photometric method was chosen for its simplicity and accuracy. Photometric methods are considered

COST OF APPLE VARIETIES AND PRODUCTS

<u>Variety or Product</u>	<u>Cost per pound</u>
Delicious apples	19¢
Golden Delicious apples	19¢
McIntosh apples	10¢
Rome Beauty apples	18¢
Winesap apples	18¢
Delicious apple sauce	22¢
Golden Delicious apple sauce	22¢
McIntosh apple sauce	12¢
Rome Beauty apple sauce	21¢
Winesap apple sauce	21¢
Evaporated apple rings	7¢
Evaporated apple sauce	8¢
Commercially canned apple pie slices	17¢
Commercially canned apple sauce	15¢

far less time consuming and far more precise than bioassays and they avoid certain of the limitations of the visual titration technics. Difficulties encountered in determining the end point of moderately turbid or colored acid extracts in visual titration can be overcome, at least partially, by the instrumentation of the photometric method. The time allowed for reaction of the ascorbic acid and the indicator reagent may also be controlled more closely in photometric methods, thus avoiding to some extent the influence of certain reducing agents other than ascorbic acid. (10)

A photometric method suggested by Morton Schmall, Charles W. Pifer and Ernest G. Wollish for the determination of ascorbic acid was first tried but this method was found unsatisfactory for the determination of ascorbic acid in the whole apple. (11) The photometric method utilized in this study is one perfected by H. J. Loeffler and J. D. Ponting. It is based on the 2, 6-dichlorophenolindophenol reagent, which is the most widely accepted reagent for ascorbic acid determinations either titrimetric or photometric. The Loeffler and Ponting procedure reads as follows:

"Blend 25-50 grams of fresh or frozen fruit or vegetable tissue with 350 ml. of 1% metaphosphoric acid in a blending machine operated for 5 minutes at high speed. If the material is of high ascorbic acid content, such as leafy vegetables, raspberries, strawberries, or asparagus, use the smaller quantity. 50 grams are used with foods containing less ascorbic acid such as stored potatoes, carrots, yams, peaches, plums and apricots. If a dehydrated fruit or vegetable is being analyzed, 5 or 10 grams of sample

are sufficient, depending upon this same classification. Some thoroughly dehydrated vegetables, such as sweet potatoes or carrots; may need 0.5 hour of soaking in the acid before blending. Frozen foods may be blended without preliminary thawing.

Filter the extract through coarse fluted filter paper. Extracts of starchy vegetables, such as potatoes and corn, filter better through a buchner funnel. They can also be cleared by centrifugation. Moderate turbidities do not interfere since the instrument is calibrated with proper blanks.

Pipet 1 ml. portions of the filtrate into 3 matched tubes from the Evelyn photoelectric colorimeter.

Add 9 ml. of distilled water to one tube and adjust the colorimeter to read 100 with this tube using filter no. 520.

To each of the other tubes add 9 ml. of the previously standardized indophenol dye solution from a pipet. Take a reading in the photoelectric colorimeter, using filter no. 520, 15 seconds after the start of the dye addition.

The dye is standardized by noting the 15 second reading with filter 520 (when the instrument is calibrated to 100 with distilled water) given by a tube containing 1 ml. of 1% metaphosphoric acid and 9 ml. of the dye solution.

The dye solution is prepared simply by dissolving enough of the dye in water so that a reading of about "30" is given with the Evelyn photoelectric colorimeter. The concentration of dye to give such a reading is roughly 13 mg. per liter. The reaction between ascorbic acid and stronger dye solution is not a linear relationship so that a calibration curve rather than a constant factor must be used with such solutions.

0.4% oxalic acid may be substituted for 1% metaphosphoric acid." (12)

An Evelyn photoelectric colorimeter was not available so a Coleman Universal Spectrophotometer was used. This substitution did not necessitate any changes in the procedure though it did involve a change in the dye standardization and the final calculation procedure. The dye was

standardized on the Coleman spectrophotometer by taking three readings. Three standard samples were prepared, one containing 2 ml. 0.4% oxalic acid and 9 ml. dye; one containing 0.6 ml. of a standard ascorbic acid solution, concentration 0.05 mg./ml., 1.4 ml. 0.4% oxalic acid and 9 ml. dye; and one containing 1 ml. of the standard ascorbic acid solution, 1 ml. 0.4% oxalic acid and 9 ml. dye. These three tubes were each placed in turn in the spectrophotometer and a reading taken with the spectrophotometer set at 100 with distilled water. These three readings were plotted on a graph of concentration of ascorbic acid against percent transmittance, forming a linear relationship, and this graph was used to calculate the ascorbic acid content of the samples by comparing the readings obtained. The dye standardization was checked before each set of determinations since the indophenol dye tends to gradually weaken even when kept under refrigeration as Loeffler and Ponting recommend. (12)

Due to the very low ascorbic acid content of apples the procedure was modified by using 2 ml. of filtrate rather than 1 ml. as recommended by Loeffler and Ponting. Oxalic acid was used in place of metaphosphoric acid.

A radial sample, 50 grams in weight for the Delicious, Golden Delicious, Rome Beauty and Winesap apples and 75 grams in weight for the McIntosh, was placed in the Waring blender and allowed to blend at high speed for 5 minutes. This

mixture was then filtered through a fluted filter paper into a 500 ml. beaker. 2 ml. portions of the filtrate were pipetted into 3 matched tubes from the spectrophotometer and 9 ml. of distilled water added to one tube. The Coleman Spectrophotometer was adjusted to read 100 with this tube and readings taken of each of the other tubes 15 seconds after the addition of 9 ml. of the indophenol dye solution. These readings were compared to the standardization graph of the indophenol dye and calculated. Loeffler and Ponting show that with fruits the volume of the solids can be neglected, since the distribution of ascorbic acid is in the liquid phase present, water plus soluble solids, rather than in the water alone. The fruits do not possess sufficient insoluble solids to alter the results materially. The formula for calculating the ascorbic acid content from the spectrophotometer readings therefore is:

$$\frac{\text{Reading in mg. asc. acid } X (350 \div \text{smpl. wgt.})}{2 \times \text{smpl. wgt.}} \times 100 \quad \text{---}$$

mg. ascorbic acid/100 grams apple

Two samples were treated in this way from each apple variety. Thus a total of four readings was obtained for each variety.

This same procedure was followed in the determination of the ascorbic acid content of the other apple products although varying sample weights were employed according to

the ascorbic acid content of the product. 100 gram samples of the commercially canned apple sauce and the commercially canned apple pie slices were used, taken from the freshly opened can. The evaporated products were first prepared according to directions on the package and then tested. If it was necessary to keep a prepared product for a few hours or a day the product was sealed, while still hot, in a glass jar and kept under refrigeration. 100 gram samples of the prepared apple sauce and 200 gram samples of the prepared apple rings were used.

Sauce was made from each of the raw apple varieties according to the following proportions: 500 grams apple to 250 ml. water. The sauce was cooked, covered, until the apples were tender or about 15 minutes. It was left unsweetened. As in the case of the evaporated products, if the sauce was to be kept for any period of time it was sealed and refrigerated. 100, 200 and 300 gram samples of the sauce were taken, giving a total of 6 readings for the sauces instead of the usual 4.

RESULTS AND DISCUSSION

The ascorbic acid content of the raw apples varied from 6.8 mg./100 grams apple for the Rome Beauty to 2.0 mg./100 grams apple for the McIntosh. Delicious, Golden Delicious and Winesap varieties contained 4.8 mg./100 grams apple, 6.3 mg./100 grams apple and 4.4 mg./100 grams apple respectively.

The prepared evaporated apples also varied. The evaporated apple sauce contained 2.1 mg./100 grams and the prepared evaporated apple rings contained 0.8 mg./100 grams.

In the commercially canned products the apple sauce was found to contain 2.1 mg. ascorbic acid/100 grams and the apple pie slices 4.2 mg./100 grams.

The sauce prepared from raw apples contained no ascorbic acid in any variety. 100, 200 and 300 gram samples were tested and the readings each time coincided with the 0 point on the standardization graph. In two cases one reading fell slightly above the 0 point but this was attributed to the extremely high sample weight utilized. The average of the readings, in both cases, fell at the 0 point.

The raw apples supplied the most ascorbic acid. Even the Rome Beauty, however, would supply, in a 100 gram portion, only about 1/11 of the daily requirement for ascorbic acid and this apple variety is most commonly used in cooking. The most popular eating apple, the Delicious, would supply about

ASCORBIC ACID CONTENT OF APPLE VARIETIES AND PRODUCTS

<u>Variety or Product</u>	<u>Content per 100 grams</u>
Delicious apples	4.8 mg.
Golden Delicious apples	6.3 mg.
McIntosh apples	2.0 mg.
Rome Beauty apples	6.8 mg.
Winesap apples	4.4 mg.
Delicious apple sauce	0.0 mg.
Golden Delicious apple sauce	0.0 mg.
McIntosh apple sauce	0.0 mg.
Rome Beauty apple sauce	0.0 mg.
Winesap apple sauce	0.0 mg.
Evaporated apple rings	0.8 mg.
Evaporated apple sauce	2.1 mg.
Commercially canned apple pie slices	4.2 mg.
Commercially canned apple sauce	2.1 mg.

1/16 the daily requirement, if eaten in 100 gram portions, the approximate size of a small apple. When the apples were cooked they lost all ascorbic acid so even the Rome Beauty would supply no ascorbic acid after cooking. In other determinations of the ascorbic acid content of the apple varieties used in this study, the content reported for any one variety varied widely from study to study. A variation of as much as 4 mg. was not uncommon. No comparisons are therefore made of the content found with that reported in other studies.

The evaporated and the commercially canned apple sauce were both superior to the sauce made from raw apples as far as ascorbic acid content was concerned. Each contained 2.1 mg./100 grams. One might thus suggest that the evaporated or commercially canned sauce would be superior to the sauce made from raw apples in the winter months in Western Montana.

The commercially canned apple pie slices were quite high, comparatively, in their ascorbic acid content but since these slices would be baked in pies one might wonder whether some or all of the ascorbic acid would be lost during the baking process. The 88% loss in the baking of apples, reported by Curran, Tressler and King would indicate that the commercially canned apple pie slices would not retain their 4.2 mg. ascorbic acid/100 grams content throughout baking. (8)

The evaporated apple rings showed a very low ascorbic

acid content as contrasted to the higher content of the evaporated apple sauce. This might be explained by the difference in their preparation. The apple sauce was prepared, according to directions on the package, using only a minimum of water while the apple rings were prepared, also according to the directions on the package, in a large quantity of water and then drained. A considerable amount of their original ascorbic acid content was probably lost in the water.

SUMMARY

The ascorbic acid content of apple varieties and products available to the Western Montana consumer during the winter months was determined. Rome Beauty apples were found to contain the most ascorbic acid, 6.8 mg./100 grams, in the raw state. They were followed, in order of ascorbic acid content, by Golden Delicious, Delicious, Winesap and McIntosh. Sauce prepared from these varieties was found to contain no ascorbic acid. Evaporated apple sauce contained 2.1 mg. ascorbic acid/100 grams as did commercially canned apple sauce. Evaporated apple rings contained only 0.8 mg./100 grams, probably because of the method employed in their preparation. Commercially canned apple pie slices had a high ascorbic acid content but this might be assumed to be lost during the baking process after they were placed in a pie.

The best ascorbic acid sources to be found in apples during the winter months in Western Montana seem to be the raw Rome Beauty and Golden Delicious apples. The best prepared sources are the evaporated apple sauces and the commercially canned apple sauces. As well as containing more ascorbic acid the cost of the evaporated and commercially canned sauces is below that of the sauce prepared from raw apples at the prevailing winter price rates in Montana.

A P P E N D I X

PROCEDURE FOLLOWED IN PREPARING EVAPORATED APPLE RINGS

The evaporated apple rings were prepared according to directions on the package which read as follows:

"Add 8 oz. of apple rings to three quarts of boiling water. Let cook, covered, for 15 minutes on medium to high flame. Drain."

PROCEDURE FOLLOWED IN PREPARING EVAPORATED APPLE SAUCE

The evaporated apple sauce was prepared according to directions on the package which read as follows:

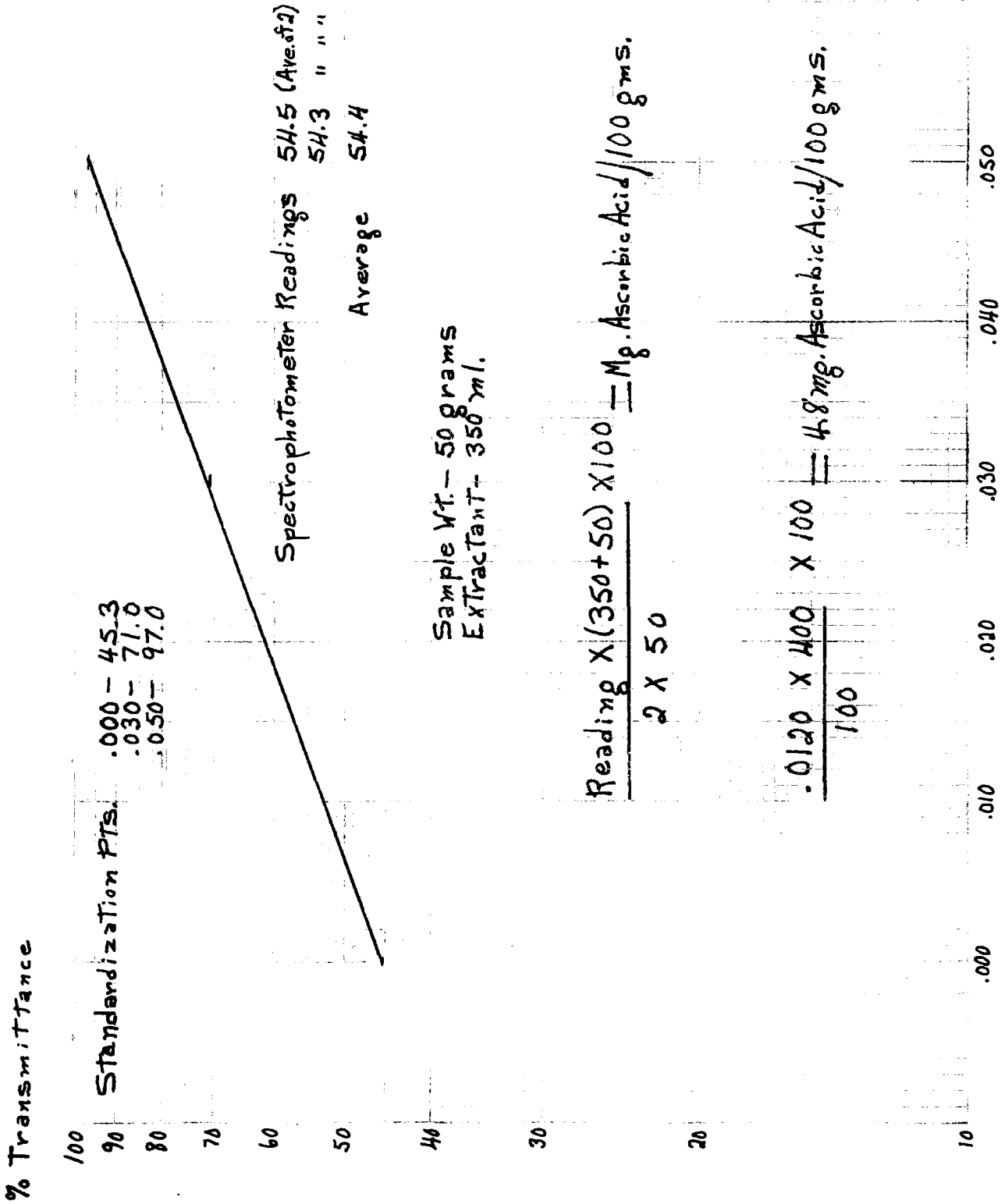
"Add contents of package (6 ozs.) to 4½ cups of boiling water, cover, cook at medium heat for 3 minutes."

PROCEDURE FOLLOWED IN PREPARING SAUCE FROM RAW APPLES

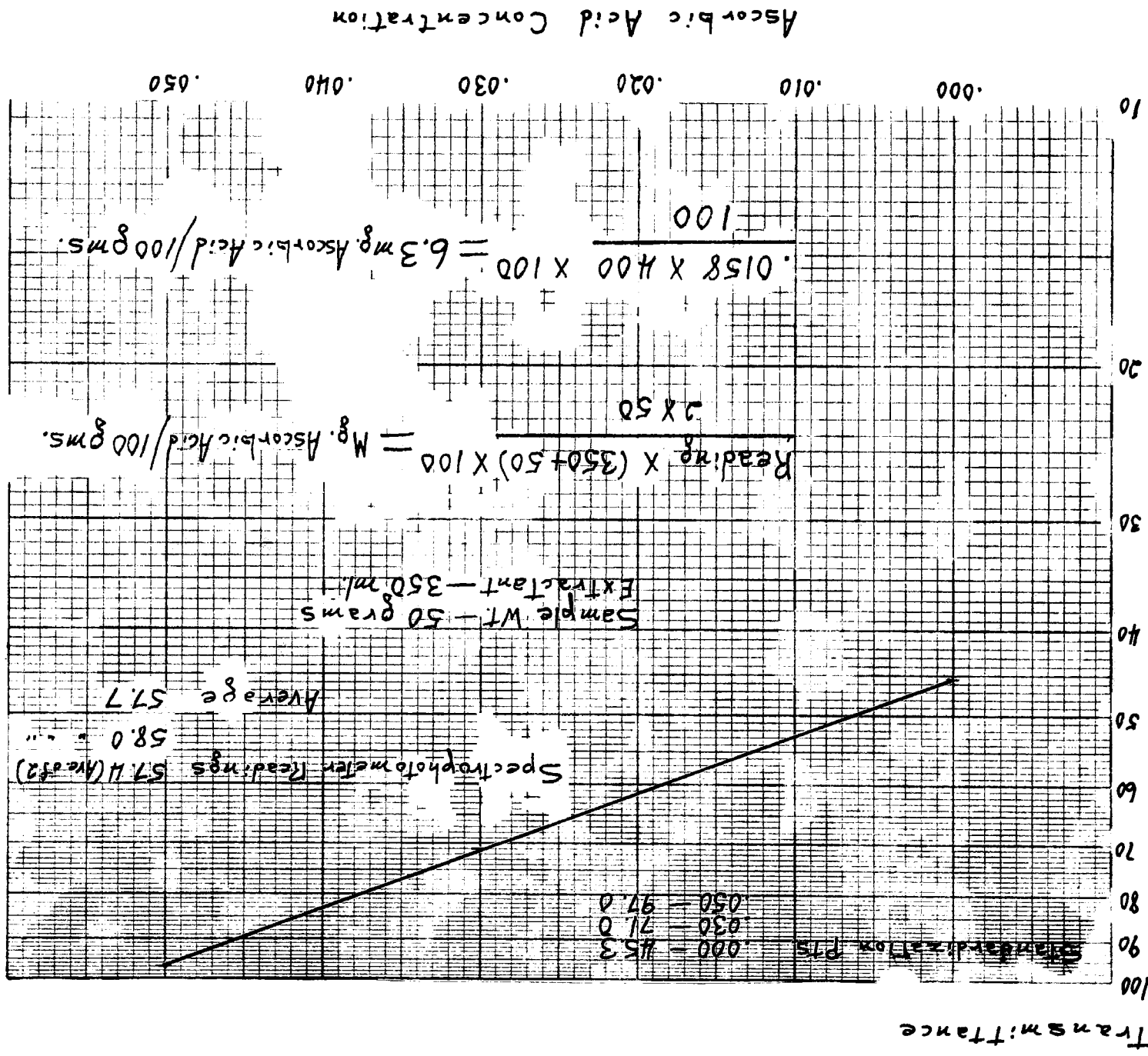
Add 500 grams raw apple, pared and sliced, to 250 ml. boiling water. Cover. Let cook for 15 minutes or until tender.

The following pages, 18 through 31, represent the standardization graphs utilized in the calculation of the ascorbic acid content of the apple varieties and products. The calculation procedure for each variety and product is included.

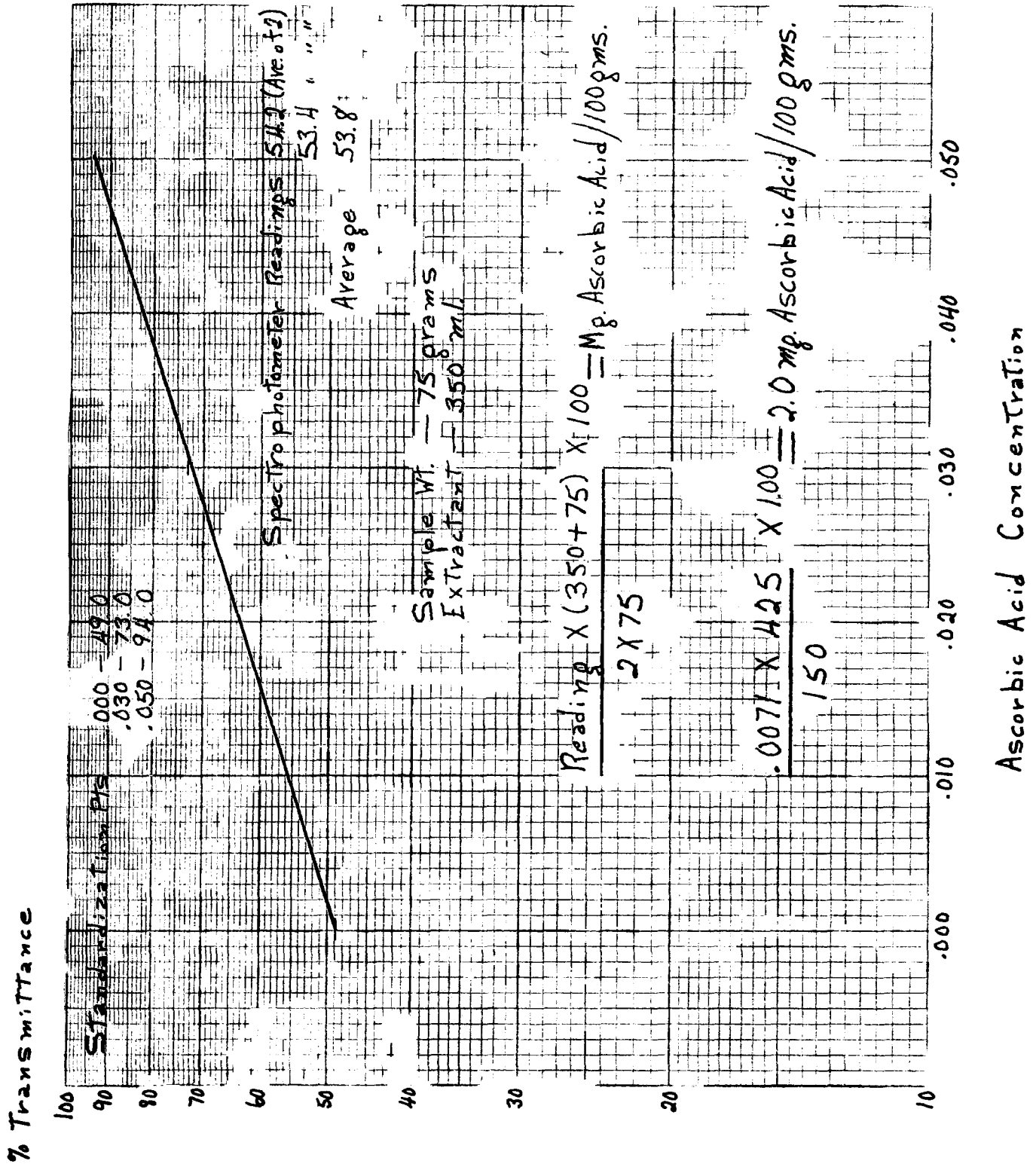
Delicious Apples



Golden Delicious Apples

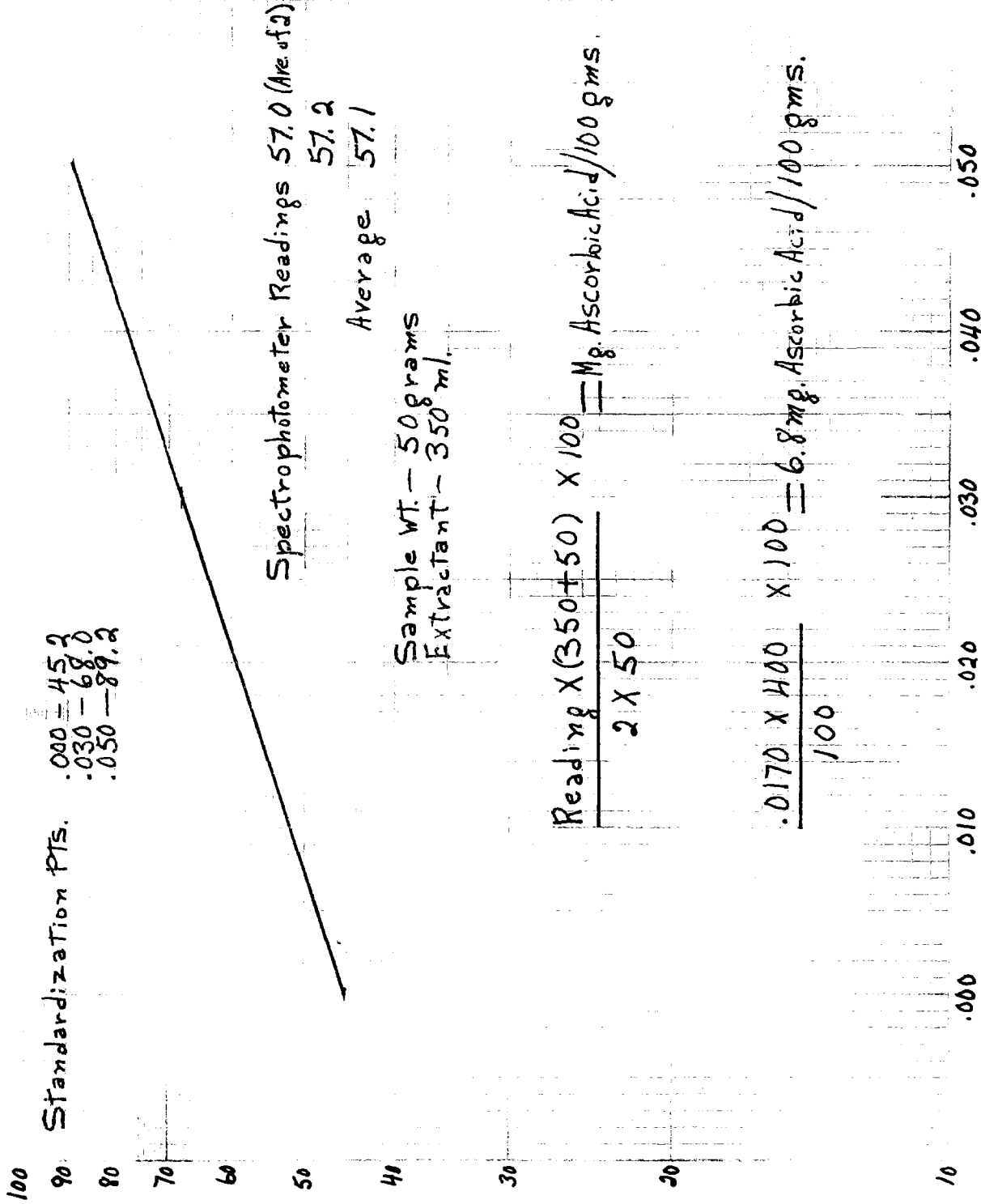


McIntosh Apples



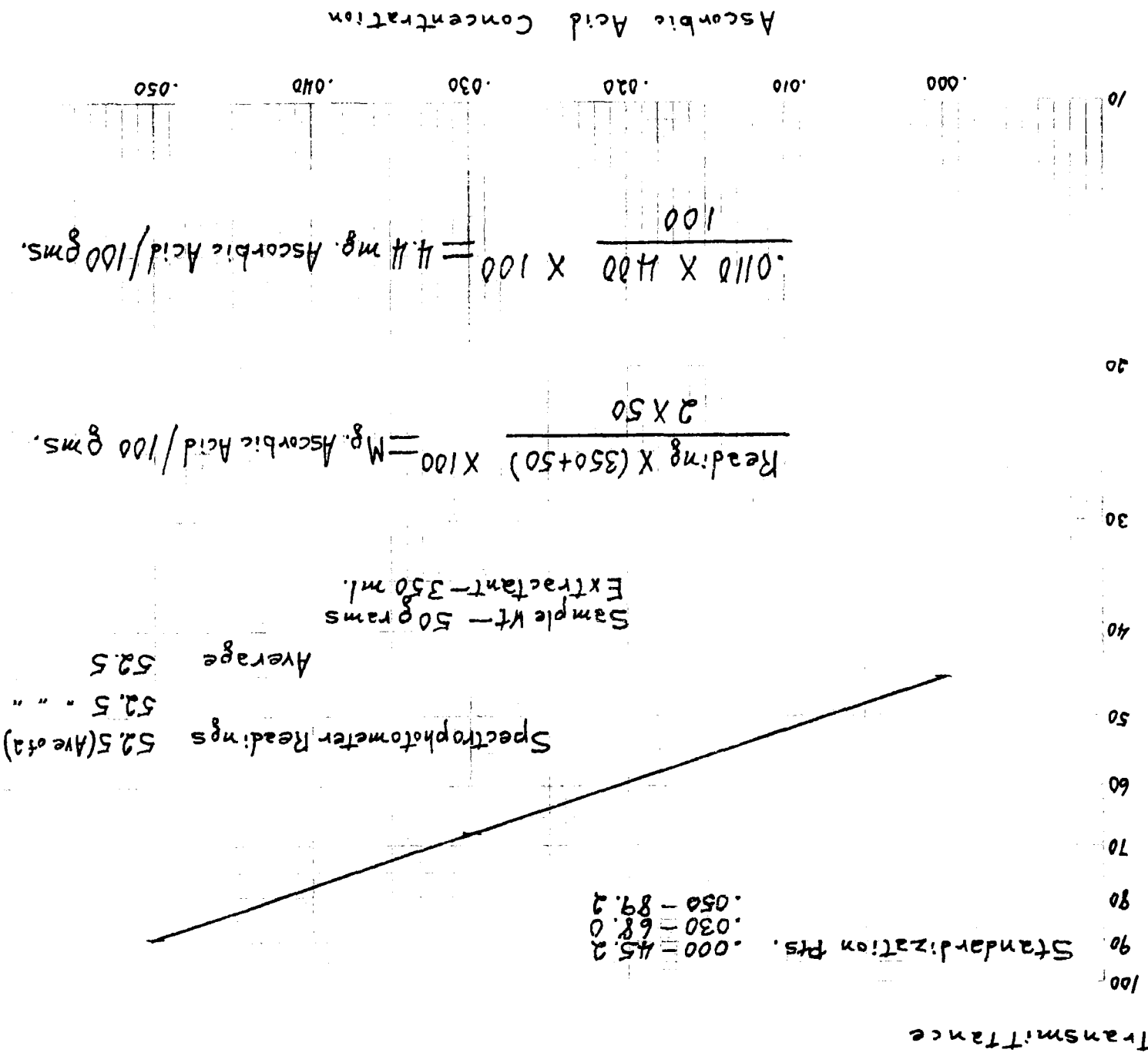
Rome Beauty Apples

% Transmittance

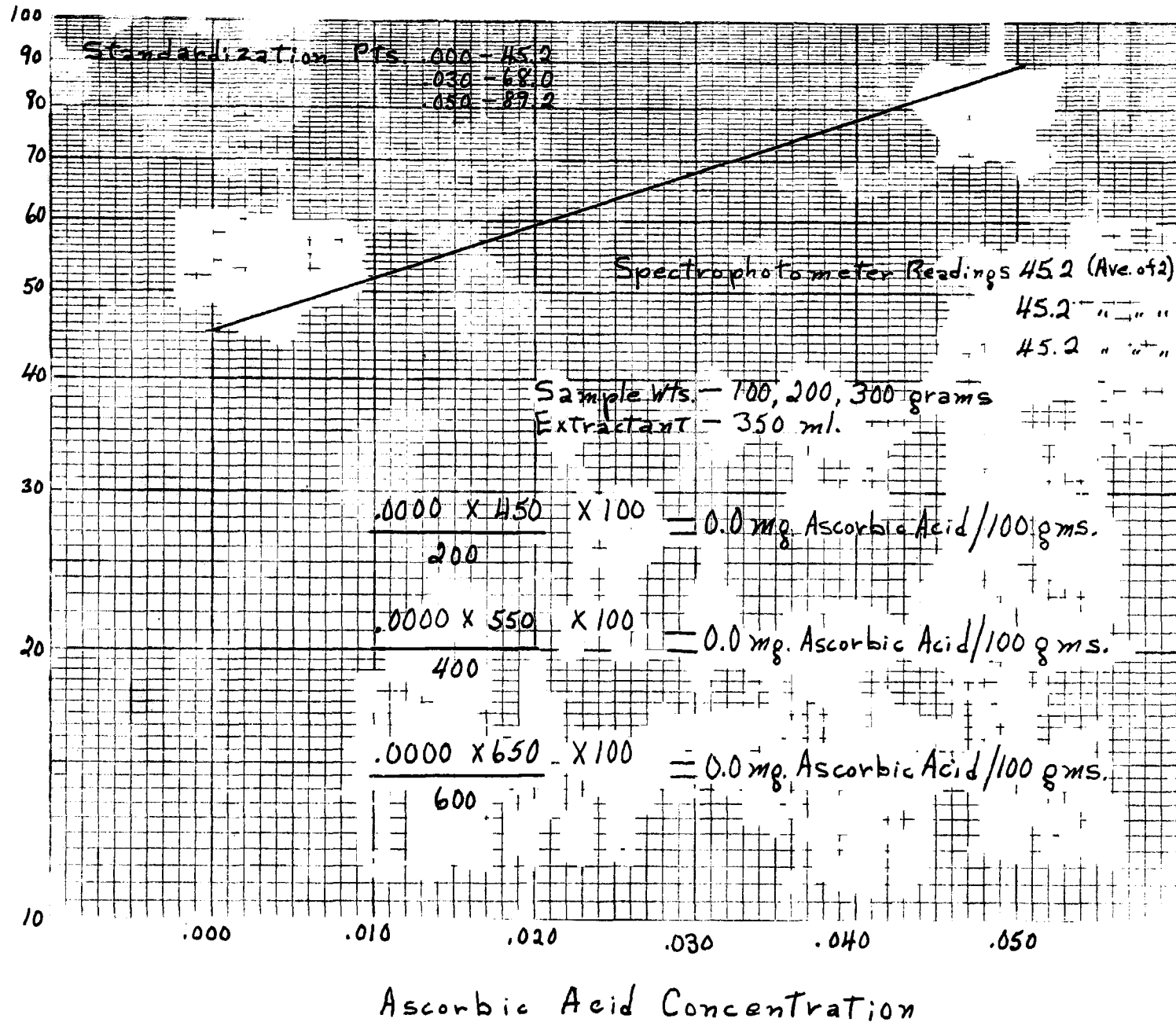


Ascorbic Acid Concentration

Winesap Apples



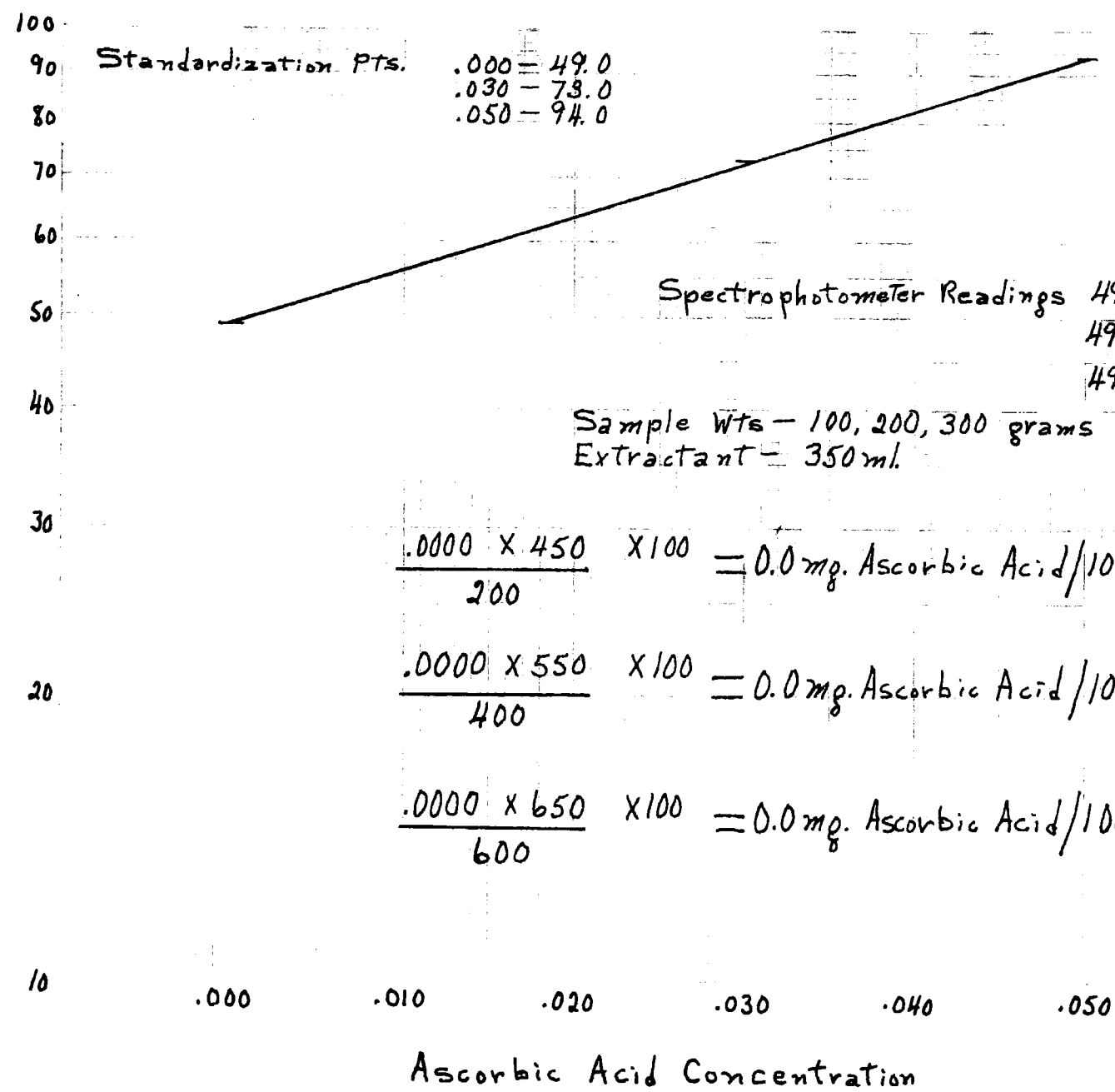
% Transmittance



Delicious Apple Sauce

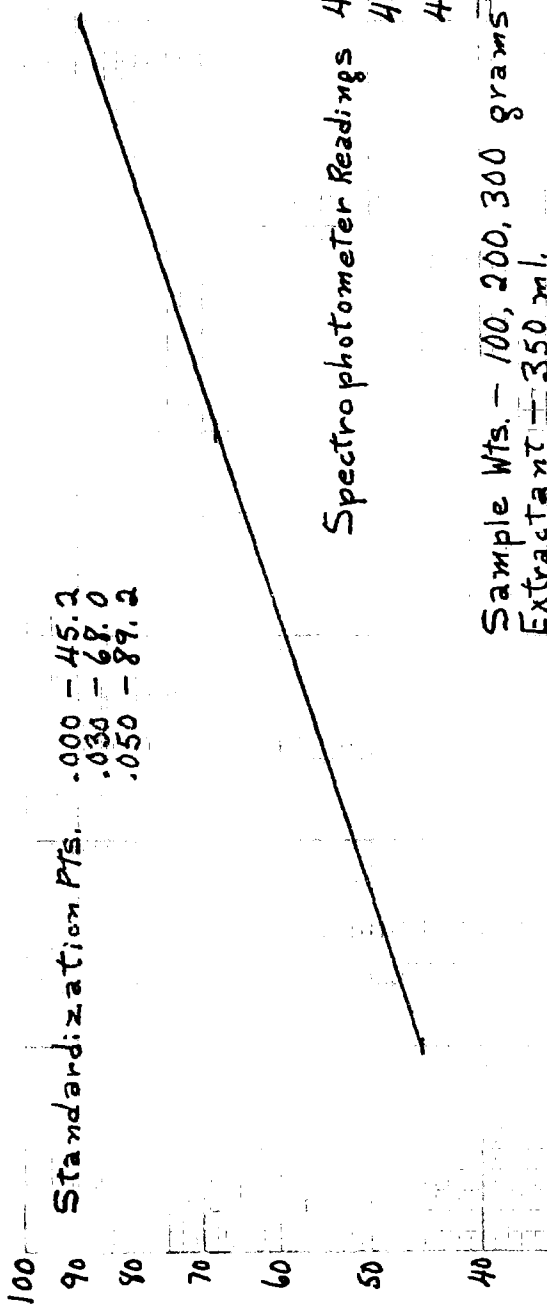
Golden Delicious Apple Sauce

% Transmittance



McIntosh Apple Sauce

% Transmittance



Standardization Pts. .000 - 45.2
 .030 - 68.0
 .050 - 89.2

Spectrophotometer Readings 45.2 (Ave. of 2)
 45.2 " " "
 45.2 " " "

Sample Wts. - 100, 200, 300 grams
 Extractant - 350 ml.

$$\frac{.0000 \times 450}{200} \times 100 = 0.0 \text{ mg. Ascorbic Acid/100 gms.}$$

$$\frac{.0000 \times 550}{400} \times 100 = 0.0 \text{ mg. Ascorbic Acid/100 gms.}$$

$$\frac{.0000 \times 650}{600} \times 100 = 0.0 \text{ mg. Ascorbic Acid/100 gms.}$$

Ascorbic Acid Concentration

% Transmittance

100

Standardization Pts. .000 - 45.2
 .030 - 68.0
 .050 - 89.2

90

70

60

50

40

30

20

10

Spectrophotometer Readings 45.2 (Ave. of 2)
 45.2 " " "
 45.2 " " "

Sample Wts - 100, 200, 300 grams
 Extractant - 350 ml.

$$\frac{.0000 \times 450}{200} \times 100 = 0.0 \text{ mg Ascorbic Acid} / 100 \text{ gms.}$$

$$\frac{.0000 \times 550}{400} \times 100 = 0.0 \text{ mg. Ascorbic Acid} / 100 \text{ gms.}$$

$$\frac{.0000 \times 650}{600} \times 100 = 0.0 \text{ mg. Ascorbic Acid} / 100 \text{ gms.}$$

.000

.010

.020

.030

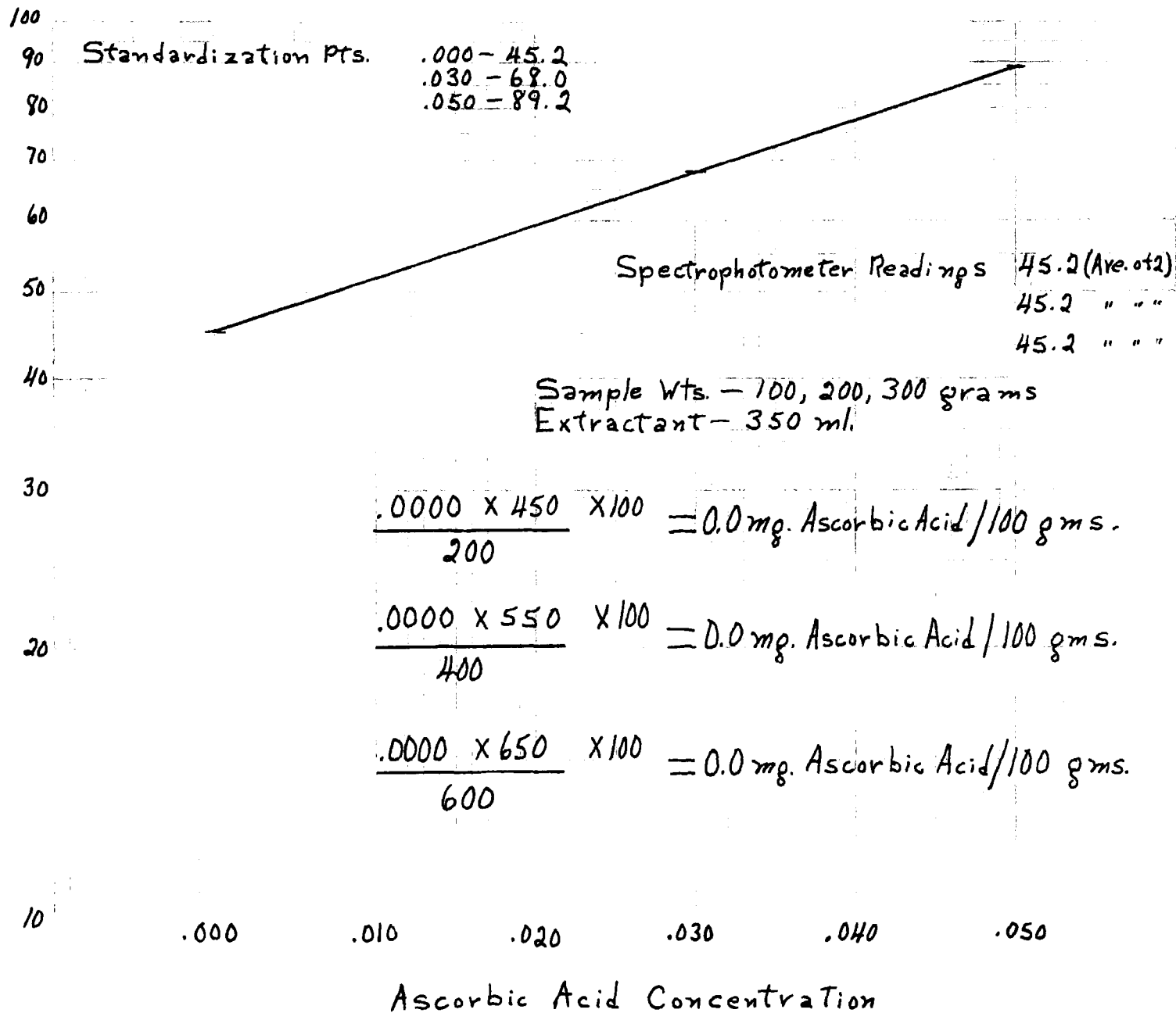
.040

.050

Ascorbic Acid Concentration

Rome Beauty Apple Sauce

% Transmittance



Winesap Apple Sauce

Evaporated Apple Rings

% Transmittance

100

90 Standardization PTS.

80

70

60

50

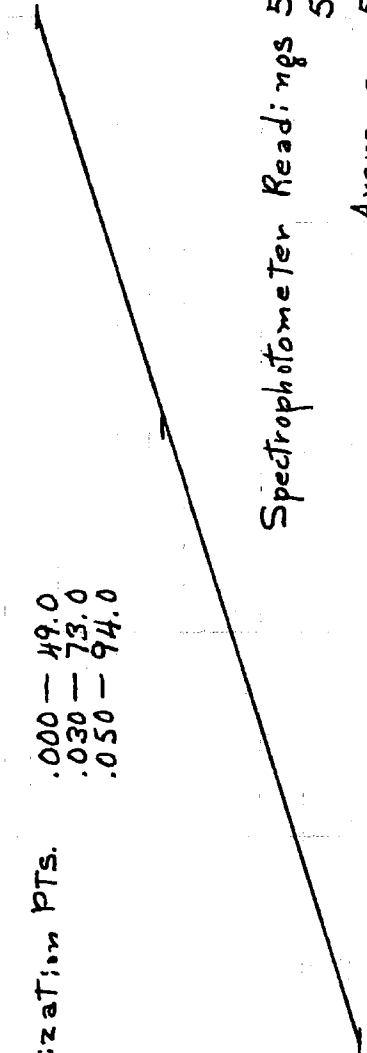
40

30

20

10

.000 — 49.0
 .030 — 73.0
 .050 — 94.0

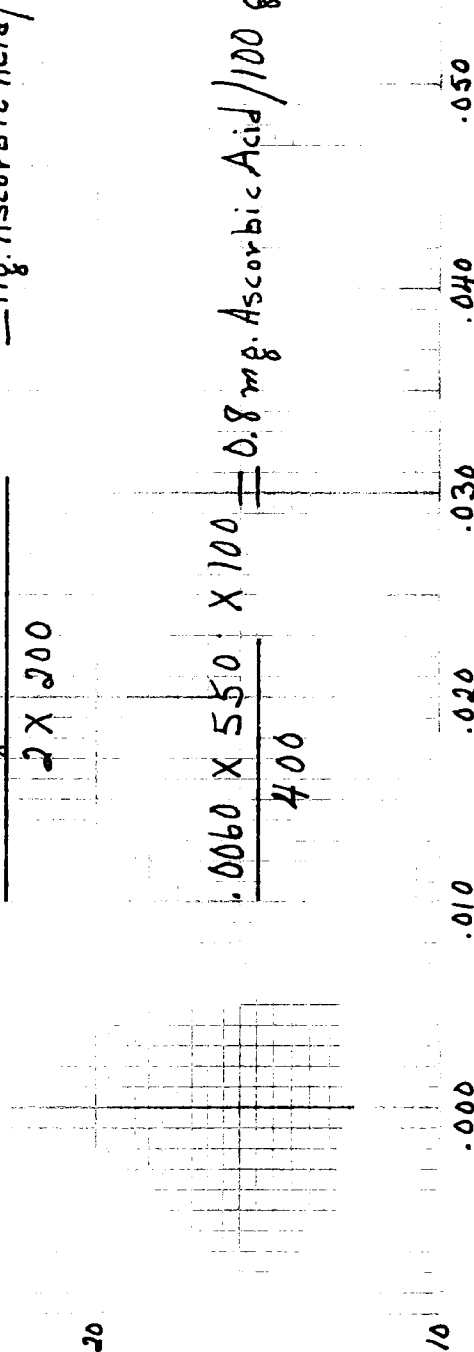


Spectrophotometer Readings 53.5 (Ave. of 2)
 52.5 " " "
 Average 53.0

Sample Wt. — 200 grams
 Extractant — 350 ml.

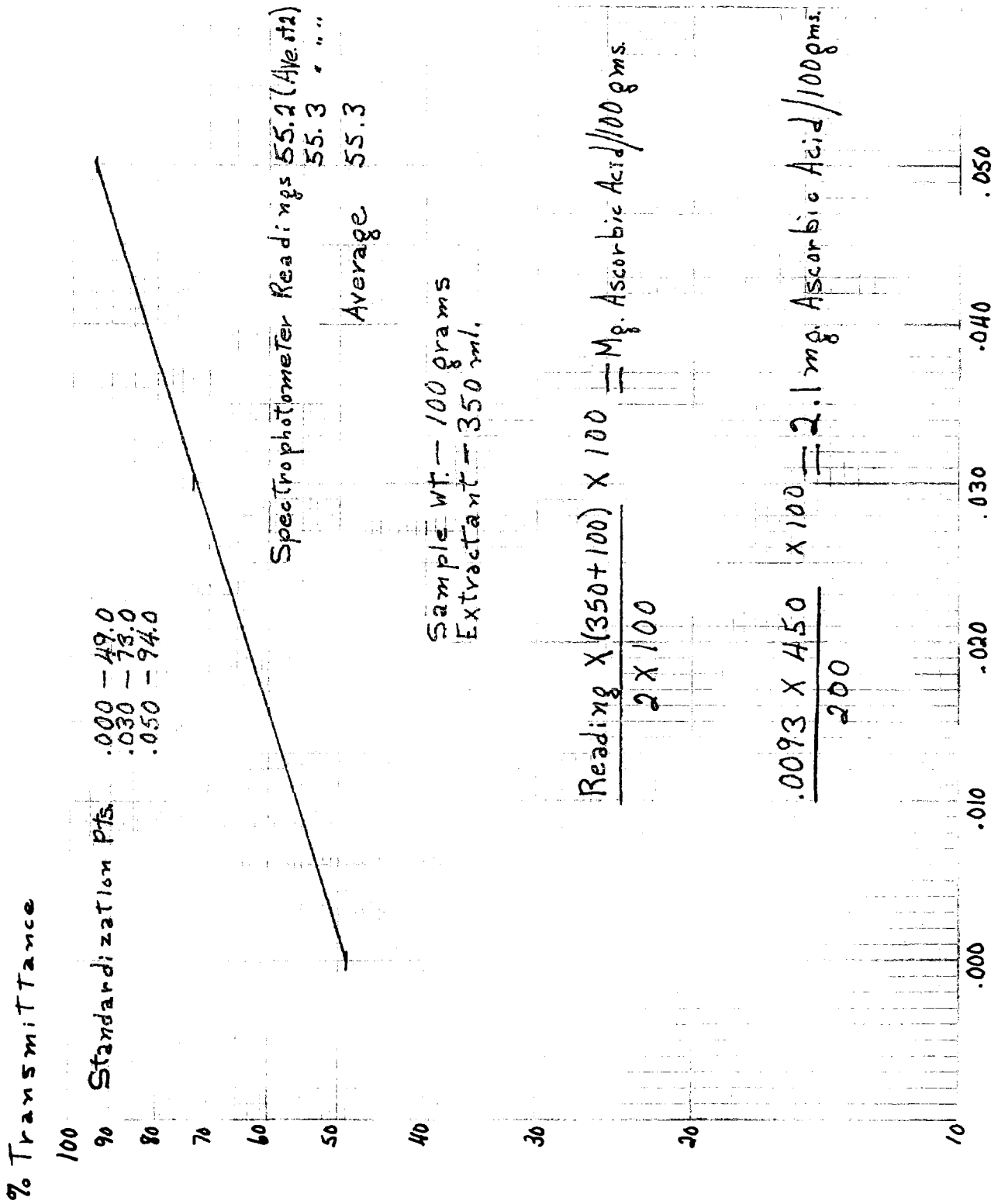
$$\frac{\text{Reading} \times (350 + 200)}{2 \times 200} \times 100 = \text{Mg. Ascorbic Acid} / 100 \text{ gms.}$$

$$\frac{.0060 \times 550}{400} \times 100 = 0.8 \text{ mg. Ascorbic Acid} / 100 \text{ gms.}$$

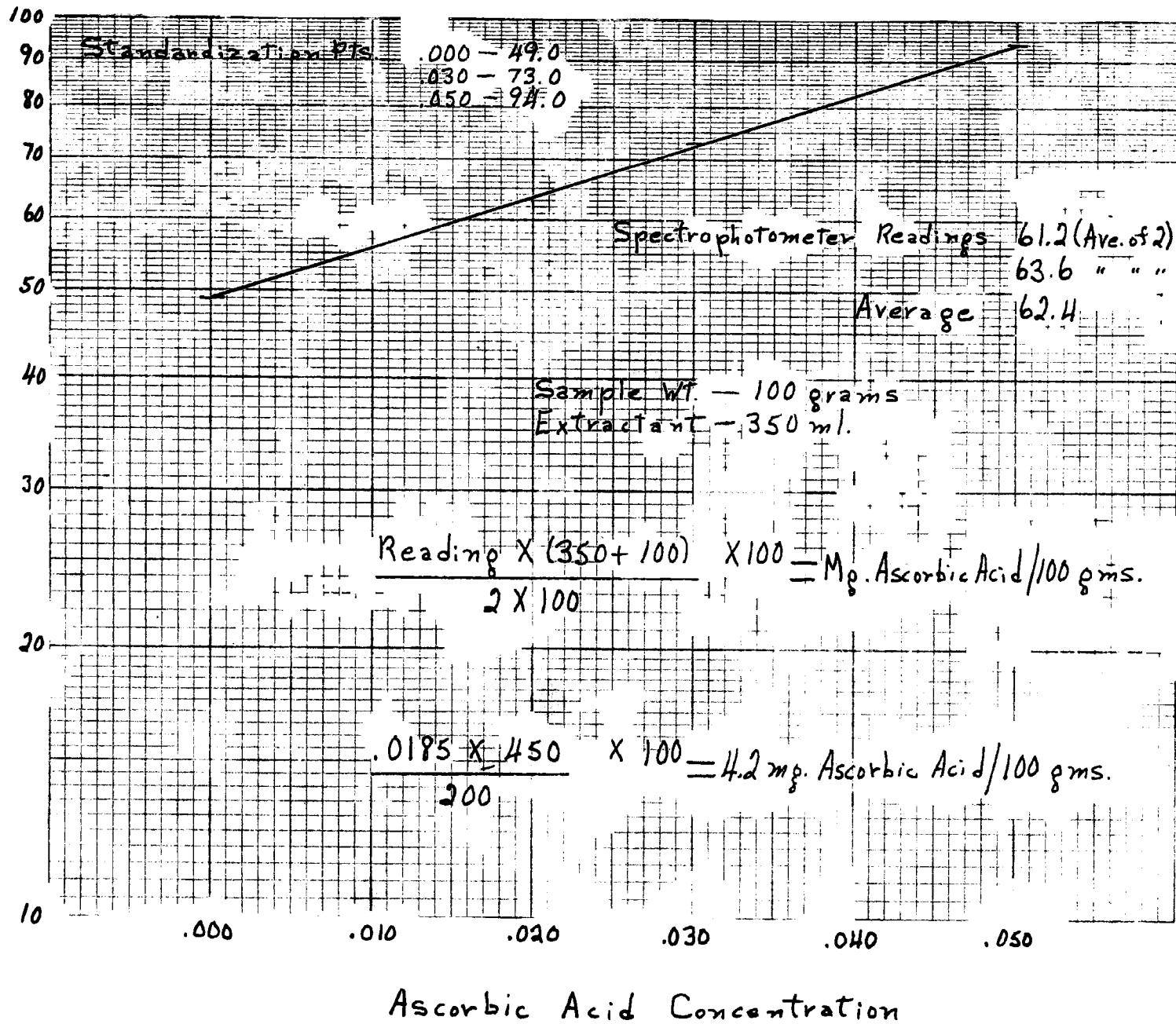


Ascorbic Acid Concentration

Evaporated Apple Sauce



% Transmittance

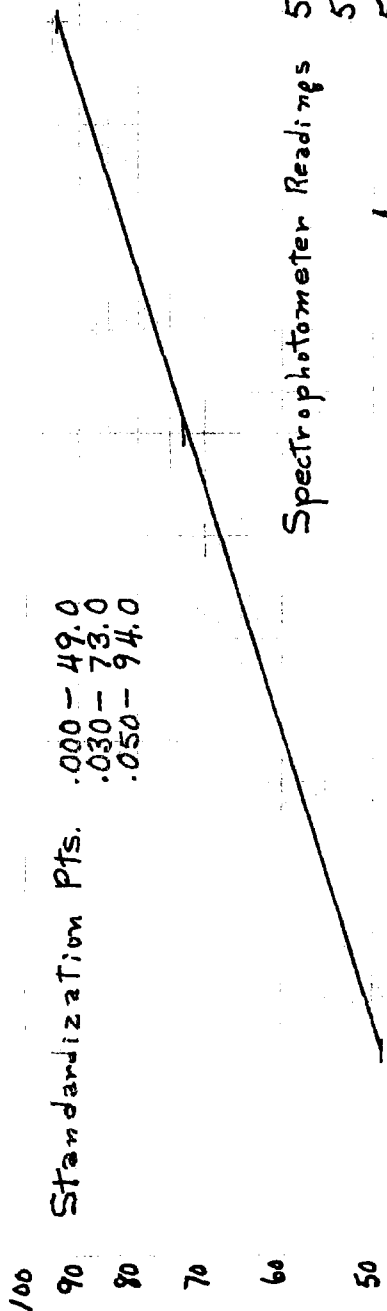


Commercially Canned Apple Pie Slices

Commercially Canned Apple Sauce

% Transmittance

Standardization Pts.
 .000 - 49.0
 .030 - 73.0
 .050 - 94.0

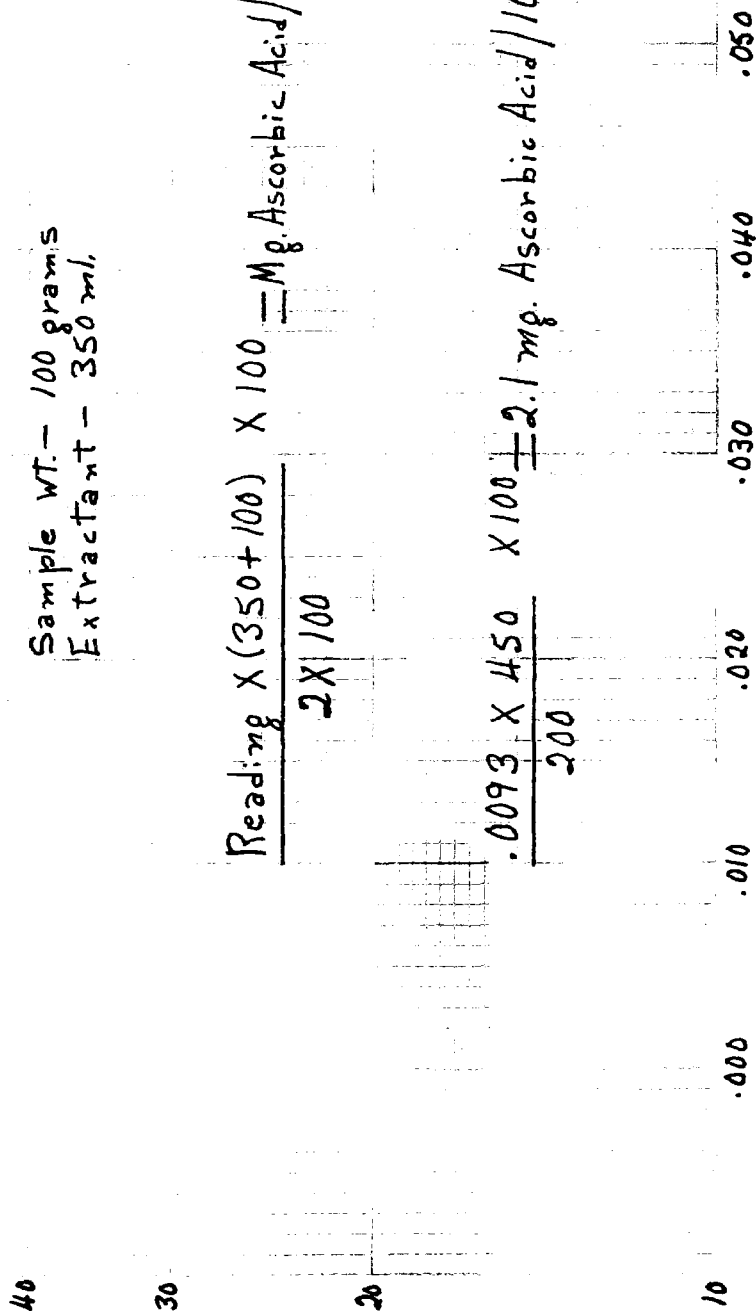


Spectrophotometer Readings
 55.2 (Ave. of 2)
 55.4 " " "
 Average
 55.3

Sample Wt. - 100 grams
 Extractant - 350 ml.

$$\frac{\text{Reading} \times (350 + 100)}{2 \times 100} \times 100 = \text{Mg. Ascorbic Acid} / 100 \text{ gms.}$$

$$\frac{.0093 \times 450}{200} \times 100 = 2.1 \text{ mg. Ascorbic Acid} / 100 \text{ gms.}$$



Ascorbic Acid Concentration

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