VITAMIN COMPOSITION OF TOMATO CULTIVARS AND COMPUTER SIMULATION OF ASCORBIC ACID STABILITY IN CANNED TOMATO JUICE

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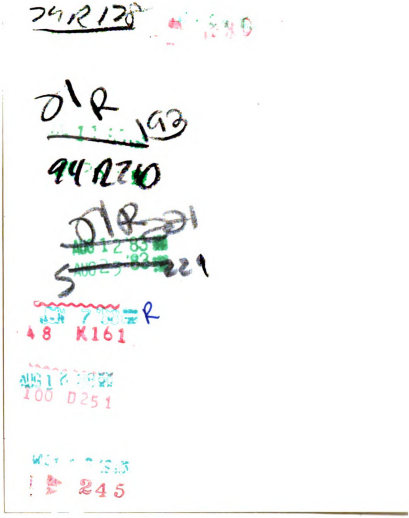
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ABSTRACT

VITAMIN COMPOSITION OF TOMATO CULTIVARS
AND
COMPUTER SIMULATION OF ASCORBIC ACID
STABILITY IN CANNED TOMATO JUICE

by

Young C. Lee

The research consisted of two parts; vitamin composition of tomato cultivars and computer simulation of ascorbic acid stability in canned tomato juice. The objectives of this research were (1) to study the vitamin content of tomatoes as affected by variety, ripening methods, harvesting time, and ethephon treatment; (2) to predict the ascorbic acid stability in tomato juice based on kinetics of ascorbic acid degradation and computer-aided prediction models. Reduced ascorbic acid was chosen as an index of nutritional quality in tomato juice.

The vitamin content of 24 tomato cultivars in 1973, 20 cultivars in 1974, and 19 cultivars in 1975 was determined. Nine standard cultivars were used to compare the vitamin content of vine ripened with that in breaker ripened tomatoes in both 1973 and 1974. Tomatoes of 9 standard cultivars in 1974 and 18 cultivars in 1975 were harvested in the early, mid, and late seasons to study the effect of harvest time on the vitamin composition of tomatoes. In 1973 and 1974, the vitamin content in tomatoes treated with ethephon one week

before harvest was compared with that in untreated tomatoes.

Highly significant differences in ascorbic acid and carotene contents were found between the tomato cultivars studied. Although there were some significant differences in the thiamin and the riboflavin contents between the cultivars studied, these differences were not as great as those noted with ascorbic acid and carotene.

Ascorbic acid and carotene contents in breaker ripened tomatoes were at least equal to those in vine ripened tomatoes. However, the results of the two years' study on thiamin and riboflavin contents in breaker ripened and vine ripened tomatoes, were inconsistent.

The ascorbic acid and the carotene contents in tomatoes harvested in the late season were significantly higher than those in the early season. The thiamin and the riboflavin contents in tomatoes decreased as the season progressed. Ethephon treatment a week before harvest did not adversely affect the vitamin composition of treated tomatoes.

The relationships between the vitamin content and organic and inorganic components of tomatoes were evaluated by the multiple linear regression, and the results were discussed.

Tomato varieties, Campbell-1327 and Campbell-28, were used to prepare tomato juice for experiments. The extracted tomato juice was deaerated and divided into 4 batches. Citrate buffer was added to each batch to adjust pH of juice to 3.53, 3.78, 4.06, and 4.36. Each batch of tomato juice

was divided into 3 lots, and $CuSO_4.5H_2O$ was added to adjust the copper level of juice to 2, 6, and 10 ppm. The treated tomato juice was processed at 265°F for 9 seconds, cooled to 200°F, filled in 8 oz. cans, closed, and cooled to 100°F. The representative lots were stored in storage boxes at 10, 18.3, 29.4, and 37.8°C. Tomato juice samples were analyzed for ascorbic acid using 2,6-dichlorophenolindophenol colorimetric method at 20 or 30 day intervals. The rate constants and other parameters were calculated by the KINFIT computer program.

The destruction of ascorbic acid under anaerobic conditions was confirmed to be a first-order reaction. The effect of storage temperature on the rate of ascorbic acid destruction was accounted for by the Arrhenius equation. The activation energy (Ea) for anaerobic destruction of ascorbic acid changed with pH, reaching a minimum near pKal of ascorbic acid.

The rate of ascorbic acid destruction was influenced by pH, reaching a maximum near pKal of ascorbic acid. Based on the changes in the rate of ascorbic acid destruction with pH, the existence of the complex form of ascorbic acid was employed to explain the kinetic results observed for ascorbic acid destruction in tomato juice. A mathematical expression, which required 4 parameters (k1, k2', k3, and Kal), was derived to compute the first-order rate constant as a function of pH. It appeared that changes in the rate of ascorbic acid destruction and Ea with pH were mainly due to the quantity of

the complex form of ascorbic acid formed at various pH's and k2'.

The rate constant of ascorbic acid destruction in the presence of copper (Kob) increased with the increase in copper concentration, and Kob changed with pH. From the plots of Kob versus copper concentration, the pseudo-first-order rate constant (K') was computed. A mathematical expression between Kob and K' was developed to compute Kob at various pH's and copper concentrations.

Mathematical expressions derived to describe kinetics of ascorbic acid destruction in tomato juice were used to develop a mathematical model for each storage condition. From the mathematical model, the computer program was developed and used to test the model and to predict ascorbic acid history during storage. The Fourier Series was employed to simulate the seasonal temperature fluctuation during storage of tomato juice. The three-factor model, which included expressions for the seasonal temperature fluctuation, metal catalyst, and pH was established and a computer program was developed. The predicted results were compared with the results obtained from shelf-life tests, whenever possible. The difference between predicted results and the shelf-life tests was in a range of $\pm$ 0 to 3% retention of ascorbic acid.

The results obtained in this study illustrate that the ascorbic acid stability in canned tomato juice can be predicted with accuracy, if the kinetic information on the ascorbic acid destruction is available.

VITAMIN COMPOSITION OF TOMATO CULTIVARS AND COMPUTER SIMULATION OF ASCORBIC ACID STABILITY IN CANNED TOMATO JUICE

by

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TABLE OF CONTENTS

To

St

RESU

I.

II

Table

LIST OF TABLES

Pages

1

2

3

4

5

6

7

8

9

10

11

12

13

14

LIST OF FIGURES

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INTRODUCTION

There has been an increased interest in the nutritional quality of foods over the past several years. More recently, this concern over the nutritional quality of the food products have given impetus to requirements for nutrition labeling of food products. Recent federal regulations covering nutrition labeling and tolerance for toxic substances in foods have brought great concern to the food industry, the major problem being variability in fresh and processed products.

The nutritional quality of fresh fruits and vegetables can be improved by breeding better varieties, good cultural practices, harvesting at right maturity, and proper post harvest handling. Many environmental factors also affect the quality of products, but they are not controllable factors.

Nutritional quality of the processed products can be improved by good processing practices and fortification of nutrients. The quality of the processed products may deteriorate during storage. This results in degradation of nutrients, development of off-flavor and off-color, and texture changes. The deterioration of canned foods is influenced by many factors, including storage temperature, pH, metal catalysts, type of container, dissolved oxygen, and some components of foods. The overall emphasis in storage

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of any food product is on keeping the deterioration mechanisms at minimum rates.

The outstanding food value of tomatoes in the diet is due to high vitamin content, especially ascorbic acid and carotenes.) The reported results indicate that many factors cause a wide variation of vitamin composition in tomatoes. The purpose of the study on the vitamin composition of tomatoes were: (1) to determine effects of variety, ripening methods, and harvesting time on vitamin composition of tomatoes; (2) to study effect of ethephon treatment upon vitamin composition of fruits; (3) to determine relationships between vitamin content and other organic and inorganic components of tomatoes. The results may be used to provide up to date data on vitamin composition of selected tomato varieties to satisfy areas of concern, such as breeding research and nutrition labeling. They may be also used to provide basic information on effects of some cultural practices and handling methods on vitamin composition of tomatoes.

To study quality stability of canned products during storage, tomato juice was selected as a model system of acid foods and reduced ascorbic acid was chosen as the quality index of the study. Since canned foods maintain anaerobic condition soon after canning, storage temperature, pH, and metal catalysts were studied as main factors which influence degradation of ascorbic acid in the system during storage. In this study, a mathematical procedure for prediction of the quality index history in a canned acid food during storage

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is developed. The mathematical functions and parameters obtained in this study are specifically for ascorbic acid in tomato juice. However, the procedures should be applicable to other canned acid foods, with minor modification.

The specific objectives of this study were: (1) to investigate kinetics of ascorbic acid degradation in the model system; (2) to develop theoretical mathematical models to describe kinetics of the ascorbic acid degradation; (3) to develop a computer-aided prediction of ascorbic acid concentration during storage; (4) to verify the computer-aided predictions of ascorbic acid history in tomato juice by comparison with the results obtained from the shelf-life tests.

This approach can be used for selection of storage environments best suited for the desired quality of canned acid food. The capability of the simulation to predict the nutrient concentration at any time during storage permits the use of such information for nutrition labeling purposes.

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LITERATURE REVIEW

Ascorbic Acid in Fresh Tomatoes

The outstanding value of the tomato in nutrition is due primarily to its vitamin content. Among these vitamins, ascorbic acid stands first in importance, based on the amount supplied in relation to human needs. On the average fresh, ripe, summer grown tomatoes contain about 25 mg of ascorbic acid per 100 g (Hamner and Maynard, 1942), and RDA of vitamin C is 45 mg for adults.

The results reported in the literature indicate that the ascorbic acid content of whole tomatoes varies considerably. Maclinn and Fellers (1938) reviewed the literature on the ascorbic acid content of tomato and reported concentrations ranging from 5 mg to 60 mg per 100 g fresh weight for American varieties. This variation is the result of a number of factors, such as the variety, the location grown, the season, and the treatment which the fruit receives before and after placing them on the market.

One of the factors that doubtless contributes to the variation in ascorbic acid content is the genetic constitution. Maclinn et al. (1938) found variations of 13 to 44 mg per 100 g of fresh weight in a study of 98 different varieties all grown in the same soil at the same time. Matthews et al. (1973) reported an average ascorbic acid content of 41 tomato varieties and breeding lines of 15.0 mg per 100 g fresh weight with a range from 10.7 to 20.9 mg/100 g fresh weight. The

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work of French (1939) indicated no difference in the ascorbic acid content of so-called red- and pink-fleshed varieties. Sansom and Zilva (1936) experimentally obtained tetraploid tomato strains from diploid plants and found a resultant doubling of ascorbic acid content in the juice of the fruit from the tetraploid strain.

The effects of acidity, total solids, sugar content, fruit size, and fruit portion on ascorbic acid content have been investigated by a number of workers. Yarbrough and Satterfield (1939) found no correlation between total acidity and vitamin C. Likewise, Cultrera (1935) found no definite relationship between acidity, reducing sugars, dry weight, and vitamin C.

Seasonal variations in fresh fruit have been reported by many investigators (Brown and Moser, 1941; Twomey and Ridge, 1970). Variations in the values of canned juice from year to year were considered by Hanning (1936) to be correlated more with season than with canning methods.

Although the results are in general agreement, it is impossible to judge just how much these variations, which occur in the environments where tomatoes are grown commercially, affect the ascorbic acid values of market tomatoes. One of the environmental factors playing a part in seasonal fluctuations and perhaps in locational differences is light intensity. Many investigators (Somers et al., 1950; Hassan and McCollum, 1954; Masui et al., 1953) reported that the ascorbic acid content in tomatoes was affected by the amount

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of sunlight falling upon the fruit. In mature tomatoes grown outdoors in a rainy season, with low light intensity, the concentration of dehydroascorbic acid was high, while L-ascorbic acid was very low.

The effects of light on the ascorbic acid content are interrelated with the temperature effects (Hamner and Maynard, 1942). In the temperature range 17 - 26°C, the higher temperature induced a high content of ascorbic acid (Hamner et al., 1945).

Data concerning the ascorbic acid content during the development and the ripening of tomato fruit are inconsistent. Some earlier investigators (Maclinn and Fellers, 1938; Works and Organ, 1943; Kaski et al., 1944) reported little changes, while more recent work has indicated an increase in ascorbic acid concentrations during maturation (Georgiev and Balzer, 1962; Kitagawa, 1973), with either a continuing rise (Fryer et al., 1954; Dalal et al., 1965) or a slight fall (Dalal et al., 1966; Malewski et al., 1971) during the final stages of ripening. Judging from these reports, it appears that immature green tomatoes are poorer in vitamin C than ripe ones, but that after a fruit has reached its full size and is in the so-called mature green stage, the increase in vitamin C during subsequent ripening is relatively slight (Hamner et al., 1942).

The effect of ripening method on the ascorbic acid content of tomatoes has been studied by numerous investigators, but there is a lack of general agreement. Craft and Heinze

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(1954), Murneek et al. (1954), and Hamner et al. (1945) reported that vitamin C content of artificially ripened tomatoes was similar to that of vine ripe tomatoes, while Scott and Kramer (1949), Pantos and Markakis (1973), and Bakulina (1970) found vine ripe tomatoes contained more ascorbic acid than artificially ripened tomatoes.

Ethylene is used for producing uniformity in the ripening of tomatoes. Jones and Nelson (1930) reported that the ethylene treatment of the green tomatoes produced no significant change in their vitamin C potency in all samples of the green fruits tested, but ethylene-ripened tomatoes and air-ripened tomatoes were richer in vitamin C than the green fruit (Hause et al., 1929).

There are some indications that soil type and cultural practices could influence ascorbic acid content. Hester and Kohman (1940) claimed a correlation between the vitamin C content of tomatoes and the soil type upon which they were grown. Hester (1940) found that the application of potassium fertilizer to certain soils resulted in an increase in the yield and vitamin C content of tomato fruits. However, Hamner et al. (1942 and 1945) indicated that ascorbic acid concentration showed little or no correlation with the macro- and micro-nutrients supply.

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Analysis of Ascorbic Acid

A large number of bioassays and chemical methods for the determination of vitamin C have been reported, since Sherman et al. (1922) described the first satisfactory bioassay using guinea pigs.

The chemical analysis of ascorbic acid generally calls for the extraction of the vitamin into an acid medium. Ponting (1943) investigated several acids for their suitability as extractants, and metaphosphoric acid and oxalic acid gave the lowest losses of ascorbic acid during extraction.

Chemical analysis for ascorbic acid and its derivatives may be divided into two groups; the determination of the reduced form and that of total vitamin C (Association of Vitamin Chemists, Inc., 1966).

The former group of analyses are usually based on the oxidation-reduction properties of ascorbic acid (Bessey and King, 1933; Bessey, 1938) or upon its ability to couple with diazotized aniline derivatives to form colored hydrozides (Schmall et al., 1953; Moor, 1957). In the oxidation-reduction methods, the reducing capacity of the extract is measured by treatment with a suitable oxidizing agent such as 2,6-dichorophenolindophenol, iodine etc. Generally, 2,6-dichlorophenolindophenol has been found to be the most satisfactory.

The latter group of analyses is usually based upon the oxidation of the vitamin C to diketogulonic acid and the subsequent formation of a highly colored hydrazone. The most

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widely used methods for the determination of total vitamin C is based on the reaction of diketogulonic acid with 2,4-dinitrophenylhydrazine to form a characteristic osazone (Roe et al., 1948).

More recently, a microfluorometric assay for vitamin C was adopted officially based on the formation of a fluorescent complex between the oxidized ascorbic acid and o-phenylenediamine (Deutsch and Weeks, 1964).

Destruction of Ascorbic Acid

Ascorbic acid in foods reversibly oxidized to dehydroascorbic acid, which has vitamin C activity. However, the oxidation reaction can continue to 2,3-diketogulonic acid which does not have vitamin C activity and which cannot be reversibly reduced to dehydroascorbic acid. A variety of compounds will be produced by further oxidation which may be enzymatic or nonenzymatic.

Barron and co-workers (1936) investigated the reaction of ascorbic acid with oxygen in the absence of cupric ion, and found that the oxidation of ascorbic acid at an immeasurably slow rate in acid and neutral solutions up to pH 7.0. Above pH 7.0, the rate of autoxidation increased considerably. Weissberger et al. (1943) studied the kinetics of the autoxidation of ascorbic acid and reported that both the monovalent and the divalent ion of ascorbic acid participated in the reaction; the divalent ion reacting 10^5 times faster than

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the monovalent ion. In the pH range below 6, the undissociated and the monovalent forms of ascorbic acid are the main species in solution (Khan and Martell, 1967). Recently Blaug and Hajratwala (1972), studying the effect of pH on the ascorbic acid oxidation using acetate and phosphate buffer, found that the pH-log rate profile showed a maximum near pK_{a1} of ascorbic acid.

Metal catalyzed autoxidation of ascorbic acid has been extensively studied by many workers (Kellie and Zilva, 1935; Barron and Klemperer, 1936; Dekker and Dickinson, 1940; Peterson and Walton, 1943; Khan and Martell, 1967). Among the metallic salts tested (Mn, Ni, Fe, Co, Ca, and Cu) copper was the most effective catalyst for the oxidation of ascorbic acid. Its catalytic action was observed in concentrations as low as 46 µg of Cu/l (Barron et al., 1936). Khan and Martell (1967) reported that the rate of the ferric and cupric ion catalyzed oxidation were found to be first order with respect to the concentration of molecular oxygen and that the rate showed an inverse dependence on the hydrogen ion concentration. They also observed that down to a partial pressure of 0.4 atm. of oxygen, the rate of oxidation was directly proportional to the partial pressure, but below 0.4 atm. linearity was not observed.

Several workers (Clegg, 1964; Curl, 1949; Harper et al., 1969; Reynold, 1965; Tatum et al., 1969), investigating the anaerobic destruction of ascorbic acid in model systems and natural food products, found that at temperatures above 30°C,

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ascorbic acid loss is followed by carbon dioxide formation and the development of brown pigments. In canned foods free oxygen is present in restricted amounts at the time of sealing and disappears entirely within one month of canning (Huelin, 1953). Nevertheless, ascorbic acid loss in canned foods continues at a steady rate throughout the storage life. This continued loss must be due to an anaerobic destruction of ascorbic acid. Finholt et al. (1963) reported that the disappearance of ascorbic acid from the model solutions found to be first order with respect to ascorbic acid at pH values from 0.4 up to 11.4.

Steinman and Dawson (1942) studied the enzymatic oxidation of ascorbic acid using an ascorbic acid oxidase preparation. The molecular weight of this enzyme was 150,000 and it contained 0.25% copper (Dawson and Magee, 1955). The pH optimum for enzyme activity in citrate-phosphate buffer was about 5.6 and the enzyme rapidly and irreversibly lost activity at pH below 4.

Thermal inactivation of ascorbic acid oxidase proceeds in two stages, the first of which is reversible, and the second irreversible. The copper is lost at the same rate as activity in the first stage, and more slowly in the second stage (Wilson, 1966).

Oxidation of ascorbic acid is temperature dependent. Barron et al. (1936) reported Q_{10} for oxidation of 1.0M-ascorbic acid to be 1.65 at 37 to 27°C. Wanninger (1972) indicated that Arrhenius expression could be used to account

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for the temperature dependence of reaction rate constant. Blaug and Hajratwala (1972) studied the effect of pH and temperature on the rate of oxidation of ascorbic acid. The activation energy (Ea) varied from 12.2 Kcal/mole at pH 3.52 to 7.8 Kcal/mole at pH 6.60. Different values of Ea at various pH indicated the possibility that a different reaction is dominant at different pH. Thermodynamic values reported by Blaug and Hajratwala (1972) compare favorably with those reported by Khan and Martell (1967) and Kato and Sugiura (1956).

The literature on the order of the reaction with respect to ascorbic acid concentration is conflicting. Barron et al. (1936) described the reaction as zero order; Schuemmer (1940) reported the reaction to be pseudo-unimolecular; Weissberger et al. (1943) expressed their results as first order constants; Peterson and Walton (1943) reported the reaction to be first order for 50 to 80% of the reaction below pH 7 and above pH 11. Dekker and Dickinson (1940) used first order constants, but noted a drift in the constant. Joslyn and Miller (1949) indicated that the reaction was first order.

Timberlake (1960) studied the stability of ascorbic acid in black currant juice and reported that the reaction appeared to be first order and this was confirmed by the independence of the half life period on the initial ascorbic acid concentration. Khan and Martell (1967), and Blaug and Hajratwala (1972), respectively, reported that the oxidation of ascorbic acid followed first order reaction. Singh (1974) stated that

the overall reaction of ascorbic acid degradation and oxygen uptake was assumed and confirmed to be a second-order reaction under limited dissolved oxygen pressure in the infant formula.

Stability of Ascorbic Acid in Tomato Juice

The ascorbic acid content in tomato juice depends upon both the inherent concentration in the fresh tomato fruit and the losses due to handling, processing and storage (Pope, 1972).

Numerous investigators have followed the variations in the ascorbic acid content of tomatoes during the canning process and the production of juices. If proper precautions are taken, little loss of ascorbic acid occurs during processing (Daggs and Eaton, 1934; Kohman et al., 1933; Robinson et al., 1970). The desirability of avoiding any treatment that permits oxidation is emphasized (Hussemann, 1935; Sanborn, 1938). With use of efficient processing procedures at least 80% of the original raw product ascorbic acid can be retained after processing the juice (Robinson et al., 1970).

When tomato juice is held at 40°F or less, there are very small losses of vitamin C from juice even after 12 months of storage (Guerrant et al., 1945; Feaster et al., 1949; Sheft et al., 1949; Kramer, 1974). Guerrant et al. (1945) held tomato juice continuously at 85°F and 110°F and found 74% retention of ascorbic acid at 85°F after 1 years and 19% retention at 110°F after 1 year.

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Fluctuation of temperature was evaluated by Feaster (1949). His results showed retention of ascorbic acid decreased with time and loss was most rapid at high temperatures. He did not find the apparent altered effect on ascorbic acid retention due to intermittent temperature changes.

Considerable research has been conducted to predict the retention of ascorbic acid in food products (Bauernfeind and Pinkert, 1970). Lamb (1946) reviewed several shelf-life studies and stated loss would be 1 per cent per month for juice stored at 70°F or below, and 2 to 5 per cent per month if storage was at 80 to 85°F.

Kwolek and Bookwatter (1971) presented a discussion on predicting food quality characteristics' storage stability from time-temperature data. They showed concentration at any time in storage could be expressed by:

$$Y = a + t\, f(Ti) \pm U$$

where Y = a measure of the product quality

a = initial quality measurement

t = storage time

$f(Ti)$ = the slope of the change in Y versus temperature at time $t = i$

U = random error associated with the deviation of observed Y.

Wanninger (1972) developed a mathematical model to predict stability of ascorbic acid in food products. He found

the most acceptable expression of the loss of ascorbic acid to be the Arrhenius equation:

$$K = Ae^{-E/RT}$$

where K = the rate of loss of ascorbic acid
A = pre-exponential constant
E = activation energy (cal/mole)
R = gas constant (1.987 cal/^{o}K.mole)
T = absolute temperature, ^{o}K.

Wanninger (1972) implied concentration effects and temperature effects were accounted for completely by the Arrhenius equation, while Kwolek and Bookwalter (1971) suggested high temperature could cause deviation from their prediction equation. Singh (1974) simulated ascorbic acid stability in infant formula, using the parameters obtained from second order reactions.

Carotene

Fresh, ripe tomatoes or juice contain 1,000 International units of vitamin A per 100 g (Munsell, 1940). On the basis of this figure, a small tomato or glass of juice would supply 20% or more of the recommended dietary adult allowance of 5,000 IU. The major carotenoid found in tomato is lycopene, which comprises 75% of the total carotenoids present (Mallia, 1967).

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tomatoes is subject to wide variation. Several individual workers have provided relative figures for carotene that reveal variations according to degree of ripeness, variety, and exposure to light (Hamner and Maynard, 1942).

Many researchers reported that the carotene content of tomatoes increased during ripening (Kirsauva, 1938; Morgan and Smith, 1928; Shivrina, 1937; Sadana and Ahmad, 1948). Some reports (Ellis and Hamner, 1943; Sadana and Ahmad, 1948; Jones and Nelson, 1930) indicated that vine-ripened fruits are more potent sources than fruits detached while partially green and ripened in air or ethylene, and that ripe fruits are richer than green fruits regardless of method of ripening.

The carotene potency also varies markedly with variety, red varieties being much more potent than so-called pink varieties (Shivrina, 1937). Variations in pigment content such as these have frequently been noted as a consequence of varietal differences (Kramer and Smith, 1946).

McCollum (1954) showed that lycopene and carotene was increased in ripe fruit by illumination at any stage during maturation. Shewfelt and Halpin (1967) concluded that the quality of the light received influenced the rate of color development of picked fruit. Boe and Salunkhe (1967) reaffirmed that light increased the amount of beta-carotene and lycopene. Tomatoes ripened at 38°C by day, and 29°C by night, never developed sufficient lycopene to make them red enough for U.S. No. 2; they turned yellow or orange when fully ripe.

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Scheunert and Wagner (1939) found the vitamin A value was not affected by fertilizer treatment, except under conditions of extreme depletion of mineral supply. Trudel and Ozbun (1971) indicated that most of the caroteniods, especially lycopene, was increased with increasing K; beta-carotene decreased with increasing K concentration.

Thiamin

Baker and Wright (1935) reported that tomato pulp contained 40 IU of thiamin per 100 g. Secomska (1971) indicated that fresh tomatoes contained 42 µg of thiamin per 100 g and fresh juice 48 µg/100 g.

Lefebure and Leclerc (1973) found that fertilizer treatment and variety had no effect on thiamin content of tomatoes from plants of similar age. Thiamin content of tomatoes increased between May and June from 40 to 80 µg/100 g fresh weight.

Riboflavin

Early studies indicated the riboflavin content of tomatoes to be rather low. A study by Hodson (1940) using the fluorometric method showed value of 52 µg per 100 g. Using rat assay, Lanford et al. (1941) found a value of 37.7 µg per 100 g. Secomska et al. (1971) showed fresh tomatoes contained 27 µg/100 g of riboflavin and tomato juice 34 µg/100 g.

Fertilizer treatment and variety have no effect on

riboflavin content of tomatoes (Lefebure and Leclerc, 1973). Riboflavin content of tomatoes increased between May and June 26 to 36 μg per 100 g.

MATERIAL AND METHODS

Effects of variety, ripening method, ethephon (2-chloroethylphosphonic acid) treatment, and harvest time on the vitamin and other composition in fresh tomatoes were studied in the 1973 and 1974 seasons. A part of this experiment, especially variety and harvest time factors, was repeated in the 1975 season. Since the experimental design of the 1974 season was developed based on the results obtained in 1973, the two designs were not the same.

Studies on kinetics of ascorbic acid destruction in tomato juice were conducted in 1974 and 1975.

Raw Material

Fresh material used in this study was obtained from the Sodus Horticultural Experimental Station, Michigan State University. The fruits were harvested randomly to provide a representative sample of the experimental plots. Each sample composed of 8 or more typical fruits of the variety.

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In the 1973 and 1974 seasons, the effect of variety and ripening methods (vine ripened versus breaker ripened) upon the nutrient composition of fresh tomatoes was studied.

Three replications of 24 cultivars were used for each study in the 1973 season. The cultivars used included Springset, Setmore, Caravelle, Jet Star, Calmart, Campbell 1327, Florida MH-1, Burpee VF, Campbell 721, Walter, Packmor, New Yorker, 71-301-2-1, 71-301-1-1, 71-302-2-1, 71-304-1-1, 71-304-2-1, 71-306-1-1, 71-307-1-1, 71-915-4-1, 71-915-5-1, 71-915-9-1, 71-915-10-11, and 71-915-11-1. The breeding lines were inbred lines developed at Michigan State University to serve as stable bases from which breeding could be accomplished.

In the 1974 season, four replications of 20 cultivars were used for each study. The 20 cultivars were Setmore, Campbell 1327, W2HF, OFHF, 33HF, Jet Star, Springset, 6718VF, Campbell 721, Ace 55VF, Redpak, Royal Flush, Prime Beefsteak, Experimental Hybrid No. 2, and No. 4 (Ferry-Morse Seed Co.), 6343 VF, 306-1-1, 307-1-1. 915-4-1, and 915-5-1. Campbell 1327 was used as check variety, serving as a basis for comparing the other varieties.

Campbell 1327 and Setmore were used to study the effect of ethephon treatment upon the nutrient composition of fresh tomatoes in 1973, while only Campbell 1327 was used in 1974. Ethephon was applied to the tomato plants at two rates, 0.375 lbs/acre and 0.75 lbs/acre, one week before harvest.

In 1974 season, tomatoes of 9 cultivars were harvested at 3 different times (Aug. 22, Aug. 30, Sept. 10) to study

effect of harvest time on nutrient content of tomatoes. The 9 cultivars were Setmore, Campbell 1327, Jet Star, Springset, Campbell 721, 71-306-1-1, 71-915-4-1,71-915-5-1, and 71-307-1-1.

Three replications of 19 cultivars were studied in the 1975 season. They are Setmore, Campbell 1327, Jet Star, Campbell 721, Royal Flush, 6718 VF, Bigset, PSX 17573, PSX 17673, Red Pak, OCNF, Rampo, Veebrite, Veeset, Vision, Ace 55VF, and Hybrid No. 9, No. 15, and No. 16 (Ferry-Morse Seed Co.).

The harvested ripe fruits were placed in perforated polyethylene bags and transported to the Food Science Building, Michigan State University. The fruits were stored in a controlled temperature cubicle maintained at 55°F and 90% relative humidity (RH). Storage time was kept at a minimum so that assay would reflect nutrient levels in the freshly harvested fruits as closely as possible. Green-mature tomatoes (breakers) were ripened at 65°F and 90% RH for a week.

Sample Handling

The fruits were removed from the storage cubicle, washed, dried, and divided into two groups, one for freezing and the other for analysis. Tomatoes for freezing were cut into quarters and frozen at -10°F in moving air.

Samples for ascorbic acid analysis were obtained from 4 randomly selected fruits. Vertical wedges were sliced from the fruits for duplicated analysis. The rest of fruits

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for assay were cut into quarters, and pooled. About 600 g of quarters were weighed and blended in a Waring blender jar at a high speed for 3 minutes. The slurry obtained was used for thiamin, riboflavin, carotene, and other analyses.

The frozen samples were crushed and 100 g of samples were weighed into tared aluminum dishes. These samples were freeze-dried at 124°F for 38 hours. The dried samples were weighed, and placed in tightly capped glass jars. These were ground to pass a 20 mesh sieve using a Wiley Laboratory Mill and the ground samples were held in well capped glass jars for mineral analysis.

Analytical Procedure

Ascorbic Acid

Ascorbic acid was determined using a modification of the method reported by Loeffler and Ponting (1942). Ponting (1943) reported that both metaphosphoric acid and oxalic acid provided equal recovery of ascorbic acid from the systems under study. Therefore, a 0.5% oxalic acid solution was substituted for the 1% metaphosphoric acid solution as an extracting media.

Fifty grams of freshly sliced tomatoes blended for 3 minutes in a Waring blender with 450 ml of 0.5% oxalic acid solution. After blending, the slurry was filtered through Whatman No. 5 filter paper to clarify.

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One ml portions of the extract were pipetted into 3 matched colorimeter tubes. Nine ml of water were added to one tube which was used to adjust the colorimeter (Bausch and Lomb Spectronic 70, Bausch and Lomb, Rochester, N.Y.) to read 100% T. To each of the other tubes, 9 ml of working dye solution was added. The reading on each tube was taken within 10 seconds from the beginning of the dye solution.

Ascorbic acid content in the tomato was calculated using the following formula:

$$\text{Ascorbic acid (mg/100 g)} = 10.0\ (L_1 - L_2)\ \frac{\text{ml acid + g sample}}{\text{g sample}},$$

where L_1 is the average absorbance of dye blanks and L_2 is the average absorbance of sample tubes. The factor 10.0 was determined as the slope of a standard curve using solutions of ascorbic acid.

Carotenes

Two 10 g samples of tomato slurry were weighed into 250 ml beakers. To each beaker was added 140 ml of an ethanol (95%) - hexane solution (2:1 v/v), and then the sample was stirred on a magnetic stirrer for 5 minutes at a rate to prevent layer separation. The samples were filtered through a coarse fritted glass filter under suction. The residue on the filter was washed with two 25 ml of 95% ethanol followed by one 25 ml of hexane.

The liquid was transferred to a 500 ml separatory

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funnel. The filter flask was rinsed with 50 ml of a 1% solution of sodium sulfate which was added to the contents of the separatory funnel. The contents of the separatory funnel were gently shaken and the layers allowed to separate.

The lower water layer was drawn off into a second separatory funnel. This fraction was then washed with three 25 ml volumes of hexane to extract any remaining pigments. Each hexane wash was added to the hexane fraction in the first separatory funnel. The water layer was then discarded.

The hexane fraction was washed with five 100 ml of distilled water followed by one 50 ml of distilled water. The distilled water wash was discarded. The hexane extract was then filtered through anhydrous sodium sulfate into a 250 ml volumetric flask, using Whatman No. 2 filter paper. The separatory funnel, filter paper, and sodium sulfate were rinsed with hexane until free of pigment. The flask was made to volume with hexane. This extract represented the total carotene fraction and an aliquot of this extract was transferred to a colorimeter tube for measurement of total carotenes at 436 nm.

A 100 ml of carotene were placed in a 150 ml beaker for further purification and separation of the alpha- and beta-carotene fraction. This aliquot was evaporated by air to a volume of 10 ml in preparation for column chromatography.

Column chromatography was accomplished using a 1 + 2 mixture (weight basis) activated magnesium oxide and diatomaceous earth. The column was packed to a depth of 10 - 15 cm

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using the method described in Methods of Vitamin Assay (Association of Vitamin Chemists, Inc., 1966).

The column was wetted with hexane before the extract was poured on. Alpha- and beta-carotenes were then eluted as a single band with acetone-hexane (1 + 9) following the procedure outlined in Official Methods of Analysis (AOAC, 1965).

The elute was collected in a 100 ml volumetric flask and diluted to volume with hexane. The absorbance was measured at 436 nm.

Both total carotene and beta-carotene elute were calculated as beta-carotene by comparison to a beta-carotene standard curve. Table 1 shows the value obtained in determining the beta-carotene standard curve. Pure crystalline beta-carotene was dissolved in hexane for the determinations.

Extraction of Thiamin and Riboflavin

Two 75 g of tomato slurry were weighed into a 400 ml beaker. Sixty-five ml of 2.5N-HCl was added, and the sample was mixed by shaking. The beaker was covered with aluminum foil and held in a boiling water bath for 30 minutes with occasional swirling. After the digestion, the beaker was placed in a 35°F refrigerator to cool. After cooling, the sample was adjusted to pH 4.5 with 10N-sodium hydroxide and 2.5M-sodium acetate using a pH meter.

The digest was then quantitatively transferred to a

Table 1.

Standa beta-car (µg/ml	
0.2	
0.4	
0.6	
0.8	
1.0	
1.2	
1.4	
1.6	
1.8	
2.0	

Regress

Table 1. Beta-carotene standard curve.

Standard beta-carotene (µg/ml)	Optical Density		
	Sample A	Sample B	Sample C
0.2	.0611	.0593	.0602
0.4	.1207	.1214	.1210
0.6	.1797	.1805	.1801
0.8	.2422	.2451	.2436
1.0	.3000	.3010	.3005
1.2	.3580	.3640	.3610
1.4	.4115	.4215	.4165
1.6	.4850	.4885	.4868
1.8	.5400	.5510	.5455
2.0	.6020	.6065	.6042

Regression Equation: O.D. = 302.24(x mg/ml), r = 0.999

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200 ml volumetric flask which contained several mg of fungal pectinase (Nutritional Biochemicals Corp.). The flask was swirled and allowed to incubate at room temperature for 3 to 4 hours or in a 35°F refrigerator overnight.

After incubation, the flask was made to volume with water and filtered through Whatman No. 5 filter paper into a brown glass bottle. The extract was stored under refrigeration and was subsequently used for analysis of thiamin and riboflavin.

All these steps were carried out under reduced light as both thiamin and riboflavin are destroyed by visible light.

Thiamin

Twenty-five ml of the vitamin extract were added to 50 ml of isbutanol in a 125 ml separatory funnel. The mixture was then shaken for 2 minutes and allowed to separate for at least 30 minutes. The lower aqueous layer was used for thiamin analysis. This procedure was employed to eliminate interfering substances in the sample.

An automated method (Kirk, 1974) was used for the analysis of thiamin. This method is basically an automation of the thiochrome methods (AOAC, 1965). Thiamin was oxidized to thiochrome with alkaline potassium ferricyanide. The thiochrome was then extracted into isobutanol and the fluorescence of this extract was measured at 436 nm using a Technicon Autoanalyzer (Technicon Instrument Corp., New York).

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Riboflavin

The vitamin extract contained high level of substances which interfered with riboflavin analysis. Therefore, the sample was treated to remove the interfering substances following the procedure outlined in Methods of Vitamin Assay (Association of Vitamin Chemists, Inc., 1966).

Ten ml of the extract were placed into a test tube. A drop of concentrated HCl and 0.5 ml of 3% $KMnO_4$ were added to it. The contents were mixed, and allowed to stand exactly 2 minutes. Then, 0.5 ml of 3% H_2O_2 was added and mixed. The red color disappeared within 10 seconds. This solution was ready for analysis.

Technicon Autoanalyzer system was used for the riboflavin analysis and the automated procedure reported by Kirk (1974) was followed. The prepared sample was pumped into the machine and dialyzed against dilute sodium chloride before the fluorescence of the sample was measured. The sample was excited with 436nm light and the fluorescence was measured at 510nm. Sample blanks were measured by quenching fluorescence with $Na_2S_2O_4$.

Acidity

pH of the tomato samples was obtained by measuring a pH of the tomato slurry using a Beckman Zeromatic pH Meter (Beckman Instruments, Inc., Fullerton, California).

Two 10 g samples of the slurry were placed into 250 ml beakers and 75 ml of water were added to each beaker to determine total acidity. Using magnetic stirrer, the mixture was titrated with 0.1N-NaOH to pH 8.0.

Miscellaneous Analysis

Total Solids

One hundred grams of tomatoes were freeze-dried and weighed to obtain total solids of the sample. The procedure was described in Sample Handling.

Soluble Solids

Tomato slurry was filtered through Whatman No. 1 filter paper to provide a sample for soluble solids determination. Soluble solids were then read with an Abbe Refractometer (Precision Model, Valentine and Co., Vista, California).

Potassium

The samples for potassium analysis were weighed into a glass jar followed by 50 ml of water. The jar was capped and agitated at every 30 minutes for 2 hours. The samples were then filtered through Whatman No. 1 filter paper.

The water extract was used for potassium analysis. Flame photometry was used for the determination on a Beckman

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Model B Flame Photometer (Beckman Instruments, Fullerton, California) adjusted to 755nm.

Other Minerals

Phosphorous, sodium, calcium, magnesium, manganese, iron, copper, boron, zinc, and aluminum were determined using an Applied Research Laboratory Quantograph (Applied Research Laboratory, Division of Bausch and Lomb, Glendale, California). One-half gram of sample of the ground freeze-dried samples was ashed at 500°F for 10 hours. The ash was dissolved in a nitric acid solution and analyzed. Levels of the elements in the sample were determined by comparison to standard curve.

Tomato Juice

Campbell 1327 and Campbell 28 were used for studies on tomato juice. Campbell 1327 was grown at Sodus Horticultural Experimental Station and Campbell 28 at Horticultural Research Center, Michigan State University. The harvested fruits were placed in wooden boxes and transported to Food Science Building, Michigan State University. They were held at 50°F and 95% RH until used for processing.

Canning Procedure

The tomatoes were sorted, washed in water, and drained. The washed tomatoes were cut into quarters and heated to

180 - 190°F with stirring in a steam jacketed kettle. The heated material was placed into the stainless steel buckets and let stand for 5 minutes. The hot pulp was then put through a pulper to extract tomato juice. Salt was added at a rate of 0.5% to the extracted juice and mixed. The juice was deaerated by pulling vacuum and let nitrogen gas flow through the juice with agitation. The deaerated juice was kept in a holding tank with a nitrogen gas distributing device.

Weighed portions of tomato juice were treated according to the experimental designs. The treated juice was processed through a Laboratory Model Spiratherm (Cherry-Burrell Corp., Newport, California) at 265°F for 9 seconds and cooled to 200°F. The tomato juice received from the cooling coil was put into 8 oz. cans with minimum head space and closed. The sealed cans were inverted, let stand for 1 minute, and then cooled to 100°F in a cooling tank. The cooled cans were kept for a few hours at room temperature to dry the surface of the can, and then stored at the desired temperatures.

Treatments

The extracted tomato juice was treated according to the purposes of various experiments. The details of the treatments for each experiment were described in each section of Results and Discussion in an effort to clarify data presentation.

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Statistical Analysis

Significance of each factor in various observations of samples was determined by analysis of variance. Mean separation was made by Duncan's Multiple Range test wherever significant differences at the 5% level were found by analysis of variance.

Relationships between variables were evaluated by calculating correlation coefficients and multiple linear regression equations.

Analysis of variance, correlation coefficients, and multiple linear regression equations were computed using MSU State System Version 3. Duncan's Multiple Range test was accomplished using DMRT, MSU Stat System. All calculations for statistical analysis were made using a CDC 6500 computer located in the Computer Laboratory of Michigan State University.

All calculations for kinetics of ascorbic acid destruction were made by a computer program, KINFIT (Dye and Nicely, 1973). This program differs from the usual least-square techniques, as it does not "Linearize" the problem; however, it uses the numerical integration procedures to provide a fit to the desired differential equation. This program is useful in plotting the data to the best fit and calculating standard deviations on the calculated parameters. This approach assists in accounting for the internal errors of vitamin assay and small variations in storage durations. The program is specially written for chemical reactions and for evaluating kinetic parameters of the reaction.

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RESULTS AND DISCUSSION

Vitamin Composition of Tomato Cultivars

Although tomato cultivars studied in the 1973 season were different from those studied in the 1974 season, nine "standard cultivars" were maintained in both seasons for comparisons.

All results were expressed on fresh weight basis, except the minerals which are expressed on a dry weight basis. Miscellaneous data are contained in the Appendix for reference.

Ascorbic Acid Content in Tomatoes

The ascorbic acid content of the cultivars of vine ripened tomatoes in 1973, 1974, and 1975 seasons are contained in Table 2.

The average ascorbic acid content of the 9 standard cultivars in 1973 was 17.9 mg/100 g and that in 1974 17.4 mg/100 g with similar standard deviations. The overall average ascorbic acid content of the varieties studied were 18.0, 16.9, and 14.0 mg/100 g in 1973, 1974 and 1975 seasons, respectively (Table 2). The differences among the overall averages of the 3 seasons might be due to different cultivars studied in each season.

There were significant differences in ascorbic acid content among cultivars studied in the three years. The varietal

Table 2. Ascorbic acid in vine ripened tomatoes.

1973		1974		1975	
Cultivars	mg/100 g	Cultivars	mg/100 g	Cultivars	mg/100 g
Campbell-1327	12.6 a[1]	Campbell-1327	13.1 a	Campbell-1327	11.4 a
Campbell-721	15.3 a	Campbell-721	16.2 a	Campbell-721	14.0 b
Setmore	21.7 b	Setmore	14.6 a	Setmore	14.5 b
Jet Star	19.7 b	Jet Star	17.9 b	Jet Star	13.3 a
Springset	20.5 b	Springset	17.8 ab	Bigset	13.8 b
306-1-1	19.1 b	306-1-1	19.5 b	Rampo	15.2 b
307-1-1	20.1 b	307-1-1	18.8 b	Veebrite	13.3 a
915-4-1	15.8 a	915-4-1	14.9 a	Veeset	15.5 b
915-5-1	16.7 ab	915-5-1	15.6 a	Vision	18.3 c
Burpee VF	21.2 b	6718VF	15.7 a	6718VF	11.9 a
Calmart	16.1 ab	Redpak	15.4 a	Redpak	11.8 a
Caravelle	23.5 b	Royal Flush	16.2 a	Royal Flush	14.2 b
Florida MH-1	15.9 ab	Ace 55 VF	16.6 a	Ace 55 VF	17.9 c
New Yorker	21.8 b	Prime Beefsteak	15.4 a	OCNF	13.5 ab
Packmore	16.7 ab	OFHF	16.5 a	PSX 17573	14.8 b
Walter	10.7 a	33 HF	19.9 b	PSX 17673	13.2 a
301-1-1	19.3 b	W2HF	21.1 b	Hybrid 9	14.2 b
301-2-1	19.0 b	6343VF	14.8 a	Hybrid 15	13.6 b
302-2-1	18.8 b	Hybrid 2	16.9 a	Hybrod 16	15.4 b
304-1-1	19.4 b	Hybrid 4	13.2 a		
304-2-1	17.4 ab				
915-9-1	18.0 ab				
915-10-11	15.8 a				
915-11-1	17.8 ab				
Mean ± SD[2]	18.0±.17		16.5±3.25		14.0±2.49

[1] Values within columns followed by the same letter are not significantly different at the 0.05 level.
[2] Mean of 72, 80 and 57 determinations, respectively.

difference in ascorbic acid content was evaluated by Duncan's Multiple Range test. The results of the statistical analysis are included in Table 2. It was found that Campbell-1327, 915-4-1 and Campbell 721 were significantly lower than other cultivars, while Jet Star, 307-1-1, and 306-1-1 were considerably higher in ascorbic acid content than other cultivars in 1973 and 1974 seasons (Table 2). In the 1975 season, Vision and Ace 55 VF were significantly higher in ascorbic acid content than other cultivars, while Campbell-1327, Redpak, 6718VF, and PSX 17673 were significantly lower in ascorbic acid content than other cultivars.

Maclinn and Fellers (1938), and Matthews et al. (1973) have reported that they observed significant variations in ascorbic acid content among varieties. Maclinn and Fellers (1938) found a variation from 15 to 22 mg/100 g of different varieties grown side by side on the same soil. The results obtained from this study are in agreement with the findings of earlier workers.

Yearly variation in the ascorbic acid content of the 9 standard cultivars was studied by analysis of variance, and the results indicated that there was no significant variation in ascorbic acid content between 1973 and 1974 seasons.

The ascorbic acid content in vine ripened tomatoes and in breaker ripened tomatoes was studied in 1973 and 1974 seasons, and the results are summarized in Table 3. The ascorbic acid content was significantly higher in the breaker ripened tomatoes than in the vine ripened tomatoes, and this

Table 3. Ascorbic acid content of tomatoes - Comparison of vine ripened and breaker ripened tomatoes in 1973 and 1974.

Cultivars	Harvested on Aug. 14, 1973		Harvested on Aug. 30, 1974	
	Vine ripened	Breaker ripened	Vine ripened	Breaker ripened
	mg/100 g			
Setmore	21.7	23.9	15.2	19.9
Campbell-1327	12.6	14.4	13.9	15.9
Jet Star	19.7	19.8	19.0	20.9
Springset	20.5	23.4	19.5	21.6
Campbell-721	15.3	15.0	17.6	16.8
306-1-1	19.1	17.7	19.7	19.0
915-4-1	15.8	17.5	15.3	20.8
915-5-1	16.7	15.7	14.7	19.1
307-1-1	20.1	24.2	19.2	20.7
Mean*	17.9	19.1	17.1	19.4
Significance		5%		1%

* Number of samples each year: 36.

trend was consistent in both seasons (Table 3).

Hamner et al. (1945) stored green mature tomatoes at 65, 70, 75, 80, and 90°F analyzing the ripened fruit at the end of 1, 2, and 3 weeks. They found 2 weeks' storage at the 3 lower temperatures did not appreciably affect the ascorbic acid content. Similar results were reported by Craft and Heinze (1954). However, Pantos and Markakis (1973) stated that tomatoes of 2 cultivars which were harvested and ripened at 55, 60, 65, and 70°F contained one-fourth to one-third less ascorbic acid than when ripened on the vine. Scott and Kramer (1949) also reported loss of ascorbic acid during storage of green-mature tomatoes at 70°F. The environmental differences affecting vine ripened tomatoes and breaker ripened tomatoes are mainly light intensity and temperature. Somers et al. (1948) reported that high temperature and CO_2 affect the accumulation of ascorbic acid in plants. Although light is not essential for ascorbic acid synthesis (Reid, 1941; Mapson et al., 1949), variation in light intensity and temperature (Harris and Loesecke, 1973) may change the rate of precursors production without affecting their conversion to ascorbic acid. Bisogni and Armbruster (1976) indicated that depending upon harvest time and cultivar, breaker ripened tomatoes could have equal amounts or only 41% of the reduced ascorbic acid content in vine ripened tomatoes. It appeared that variety and harvest time should be considered together, when ascorbic acid contents in vine ripened and breaker ripened tomatoes were compared.

In 1974 and 1975 the relationship between harvest time and ascorbic acid content was determined. In 1974 representative samples were harvested on August 22, 30 and September 10 and in 1975 August 13, 20 and 27, representing early, middle and late season.

The results indicated that the ascorbic acid content in the early harvested tomatoes was significantly lower than that of the mid or late season harvested tomatoes (Table 4). In 1974 the difference in the ascorbic acid content between mid season and late season was not significant but in 1975 the late season harvest was significantly higher.

Twomey and Ridge (1970) studied the ascorbic acid content of English early tomatoes harvested in the spring and early summer. They found that the ascorbic acid content increased from 12.3 mg/100 g in May to 22.1 mg/100 g in July. Brown and Maser (1941), Somers et al. (1950), and Masui et al. (1953) indicated that light intensity and temperature (Hamner and Maynard, 1942) affected the ascorbic acid content in tomatoes. It appears that high ascorbic acid content in the mid and the late season may be partially due to an increase in sunlight falling on fruits and higher temperatures.

Ethephon has been used for uniform ripening of tomatoes for once-over mehcanical harvesting or for early ripening of fresh market fruits. The effect of ethephon treatment on the ascorbic acid content of tomatoes for the 1973 and 1974 seasons is given in Table 5.

No significant dose effect was observed in the two years.

Table 4. Ascorbic acid content of vine ripened tomatoes - Effect of harvest time in 1974 and 1975.

Cultivars	Harvest Date (1974) Aug. 22	Aug. 30	Sept. 10	Cultivars	Harvest Date (1975) Aug. 13	Aug. 20	Aug. 27
			mg/100 g				
Campbell-1327	11.0	14.5	13.9	Campbell-1327	11.1	10.4	12.8
Campbell-721	14.3	16.6	17.6	Campbell-721	12.6	13.0	16.5
Setmore	12.9	15.7	15.2	Setmore	12.7	12.4	18.4
Jet Star	14.7	19.9	19.0	Jet Star	11.6	12.2	16.1
Springset	16.5	17.5	19.5	Royal Flush	13.2	12.6	16.9
306-1-1	18.9	19.8	19.7	Bigset	12.2	12.3	16.8
307-1-1	17.3	19.9	19.2	Redpak	9.6	10.7	15.1
915-4-1	14.1	15.3	15.3	Rampo	13.3	15.0	17.3
915-5-1	15.1	17.1	14.7	Veebrite	12.2	13.4	14.3
				Veeset	15.0	15.0	16.6
				Vision	16.8	17.7	20.3
				Hybrid 9	13.9	13.0	15.5
				Hybrid 15	12.1	13.3	15.6
				Hybrid 16	13.5	14.7	17.9
				6718 VF	11.8	11.0	12.8
				PSX 17573	12.7	12.9	18.8
				PSX 17673	11.6	11.4	16.5
				OCNF	11.8	15.3	13.3
Mean ± DS	15.0±2.96	17.4±3.20	17.1±3.33		12.6±1.63	13.1±1.95	16.2±2.20
Duncan's Multiple Range test at 1% :	15.0, 17.1, 17.4				12.6, 13.1, 16.2		

Table 5. Effect of ethephon treatment - Ascorbic acid content in tomatoes.

Ethephon treatment	Year	
	1973	1974
Control	13.0	14.4
0.375 lb/acre	15.5	14.7
0.70 lb/acre	17.1	13.3
Significance	N.S.	N.S.

In 1973 the ethephon treated tomatoes were slightly higher in ascorbic acid than the control. However, no significant effect was detected by analysis of variance, due to large error term.

Jones and Nelson (1930) studied the effect of ethylene treatment of the green tomatoes on the ascorbic acid content of ethylene-ripened tomatoes. They found no significant changes in the ascorbic acid potency in all green fruits tested. Based on these observations, it can be concluded that ethephon treatment of the green fruits does not significantly change ascorbic acid content of tomatoes.

The relationships between the ascorbic acid content and other components of tomatoes (organic and mineral components) were evaluated by the multiple linear regression, and the results are summarized in Tables 6 and 7. The ascorbic acid content had a negative relationship with pH and a positive

Table 6. Multiple linear regression equation between ascorbic acid and organic components of tomatoes.

No. of cases	Variable	Regression Coefficients	Beta Weight	Significance
	Constant	33.92	0.00	0.2 %
80	pH	-6.18	-0.26	1.5 %
80	Tot. Solids	1.34	0.35	0.1 %

Ascorbic acid (mg/100 g) = -6.18(pH)+1.34(Tot. solids)+33.92

Standard error of estimate = 3.00

Multiple Correlation Coefficient = 0.411 (Sig. at 0.1% level)

Table 7. Multiple linear regression equation between ascorbic acid and minerals of tomatoes.

No. of cases	Variable	Regression Coefficients	Beta Weight	Significance
	Constant	25.67	0.00	0.05 %
80	Potassium	-4.18	-0.57	0.05 %
80	Magnesium	28.24	0.26	3.7 %

Ascorbic acid (mg/100 g) = -4.18 (K) + 28.24 (mg) + 25.67

Standard error of estimate = 2.90

Multiple correlation coefficient = 0.473 (Sig. at 0.05% level).

relationship with total solids. The calculated multiple correlation coefficient was 0.411 with a high significance (0.1% level). The beta weight indicated that total solids influenced ascorbic acid content more than pH did.

Yarbrough and Satterfield (1937) found no correlation between total acidity and ascorbic acid content. Cultrera (1935) found no definite relationship between acidity, reducing sugars, dry weight, and ascorbic acid content. A part of the results reported by Cultrera (1935) (correlation between dry weight and ascorbic acid) was not in agreement with the results of this study. The fruits with high total solids have more precursors of ascorbic acid (the simple correlation between total solids and soluble solids was 0.69, and total solids and reducing sugars was 0.68, respectively). Therefore, the fruits with high total solids could have higher ascorbic acid content.

The relationship between ascorbic acid content and mineral composition was evaluated. Among the 11 minerals tested, only potassium and magnesium content could be correlated to the ascorbic acid content. It had a negative correlation with the potassium content and a positive relationship with the magnesium content. The multiple correlation coefficient was 0.473 with very high significance (0.05%). Judging from the beta weights, the ascorbic acid content was affected more by the potassium content than by the magnesium content.

Carotene Content in Tomatoes

The carotene content in tomato fruits was studied in the 1973, 1974, and 1975 seasons. The carotene content of the cultivars studied are summarized in Table 8.

It was found that the carotene content varied significantly between cultivars. Duncan's Multiple Range test was employed to compare the carotene content of different cultivars. In the 1973 season, Florida MH-1, Jet Star, 301-1-1, 304-2-1, and Springset had the higher carotene content, while 915-4-1, 915-9-1, 915-5-1, 915-10-1, and Campbell-721 contained less carotene than the other cultivars. In the 1974 season, Springset, Jet Star, 6718 VF, and Setmore had the higher carotene content and Hybrid 2, Royal Flush, 307-1-1, and Hybrid 4 the less carotene content than the other cultivars. In the 1975 season, Veeset, Vision, and Jet Star contained significantly more carotene and Rampo, Royal Flush, and Redpak less carotene than other cultivars (Table 8).

Early researchers (Peragallo, 1936; Shivrina, 1937) indicated that vitamin A potency varied markedly with tomato variety. Hoffman et al. (1938) reported that the total pigment content of 50 varieties of mature tomato fruits varied from 1.8 to 97.0 µg/g, while Bohart (1940), in studies on the composition of 12 tomato varieties, recorded a range of values from 72 to 140 µg/g with an average of 104 µg lycopene/g fruit. Goodwin (1952) summarized the results of many workers with the limits of total carotene content a range from 1 to

Table 8. Carotene content - Vine ripened tomatoes.

1973		1974		1975	
Cultivars	mg/100 g	Cultivars	mg/100 g	Cultivars	mg/100 g
Campbell-1327	0.66 ab[1]	Campbell-1327	0.80 ab	Campbell-1327	0.81 ab
Campbell-721	0.55 a	Campbell-721	0.76 a	Campbell-721	0.66 a
Setmore	0.66 ab	Setmore	0.85 b	Setmore	0.76 ab
Jet Star	0.74 b	Jet Star	0.92 b	Jet Star	0.85 b
Springset	0.77 b	Springset	0.95 b	Bigset	0.81 ab
306-1-1	0.63 ab	306-1-1	0.78 ab	Rampo	0.64 a
307-1-1	0.56 a	307-1-1	0.66 a	Veebrite	0.84 b
915-4-1	0.49 a	915-4-1	0.77 ab	Veeset	0.89 b
915-5-1	0.53 a	915-5-1	0.68 a	Vision	0.87 b
Burpee VF	0.65 ab	6718 VF	0.86 b	6718 VF	0.77 ab
Calmart	0.59 ab	Redpak	0.72 a	Redpak	0.65 a
Caravelle	0.72 b	Royal Flush	0.64 a	Royal Flush	0.65 a
Florida MH-1	0.80 b	Ace 55 VF	0.77 ab	OCNF	0.71 ab
New Yorker	0.68 ab	Prime Beefsteak	0.77 ab	PSX 17573	0.77 ab
Packmore	0.60 ab	OFHF	0.67 a	PSX 17673	0.77 ab
Walter	0.55 a	33 HF	0.67 a	Hybrid 9	0.78 ab
301-1-1	0.75 b	W2HF	0.73 a	Hybrid 15	0.67 a
301-2-1	0.68 ab	6343 VF	0.84 b	Hybrid 16	0.74 ab
302-2-1	0.58 a	Hybrid 2	0.64 a		
304-1-1	0.68 ab	Hybrid 4	0.67 a		
304-2-1	0.74 b				
915-9-1	0.50 a				
915-10-1	0.54 a				
915-11-1	0.55 a				
Mean ± SD[2]	0.61±.13		0.76±.13		0.76±.13

[1] Values within columns followed by the same letter are not significantly different at the 0.05 level.

[2] Mean of 72, 80 and 54 determinations respectively.

to 191 µg/g fresh weight. The average carotene contents of tomatoes studied in 1973, 1974, and 1975 were 0.61, 0.76, and 0.76 mg/100 g, respectively.

The yearly variation in the carotene content of the 9 standard cultivars between 1973 and 1974 seasons was evaluated by analysis of variance. It was found that the total carotenoids content changed significantly with season, while the carotene content did not. This might indicate that the total carotenoids content, mostly lycopene, was mainly affected by the environmental factors, such as light intensity and temperature. McCollum (1954) demonstrated that lycopene and carotene were increased in ripe fruit by illumination at any stage. Shewfelt and Holpin (1967) indicated that the light intensity received influenced the rate of color development of picked tomatoes.

The carotene content of tomatoes harvested at breaker ripe stage and ripened was not significantly different from that of the vine ripened tomatoes in either year (Table 9). Morgan and Smith (1928) reported that ethylene or air ripened fruits were equivalent to vine ripened fruits in vitamin A potency. Sayre et al. (1953) and Matthews et al. (1973) showed that tomatoes picked at either breaker or pink stage and ripened did not differ significantly in beta-carotene content from tomatoes picked at the ripe stage. However, Sadana and Ahmad (1948) and Jones and Nelson (1930) reported that vine ripened fruits were more potent sources of vitamin A than fruits detached while partially green and ripened in air or ethylene.

Table 9. Carotene content of tomatoes - Comparison of vine ripened and breaker ripened tomatoes.

Cultivars	1973		1974	
	Vine ripened	Breaker ripened	Vine ripened	Breaker ripened
	mg/100 g			
Setmore	0.66	0.66	1.06	1.09
Campbell-1327	0.66	0.80	1.04	1.06
Jet Star	0.74	0.72	1.15	1.14
Springset	0.77	0.58	1.14	0.93
Campbell-721	0.55	0.64	0.93	1.03
306-1-1	0.63	0.64	0.98	0.94
915-4-1	0.49	0.50	0.93	0.84
915-5-1	0.53	0.40	0.78	0.82
307-1-1	0.56	0.59	0.88	0.89
Mean*	0.62	0.61	0.99	0.97
Significance	N.S.		N.S.	

* Number of samples each year: 36.

Changes in the carotene content of tomatoes with harvest time were studied in 1974 and 1975 seasons. It was found that there was no significant difference in carotene content of tomatoes harvested on August 22 and August 30, but it was significantly higher on September 10 in 1974 (Table 10). In 1975, there was significant difference only between tomatoes harvested on Aug. 13 and Aug. 27.

The marked effect of the environmental temperature upon carotenogenesis in ripening tomatoes was noted by Vogele (1973), Rosa (1926), and MacGillivray (1934). They indicated that fruits stored at temperatures lower than 20°C and higher than 37°C showed little lycopene formation. They stated that 24°C was the optimum temperature for lycopene formation. Although not essential for carotenogenesis in normal tomatoes, light was claimed to have a stimulatory effect. However, the thermal effect is quantitatively of greater importance than the light effect (Edwards and Reuter, 1965). The significant increase in carotene content of tomatoes harvested on September 10, 1974 and August 27, 1975 could be due to optimum environmental factors around the harvest time.

Tomato fruits, treated with ethephon one week before harvesting, were subjected to carotene analysis to see whether ethephon treatment affected the carotene content. The study was conducted in the 1973 and 1974 seasons, and the results are contained in Table 11. It was found that there is no significant effect of ethephon treatment on the carotene content in either year. In the case of total carotenoids,

Table 10. Carotene content of vine ripened tomatoes - Effect of harvest time in 1974 and 1975.

Cultivars	Harvest date (1974)			Cultivars	Harvest date (1975)		
	Aug. 22	Aug. 30	Sept. 10		Aug. 13	Aug. 20	Aug. 27
	mg/100 g						
Campbell-1327	0.67	0.70	1.04	Campbell-1327	1.05	0.55	0.82
Campbell-721	0.65	0.71	0.93	Campbell-721	0.62	0.66	0.71
Setmore	0.74	0.75	1.06	Setmore	0.79	0.65	0.83
Jet Star	0.79	0.82	1.15	Jet Star	0.90	0.81	0.85
Springset	0.88	0.85	1.14	Bigset	0.83	0.66	0.95
306-1-1	0.71	0.63	0.98	Rampo	0.56	0.67	0.70
307-1-1	0.54	0.55	0.88	Veebrite	0.94	0.92	0.64
915-4-1	0.69	0.67	0.93	Veeset	0.92	0.87	0.89
915-5-1	0.67	0.60	0.78	Vision	0.92	0.78	0.90
				6718 VF	0.89	0.75	0.67
				Redpak	0.70	0.65	0.56
				Royal Flush	0.67	0.63	0.65
				OCNF	0.67	0.78	0.70
				PSX 17573	0.80	0.77	0.75
				PSX 17673	0.77	0.65	0.75
				Hybrid 9	0.74	0.72	0.88
				Hybrid 15	0.73	0.63	0.64
				Hybrid 16	0.97	0.59	0.68
Mean ± SD	0.70±.13	0.70±.13	0.99±.17		0.80±.14	0.71±.12	0.75±.13
Duncan's Multiple Range test at 5% :	0.70,	0.70,	0.99		0.71,	0.75,	0.80

Table 11. Effect of ethephon treatment on carotene content of tomatoes.

Ethephon treatment	1973		1974	
	Total carotenoids	Carotene	Total carotenoids	Carotene
	mg/100 g			
Control	5.0 a[1]	0.87 a	7.75 a	1.08 a
0.375 lb/acre	6.0 b	0.99 a	7.55 a	1.17 a
0.750 lb/acre	6.3 b	1.04 a	7.43 a	1.01 a

[1] Means within columns followed by the same letter are not significantly different at the 0.05 level.

the results were not conclusive. The control tomatoes had a significantly lower total carotenoids content than the treated tomatoes in the 1973 season, while no considerable differences were observed in total carotenoids content between the control and ethephon treated tomatoes in the 1974 season.

Morgan and Smith (1928) reported that ethylene - ripened fruits were equivalent to vine ripened fruits in vitamin A potency. The results of Salunkhe et al. (1971) indicated no significant difference in color between the control fruits and those treated with 1000 ppm ethephon. Based on the experimental results, it appears that ethephon treatment a week before harvest does not adversely affect carotene content of the treated tomatoes.

The relationships between carotene and pH, total acidity, soluble solids, reducing sugar, total carotenoids, ascorbic

acid, and total solids were evaluated by multiple linear regression. It was observed that there was no significant relationship between the carotene content and the above mentioned components, including total carotenoids.

When the relationships between carotene content and K, P, Na, Ca, Mg, Fe, and Cu were tested, significant correlations between carotene and Cu, P, Na, and Fe was obtained. The multiple linear regression equation and its statistics are shown in Table 12.

Table 12. Multiple linear regression between carotene and minerals of tomatoes.

No. of Cases	Variable	Regression Coefficients	Beta Weight	Significance
	Constant	0.710	0.00	0.05 %
80	Cu	-0.029	-0.30	2.6 %
80	P	-0.531	-0.34	0.6 %
80	Na	0.00042	0.36	1.2 %
80	Fe	0.0226	0.28	2.4 %

Carotene (mg/100 g)= -0.029(Cu) - 0.531(P) + 0.00042(Na) + 0.0226(Fe) + 0.710.

Standard error of estimate = 0.117

Multiple correlation coefficient = 0.454 (Sig. at 0.2% level).

Positive relationships were observed between carotene content and Na and Fe content of tomatoes, while negative correlations were found between carotene content and P and Cu

content of tomatoes. The multiple correlation coefficient, 0.454, was highly significant ($P<0.002$).

The relationships between the total carotenoids content and organic components, and the mineral content were evaluated in the same manner. Only potassium content had a significant correlation with total carotenoids content.

Total carotenoids (mg/100 g) = 0.222 (K) + 3.266

The regression and the correlation coefficient were significant at 0.6% level. This finding was in agreement with the report by Trudel and Ozbeen (1971). They indicated that most of the carotenoids, especially lycopene, was increased with increasing K concentration.

Thiamin and Riboflavin in Tomatoes

The thiamin and riboflavin contents of tomatoes are low in terms of human need, in contrast to ascorbic acid and carotene in tomatoes. The literature available on thiamin and riboflavin in tomatoes is limited. Thiamin and riboflavin contents of tomato cultivars studied in 1973 and 1974 are shown in Table 13.

The average thiamin and riboflavin contents of all cultivars studied were 0.050 and 0.053 mg/100 g in 1973 and 0.051 and 0.046 mg/100 g in 1974, respectively. Bedford et al. (1972) found thiamin and riboflavin contents of 42 tomato cultivars in 1972 were 0.048 ± 0.008 and 0.048 ± 0.015 mg/100 g, respectively. These values were in agreement with the reports

Table 13. Thiamin and riboflavin content of vine ripened tomatoes, 1973 and 1974.

1973			1974		
Cultivars	Thiamin	Riboflavin	Cultivars	Thiamin	Riboflavin
	mg/100 g				
Campbell-1327	0.068 ab[1]	0.043 a	Campbell-1327	0.051 a	0.040 a
Campbell-721	0.061 ab	0.060 ab	Campbell-721	0.060 b	0.045 ab
Setmore	0.053 a	0.036 a	Setmore	0.051 ab	0.046 ab
Jet Star	0.050 a	0.052 ab	Jet Star	0.046 a	0.044 ab
Springset	0.066 ab	0.053 ab	Springset	0.051 a	0.042 ab
306-1-1	0.065 ab	0.058 ab	306-1-1	0.063 b	0.063 b
307-1-1	0.068 ab	0.048 ab	307-1-1	0.057 b	0.047 ab
914-4-1	0.050 a	0.058 ab	915-4-1	0.047 a	0.055 b
915-5-1	0.048 a	0.038 a	915-5-1	0.042 a	0.043 ab
Burpee VF	0.078 b	0.051 ab	6718 VF	0.045 a	0.043 ab
Calmart	0.068 ab	0.050 ab	Redpak	0.046 a	0.046 ab
Caravelle	0.050 a	0.051 ab	Royal Flush	0.056 b	0.045 ab
Florida MH-1	0.060 ab	0.046 ab	Ace 55 VF	0.058 b	0.049 ab
New Yorker	0.056 a	0.044 a	Prime Beefsteak	0.060 b	0.047 ab
Packmore	0.066 ab	0.052 ab	OFHF	0.057 b	0.048 ab
Walter	0.057 a	0.051 ab	33 HF	0.054 ab	0.043 ab
301-1-1	0.057 a	0.042 a	W2HF	0.043 a	0.045 ab
301-2-1	0.055 a	0.075 b	6343 VF	0.045 a	0.042 ab
302-2-1	0.051 a	0.070 b	Hybrid 2	0.046 a	0.038 a
304-1-1	0.059 a	0.067 ab	Hybrid 4	0.040 a	0.049 ab
304-2-1	0.054 a	0.062 ab			
915-9-1	0.057 a	0.078 b			
915-10-1	0.054 a	0.044 a			
915-11-1	0.050 a	0.050 ab			
Mean ± SD[2]	0.050±.012	0.053±.019		0.051±.009	0.046±.007

[1] Values within colums followed by the same letter are not significantly different at the 0.05 level.
[2] Mean of 72 determinations in 1973 and 80 in 1974.

by earlier researchers (Hodson, 1940; Lanford et al., 1941; Secomska et al., 1971; Bedford et al., 1972). Even though the average values of thiamin and riboflavin contents varied slightly from year to year, this variation was not stastically significant.

There were significant differences in both thiamin and riboflavin contents between cultivars. However, the degree of difference was much less than that obtained for ascorbic acid and carotene contents and of little effect in terms of human nutrition based on percentage of the RDA supplied. The results obtained from the 2 years of this study were in disagreement with the results of Lefebure and Leclerc (1973) who reported that variety had no effect upon the thiamin and riboflavin contents of tomatoes.

The thiamin content in vine ripened tomatoes was significantly higher, averaging 18% more, than in breaker ripened tomatoes in the 1973 season ($p<0.006$). However, in the 1974 season, breaker ripened tomatoes had significantly higher thaimin content, averaging 25% more, than vine ripened tomatoes (Table 14). Because of these conflicting results, it was not possible to evaluate the effect of ripening method upon the thiamin content of tomatoes.

Johns and Nelson (1930) observed that mature, green, full-grown tomatoes were equivalent to immature ones in thiamin and contained less than vine ripened fruits. But they did not study the difference in the thiamin content between the vine ripened and artificially ripened tomatoes.

Table 14. Thiamin content of tomatoes - Comparison of vine ripened and breaker ripened tomatoes.

Cultivars	1973		1974	
	Vine ripened	Breaker ripened	Vine ripened	Breaker ripened
	mg/100 g			
Setmore	0.053	0.042	0.048	0.051
Campbell-1327	0.068	0.045	0.039	0.055
Jet Star	0.050	0.046	0.042	0.050
Springset	0.066	0.046	0.047	0.061
Campbell-721	0.061	0.057	0.053	0.058
306-1-1	0.065	0.067	0.057	0.064
915-4-1	0.050	0.041	0.034	0.051
915-5-1	0.048	0.046	0.033	0.046
307-1-1	0.068	0.063	0.045	0.060
Mean*	0.059	0.050	0.044	0.055
Significance	0.6 %			0.05 %

* Number of samples each year: 36.

In the 1973 season, the riboflavin content in vine ripened tomatoes was very significantly higher than in breaker ripened tomatoes ($p<0.0005$). However, in 1974 no significant difference in the riboflavin content was obtained between the vine ripened tomatoes and breaker ripened tomatoes (Table 15). Judging from the results obtained, it appears that more work is required to evaluate the effect of ripening upon the riboflavin content of tomatoes.

The thiamin and riboflavin contents in the vine ripened tomatoes decreased considerably as the season progressed (Table 16). The thiamin contents in tomatoes harvested at different times were significantly different from each other. Although the thiamin content in tomatoes decreased between the August 30 and September 10 harvests, the rate of decrease was less than that between the August 22 and August 30 harvests. The riboflavin content in the vine ripened tomatoes harvested on August 22 was significantly higher than those harvested on August 30 and September 10 (Table 16). There was no significant difference in the riboflavin content between tomatoes harvested on August 30 and September 10.

Although there is a lack of literature available on this subject, the results obtained from this study indicated that the thiamin and riboflavin content in vine ripened tomatoes decreased considerably as the season progressed.

Ethephon has been used for uniform ripening of tomatoes, but the effect of the ethephon treatment on the thiamin and

Table 15. Riboflavin content of tomatoes - Comparison of vine ripened and breaker ripened tomatoes.

Cultivars	1973		1974	
	Vine ripened	Breaker ripened	Vine ripened	Breaker ripened
	mg/100 g			
Setmore	0.036	0.032	0.039	0.040
Campbell-1327	0.043	0.031	0.030	0.037
Jet Star	0.052	0.030	0.031	0.033
Springset	0.053	0.031	0.033	0.040
Campbell-721	0.060	0.034	0.038	0.043
306-1-1	0.058	0.033	0.048	0.046
915-4-1	0.058	0.043	0.043	0.037
915-5-1	0.038	0.023	0.032	0.033
307-1-1	0.048	0.029	0.041	0.041
Mean*	0.050	0.033	0.037	0.039
Significance	0.05 %		N.S.	

* Number of samples each year: 36.

Table 16. Thiamin and riboflavin content of vine ripened tomatoes - Effect of harvest time in 1974.

Cultivars	Aug. 22		Aug. 30		Sept. 10	
	Thiamin	Riboflavin	Thiamin	Riboflavin	Thiamin	Riboflavin
	mg/100 g					
Setmore	0.058	0.060	0.048	0.039	0.048	0.039
Campbell-1327	0.059	0.053	0.047	0.038	0.039	0.030
Jet Star	0.050	0.061	0.045	0.039	0.042	0.031
Springset	0.060	0.052	0.047	0.041	0.047	0.033
Campbell-721	0.069	0.056	0.057	0.041	0.053	0.038
306-1-1	0.074	0.090	0.057	0.050	0.057	0.048
915-4-1	0.057	0.071	0.050	0.050	0.034	0.043
915-5-1	0.049	0.057	0.043	0.039	0.033	0.032
307-1-1	0.069	0.061	0.057	0.040	0.045	0.041
Mean*	0.061	0.062	0.050	0.042	0.044	0.037

Duncan's Multiple Range test at 5% level:

Thiamin; 0.061, 0.050, 0.044

Riboflavin; 0.062, 0.042, 0.037

* Number of samples each date: 36.

riboflavin contents has not been studied. It was found that the thiamin and riboflavin contents in tomatoes were not significantly affected by ethephon treatment, and these results were observed in two consecutive years (Table 17).

Table 17. Effect of ethephon treatment on thiamin and riboflavin content of tomatoes.

Ethephon treatment	1973		1974	
	Thiamin	Riboflavin	Thiamin	Riboflavin
	mg/100 g			
Control	0.073	0.028	0.064	0.057
0.375 lb/acre	0.085	0.029	0.065	0.053
0.75 lb/acre	0.085	0.030	0.073	0.048
Significance	N.S.	N.S.	N.S.	N.S.

The relationships between the thiamin content and pH, total acidity, soluble solids, reducing sugars, carotenoids, ascorbic acid, and total solids were evaluated by the multiple linear regression, and the results are shown in Table 18.

The positive relationships were observed between the thiamin content and pH, total acidity, and total solids. The multiple correlation coefficient, 0.453, was highly significant ($p<0.001$). The multiple linear regression equation indicated that the thiamin content increased as pH, total acidity, and total solids contents in tomatoes increased. Judging from beta-weight, pH and total acidity of tomatoes

Table 18. Multiple linear regression equation between thiamin and organic components of tomatoes.

No. of Cases	Variable	Regression Coefficients	Beta Weight	Significance
	Constant	-0.075	0.00	6.9%
80	pH	0.022	0.34	1.9%
80	Total acidity	0.039	0.36	1.5%
80	Total solids	0.002	0.24	3.3%

Thiamin (mg/100 g) = 0.022(pH) + 0.039(T.A.) + 0.002 (T.S.) - 0.075.

Standard error of estimate = 0.0078.

Multiple correlation coefficient = 0.453 (Sig. at 0.1% level).

affected the thiamin content more than total solids did. Since pH and total acidity are closely related to the buffering system of tomatoes, it appears that the buffering property of tomato fruits has a relationship with the thiamin content of tomatoes.

In a similar manner, the relationships between the thiamin content and K, P, Na, Ca, Mg, Fe, and Cu were tested by the multiple linear regression, and the results are contained in Table 19.

Table 19. Multiple linear regression equation between thiamin and minerals in tomatoes.

No. of Cases	Variable	Regression Coefficient	Beta Weight	Significance
	Constant	0.059	0.00	0.05 %
80	Cu	-0.002	-0.27	1.7 %
80	Ca	-0.055	-0.29	1.0 %

Thiamin (mg/100 g) = -0.002(Cu) - 0.055(Ca) + 0.059

Standard error of estimate = 0.0082

Multiple correlation coefficient = 0.345 (Sig. at 0.8% level)

It was found that there were negative correlations between the thiamin content and copper, and calcium contents of tomatoes. The multiple correlation coefficient was 0.345 which was highly significant ($p<0.008$). The multiple linear

regression equation indicated that the thiamin content decreased as copper and calcium contents in tomatoes increased.

The relationships between the riboflavin content and organic components and between the riboflavin content and mineral components of tomatoes were also studied by the multiple linear regression. The components studied were the same as the cases of thiamin. The results obtained are shown in Tables 20 and 21.

There were positive correlations between the riboflavin content and total carotenoids, total acidity, and soluble solids contents of tomatoes. According to beta-weight, soluble solids content was the most important factor which influenced the riboflavin content of tomatoes. The equation

Table 20. Multiple linear regression equation between riboflavin and organic components of tomatoes.

No. of Cases	Variable	Regression Coefficient	Beta Weight	Significance
	Constant	-0.008	0.00	2.5 %
80	Total carotenoids	0.002	0.26	0.4 %
80	Total acidity	0.022	0.23	1.4 %
80	Soluble solids	0.006	0.60	0.05 %

Riboflavin (mg/100 g) = 0.002(tot. carotenoids) + 0.022(T.A.) + 0.006(S.S.) -0.008

Standard error of estimate = 0.0054

Multiple correlation of coefficient = 0.69(sig. at 0.05% level)

Table 21. Multiple linear regression equation between riboflavin and mineral content of tomatoes.

No. of Cases	Variable	Regression Coefficient	Beta Weight	Significance
	Constant	0.049	0.00	0.05 %
80	K	-0.005	-0.28	2.5 %
80	Fe	0.001	0.26	3.3 %

Riboflavin (mg/100 g) = -0.005(K) + 0.001(Fe) + 0.049

Standard error of estimate = 0.0071

Multiple correlation coefficient = 0.29(Sig. at 3.5% level)

indicated that the riboflavin content increased as total carotenoids, total acidity, and soluble solids contents in tomatoes increased (Table 20). The multiple correlation coefficient calculated was very highly significant ($p<0.0005$). Potassium had a negative correlation with the riboflavin content, and iron a positive correlation. The multiple correlation coefficient calculated was 0.29 and significant at 3.5% level (Table 21).

Based on the multiple correlation coefficients and significances of the statistical parameters, it appears that the riboflavin content has a closer relationship with total carotenoids, total acidity, and soluble solids than with K and Fe.

Acidity in Tomatoes

Acidity of tomatoes is important for taste, processing, and quality stability of tomato products. Acidity of tomatoes was studied in 1973, 1974 and 1975 (Table 22).

The average pH and total acidity for all cultivars studied were 4.3 and 0.41 in 1973, 4.2 and 0.43 in 1974, and 4.4 and 0.43 in 1975. When the average pH and total acidity for 9 standard cultivars in 1973 and 1974 were compared, the statistical analysis indicated that the average pH values had no significant difference, while total acidity in 1974 was significantly higher than that in 1973 ($p<0.05$).

There was significant varietal difference in pH and total acidity in all seasons. Springset and Campbell-721 were the popular cultivars which had markedly lower pH than the other cultivars, while Campbell-1327 which is the most popular variety in Michigan, had considerably higher pH than other cultivars in all seasons.

Saywell and Cruess (1932), Lambeth et al. (1964), and Koch (1960) indicated that the acidity of tomatoes varied significantly between the varieties they studied. Bradley (1962) reported that changes in total acidity were attributable to the changes in the citric acid content alone, while Davies (1964) indicated that it was attributed to changes in both citric and malic acid content.

Table 22. Total acidity and pH of vine ripened tomatoes in 1973, 1974, and 1975.

Cultivars	1973		Cultivars	1974		Cultivars	1975	
	pH	T.A.		pH	T.A.		pH	T.A.
		%			%			%
Campbell-1327	4.4	.40	Campbell-1327	4.4	.35	Campbell-1327	4.6	.35
Campbell-721	4.2	.44	Campbell-721	4.1	.52	Campbell-721	4.3	.52
Setmore	4.3	.44	Setmore	4.4	.41	Setmore	4.5	.40
Jet Star	4.4	.33	Jet Star	4.3	.35	Jet Star	4.5	.35
Springset	4.2	.40	Springset	4.2	.40	Bigset	4.4	.45
306-1-1	4.3	.38	306-1-1	4.3	.46	Rampo	4.4	.48
307-1-1	4.4	.36	307-1-1	4.4	.40	Veebrite	4.4	.43
915-4-1	4.4	.35	915-4-1	4.3	.45	Veeset	4.3	.45
915-5-1	4.3	.45	915-5-1	4.2	.43	Vision	4.4	.42
Burpee VF	4.3	.43	6718 VF	4.2	.48	6718 VF	4.4	.44
Calmart	4.4	.34	Redpak	4.2	.48	Redpak	4.4	.43
Caravelle	4.2	.43	Royal Flush	4.2	.42	Royal Flush	4.5	.40
Florida MH-1	4.3	.46	Ace 55 VF	4.5	.40	Ace 55 VF	4.6	.40
New Yorker	4.2	.40	Prime Beefsteak	4.4	.39	OCNF	4.4	.43
Packmore	4.3	.40	OFAF	4.1	.45	PSX 17573	4.5	.41
Walter	4.4	.45	33 HF	4.1	.43	PSX 17673	4.4	.45
301-1-1	4.3	.45	W2HF	4.2	.43	Hybrid 9	4.5	.45
301-2-1	4.3	.43	6343 VF	4.2	.48	Hybrid 15	4.4	.42
302-2-1	4.3	.39	Hybrid 2	4.2	.45	Hybrid 16	4.4	.50
304-1-1	4.3	.44	Hybrid 4	4.2	.42			
304-2-1	4.4	.42						
915-9-1	4.3	.40						
915-10-11	4.4	.33						
915-11-1	4.3	.40						
Mean ± SD	4.3±.10	0.41±.061		4.2±.14	0.43±.078		4.4±.10	.43±.052

CONCLUSION

The purposes of this study were to determine 1) effects of variety, ripening methods, harvesting time, and ethephon treatment on the vitamin composition of tomatoes; and 2) relationships between the vitamin content and other components of tomatoes.

The effect of variety on the ascorbic acid and the carotene contents was highly significant. This significant varietal effect was observed in all three seasons. Although there were some significant differences in the thiamin and riboflavin contents among the cultivars studied, these differences were not as great as those noted with ascorbic acid and carotene.

The ascorbic acid and the carotene contents in breaker ripened tomatoes were at least equal to those in vine ripened tomatoes. The effect of ripening methods on the thiamin and the riboflavin contents was inconsistent.

It was found that the ascorbic acid content in tomatoes harvested in the mid or late season was significantly higher than that in the early season. The carotene content in tomatoes harvested in the late season was also significantly higher than that in tomatoes harvested in either early or mid season. However, it was observed that the thiamin and the riboflavin contents of tomatoes decreased as the season progressed.

Ethephon treatment a week before harvest did not

adversely affect the vitamin composition of treated tomatoes. These results were consistent in both years.

The relationships between the vitamin content and other components of tomatoes were evaluated by the multiple linear regression. The ascorbic acid content had positive correlations with total solids and magnesium content, while it had negative correlations with pH and potassium content. The carotene content did not show any correlation with organic components. But it had significant positive correlations with Na and Fe, and significant negative correlations with Cu and P contents of tomatoes.

There were significant positive correlations between the thiamin content and pH, total acidity, and total solids in tomatoes and negative correlations between the thiamin content and Cu and Ca. Since both pH and total acidity had significant correlations with the thiamin content, it appeared that the buffering property of tomatoes has a relationship with the thiamin content. The riboflavin content had significant positive correlations with total carotenoids, total acidity, soluble solids and Fe, while it had significant negative correlation with potassium.

Computer Simulation of Ascorbic Acid Stability in Canned Tomato Juice

The quality of the processed products may deteriorate during storage. This results in degradation of nutrients, development of off-flavor and off-color, and other quality changes. The deterioration of canned foods is influenced by many factors, including storage temperature, pH, metal catalysts, dissolved oxygen, type of container, light, and some components of foods.

Tomato juice was selected as a model system of acid foods and reduced ascorbic acid was chosen as a quality index to study quality stability of canned acid foods during storage. Since canned acid foods maintain anaerobic condition soon after canning, storage temperature, pH, and metal catalysts were studied as main factors which influenced the degradation of ascorbic acid in the system during storage.

In this study, mathematical models were developed based on kinetics of ascorbic acid degradation. The mathematical models and parameters obtained were used for computer simulation to predict ascorbic acid stability in canned tomato juice under various storage conditions.

Order of Reaction with Respect to Ascorbic Acid

The half-life ($t_{1/2}$) of a reaction is the time required for half of a substance to react (oxidation of reduced ascorbic acid in this case). For a first-order reaction the half-

life is dependent of the initial concentration of the reactant, and this fact is often used to verify a first-order reaction.

Canned tomato juice with two initial ascorbic acid concentrations was stored at 37.8°C for 140 days, and samples were analyzed for ascorbic acid at 20 day intervals. The half-life of ascorbic acid was calculated using the equation: $t_{1/2} = \frac{0.693}{K}$, where K is a rate constant for ascorbic acid destruction. The plot of logarithem of ascorbic acid versus storage time gave straight lines (Fig. 1) which indicated a first-order reaction. The half-lives calculated from rate constants were almost identical (290 days) within reasonable experimental error.

It was found that the initial ascorbic acid concentration obtained from experiment was greater than the one calculated from the intercept of the plot (Fig. 1). This result indicated that the degradation of ascorbic acid in canned tomato juice during the first 20 days did not follow a first-order reaction. Kahn and Martell (1967) and Singh (1974) reported the dependence of ascorbic acid destruction on dissolved oxygen, the rate of ascorbic acid destruction decreased as the concentration of dissolved oxygen reduced. Horner (1933) stated that in canned acid foods oxygen was present in restricted amounts at the time of sealing and disappeared entirely within 2 to 4 weeks of canning. Based on these results reported, it appeared that the destruction of ascorbic acid in canned tomato juice followed a second-

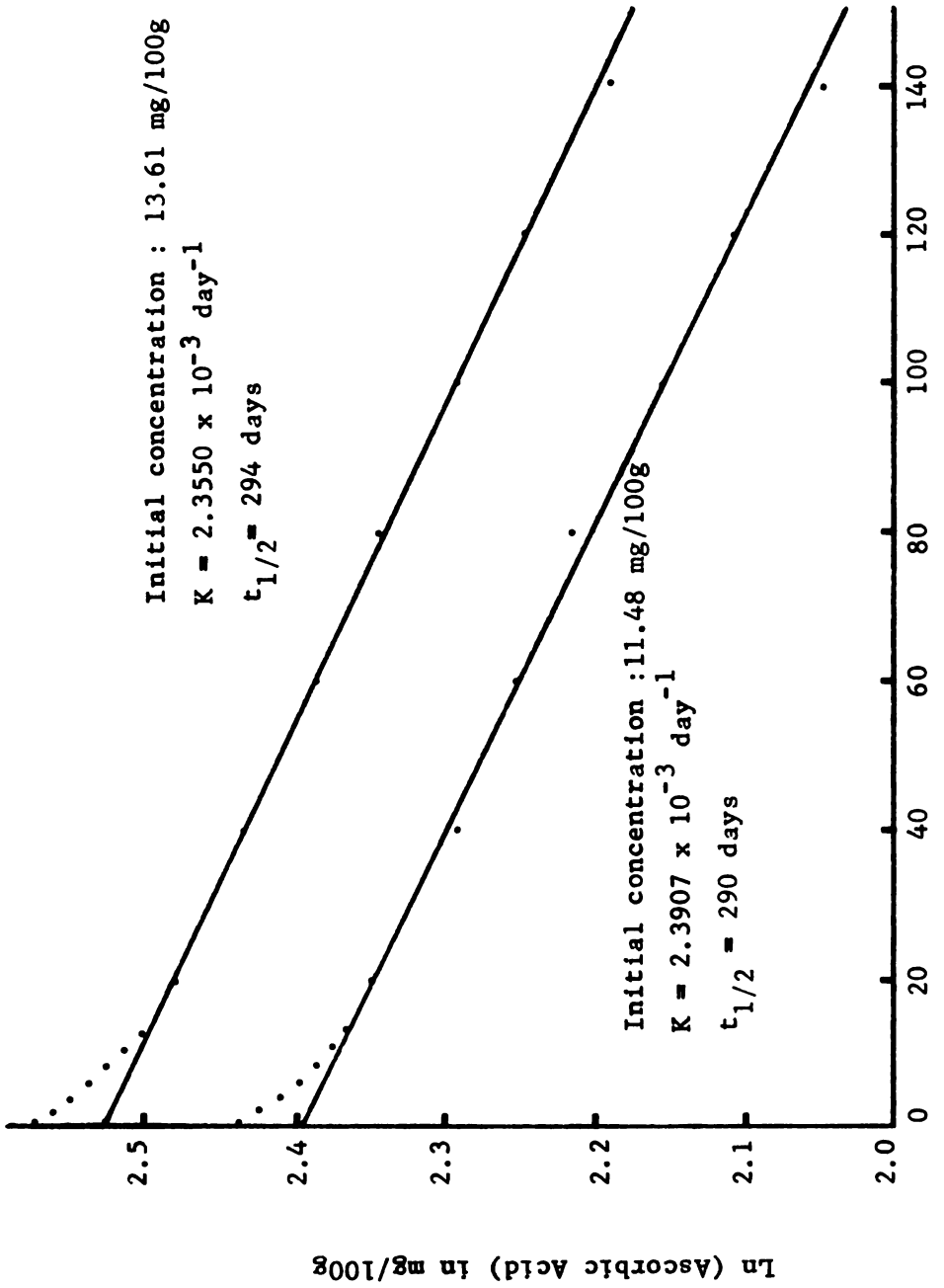


Figure 1.--First-order plots for anaerobic degradation of ascorbic acid in tomato juice.

order reaction for the first 20 days when a small amount of oxygen was available, and then followed a first-order reaction under the anaerobic condition.

Effect of Temperature on Anaerobic Degradation of Ascorbic Acid

Canned tomato juice was stored at 10, 18.3, 29.4, and 37.8°C, and representative samples were taken at 30 day intervals (20 day intervals for the samples held at 37.8°C) for ascorbic acid analysis in order to study the temperature dependence of ascorbic acid destruction. First-order rate constants calculated using the KINFIT program are contained in Table 25, and the Arrhenius plot is shown in Fig. 2.

Table 25. First-order rate constants determined at various storage temperatures (pH = 4.06).

Storage Temperature	Rate Constants ($K \times 10^{-3} day^{-1}$)
10.0 ± 0.8°C	1.4575 ± 0.1510
18.3	1.7366 ± 0.0589
29.4	2.1228 ± 0.0346
37.8	2.4788 ± 0.0682

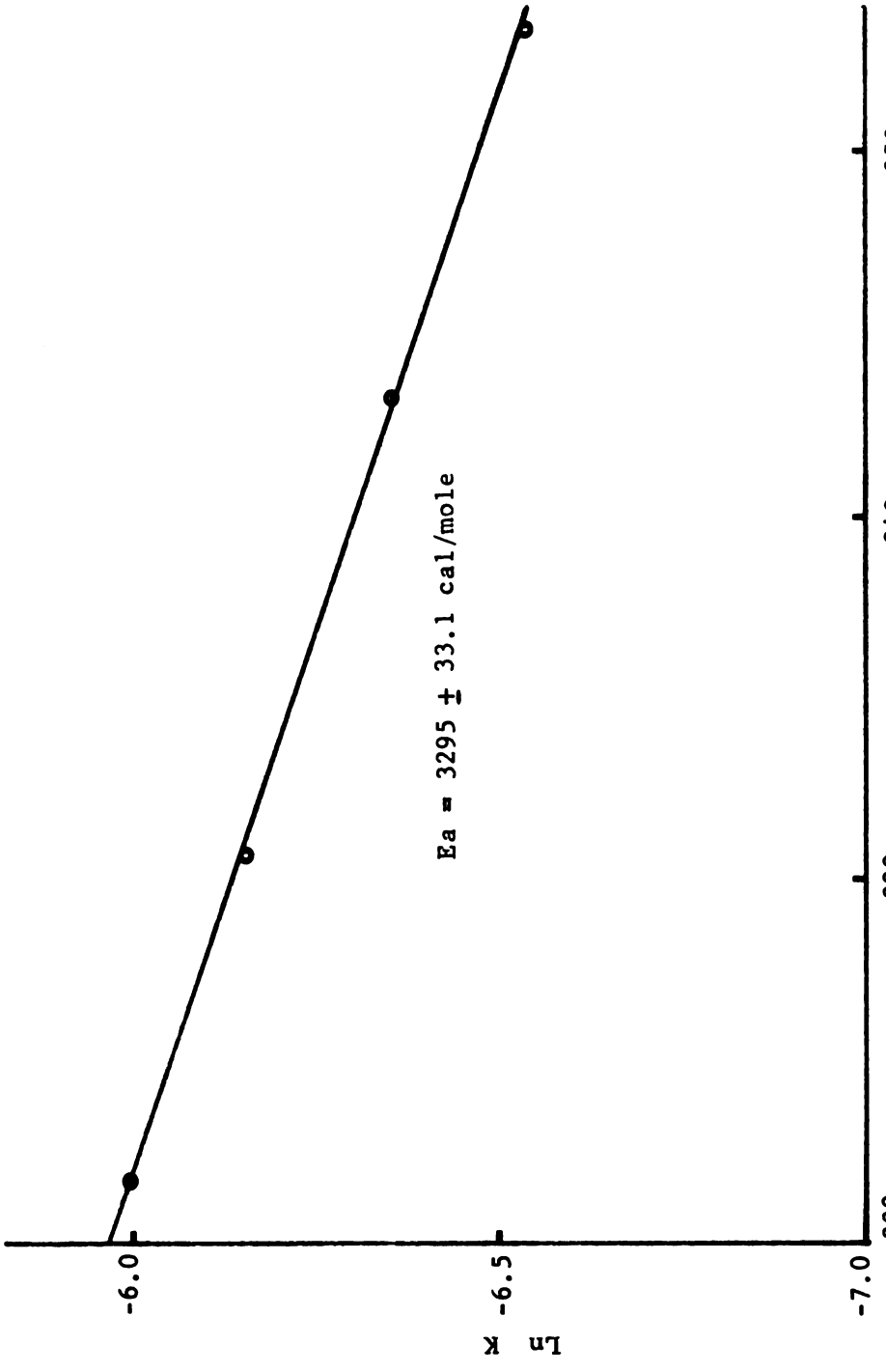


Figure 2.--Arrhenius plot of ascorbic acid destruction in tomato juice (pH= 4.06).

A number of methods are available for quantitatively expressing the effect of temperature on the rate of reaction. Of the methods available, Q_{10} and the Arrhenius equation are often used in biology and related areas. Wanninger (1972) developed a model to specifically predict the stability of ascorbic acid in food products. He found the most acceptable expression to predict the loss of ascorbic acid was the Arrhenius equation. Figure 2 shows the dependence of the rate of ascorbic acid destruction in tomato juice on storage temperature. The estimated activation energy for the anaerobic degradation of ascorbic acid was 3.295 Kcal/mole. There is no reported Ea for the anaerobic degradation of ascorbic acid in food systems. Blaug and Hajratwala (1972) reported an Ea for the aerobic oxidation of ascorbic acid in a pure system (an acetate buffer solution with ionic strength 0.4) would correspond to 10.9 Kcal/mole at pH 4.55.

Pope and Gould (1973) investigated the storage stability of ascorbic acid in canned tomato juice. The rate constants reported were 0.0024/month at 35°F, 0.0112 at 55°F, 0.040 at 68°F, and 0.228 at 88°F. These results indicated that the temperature dependence of the rate constant was much greater than that observed in this study. This might be due to insensitive analytical method and low storage temperatures used for his experiment.

Prediction of Ascorbic Acid Stability in Tomato Juice Based on Temperature Dependence of the Rate Constants

In this model, temperature was the only factor taken into consideration for the prediction of ascorbic acid stability in the stored tomato juice. A mathematical model was developed based on the information that the destruction of ascorbic acid followed a first-order reaction (equation 2) and effect of temperature upon the reaction rate constants could be accounted for by the Arrhenius equation (equation 1).

Arrhenius equation; $K = A\ EXP\ (-Ea/RT)$, or $\log \frac{K_2}{K_1} =$

$$\frac{Ea}{2.303R}\left(\frac{T_2-T_1}{T_2 x T_1}\right)\text{----(1)}$$

where Ea = activation energy (cal/mole)

T = absolute temperature (^oK)

R = 1.987 (cal/^oK-mole)

A = pre-exponential constant ($time^{-1}$)

K_2 = rate constant at temperature T_2

K_1 = rate constant at temperature T_1

The degradation of ascorbic acid can be expressed: $AH_2 \longrightarrow$ product. The rate of this reaction can be expressed: $\frac{d(AH_2)}{dt} = -Kt$. Integration of this equation gives: $C_t = Co/EXP(Kt)$ ----------(2)

where AH_2 = ascorbic acid

C_t = concentration of ascorbic acid at time t

Co = initial concentration of ascorbic acid.

Equation 3 may be used for calculation of % retention at time t and can be derived from equation 2: % retention = EXP(-Kt) x 100 ---------- (3).

A flowchart of the temperature-model is shown in Figure 15 in Appendix. The model calculates the reaction rate constants at the storage temperatures selected using the Arrhenius equation. The calculated rate constants are used for the computation of the ascorbic acid concentration at various storage times. The calculations are repeated within each loop, and the calculated information is printed out.

The history of the ascorbic acid concentration in tomato juice during storage was predicted using this simple computer program. The results of the shelf-life tests and the computer-aided predictions at selected temperatures were compared in Figure 3.

It was found that the results of shelf-life tests were very close to the prediction by the computer program. The difference between the results of the shelf-life tests and those of prediction was in the range of $\pm$ 0 to 2.5% retention with a mean difference of 1.06% retention. These results indicated that the temperature dependence of the rate constants could be accounted for by the Arrhenius equation, and the degradation of ascorbic acid in tomato juice during storage followed a first-order reaction.

It was known in the 1940's that oxidation of ascorbic acid followed a first-order reaction. However, this fact was

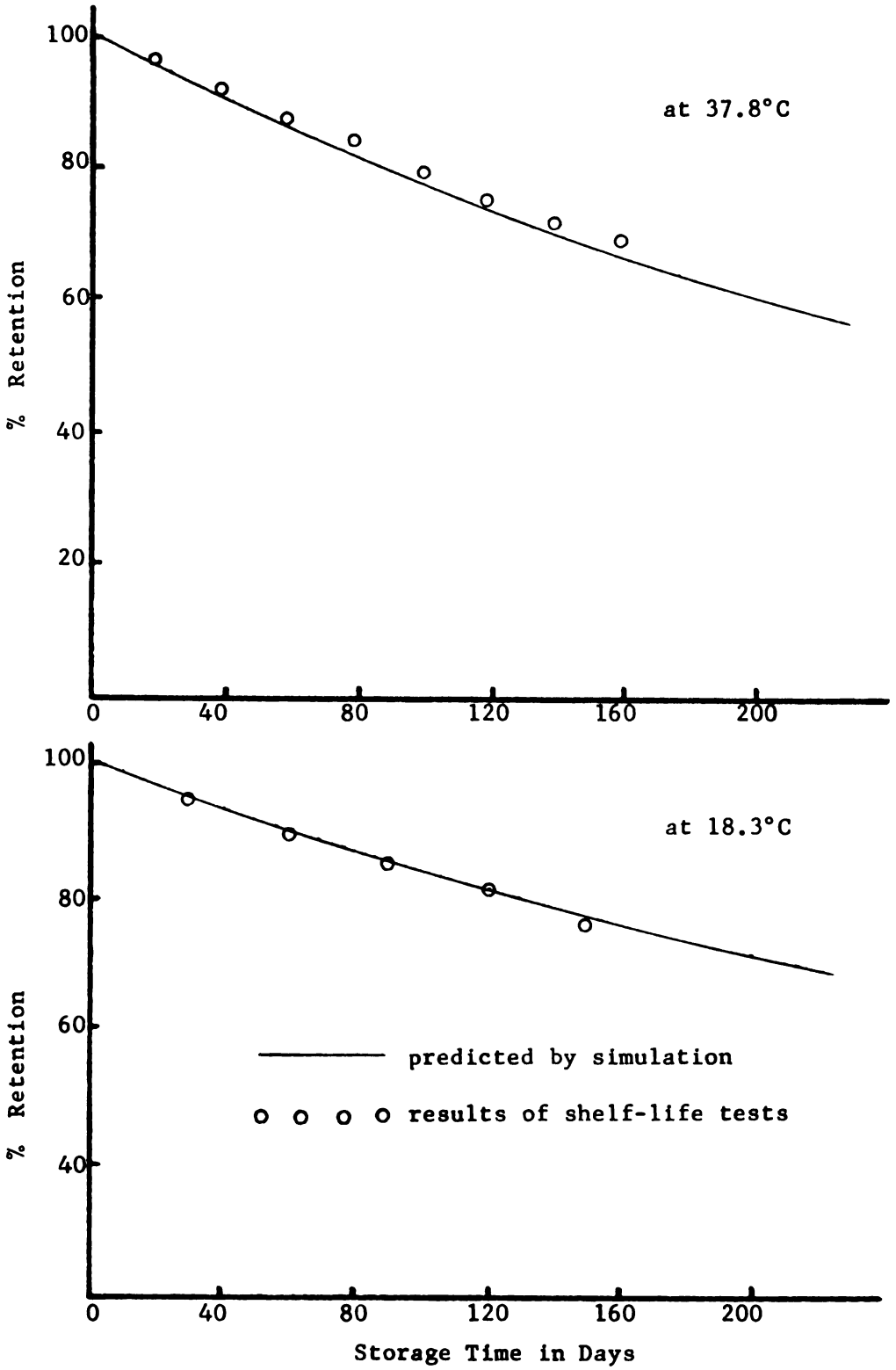


Figure 3. -- Percent retention of ascorbic acid in tomato juice during storage.

not taken into consideration to calculate the retention of ascorbic acid in foods. Cameron (1955) and Siemers (1960) in their review articles concluded that tomato juice held at room temperature would lose 1% of its ascorbic acid per month. This conclusion has been widely quoted and has appeared in consumer oriented magazines and surveys of food processor. In the survey of New Jersey food processors, the Rutgers University Food Science Department (1971) found food processors used the following procedure to determine shelf-life; 12 weeks at 120°F provides acceleration 10:1 over 70°F storage and 18 months at 100°F provides acceleration of 2 to 3:1 over 70°F storage. Pope and Gould (1973) investigated the storage stability of ascorbic acid in tomato juice. They found the loss of ascorbic acid from the anaerobic food system followed a first-order reaction. However, they reported that ascorbic acid concentration decreased at each storage temperature at a constant rate during the nine months storage, and that the rate constant did not fit the Arrhenius equation.

Effect of pH on Anaerobic Degradation of Ascorbic Acid

Calculated amounts of citrate buffer were added to tomato juice to adjust pH of tomato juice to 3.53, 3.78, 4.06, and 4.36 (pH of natural tomato juice was 4.06). The canned tomato juice was stored at 37.8°C and representative samples were analyzed for ascorbic acid at 20 day intervals. The reaction rate constants calculated by the KINFIT program are shown in Table 26.

Table 26. A comparison of the predicted and the experimentally determined rate constants at 37.8°C.

pH	Predicted rate constants	Rate constants from shelf-life tests
3.53	$1.8642 \times 10^{-3} day^{-1}$	$1.8408 \times 10^{-3} day^{-1}$
3.78	2.2742×10^{-3}	2.2793×10^{-3}
4.06	2.4797×10^{-3}	2.4788×10^{-3}
4.36	2.2410×10^{-3}	2.2749×10^{-3}

It was found that the rate constants increased as pH increased until pH 4.06, and then decreased. These results indicated that the overall reaction rate represented a summation of several separate reactions. Finholt (1963) suggested several possible reactions to account for the overall degradation of ascorbic acid:

$AH^- \xrightarrow{k_1}$ product (reaction 1)

$AH_2.AH^- \xrightarrow{k_2}$ product (reaction 2)

$AH_2 \xrightarrow{k_3}$ product (reaction 3)

$AH_2 + H^+ \xrightarrow{k_4}$ product (reaction 4)

$A^= \xrightarrow{k_5}$ product (reaction 5)

$AH_2 + AH^- \xrightarrow{k_6}$ product (reaction 6)

where AH_2 = undissociated ascorbic acid

AH^- = monohydrogen ascorbate ion

$A^=$ = ascorbate ion

$AH_2.AH^-$ = a complex of undissociated ascorbic acid and monohydrogen ascorbate ion.

In an acidic system, $A^{=}$ does not practically exist, and early experimental results indicated that the rate constants actually decreased as H^{+} concentration increased. Therefore, reactions 4 and 5 could be ignored in acid food systems. The formation of a complex of undissociated ascorbic acid and monohydrogen ascorbate ion can be expressed:

$AH_2 + AH^- \xrightarrow{Kf} AH_2.AH^-$ (reaction 7)

where Kf is a formation constant. Considering all of these reactions, there are three probable reactions involved in the degradation of ascorbic acid:

$AH^- \xrightarrow{k_1}$ product; $-\frac{d(AH^-)}{dt} = k_1(AH^-)$

$AH_2 + AH^- \xrightarrow{Kf} AH_2.AH^- \xrightarrow{k_2}$ product; $-\frac{d(AH_2.AH^-)}{dt} = k_2(AH_2.AH^-)$

$AH_2 \xrightarrow{k_3}$ product; $-\frac{d(AH_2)}{dt} = k_3(AH_2)$

From reaction 7, $Kf = \frac{(AH_2.AH^-)}{(AH_2)\ (AH^-)}$ ----------(4)

and $k2' = k2 \times Kf$ ----------(5)

The rate of ascorbic acid degradation is the sum of the 3 reactions:

$-\frac{d(At)}{dt} = k1(AH^-) + k2(AH_2.AH^-) + k3(AH_2)$ ----------(6)

where $(At) = (AH_2) + (AH^-)$

Combining equations 5 and 6 gives:

$-\frac{d(At)}{dt} = k1(AH^-) + k2'(AH_2)\ (AH^-) + k3(AH_2)$ ----------(7)

Because of the overall first-order character of the reaction:

$-\frac{d(At)}{dt} = K(At)$ ----------(8)

The dissociation constant of ascorbic acid:

$$Ka_1 = \frac{(H^+)\ (AH^-)}{(AH_2)} \quad \text{----------} \quad (9)$$

From equations 7 and 8:

$$K(At) = k1(AH^-) + k2'(AH_2)\ (AH^-) + k3(AH_2) \quad \text{----------} \quad (10)$$

From equations 9 and 10:

$$K = \frac{k1\ Ka_1 + k3\ (H^+)}{Ka_1 + (H^+)} + \frac{k2'\ Ka_1\ At\ (H^+)}{(Ka_1 + (H^+)\ )^2} \quad \text{----------} \quad (11)$$

Equation 11 indicates that an overall rate constant, K, can be calculated when k1, k2', k3, Ka_1, and (H^+) are known.

Estimation of k1, k2', and k3 can be made by graphical method or by using the KINFIT program. In acidic solution, where $H^+ \gg Ka_1$, equation 11 reduces to:

$$K = k3 + \frac{k1\ Ka_1 + k2'\ Ka_1\ At}{(H^+)} \quad \text{----------} \quad (12)$$

For solutions where $H^+ \ll Ka_1$, equation 11 reduces to:

$$K = k1 + \frac{k3\ (H^+) + k2'(H^+)At}{Ka_1} \quad \text{----------} \quad (13)$$

From equation 12, the plot of K versus $1/(H^+)$ at pH values much less than pKa_1 gives a straight line, and the intercept is k3. From equation 13, the plot of K versus (H^+) gives a straight line whose intercept is k1. Knowing k1 and k3, k2' can be calculated from either equation 12 or 13. This graphic method is theoretically sound. However, when pH of a food system is adjusted too high or too low, chemical activities of other components in a food system (anthocyanin, sugars, organic acids, and catalysts), which may directly or indirectly affect the rate of ascorbic acid degradation, are significantly changed. Therefore, the estimated rate constants may

not change as a function of (H^+).

This problem can be avoided by using the KINFIT program. The pH of a food can be adjusted to the desired range, and the rate constants at different pH's are estimated. With equation 11 and the approximate k1, k2', and k3, which can be obtained from the literature or by approximate calculation, the KINFIT program determines k1, k2', and k3 which best fit the experimental data. The calculated k1, k2', and k3 using the KINFIT program are contained in Table 27. It was found that k2' was inversely proportional to total concentration of ascorbic acid (At) in the system.

Table 27. Specific rate constants: k1, k2', and k3 calculated by the KINFIT program.

Parameters	Calculated values	Standard deviation
k1	0.21062×10^{-3}	0.311×10^{-4}
k2'	0.0085625/At	
k3	0.46372×10^{-3}	0.101×10^{-3}

The Ka_1 of ascorbic acid was determined from the titration curve by measuring pH using glass and calomel electrodes on a pH meter (Corning Digital 110 pH meter). A solution containing 0.003 mole of ascorbic acid was prepared and a calculated amount of NaCl was added to give an ionic strength of 0.23, which was an estimated ionic strength in tomato

juice. The solution was titrated with 0.1N-NaOH at 37.8°C and the average of 3 measurements gave a pKa_1 = 4.087 (Ka_1 = 8.185 x 10^{-5}). A titration curve of the ascorbic acid solution is shown in Figure 4. Using the Henderson-Hasselbach equation, the fraction of ascorbic acid species as a function of pH was calculated, and the species profile is shown in Figure 5.

The pKa_1 values reported for ascorbic acid were 3.98 at 67°C and μ=0.4 (Blaug and Hajratwala, 1972), 3.94 at 96°C and μ=0.5 (Finholt et al., 1963), and 4.04 at 25°C and μ=0.1. The result obtained in this research was in agreement with the reported values.

The reaction rate constants at the selected pH values were predicted using calculated k1, k2', k3 and Ka_1. The predicted rate constants and the rate constants obtained from shelf-life tests are contained in Table 26 for comparison.

The predicted rate constants from equation 11 at 4 selected pH's were very close to those determined from the shelf-life tests. These results indicated that the reaction mechanism of the overall degradation of ascorbic acid in tomato juice was a sum of 3 separate reactions (reactions 1, 2, and 3), and k1, k2', and k3 calculated by the KINFIT program were accurate and acceptable.

Based on equations 11 and 2, a computer simulation program was developed to predict ascorbic acid stability in tomato juice at different pH's. A flowchart of the computer program is given in Figure 16 in Appendix. The program

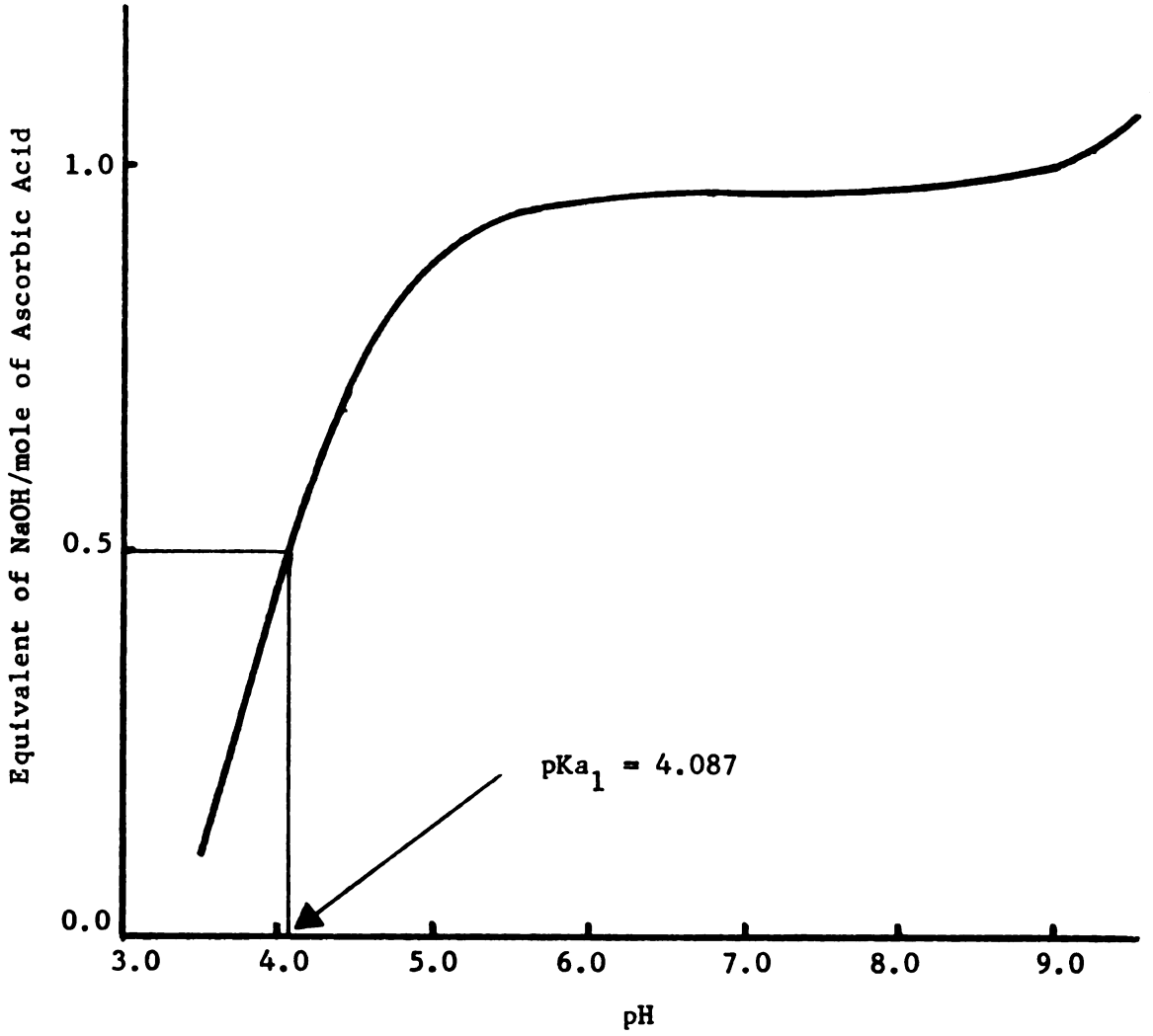


Figure 4.-- Potentiometric titration curve of ascorbic acid (3×10^{-3}mole) at 37.8°C and μ= 0.23.

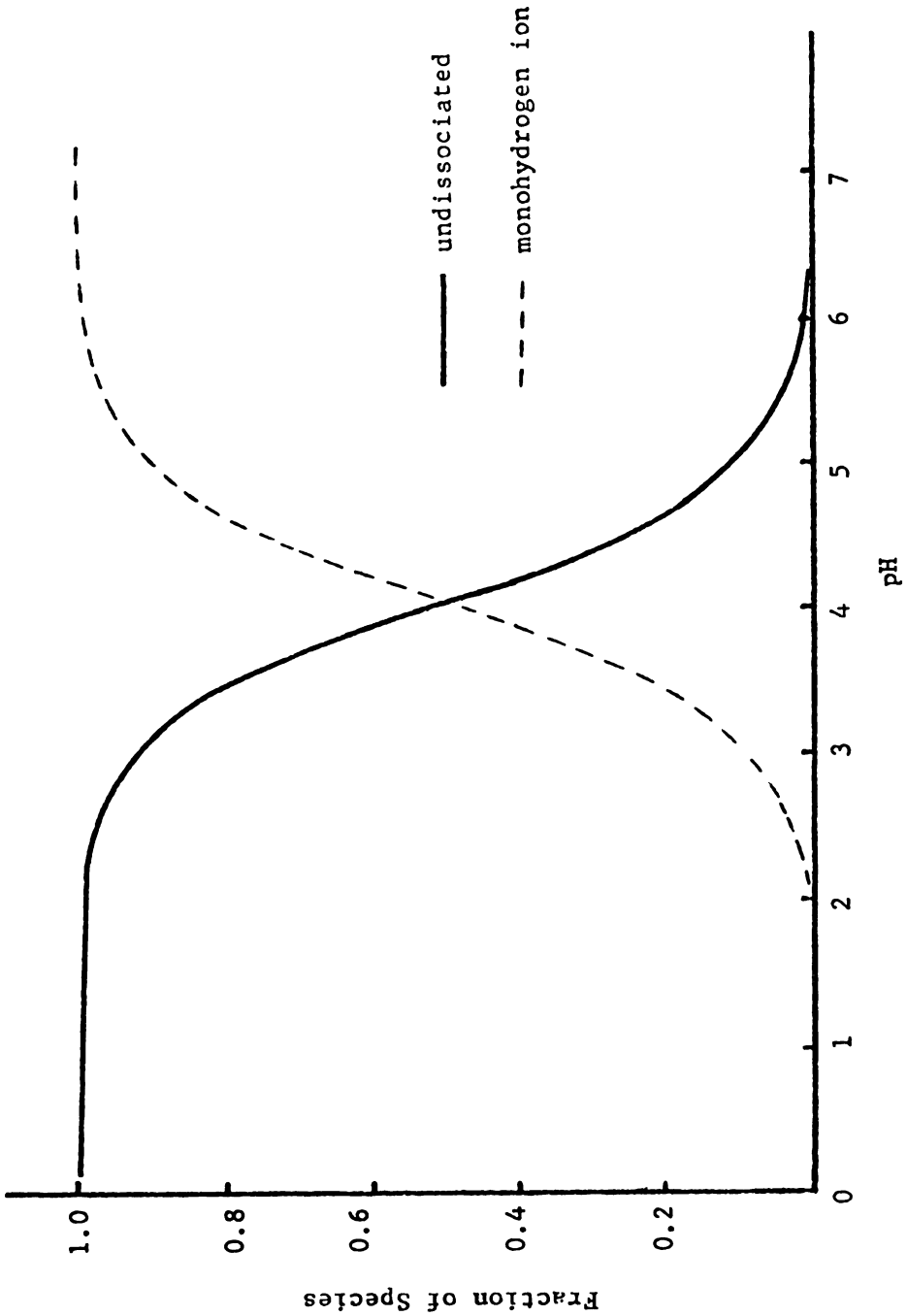


Figure 5. -- Fraction of ascorbic acid species in solution as a function of pH at 37.8°C and μ= 0.23.

requires initial concentration of ascorbic acid, k1, k3, and Ka_1. The rate constants at the selected pH's are calculated using equation 11, and the ascorbic acid concentration at the selected storage time is then computed by equation 2. The percent retention of ascorbic acid is also computed at the same time by equation 3. The ascorbic acid history and the necessary information are printed out. These calculations may be repeated as many times as required within each loop of the program. The rate constants predicted by this program are given in Table 26, and the history of ascorbic acid concentration obtained from the shelf-life tests and predicted by the program are compared in Figure 6.

It was found that the results of the shelf-life tests were very close to the computer-aided prediction at pH 3.53 to 4.36. The difference between the predicted results and the shelf-life tests was in a range of $\pm$ 0 to 2.5% retention with a mean difference of 0.95% retention. These results indicated that the ascorbic acid stability in tomato juice at different pH's could be predicted with accuracy using this pH-model.

Combined Effects of pH and Temperature on Ascorbic Acid Stability in Tomato Juice

In the previous experiments, temperature and pH were considered separately as factors affecting the degradation of ascorbic acid in tomato juice. In this model, temperature

% Retention

% Retention

Figure

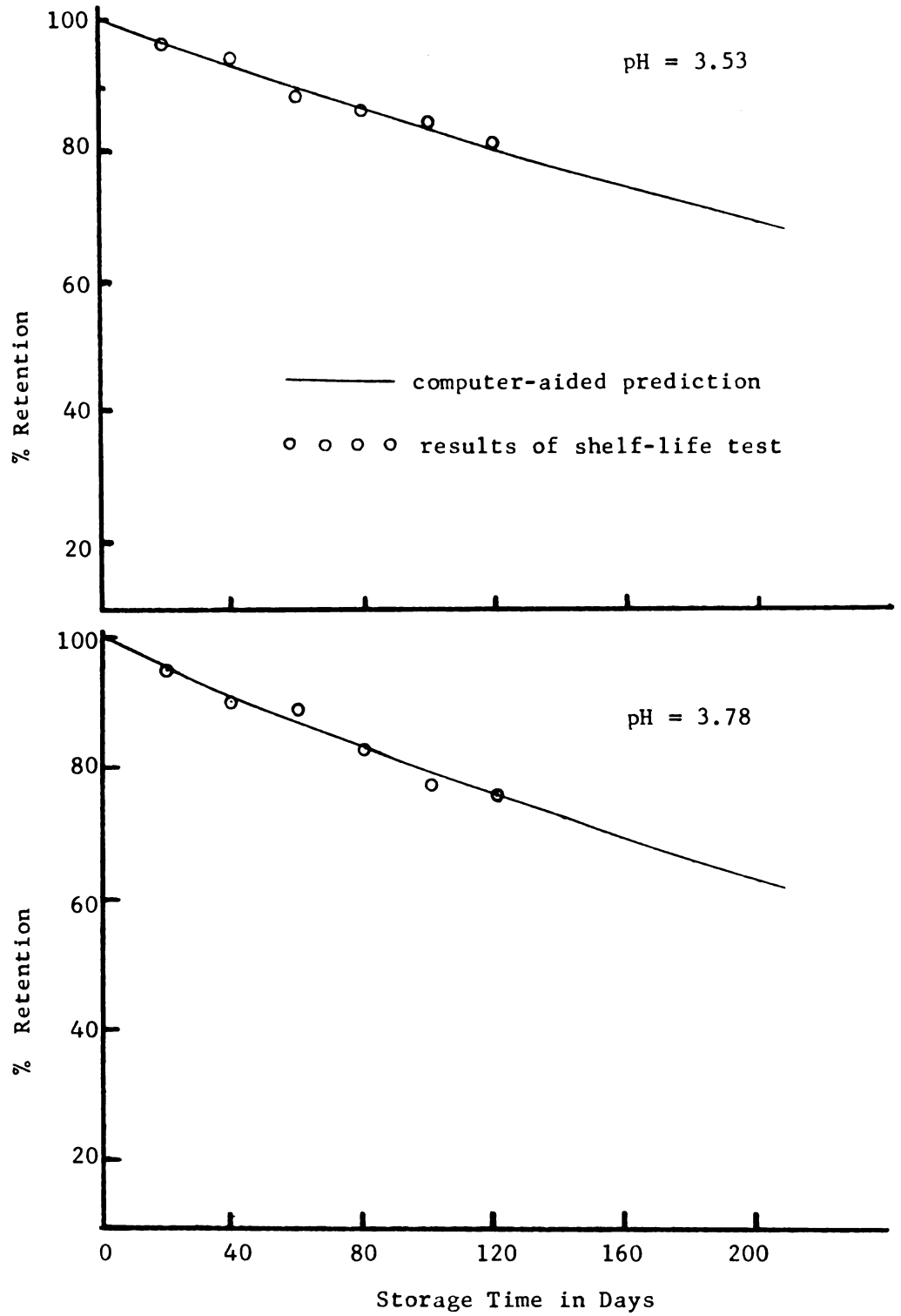


Figure 6.--% retention of ascorbic acid in tomato juice during storage at 37.8°C.

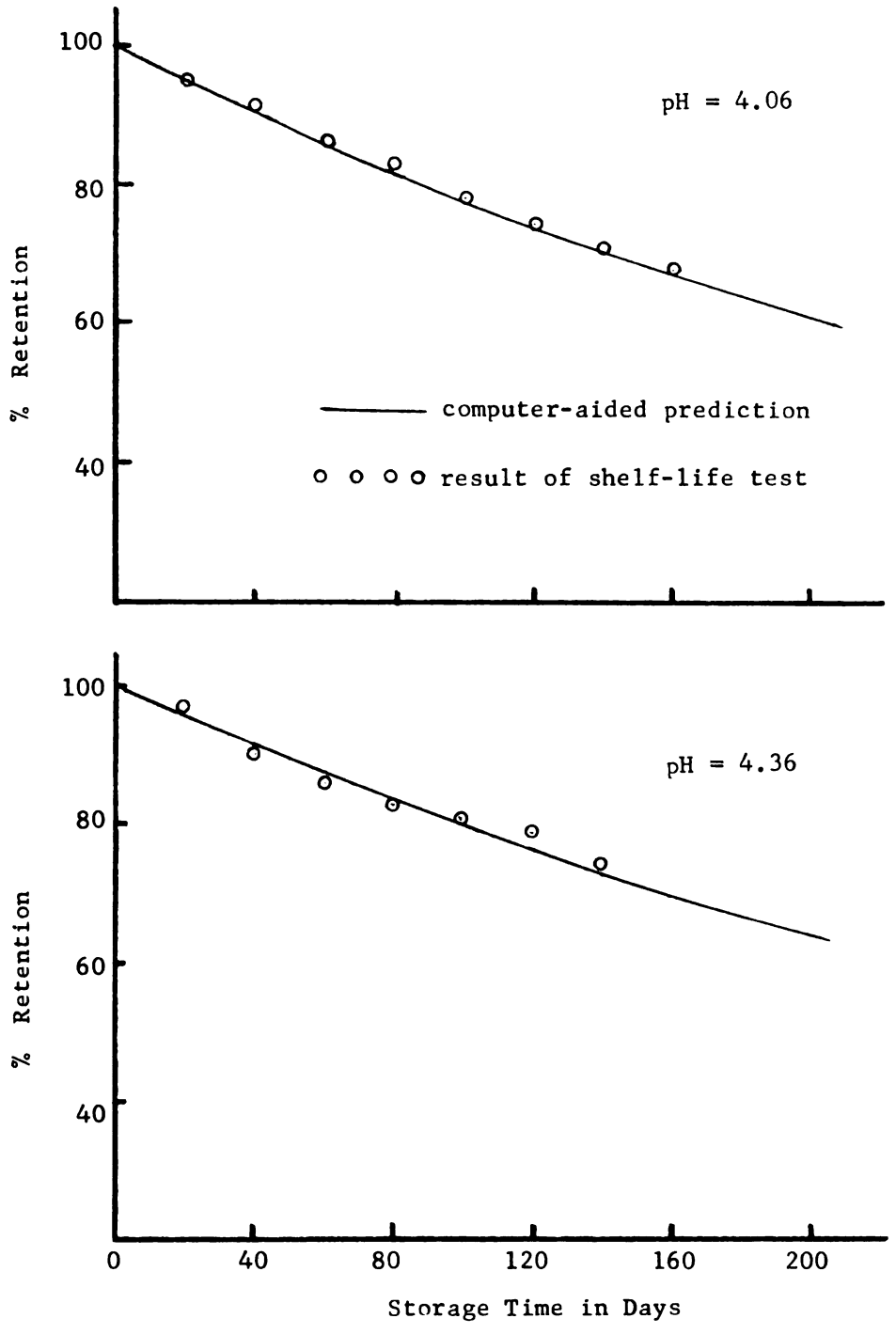


Figure 6. -- Continued

and pH were considered together in order to more realistically simulate the storage condition.

The pH of tomato juice was adjusted to 3.53, 3.78, 4.06, and 4.36 with the citrate buffer, and canned tomato juice was stored at 10, 18.3, 29.4, and 37.8°C. Representative samples were analyzed for ascorbic acid concentration at 30 day intervals (20 day intervals at 37.8°C). The rate constants of ascorbic acid destruction and Ea determined using the KINFIT program are shown in Table 28.

The results in Table 28 showed that the first-order rate constants increased as pH increased to pH 4.06, and then decreased with increasing pH. This trend was observed at each storage temperature but was more obvious at the higher storage temperatures. Finholt et al. (1963) reported that the rate of disappearance of ascorbic acid from aqueous solution under anaerobic conditions showed an apparent maximum at pH= pKa_1 of ascorbic acid. Blaug and Hajratwala (1972) observed similar results under the aerobic conditions. The pH dependence of the rate constants shown in Table 28 was in agreement with the reports by Finholt et al. (1963) and Blaug and Hajratwala (1972). The maximum rate constants of ascorbic acid destruction at pH 4.06 appeared to be due to the facts that maximum quantity of the complex form of ascorbic acid could be formed at pH near pKa_1 of ascorbic acid and k2' was greater than k1 and k3 (Table 27).

This finding indicated that the rate of ascorbic acid degradation might increase when foods are acidified to avoid

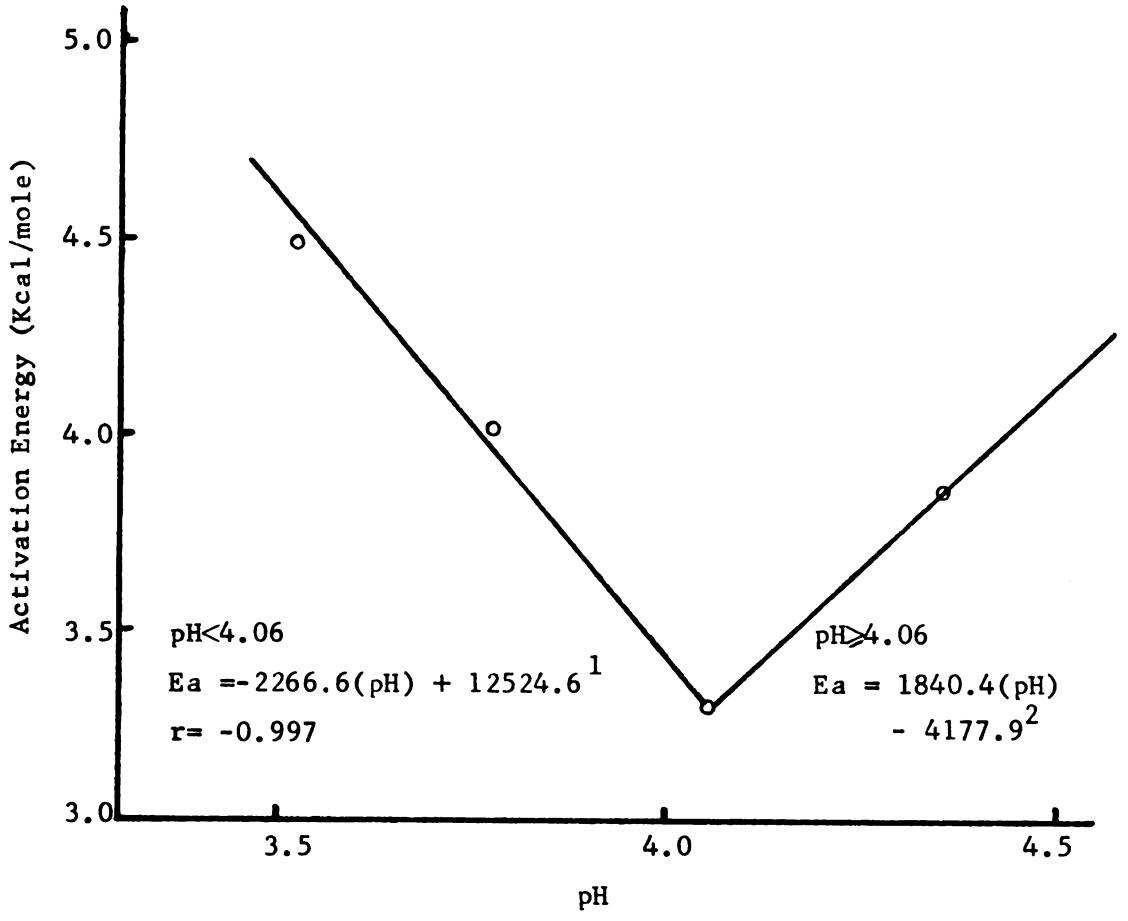
Table 28. Reaction rate constants (K x $10^{-3}day^{-1}$) and activation energy determined at 4 pH's and 4 temperatures.

Temp.	pH			
	3.53	3.78	4.06	4.36
10°C	0.8983 ± 0.0133	1.2054 ± 0.0995	1.4575 ± 0.1510	1.2314 ± 0.1640
18.3°C	1.1132 ± 0.1410	1.4580 ± 0.1960	1.7366 ± 0.0589	1.5034 ± 0.0643
29.4°C	1.5034 ± 0.2760	1.9017 ± 0.1060	2.1228 ± 0.0346	1.9208 ± 0.1540
37.8°C	1.8404 ± 0.2010	2.2793 ± 0.2200	2.4788 ± 0.0682	2.2749 ± 0.2240
Ea (Kcal/mole)	4.493 ± 0.055	4.015 ± 0.050	3.295 ± 0.033	3.847 ± 0.029

microbial spoilage. Tomato juice and other tomato products whose pH's are higher than 4.3, are often acidified with citrate buffer to avoid the flat sour spoilage. If pH of a product is lowered to about 4.1, which is often practiced, the rate of ascorbic acid destruction would increase significantly.

The first-order rate constants determined from shelf-life tests at each pH increased as the storage temperature increased. The activation energy calculated at each pH decreased as pH increased to pH 4.06, and then increased at pH over 4.06. The relationship between pH and activation energy is shown in Figure 7. The change of Ea with pH might be due to the facts that conversion of the complex form of ascorbic acid to degradated product required less Ea than that of dissociated and undissociated forms of ascorbic acid, and amount of the complex form might reach maximum at pH near pKa_1 of ascorbic acid.

A mathematical model as functions of pH and storage temperature was developed, based on equations 11, 1, and 2. Equation 11 was used to calculate the first-order rate constants as a function of pH at a reference temperature where k1, k2', and k3 were determined. The effect of storage temperature on the rate constants was then considered using equation 1. As shown in Figure 7, activation energy changed with pH change, and the linear regression equations were developed to calculate activation energy at various pH's. The calculated Ea at the selected pH's was used for computation



1 Equation 14.

2 Equation 15.

Figure 7. -- Relationship between pH and activation energy.

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in equation 1. Using the rate constants calculated, the ascorbic acid concentration in tomato juice at various storage times could be calculated by equation 2.

A computer program based on this mathematical model was developed to predict the ascorbic acid concentration in tomato juice during storage at various pH's and storage temperatures. A flowchart of the program is shown in Figure 17 in Appendix. The main program reads all parameters required for calculations and calls three subroutines for various computations. The computed results, including percent loss and percent retention of ascorbic acid, are printed out.

The first-order rate constants predicted by this program at selected pH's and storage temperatures are contained in Table 29. The determined rate constants from shelf-life tests (Table 28) and the predicted rate constants (Table 29) are compared at different pH's and storage temperatures, and the results are shown in Figure 8.

It was found that the determined and predicted rate constants for ascorbic acid degradation were in close agreement at all pH's and the storage temperatures. The difference between the determined and predicted rate constants was in a range of $\pm$ 0 to 1.3% (Fig. 8).

Table 29. The rate constants predicted by the computer program at selected pH's and storage temperatures.

Temp.	pH			
	3.53	3.78	4.06	4.36
10°C	0.908 x 10^{-3} day^{-1}	1.212 x 10^{-3} day^{-1}	1.468 x 10^{-3} day^{-1}	1.216 x 10^{-3} day^{-1}
18.3°C	1.142	1.481	1.735	1.477
29.4°C	1.521	1.903	2.138	1.885
37.8°C	1.864	2.274	2.480	2.241
Ea (Kcal/mole)	4.524	3.958	3.292	3.846


K x 10^-3 day^-1
K x 10^-3 day^-1

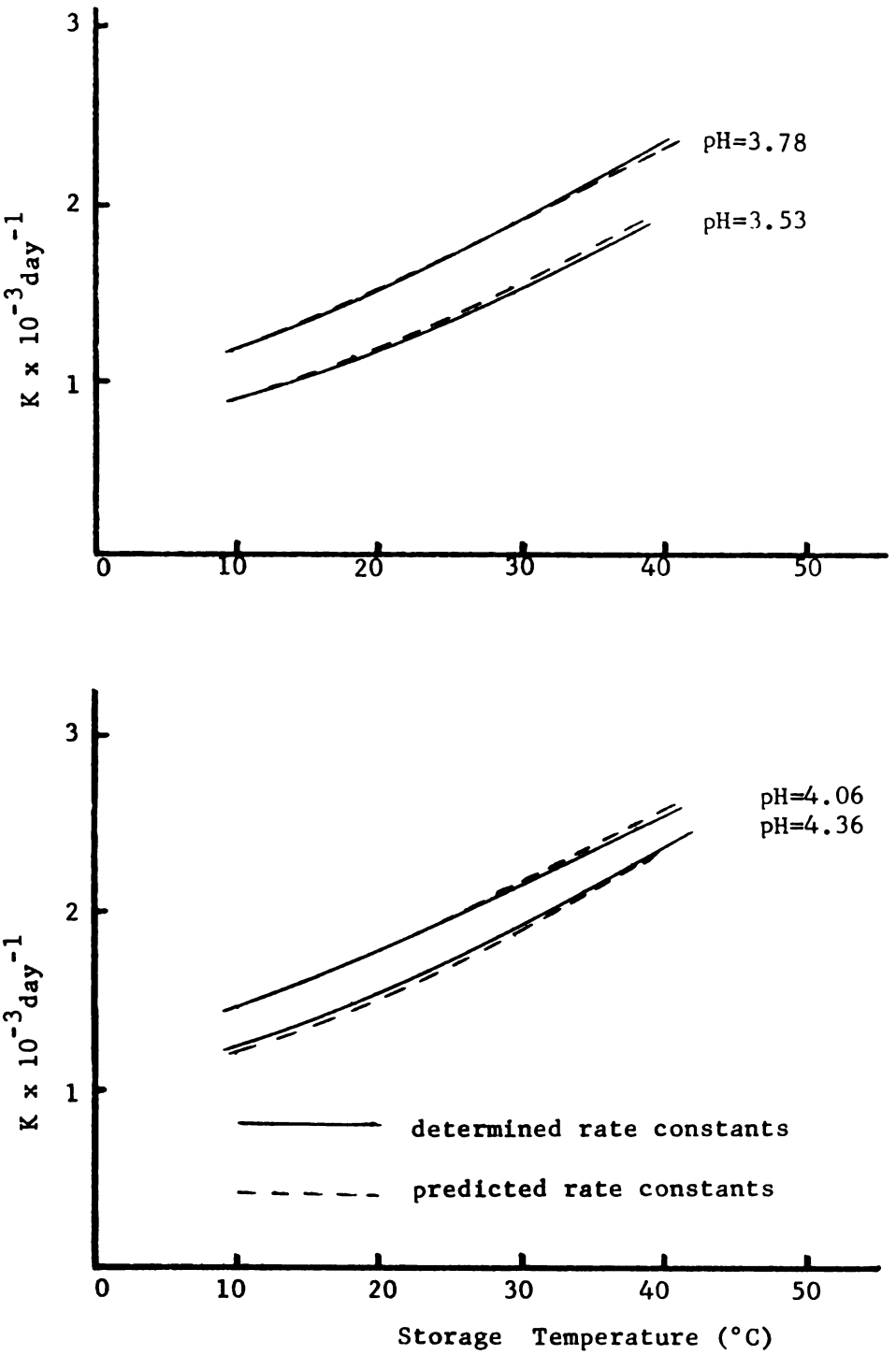

Figure 8. --A comparison of determined rate constants with predicted rate constants.

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Effect of Metal Catalyst on Anaerobic Degradation of Ascorbic Acid in Tomato Juice

Barron et al. (1936) and Kato and Sugiura (1957) reported that copper and iron were found to be effective catalysts for the oxidation of ascorbic acid. They also indicated that the catalytic effect of copper was stronger than that of iron.

Copper was chosen as a catalyst in the model system. A calculated amount of $CuSO_4.5H_2O$ was added to the extracted tomato juice, whose pH was adjusted to 3.53, 3.78, 4.06, and 4.36, to modify copper levels; natural (2ppm), level 1 (6ppm), and level 2 (10ppm). The canned tomato juice was stored at 37.8°C and representative samples were analyzed for ascorbic acid at 20 day intervals. The concentration of copper in tomato juice was determined by atomic absorption spectography.

The rate constants of ascorbic acid destruction increased as the copper concentration increased. This trend was observed at all 4 pH's, although maximum copper effect was found at pH 4.06 (Table 30). Dekker and Dickinson (1940) postulated the following copper-catalyzed oxidation scheme for ascorbic acid: $Cu^{+2} + At \longrightarrow CuA \longrightarrow$ Dehydroascorbic acid + Cu^{+2}. The rate of this reaction can be expressed:

$$- \frac{d(At)}{dt} = K' (At) (Cu^{+2}) \text{ ---------- (16).}$$

As the concentration of copper does not change during the course of the reaction, the reaction was referred to as a pseudo-first-order reaction.

Table 30. The rate constants of ascorbic acid destruction obtained from shelf-life tests (Kob) and the ones predicted (K) at various copper concentrations and 4 different pH's (temperature = 37.8°C).

pH	Treatment	Cu(ppm)	Kob x $10^{-3}day^{-1}$	K x $10^{-3}day^{-1}$
	Natural	2.15	1.8408 ± 0.2010	1.8956
3.53	Level 1	6.25	2.4541 ± 0.3310	2.3495
	Level 2	10.20	2.8089 ± 0.3310	2.7868
	Natural	2.50	2.2793 ± 0.2200	2.3141
3.78	Level 1	6.10	2.7700 ± 0.3740	2.7617
	Level 2	10.25	3.1620 ± 0.3740	3.2777
	Natural	2.25	2.4788 ± 0.0682	2.4781
4.06	Level 1	6.90	3.0624 ± 0.4780	3.1384
	Level 2	11.25	3.7955 ± 0.4780	3.7561
	Natural	2.45	2.2749 ± 0.2240	2.2380
4.36	Level 1	6.58	2.8695 ± 0.2860	2.7838
	Level 2	10.55	3.3400 ± 0.2860	3.3085

The rate constants (Table 30) versus the copper concentrations at 4 different pH's were plotted in Figure 9, and a linear relationship was found between the rate constants determined and the copper concentrations at each pH. The plots also demonstrated effect of pH on the copper-catalyzed degradation of ascorbic acid in canned tomato juice.

$Kob = K' (Cu^{+2}) + Ko$ ---------- (17),

where Kob = the rate consant determined at the constant copper concentration

Ko = the rate constant at zero copper concentration

K' = the pseudo-first-order rate constant.

The Ko and K' values at the 4 different pH values were calculated by the KINFIT program and are given in Table 31.

Table 31. Pseudo-first-order rate constants (K') and Ko calculated by the KINFIT program (at 37.8°C).

pH	K' x $10^{-3}day^{-1}$	Ko x $10^{-3}day^{-1}$
3.53	0.11220 ± .0116	1.6402 ± .0660
3.78	0.12303 ± .0103	2.0005 ± .0591
4.06	0.14203 ± .0087	2.1584 ± .0256
4.36	0.13217 ± .0066	1.9624 ± .0456

4

3

$K \times 10^{-3}$ day^{-1}

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Fig

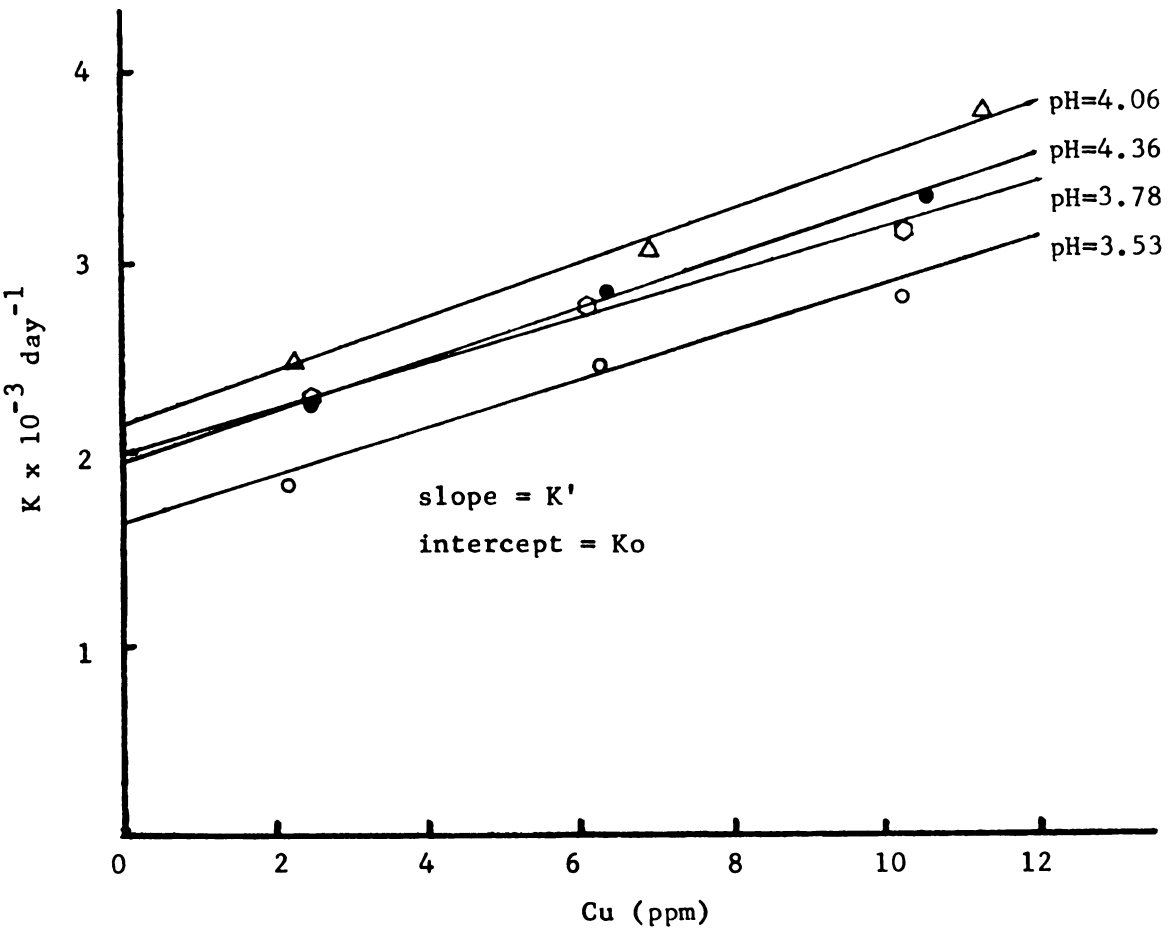

Figure 9. -- The rate constant versus copper concentration at 37.8°C.

It was found that the pseudo-first-order rate constants (K') and Ko were pH dependent with a small but apparent maximum at pH 4.06 (Table 31). The relationship between pH and the pseudo-first-order rate constants is illustrated in Figure 10. Two exponential functions, one for pH less than 4.06 and the other for pH greater than or equal to 4.06, were developed based on the results shown in Table 31.

Ko as a function of pH could be calculated using equation 11. The parameters (k1, k2', and k3) necessary for the calculation were computed by the KINFIT program, based on Ko values given in Table 31. The parameters estimated by this method are contained in Table 32.

Table 32. k1, k2', and k3 estimated to calculate Ko as a function of pH (at 37.8°C).

Parameters	Estimated values	Standard deviation
k1	0.3503×10^{-4}	0.2430×10^{-4}
k2'	0.0076547/At	
k3	0.44561×10^{-3}	0.0718×10^{-3}

Having parameters (k1, k2', and k3) calculated to compute Ko and the relationships between pH and pseudo-first-order rate constants (Fig. 10), Kob at various Cu concentrations could be predicted by equation 17. The rate

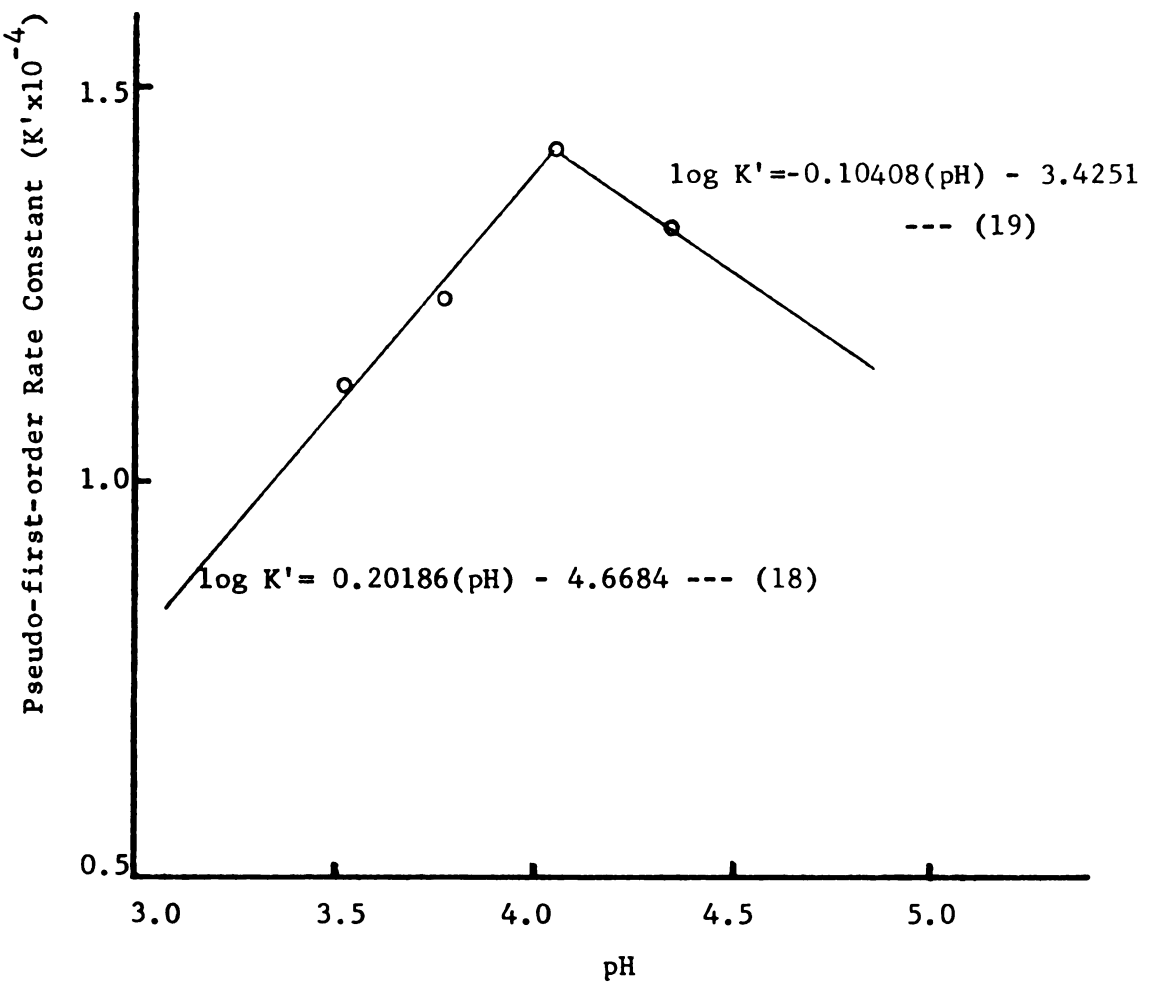

Figure 10. -- Relationships between pH and pseudo-first-order rate constants.

constants of ascorbic acid degradation (K) predicted by this method were compared with those obtained from shelf-life tests in Table 30.

It was found that the rate constants predicted by equations 11, 18 or 19, and 17 were in close agreement with the rate constants obtained from the shelf-life tests at various Cu concentrations and pH's. These results indicated that equations 11, 18 or 19, and 17 could be used as a mathematical model to describe the Cu catalyzed oxidation of ascorbic acid in tomato juice.

pH, Metal Catalyst, and Temperature Model

Oxygen, pH, temperature, and metal catalyst are the most important factors affecting the ascorbic acid degradation in food systems. Because of the anaerobic condition in the canned foods, pH, temperature, and metal catalyst are the main factors which control the rate of the ascorbic acid degradation in the canned foods. These three factors were studied either separately or as a combination of two factors, so far. In this model, the three factors were combined to simulate the real storage condition of acid foods.

The limitations of this system are:

1) acid food system - when pH of a system was over 5, the predicted rate constants by equation 11 deviated significantly from the determined ones.

2) canned food system - since oxygen was not included as a

factor, this model would simulate only canned food systems.

3) foods with high water content - since water activity was not taken into consideration for ascorbic acid stability, this system would be restricted to those canned foods in which the moisture content might be so high that it would not affect the reaction rate. Most canned fruit and vegetable products belong to this category.

4) packaging material - the container of the canned foods should be an absolute barrier to gas and vapor permeability. Metal and glass containers would meet this requirement.

5) other factors - there could be some other minor factors in the food system which might affect stability of ascorbic acid during storage. It was assumed that these minor factors would not significantly effect the reaction rate of ascorbic acid degradation.

The mathematical model developed for this system was:

1) equation 11; $Ko = \frac{k1\ Kal + k3(H^+)}{Kal + (H^+)} + \frac{k2'\ Kal\ At\ (H^+)}{(Kal + (H^+))^2}$

(parameters; Table 32)

2) equation 18 or 19;

$\log K' = 0.20186\ (pH) - 4.6684$, when $pH < 4.06$;

$\log K' = -0.10408\ (pH) - 3.4251$, when $pH \geq 4.06$.

3) equation 17; $Kob = K'\ (Cu^{+2}) + Ko$

4) equation 14 or 15;

$Ea = -2266.6\ (pH) + 12524.6$, when $pH < 4.06$;

$Ea = 1840.4\ (pH) - 4177.9$, when $pH \geq 4.06$.

5) equation 1; $\log \frac{K_2}{K_1} = \frac{Ea}{2.303\ R} \left(\frac{T_2 - T_1}{T_2 \times T_1} \right)$

6) equation 2; Ct = Co / EXP (K t)

Equation 11 was used to calculate the rate constant at zero copper concentration (Ko) at the selected pH. Either equation 18 or 19 was employed to compute the pseudo-first-order rate constant (K') at the selected pH. These results were combined to calculate the observed rate constant (Kob) by equation 17. Therefore, Kob depended upon pH and the copper concentration of the food system. Equation 14 or 15 was used to calculate activation energy at different pH's. The calculated activation energy was used in equation 1 which accounted for the effect of storage temperature on the rate of ascorbic acid destruction. With the rate constant calculated as functions of pH, copper catalyst, and storage temperature, the ascorbic acid destruction at various storage times could be calculated by equation 2.

A flowchart of the computer program based on this mathematical model to predict the storage stability of ascorbic acid in tomato juice is shown in Figure 18 in Appendix. The main program reads all parameters necessary for the various calculations. Then, it calls a subroutine PHRATE which calculates the rate constant (Ko) as a function of pH using equation 11. The main program calls a subroutine CURATE which computes Kob using equations 18 or 19 and 17. If the storage temperature is a constant, the program calls a subroutine THERMO which computes the rate constant as a function of temperature using equations 14 or 15 and 1. When the final rate constant as functions of pH, copper catalyst, and

temperature is calculated, the program calls a subroutine COMPUTE which calculates ascorbic acid concentrations, percent loss of ascorbic acid, percent retention of ascorbic acid at various storage times. If the storage temperature is a function of time, the main program calls a subroutine CHANGE. The subroutine CHANGE calculates the storage temperature at the selected storage time. The rate constant at that temperature is then calculated by equation 1 and the ascorbic acid stability at the storage time is calculated by equation 2. All calculations in this program are repeated with each loop.

The results predicted by the program at selected pH's, temperatures, and Cu concentrations are shown in Figure 11. The determined percent retentions at 37.8°C were included in Figure 11 to compare with the predicted results. The determined results were very close to the predicted results at all pH's and copper concentrations. The difference between the determined results and the predicted values was in a range of $\pm$ 0 to 3% retention with a mean difference of 0.78% retention. The good agreement between the predicted and the estimated results indicated that the model could predict the ascorbic acid stability in canned tomato juice with good accuracy, as functions of storage temperature, metal catalyst, and pH.

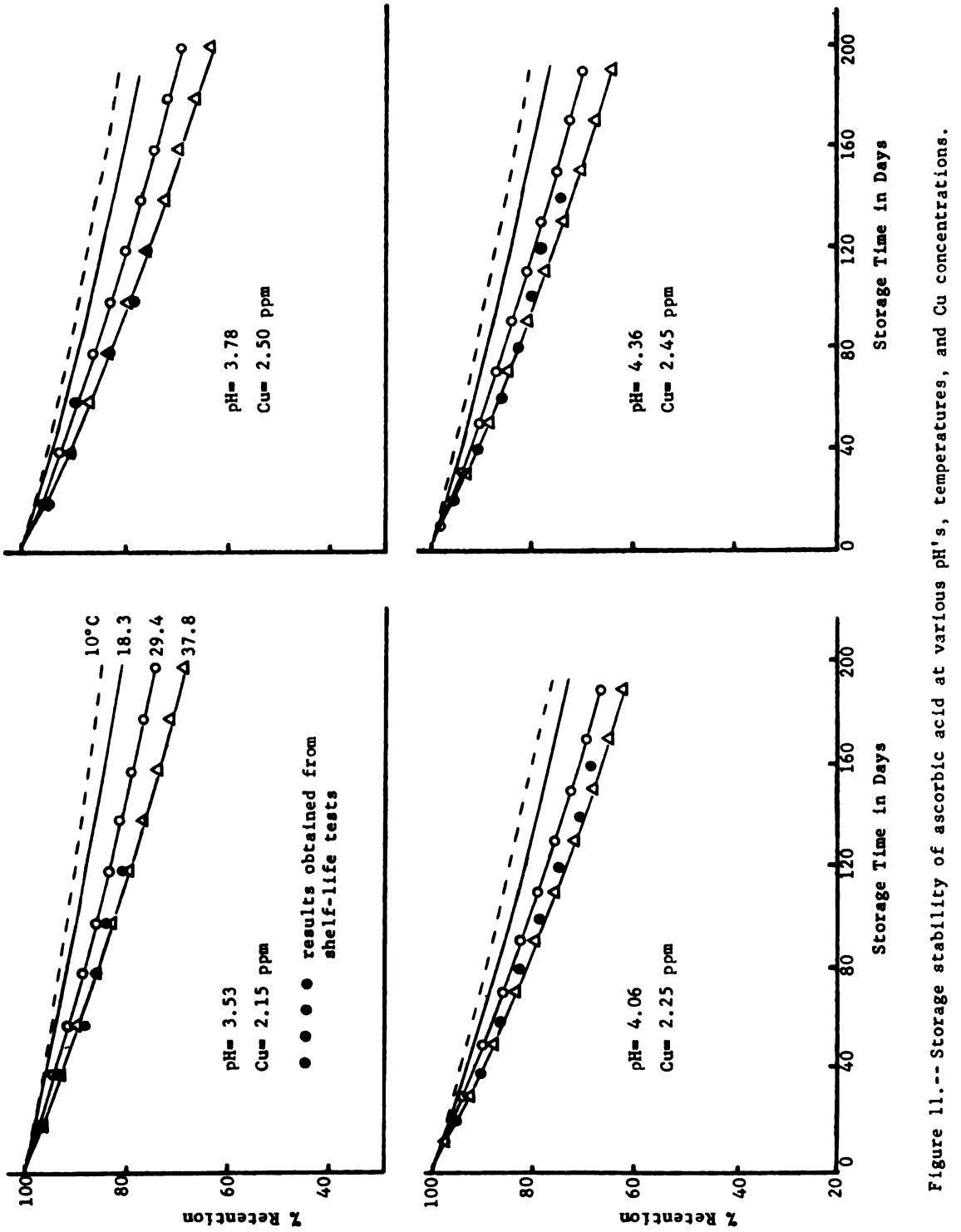

Figure 11.-- Storage stability of ascorbic acid at various pH's, temperatures, and Cu concentrations.

Temperature Fluctuation During Storage

Unless canned foods are stored under the controlled temperature conditions, the product temperature will fluctuate with changes in environmental temperature. The product temperature will also change during transportation and in the marketing channel.

The temperature changes during storage could be a continuous cycle, like a seasonal temperature change, or a discontinuous function of storage time. To study effect of temperature changes as a step function of storage time on the destruction of ascorbic acid, canned tomato juice was stored at 50°F for one month, and then storage temperature was changed to 65, 85, 100, 85, 65, and 50°F after one month storage at each temperature. Tomato juice samples were taken at 20 day intervals for the determination of ascorbic acid concentration. Percent retention of ascorbic acid obtained from shelf-life test and that predicted by the simulation program are shown in Figure 12.

The retention of ascorbic acid predicted by the simulation program was affected by the temperature fluctuation during storage. The percent retention of ascorbic acid determined by shelf-life test was close to that predicted by the simulation program. The difference between the experimentally determined and the predicted percent retentions of ascorbic acid was in a range of $\pm$ 0.2 to 3.5% retention with a mean difference of 2.1% retention. The correlation coefficient between the determined and the predicted values

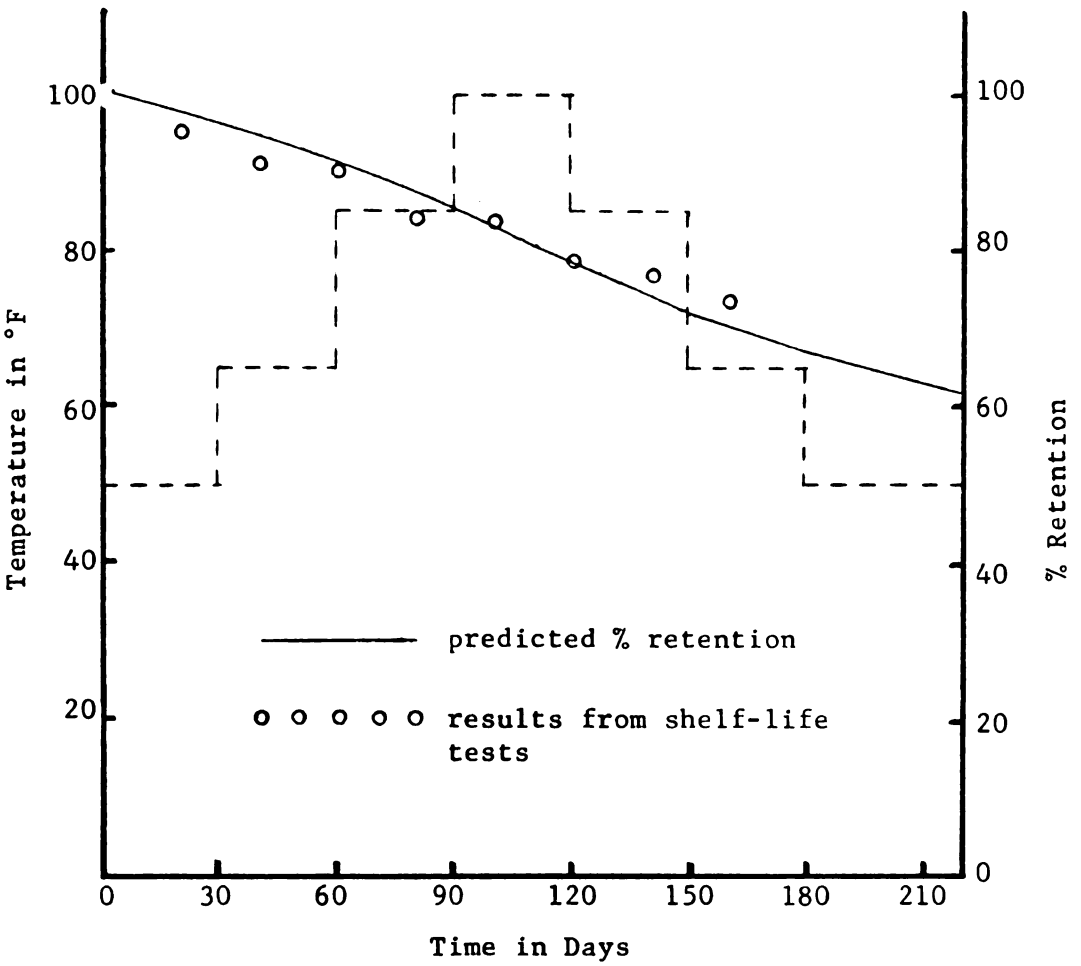

Figure 12. -- Ascorbic acid stability with temperature fluctuation as a step function.

was 0.99.

The seasonal temperature change throughout a year is a continuous cycle with considerable daily temperature fluctuation. An attempt was made to simulate the seasonal temperature change by using the Fourier Series.

Fourier Series:

$$f(x) = \frac{a_o}{2} + \sum_{n=1}^{\infty} \left(a_n \text{ COS } \frac{n\pi x}{L} + b_n \text{ SIN } \frac{n\pi x}{L}\right) \text{ ----------(20)}$$

where $a_n = \frac{1}{L} \int_{-L}^{L} f(x) \text{ COS } \frac{n\pi x}{L} dx$, n = 0,1,2,3, ----

$b_n = \frac{1}{L} \int_{-L}^{L} f(x) \text{ SIN } \frac{n\pi x}{L} dx$, n = 1,2,3, ------

L = limit of cycle

x = time in days

A computer program was developed to simulate the seasonal temperature change using the Fourier Series. A flowchart of the computer program is given in Figure 19 in Appendix. The program was designed to calculate the coefficients, a_n and b_n, through numerical integration procedure. After the coefficients were calculated, the program computed temperatures at any time (x) using equation 20. The number of terms, n, to be used for calculation could be determined by the accuracy needed.

The maximum daily temperature in Lansing area reported by Weather Bureau in 1974 was used to test the program. The maximum daily temperature was used because it fluctuated more than the average daily temperature and was more difficult

to simulate. The reported temperature was compared with the calculated temperature by the Fourier Series at 10 day intervals, and the results are shown in Figure 13.

The temperature calculated by the Fourier Series simulated the seasonal temperature change with good accuracy, when ten terms were used for calculation (correlation coefficient between input temperature data and the calculated data was 0.94). These results indicated that the Fourier Series could be used to simulate the seasonal temperature change of the canned food during storage with accuracy.

The computer program described in Figure 18 in Appendix was modified to accomodate the Fourier Series, which was used to calculate the storage temperature as a function of time. The main program and the subroutine CHANGE were modified and the subroutine FOURIER was added. Flowcharts of subroutine FOURIER and subroutine CHANGE are shown in Figure 20 in Appendix.

The added functions of the main program are:
(1) to read temperature data to be used for simulation of temperature changes (statement added at connector 1 in Figure 18 in Appendix).
(2) to call subroutine FOURIER (statement added at connector 2 in Figure 18).

The function of the subroutine FOURIER is to compute coefficients of the Fourier Series. These coefficients are then used for the calculation of temperature as a function of storage time in the subroutine CHANGE. The subroutine

Figure 13.-- Simulation of seasonal temperature changes by using the Fourier Series.

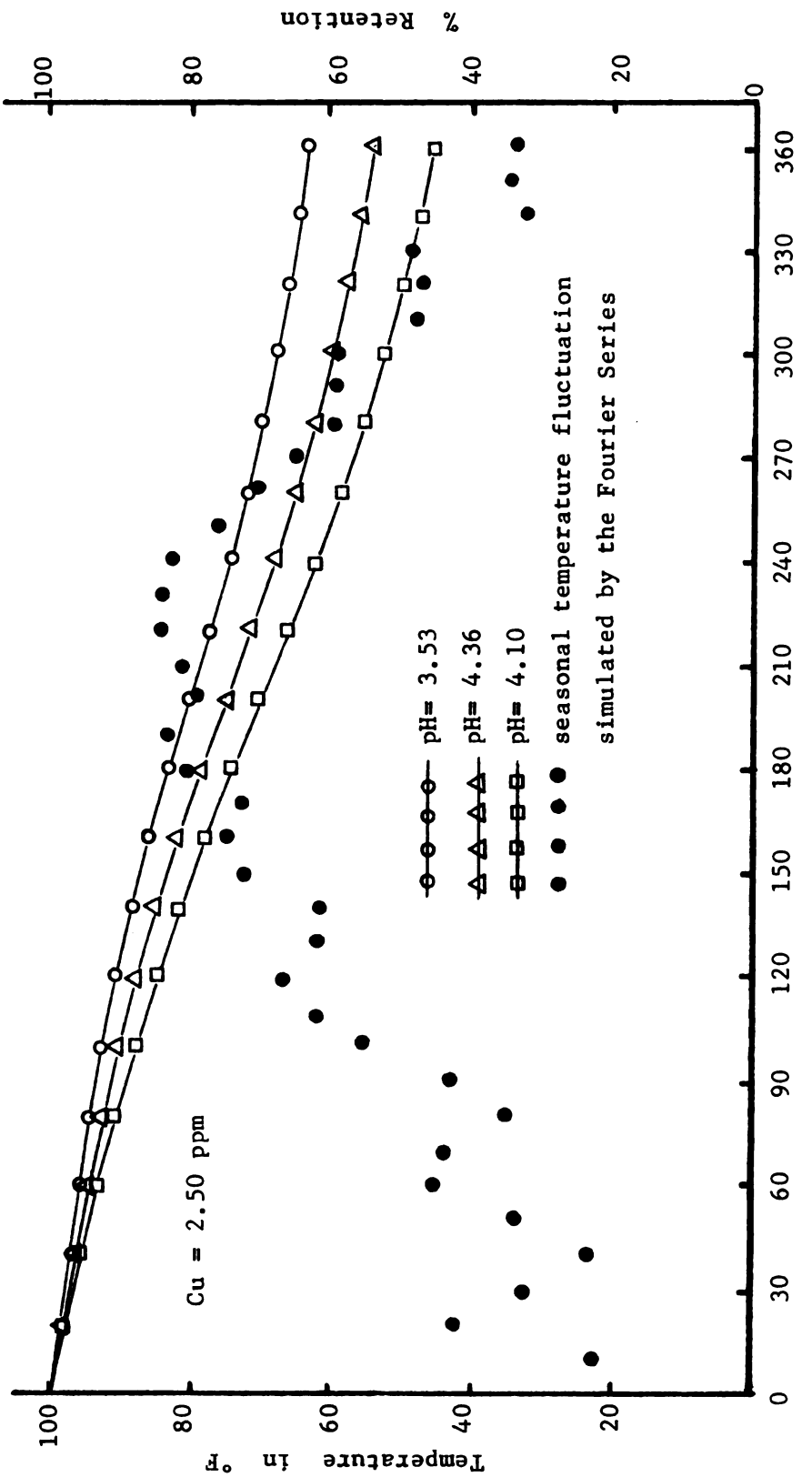

Figure 14.-- Effect of seasonal temperature fluctuation on retention of ascorbic acid.

CHANGE also computes and prints ascorbic acid history during storage.

The stability of ascorbic acid in tomato juice during storage was predicted using the simulation model with the Fourier Series, and the results are shown in Figure 14. The temperature history used for the simulation was the maximum daily temperature in Lansing area in 1974.

The results indicated that the rate of ascorbic acid destruction varied with temperature changes. Among the three pH values tested, ascorbic acid was most stable at pH 3.53 and least stable at pH 4.10. Effect of pH on the stability of ascorbic acid became more obvious as the storage temperature and time increased. Due to the complicated temperature fluctuation, experimental shelf-life tests to verify the computer predicted stability of ascorbic acid was not attempted.

CONCLUSION

The objectives of this research were to study kinetics of ascorbic acid destruction as affected by storage temperature, pH, and metal catalyst; to develop mathematical models which describe kinetics of ascorbic acid destruction; and to develop the computer simulation program to predict ascorbic acid stability in canned tomato juice as affected by seasonal temperature fluctuation, pH, and metal catalyst. Tomato juice was chosen as a model system of high acid foods, and ascorbic

acid was selected as an index of nutritional quality in this study.

The ascorbic acid destruction under anaerobic conditions was confirmed to be a first-order reaction with respect to unreacted ascorbic acid concentration.

The effect of storage temperature on the rate of ascorbic acid destruction was accounted for by the Arrhenius equation. The calculated activation energy (Ea) for the anaerobic degradation of ascorbic acid was 3.295 Kcal/mole at pH 4.06. Ea changed with changes in pH, reaching a minimum near pKal of ascorbic acid which was 4.09 at 37.8°C and μ=0.23.

The rate of ascorbic acid destruction was significantly influenced by pH, reaching a maximum near pKal of ascorbic acid. Based on the changes in the rate of ascorbic acid degradation with pH, existence of a complex form of ascorbic acid was employed to explain the kinetic results observed for ascorbic acid destruction in tomato juice. A mathematical expression, which required 3 specific rate constants (k1, k2', and k3) and Kal, was derived to calculate the first-order rate constant as a function of pH. It was found that k2' was significantly greater than k1 and k3 and inversely proportional to ascorbic acid concentration. The maximum rate of ascorbic acid destruction and the minimum Ea for ascorbic acid destruction near pKal of ascorbic acid could be explained by the facts that the formation of the complex form of ascorbic acid could reach a maximum at pKal

of ascorbic acid and k2' would require less Ea than k1 and k3. The inverse relationship of k2' with ascorbic acid concentration implied that the rate of ascorbic acid destruction would change with significant changes in initial concentration of ascorbic acid.

The rate constant of ascorbic acid destruction in the presence of copper (Kob) increased with increase in copper concentration, and Kob changed with pH. Based on the results, the pseudo-first-order rate constant (K') and the rate constant of ascorbic acid destruction in the absence of copper (Ko) were computed. A mathematical expression between Kob and K' and Ko was developed to calculate Kob at various pH's and copper concentrations.

A computer program employing the Fourier Series was used to describe the seasonal temperature fluctuation during storage of tomato juice. The predicted results showed the effect of temperature fluctuation on the ascorbic acid stability in tomato juice.

Mathematical expressions derived to describe kinetics of ascorbic acid destruction in tomato juice were used to develop a mathematical model for each storage condition. From the mathematical model, the computer program was developed and used to test the model and to predict ascorbic acid history during storage. The three-factor model, which included expressions for seasonal temperature fluctuation, metal catalyst, and pH was established and a computer simulation program was developed. The predicted results using each computer

program were compared with the results obtained from shelf-life tests, whenever possible. The difference between predicted results and the shelf-life tests was in a range of $\pm$ 0 to 3% retention of ascorbic acid with a mean difference of 1.3% retention.

The rate constants of ascorbic acid destruction and the parameters obtained in this study might be different in other canned high acid foods. However, the mathematical expressions and the procedures should be applicable to other canned high acid foods for prediction of ascorbic acid stability.

The results obtained in this study illustrate that the ascorbic acid stability in canned tomato juice can be predicted with accuracy, if the kinetic information on the ascorbic acid destruction is available.

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A P P E N D I X

Table 23. Total and soluble solids content of vine ripened tomatoes.

Cultivars	1973		Cultivars	1974		Cultivars	1975	
	T.S.	S.S.		T.S.	S.S.		T.S.	S.S.
	%			%			%	
Campbell-1327	6.2	4.3	Campbell-1327	6.0	4.5	Campbell-1327	5.6	4.4
Campbell-721	5.9	4.2	Campbell-721	7.0	5.5	Campbell-721	6.3	5.1
Setmore	6.1	4.4	Setmore	6.4	4.8	Setmore	5.8	4.8
Jet Star	6.2	4.3	Jet Star	7.1	5.2	Jet Star	6.2	5.1
Springset	5.9	4.3	Springset	6.5	4.7	Bigset	6.1	5.1
306-1-1	6.4	5.1	306-1-1	8.3	6.4	Rampo	6.5	5.3
307-1-1	6.9	5.4	307-1-1	8.0	6.1	Veebrite	5.4	4.1
915-4-1	6.2	4.2	915-4-1	7.5	6.0	Veeset	5.8	4.3
915-5-1	5.3	3.4	915-5-1	6.5	4.7	Vision	5.8	4.5
Burpee VF	6.9	5.0	6718 VF	6.3	5.2	6718 VF	5.8	4.6
Calmart	6.1	4.4	Redpak	6.5	5.6	Redpak	6.1	4.5
Caravelle	5.9	4.1	Royal Flush	7.0	5.2	Royal Flush	6.4	5.0
Florida MH-1	6.5	4.8	Ace 55 VF	7.9	6.3	Ace 55 VF	6.0	5.2
New Yorker	5.8	4.0	Prime Beefsteak	7.2	5.8	OCNF	7.1	5.6
Packmore	5.9	4.7	OFHF	6.2	5.0	PSX 17573	6.0	4.8
Walker	5.6	3.6	33 HF	6.2	4.9	PSX 17673	5.8	4.5
301-1-1	7.8	5.7	W2HF	7.3	5.8	Hybrid 9	6.3	5.1
301-2-1	7.7	6.1	6343 VF	6.7	5.4	Hybrid 15	5.8	4.7
302-2-1	7.5	5.4	Hybrid 2	5.8	4.6	Hybrid 16	6.1	5.1
304-1-1	6.9	5.8	Hybrid 4	7.2	5.7			
304-2-1	6.4	4.9						
915-9-1	6.5	4.9						
915-10-1	6.5	4.7						
915-11-1	7.0	5.1						
Means	6.3±.75	4.7±.72		7.0±.92	5.4±.87		6.0±.52	4.8±.46

Table 24. Mineral content of vine ripened tomatoes in 1973 and 1974.

Mineral	1973			1974		
	Mean	Range	Sig.	Mean	Range	Sig.
%						
Nitrogen	2.1 ± .40	1.6 - 2.9	0.05%	2.4 ± .33	2.0 - 3.1	0.05%
Potassium	3.3 ± .46	2.0 - 3.8	0.05%	3.3 ± .44	2.7 - 3.9	0.05%
Phosphorus	0.44 ± .09	.32 - .58	0.05%	0.38 ± .08	.27 - .48	0.05%
Sodium	0.02 ± .006	.02 - .03	N.S.	0.02 ± .01	.01 - .03	0.05%
Calcium	0.03 ± .034	.01 - .08	N.S.	.11 ± .04	.07 - 1.82	1.9 %
Magnesium	0.17 ± .03	.14 - .22	0.05%	0.18 ± .03	.14 - .22	0.05%
mg/100 g						
Manganese	1.57 ± .63	0.5 - 2.7	0.1 %	2.45 ± .73	1.63 - 3.63	0.5 %
Iron	9.2 ± 3.23	7.3 - 18.0	N.S.	7.8 ± 1.52	6.2 - 9.9	0.05%
Copper	1.4 ± .36	1.0 - 2.2	0.7 %	1.8 ± 1.34	1.0 - 3.3	N.S.
Boron	1.2 ± .29	0.8 - 1.8	0.05%	1.2 ± .92	0.8 - 3.3	N.S.
Zinc	0.7 ± .68	0.01 - 1.6	0.05%	1.4 ± .76	0.7 - 2.8	0.1 %

Note: 1973 - mean value is an average of 144 analyses (dry weight basis)

1974 - mean value is an average of 80 analyses (dry weight basis)

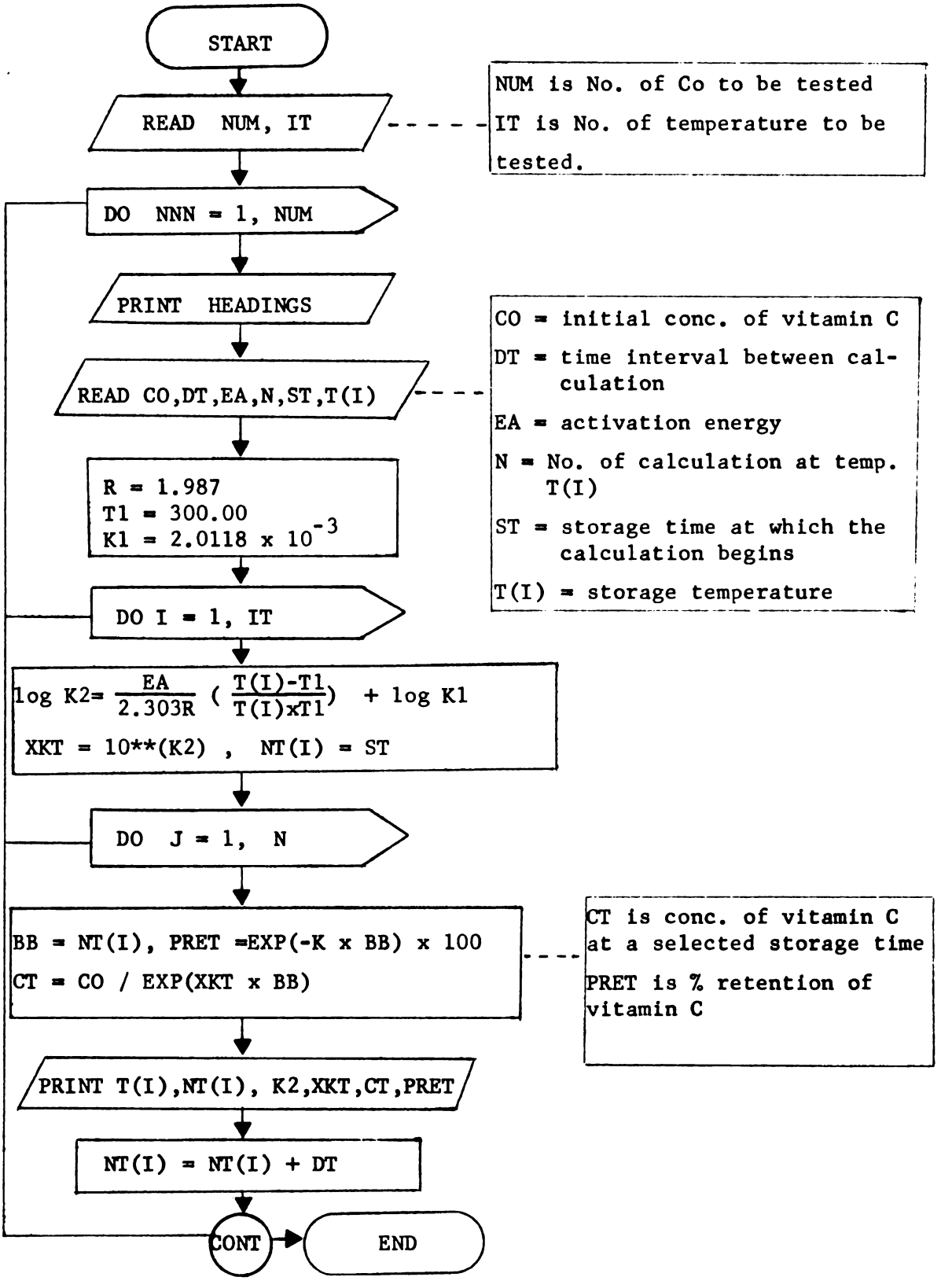


Figure 15.-- A flowchart of the temperature model.

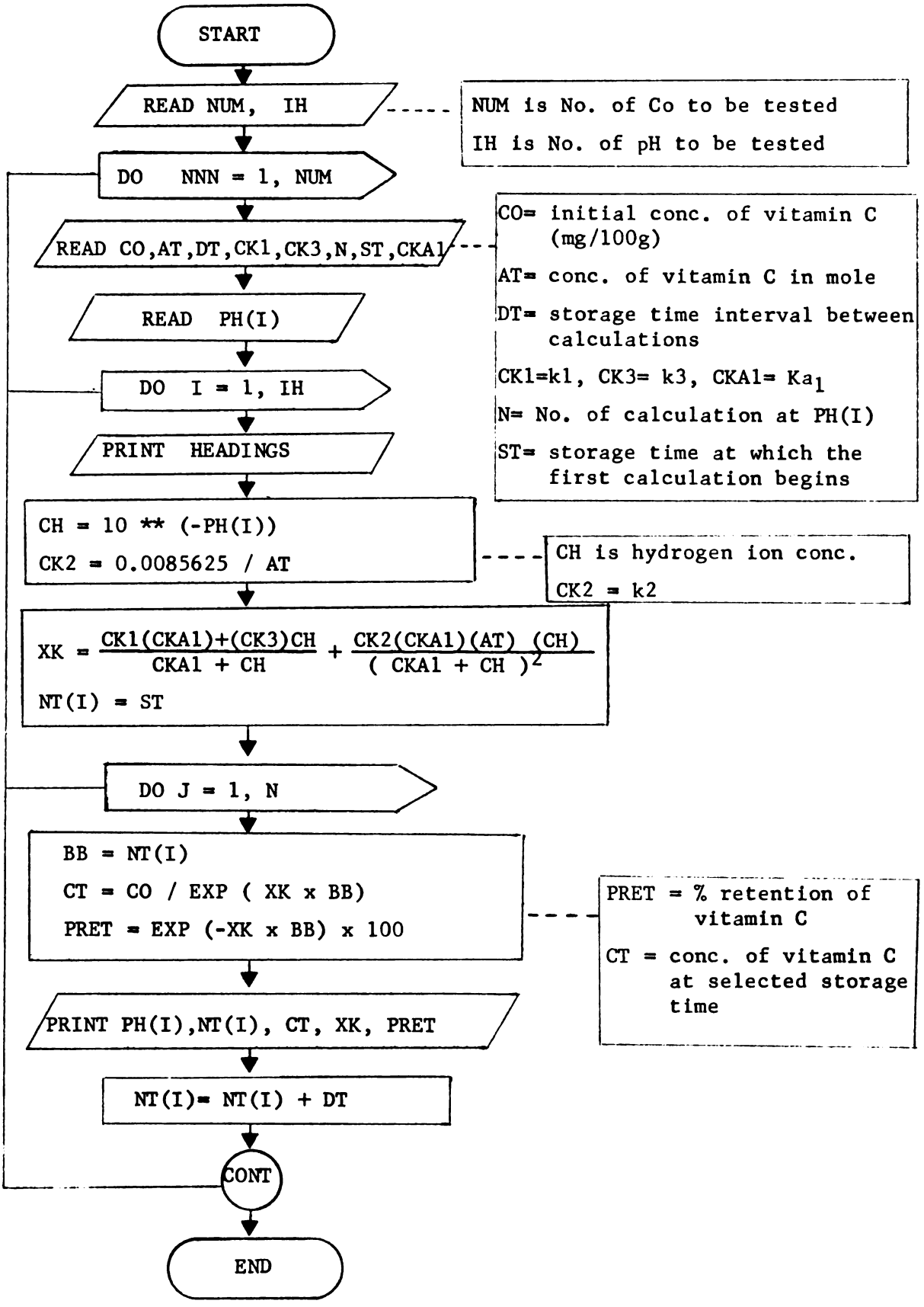
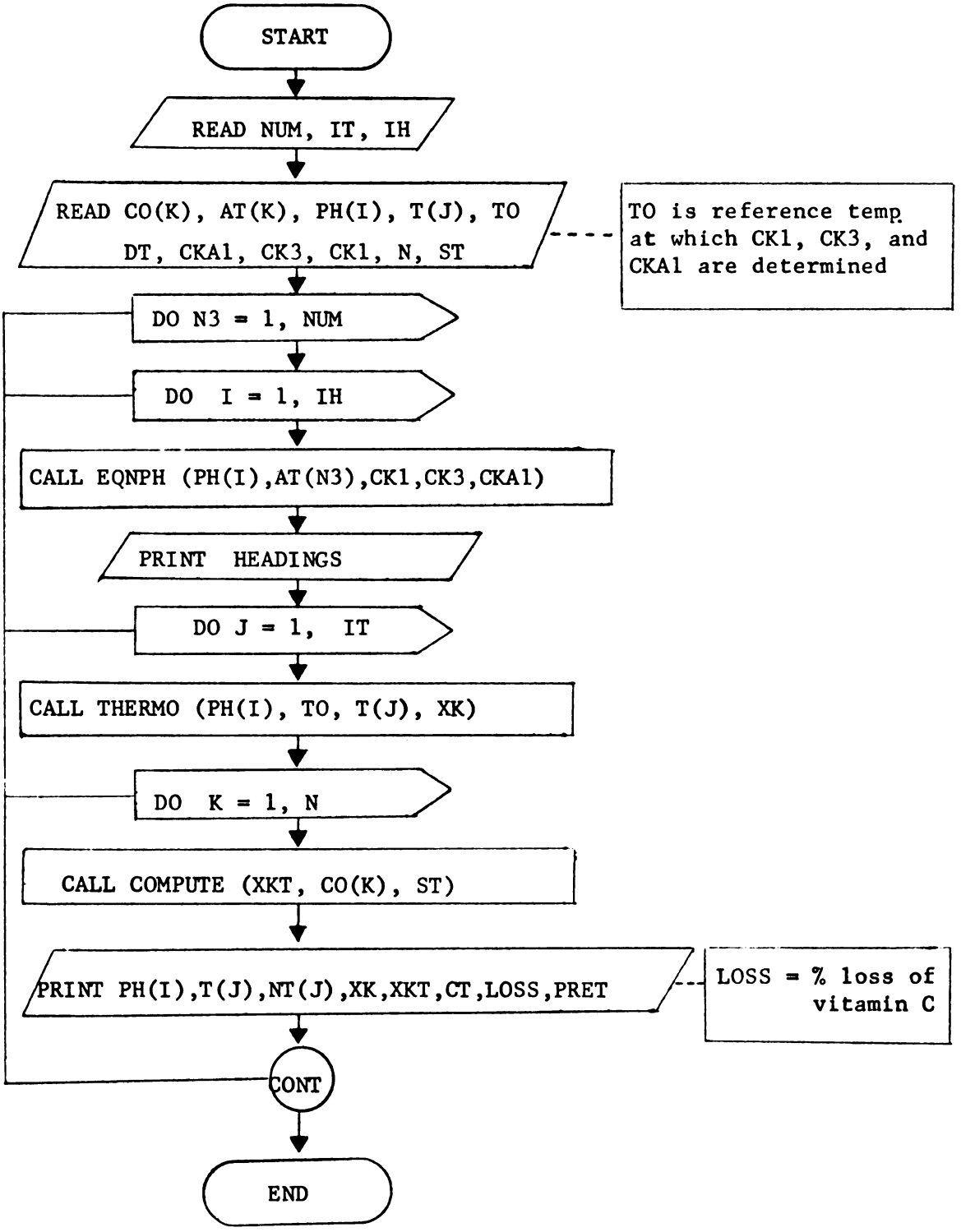
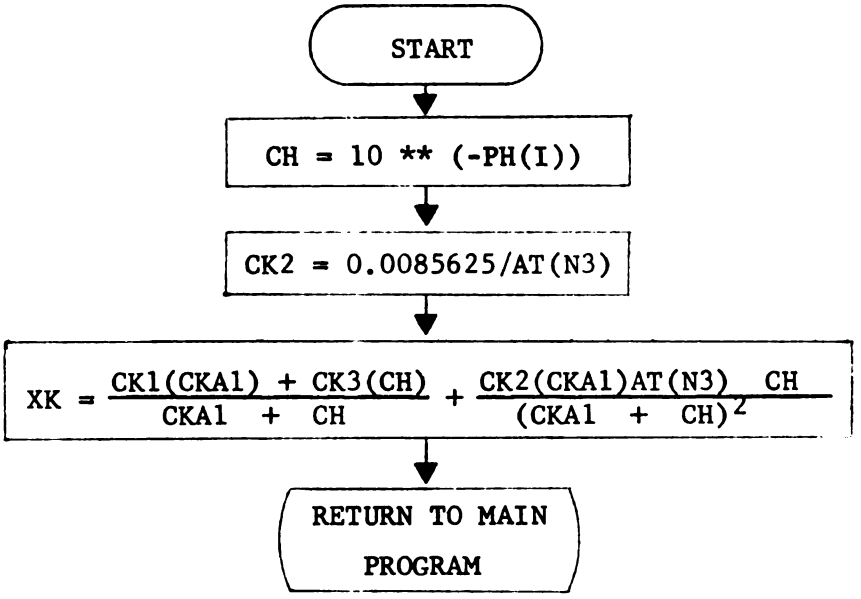


Figure 16. -- A flowchart of the pH model.

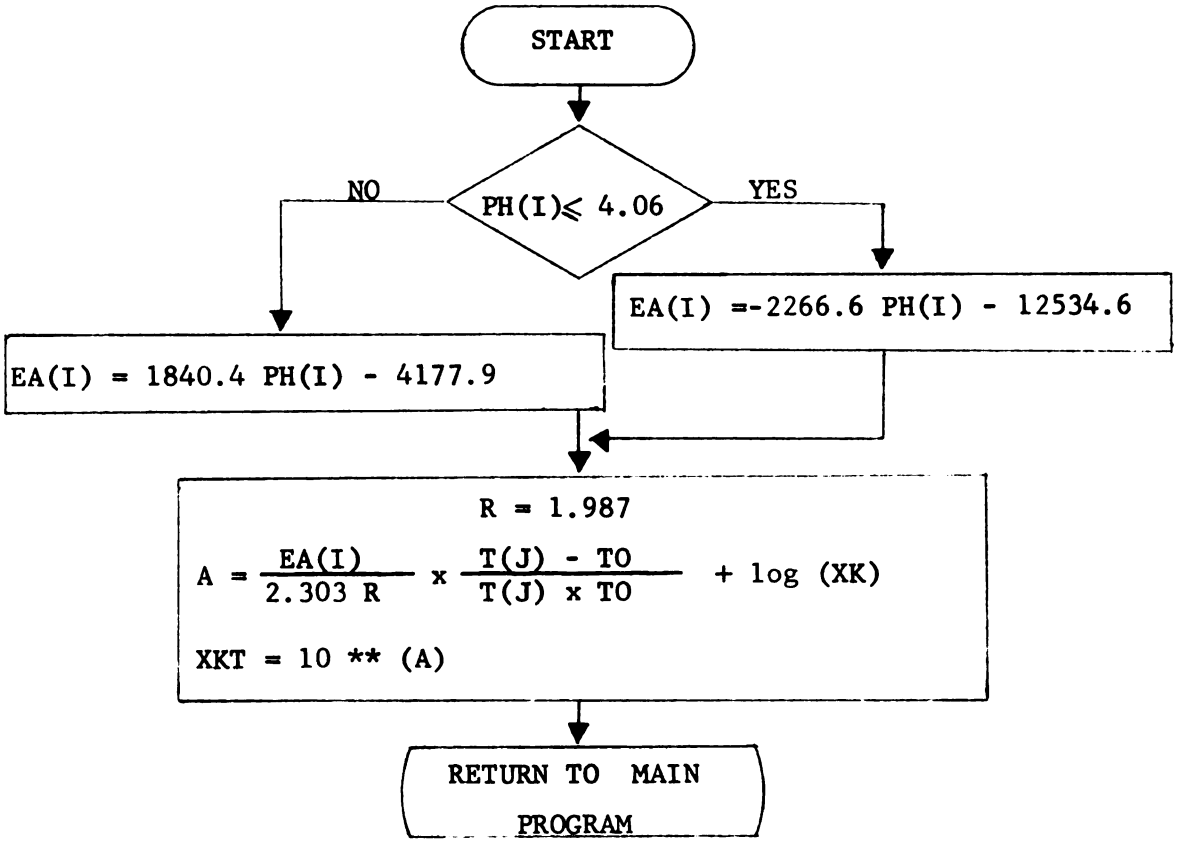


(1) Main Program

Figure 17. -- A flowchart of temperature and pH model.

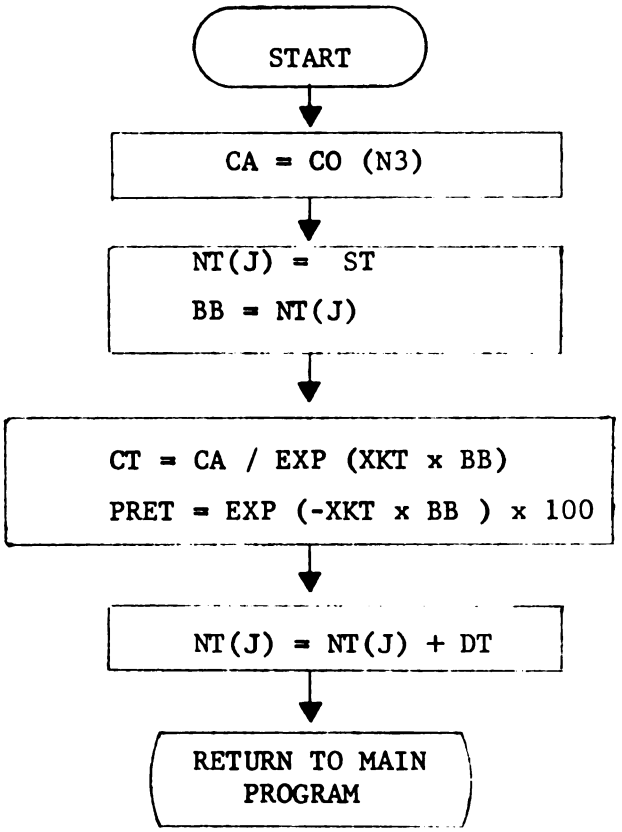


(2) Subroutine EQNPH



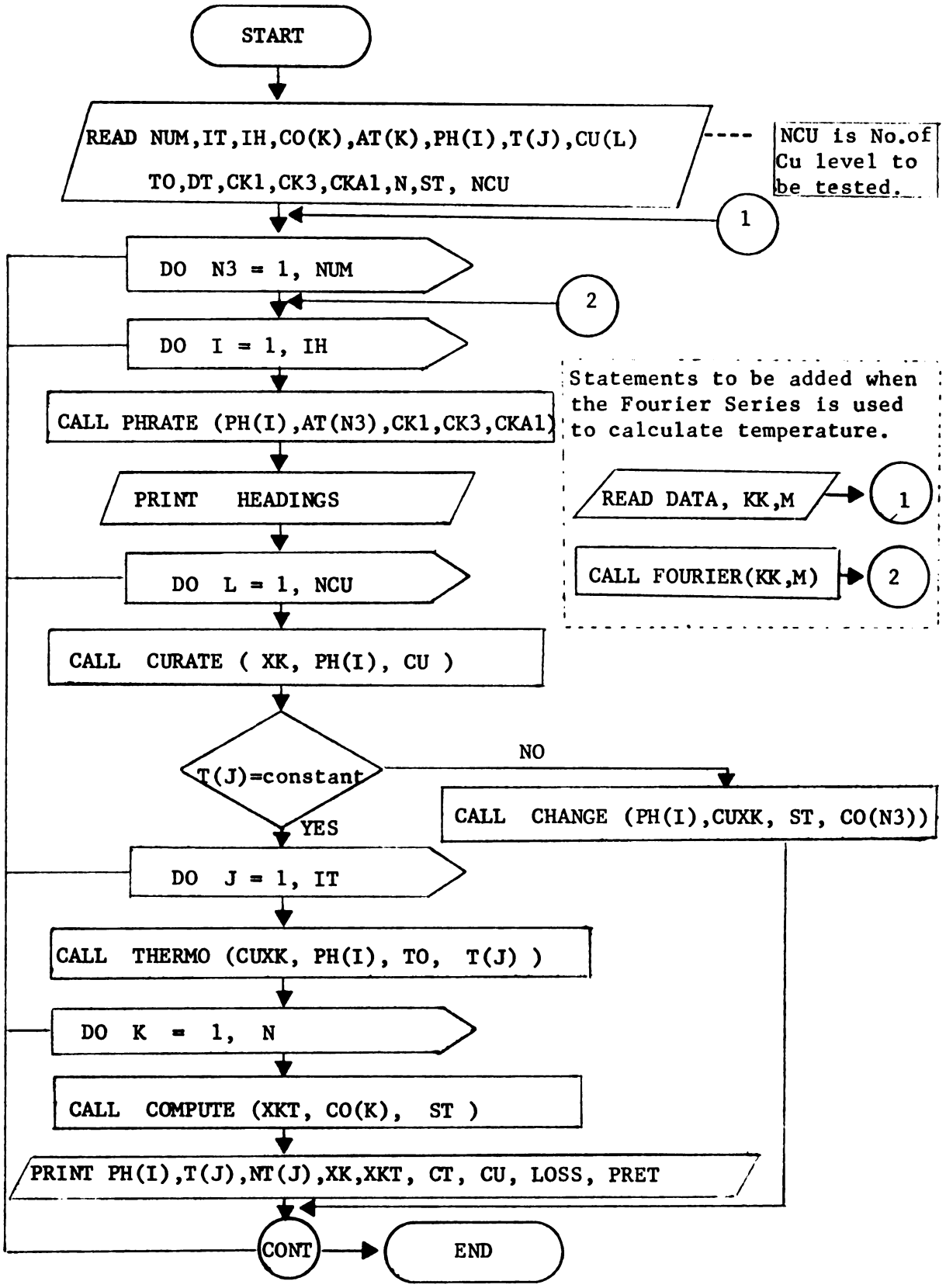
(3) Subroutine THERMO

Figure 17. -- Continued.



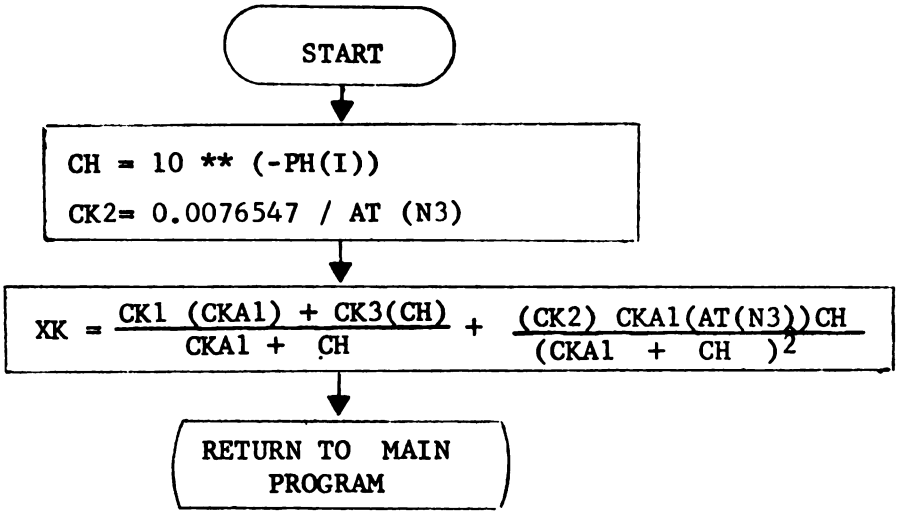
(4) Subroutine COMPUTE

Figure 17. -- Continued.

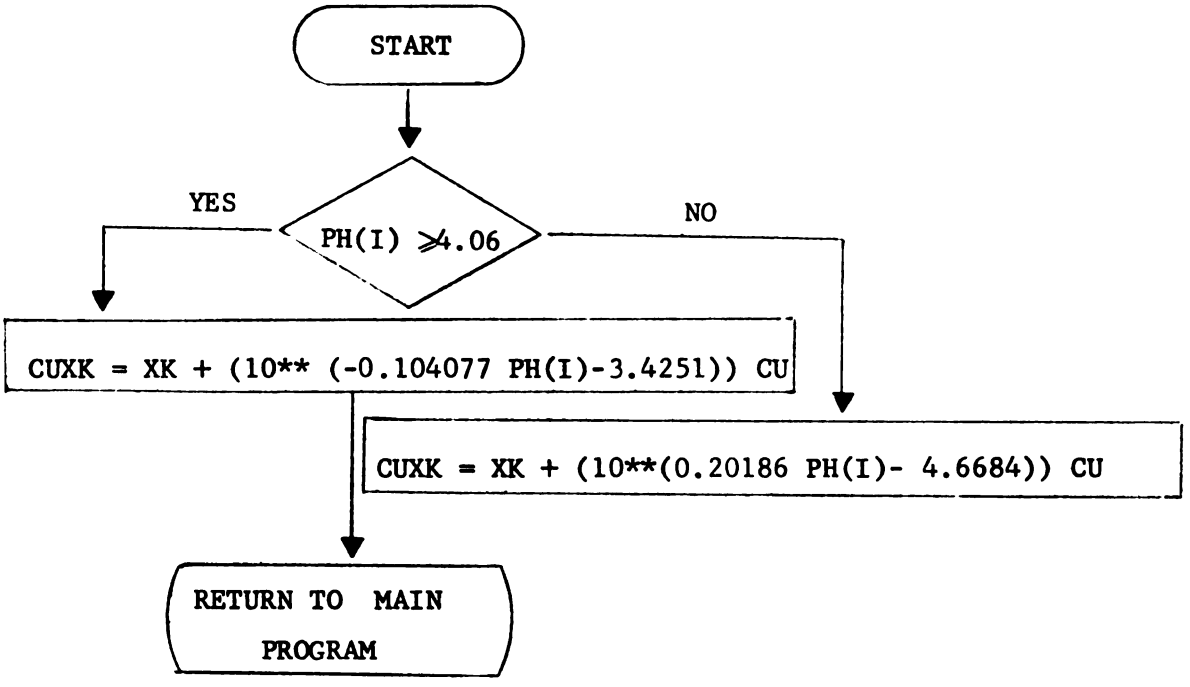


(1) Main Program

Figure 18. -- A flowchart of pH, temperature, and metal catalyst model.

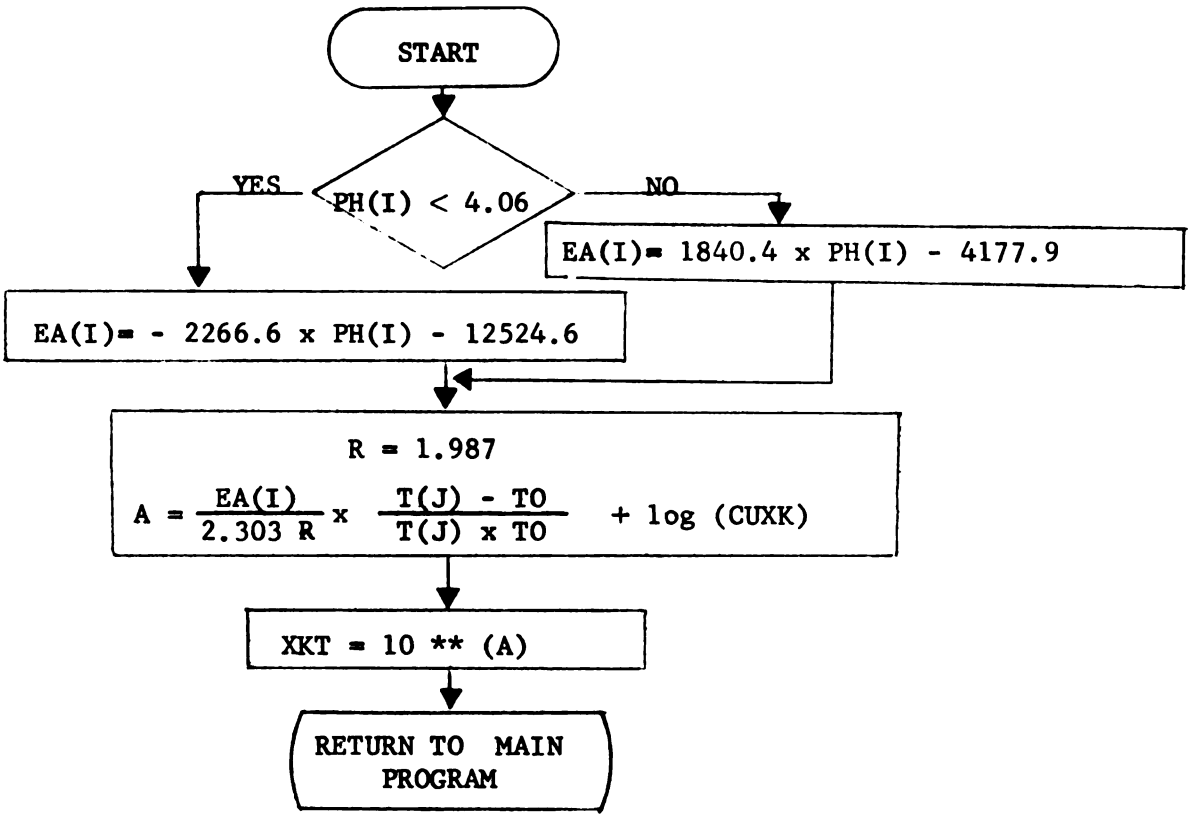


(2) Subroutine PHRATE

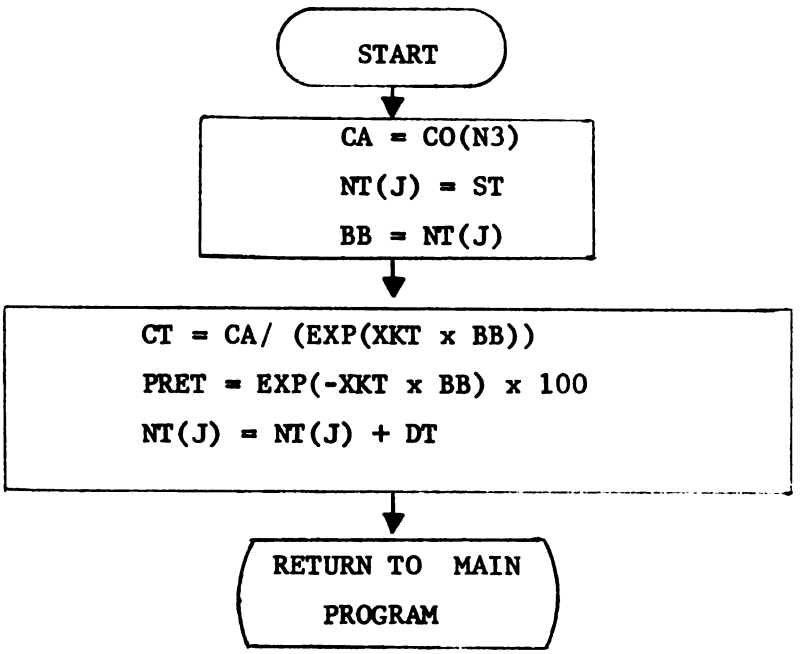


(3) Subroutine CURATE

Figure 18. -- Continued.

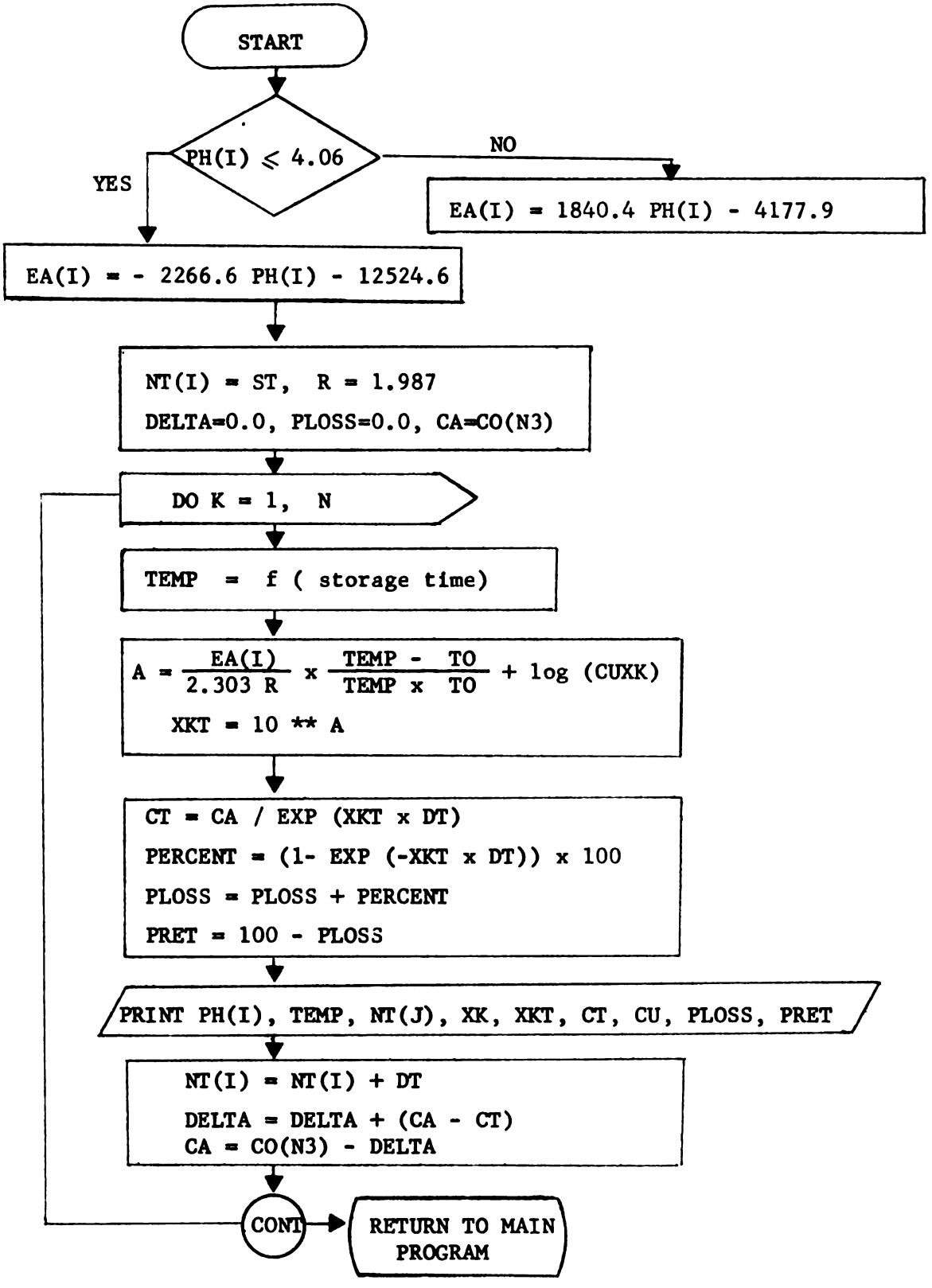


(4) Subroutine THERMO



(5) Subroutine COMPUTE

Figure 18. -- Continued.



(6) Subroutine CHANGE

Figure 18. -- Continued.

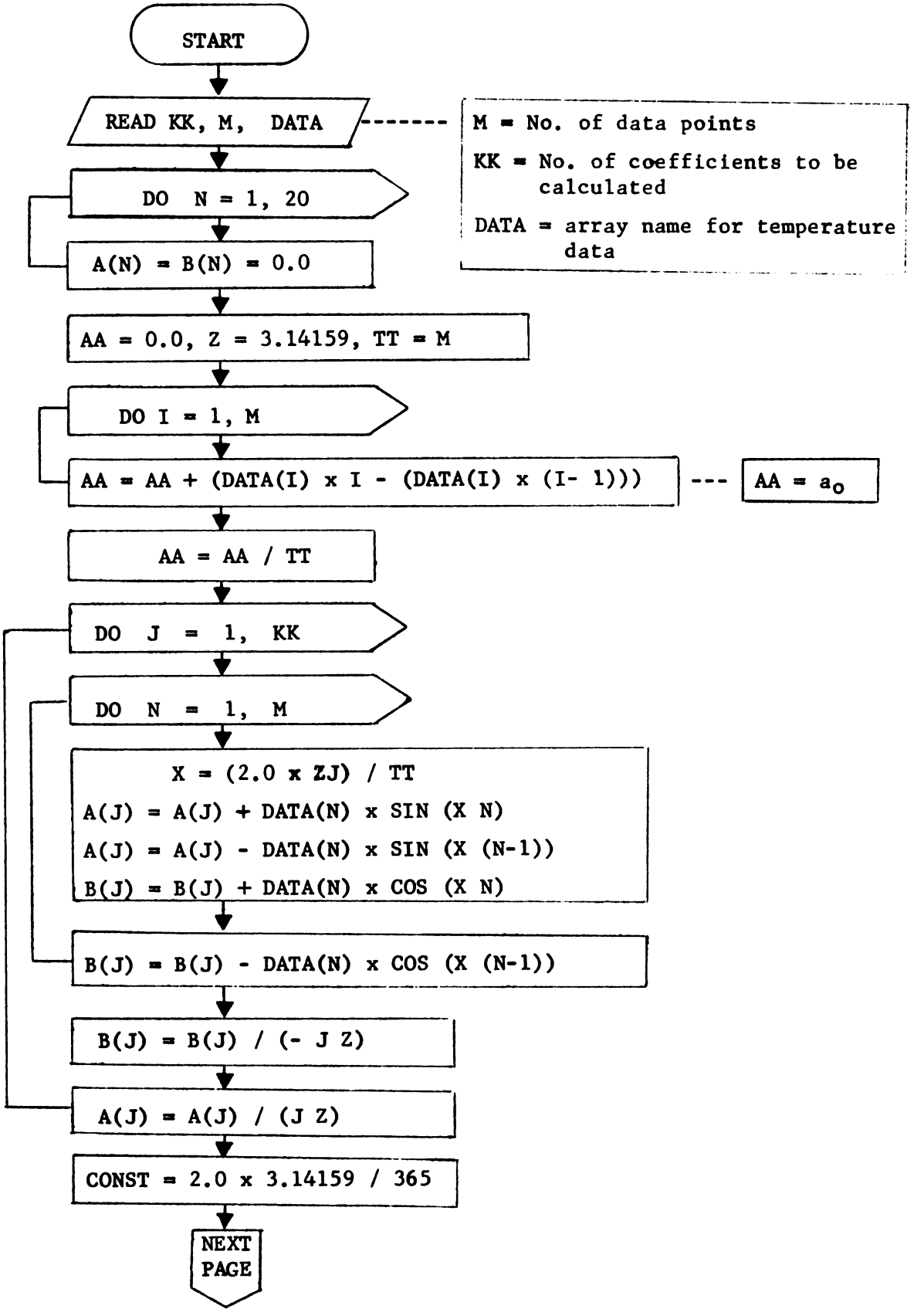


Figure 19. -- A flowchart to compute the Fourier Series.

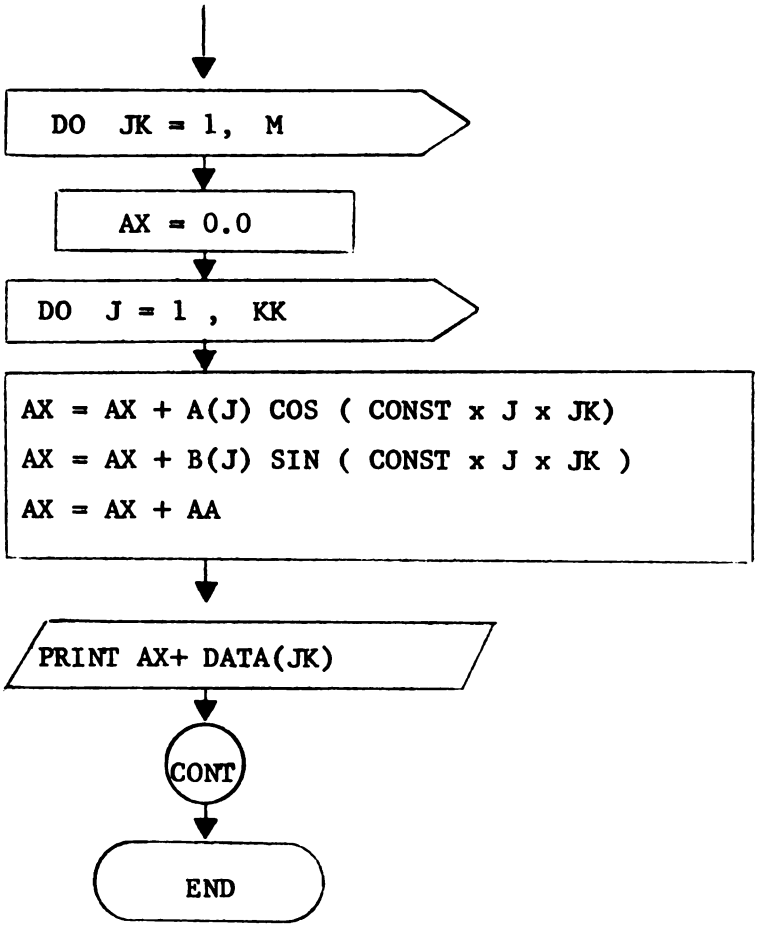
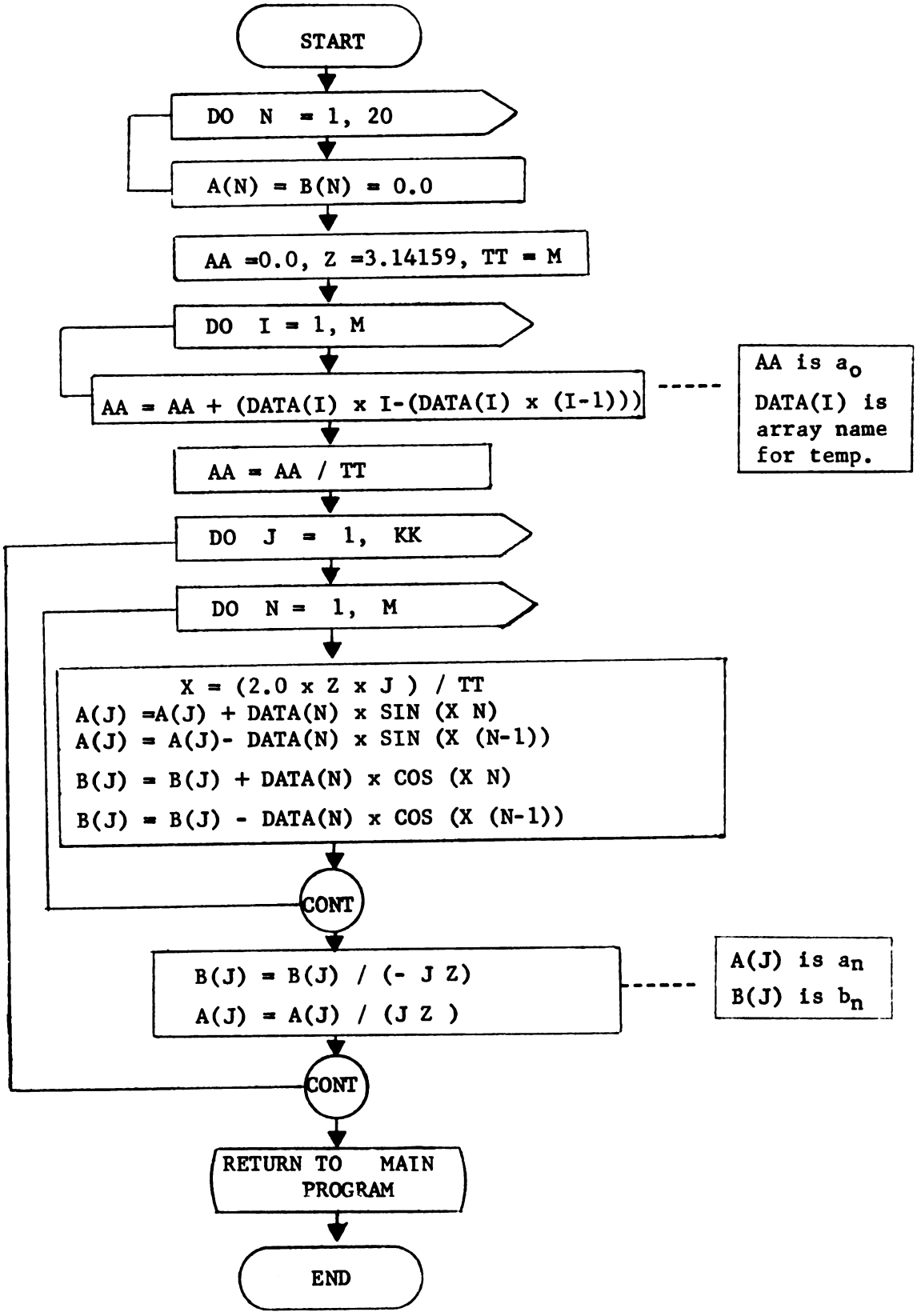
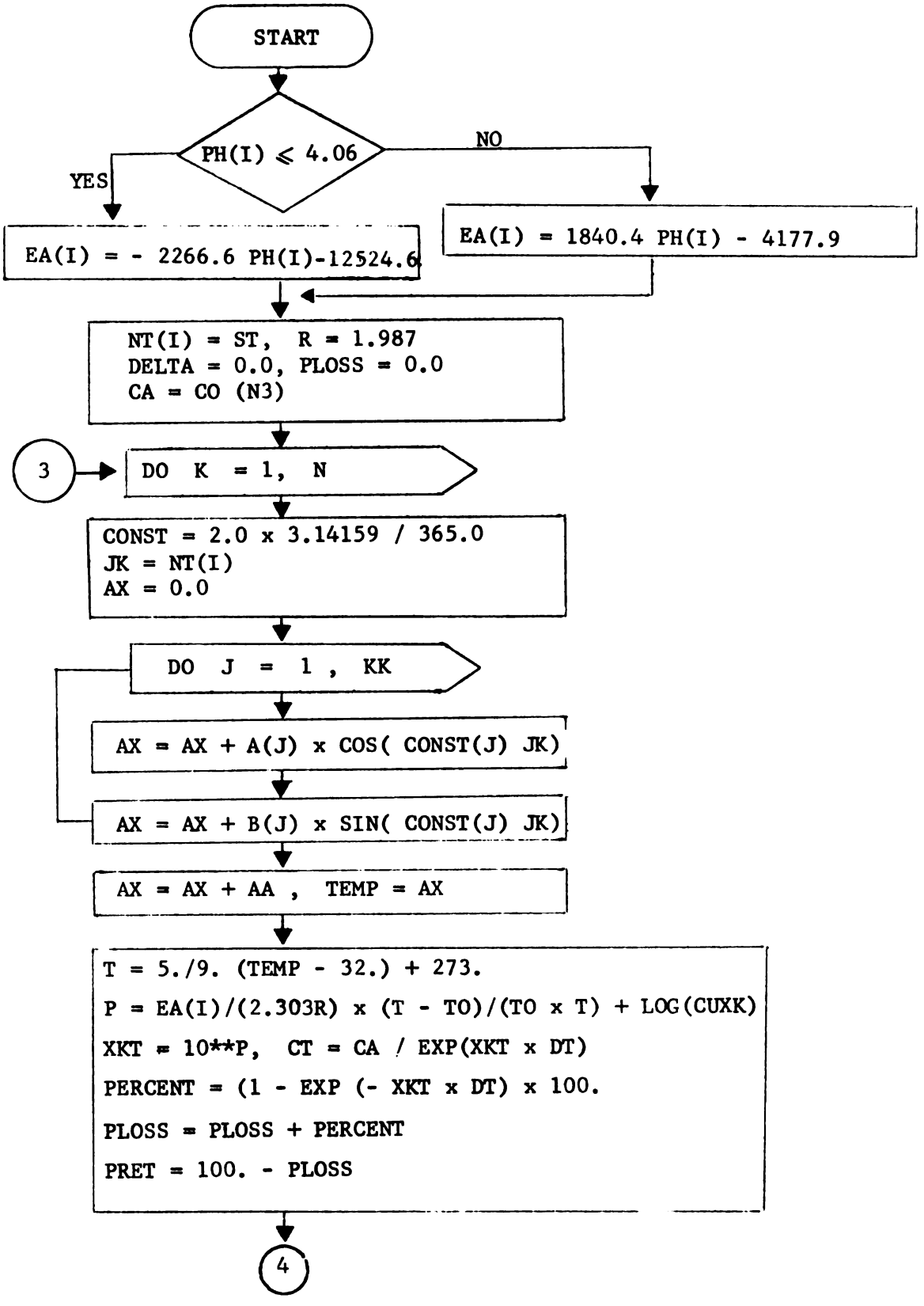


Figure 19. -- Continued.



(1) Subroutine FOURIER

Figure 20. -- Fowcharts of subroutine FOURIER and CHANGE.



(2) Subroutine CHANGE

Figure 20. -- Continued.

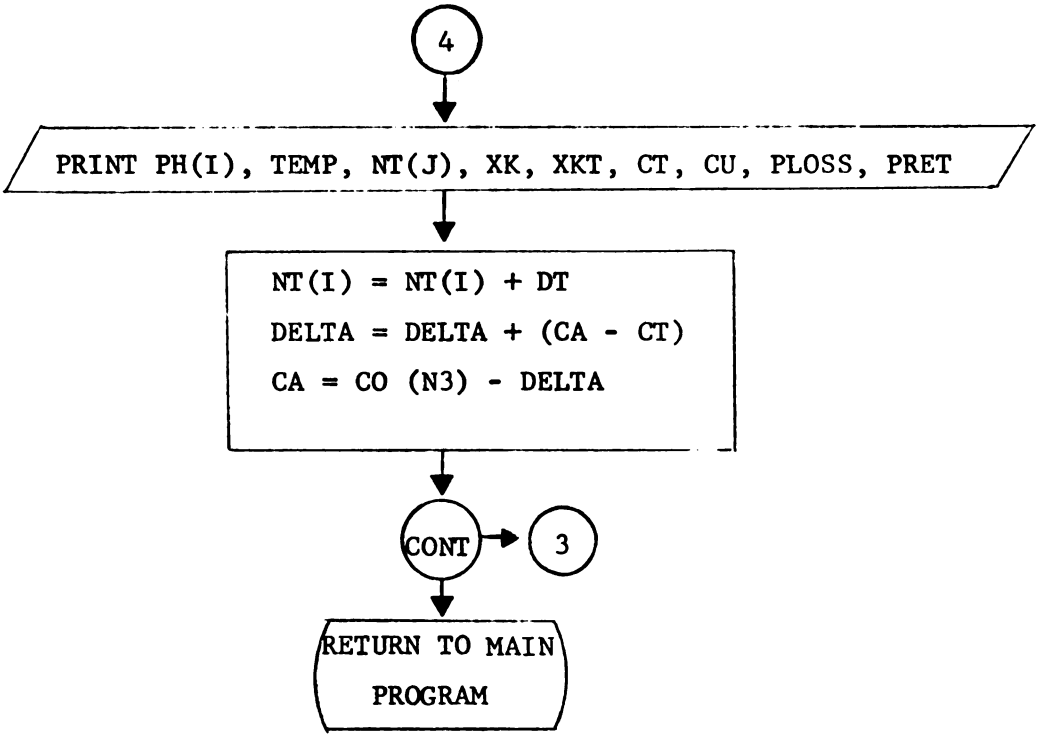


Figure 20. -- Continued.