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Edited by D. R. Heldman, Michigan State University

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CONTENTS

Meetings vii

Proteolysis by Immobilized Trypsin
ERIC A. GRULKE, MARTIN R. OKOS and **ALDRICH SYVERSON**, The Ohio State University, Columbus, Ohio 115

Indirect Energy Requirements for Vegetable Canning
W. VERGARA and **M. A. RAO**, New York State Agricultural Experiment Station, Cornell University, Geneva, New York 137

Retention of Sparingly Soluble Volatile Compounds During the Freeze Drying of Model Solutions
T. G. SMYRL and **MARC LEMAGUER**, University of Alberta, Edmonton, Alberta, Canada 151

Pasteurization of Cherry Brine in a Helically Coiled Heat Exchanger
PETROS Z. MINTZIAS, ALVIN L. RIPPEN and **LLOYD E. LEREW**, Michigan State University, East Lansing, Michigan . 171

Literature Abstracts 181

MEETINGS

JANUARY 1979

January 21—24: INTERNATIONAL EXPOSITION FOR FOOD PROCESSORS. Sponsored by Food Processing Machinery and Supply Association. Brooks Hall—Civic Center, San Francisco, California. Contact T. J. Gorman, Food Processing Machinery and Supply Association, Suite 700, 1828 L St. N.W., Washington, D.C. 20036.

FEBRUARY 1979

February 4—7: SEVENTY-FIFTH ANNUAL CONVENTION AND EDUCATION EXPOSITION OF THE UNITED FRESH FRUIT AND VEGETABLE ASSOCIATION. New Orleans, Louisiana. Contact D. Haropulos, Registrar, United Fresh Fruit and Vegetable Association, 1019 19th St. N.W., Washington, D.C. 20036.

February 14—15: DAIRY AND FOOD INDUSTRY CONFERENCE. The Ohio State University. Contact J. Lindamood, Department of Food Science and Nutrition, 2121 Fyffe Road, The Ohio State University, Columbus, Ohio 43210.

February 20—21: APPLYING STATISTICAL QUALITY CONTROL IN CANNING AND FREEZING PLANTS. Wisconsin Center, University of Wisconsin, Madison. Contact Engineering Registration, The Wisconsin Center, 702 Langdon St., Madison, Wisconsin 53706.

February 20—23: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. Louisiana State University. Contact A. F. Novak, Department of Food Science, Louisiana State University, Baton Rouge, Louisiana 70803.

February 26—28: SIXTH ENERGY TECHNOLOGY CONFERENCE AND EXPO 79. Sheridan Park Hotel, Washington, D.C. Contact Martin Heavner, Energy Technology Conference, 4733 Bethesda Avenue N.W., Washington, D.C. 20014.

February 26—29: WASTE MANAGEMENT '79. Double Tree Inn, 445 South Alvernon Way, Tuscon, Arizona 85711.

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February 26—Mar. 1: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. University of Washington, Seattle. Contact John Matches, University of Washington, Institute of Food Science and Technology, Seattle, Washington 98195.

MARCH 1979

March 1—2: ANNUAL FOOD TECHNOLOGY CONFERENCE. Ramada Inn, Columbia, Missouri. Sponsored by IFT Kansas City and St. Louis Sections. Theme: Food Ingredients — Sweetener and Preservatives. Contact S. A. Taillie, Paniplus Company, ITT Continental, 100 Paniplus Road Way, Olathe, Kansas 66061.

March 6—9: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. University of Minnesota, St. Paul, Minnesota. Contact E. A. Zottola, Department of Food Science & Human Nutrition, University of Minnesota, St. Paul, Minnesota 55101.

March 7—9: SHORT COURSE ON REACTION KINETICS OF FOOD DETERIORATION. Directed by Prof. Theodore P. Labuza, University of Minnesota, assisted by Daryl B. Lund, University of Wisconsin. Contact Food & Nutrition Press, Inc., 265 Post Road West, Westport, Connecticut 06880.

March 12—16: CORROSIONS/79. Atlanta Hilton Hotel, Atlanta, Georgia. Contact P. Larsons, Conference Coordinator, National Association of Corrosion Engineers. P.O. Box 986, Katy, Texas 77450.

March 19—22: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. The Ohio State University, Columbus, Ohio. Contact W. A. Gould, Department of Horticulture, The Ohio State University, 2001 Fyffe Court, Columbus, Ohio 43210.

March 26—29: WORLD SOYBEAN RESEARCH CONFERENCE — II. North Carolina State University, Raleigh. Contact B. E. Caldwell, World Soybean Research Conference, North Carolina State University, P.O. Box 5155, Raleigh, North Carolina 27650.

March 27—30: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. University of Maryland and Rutgers University. Contact R.C. Wiley, Department of Horticulture, University of Maryland, College Park, Maryland 20742.

APRIL 1979

April 10—13: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. Pennsylvania State University, University Park, Pennsylvania. Contact G. D. Kuhn, Department of Food Science, 106 Borland Building, Pennsylvania State University, University Park, Pennsylvania 16802.

April 23—26: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. Purdue University. Contact A. F. Badenhop, Institute of Food Science, Purdue University, West Lafayette, Indiana 47906.

MAY 1979

May 14—17: FDA-FPI-NFPA BETTER PROCESS CONTROL SCHOOL. Rochester, New York. Contact D. L. Downing, Department of Food Science Technology, Cornell University, Geneva, New York 14456.

JUNE 1979

June 10—13: 39TH ANNUAL MEETING & FOOD EXPO FOR INSTITUTE OF FOOD TECHNOLOGY. Alfonzo J. Cerdantes Convention Center, St. Louis, Missouri. Contact C. L. Willey, Institute of Food Technologist, Suite 2120, 221 North LaFalle Street, Chicago, Illinois 60601.

June 24—27: SUMMER MEETING OF THE AMERICAN SOCIETY OF AGRICULTURAL ENGINEERS. In cooperation with the Canadian Society of Agricultural Engineers. University of Manitoba, Winnepeg, Canada. Theme: International Dimensions in Engineering. Contact R. R. Castenson, Manager of Public Relations, American Society of Agricultural Engineers, 2950 Niles Road, St. Joseph, Michigan 49085.

AUGUST 1979

August 27—31: SECOND INTERNATIONAL CONGRESS ON ENGINEERING & FOOD, FOOD PROCESSING AND ENGINEERING 1979. Helsinkie University of Technology, Helsinkie, Finland. Contact Dr. J. Larinkari, P.O. Box 244, SF-101031 Helsinkie, Finland.

PROTEOLYSIS BY IMMOBILIZED TRYPSIN

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ABSTRACT

Trypsin immobilized on a phenol-formaldehyde resin was used as a model system to hydrolyze bovine serum albumin. An inhibitor was used during coupling to reduce autolysis. An automated GPC column showed that the reaction product distribution of the immobilized trypsin was different from that of the soluble enzyme. Enzyme loading affected the reaction product distribution. A 5% *loss in proteolytic activity was found after* 31 *days of use.*

INTRODUCTION

Treating protein with immobilized enzymes might be useful for causing specific alterations in the protein structure. The product of an enzymatic change in protein structure would probably have to command a premium price or result in a significant cost savings to be considered economical. The coupling efficiency, the catalytic activity and specificity, the catalyst life and the total cost of the supported enzyme system will determine the usefulness of the process.

Proteolytic enzymes have been widely studied. These enzymes hydrolyze peptide bonds. Depending on the degree of hydrolysis achieved, proteolytic enzymes can change the functional properties, the solubility or cause the degradation of the substrate proteins. Proteolytic enzymes can often catalyze their own degradation (this process is termed autolysis). Reducing autolysis during coupling may lead to more active catalyst systems. Steric hindrance of substrate diffusion to enzyme active sites can also affect the efficiency of the catalyst. Depending on the substrate, soluble enzymes may not be economically recoverable from

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a modified protein mixture and might be used only once. On the other hand, immobilized enzymes could be reused many times. Immobilized enzymes can be considered in the process design if their coupling efficiency, their activity at process conditions and their ability to perform the desired modifications are high. Trypsin was chosen as the proteolytic enzyme for this study since there was much information on its reaction with large and small substrates. Bovine serum albumin (BSA) was chosen as the protein substrate since its soluble hydrolysis by trypsin had been studied.

One of the problems of studying proteolysis is determining the extent of reaction. The molecular weights of the proteolysis products can be of interest to the food industry. In this work, gel permeation chromatography (GPC) was used to separate protein mixtures by molecular weight. The GPC column detector output was digitized and stored on a PDP-15 computer to increase the accuracy of the method.

LITERATURE REVIEW

The design of a proteolysis process requires information on the types of products formed and the rate of product formation at various process conditions. When using soluble enzymes, traditional activity assays can often be used to determine enzyme activities and rates. In these assays, the hydrolysis of a low molecular weight substrate is followed spectrophotometrically or by an automatic titration device. The extent of protein hydrolysis by soluble enzymes has been followed by viscosity and sedimentation measurements, free end-group titrations and peptide fragment separations (i.e. dialysis and precipitation). In the food and beverage industry, researchers are interested in the taste of the product. Since some low molecular weight polypeptides can alter taste, the identification of these materials is important. Evaluation of enzyme proteolysis can range from chill-haze tests on papain treated beer (Venkatasvbramanian *et al.* 1975) to the use of gel permeation chromatography, ion exchange chromatography and thin layer chromatography. King and Spencer (1970) and Markus *et al.* (1967) have used gel permeation chromatography to identify reaction products of albumin hydrolysis by soluble trypsin. They both noticed the rapid formation of large protein fragments which were later broken down to lower molecular weight polypeptides. Fujimaki *et al.* (1970) used GPC along with ion exchange and thin layer chromatography to identify some bitter

components of peptic hydrolysis of soybean protein. Cheftel *et al.* (1971) separated enzymatically solubilized fish protein by GPC and used the ninhydrin method for determining the number of free amino groups. GPC was used because it could separate the reaction products by molecular weight.

Immobilizing trypsin for use in hydrolyzing proteins presents special problems. Since trypsin undergoes autolysis, coupling conditions must minimize the tryptic self-digestion. Coupling should probably be irreversible, since active trypsin leaching off the support under reaction conditions could cause catalyst deactivation by undergoing autolysis and/or denaturing in the pore of the support. Two primary candidates for trypsin coupling methods are adsorption and covalent binding because these methods tend to reduce enzyme leaching. Since proteins are to be the substrates, the support should not sterically block the protein from catalytic sites or allow protein sorption on the support under reaction conditions. The microstructure of the support will affect protein diffusion, protein reaction and unfolding and diffusion of products back to the catalyst surface.

Other researchers have chosen rigid supports for coupling because of their versatility. Taylor and Swaisgood (1972) bound trypsin to polymer chains synthesized on a polystyrene matrix. The enzyme loading was 0.0024 g trypsin/g dry resin and no destabilization of the bound trypsin was observed. Several investigators have recently used immobilized trypsin catalysts for proteolysis. Lee *et al.* (1974) used trypsin immobilized on porous glass to hydrolyze proteins in milk. Trypsin leaching from the support caused them problems initially. Their later preparations had high enzyme loadings (0.025 g trypsin/g dry support), excellent storage life (94% retention of activity after 156 days at 5 °C) and good operational stability (50% loss in activity over 90 days with 1% casein). Knights and Light (1974) used Sepharose-bound trypsin to activate trypsinogen. The activity of the immobilized enzyme towards trypsinogen was only 40% of its activity toward a low molecular weight substrate. They attributed the reduction in activity to steric effects, both in the binding of the enzyme and in the movement of the protein through the support. Van Leemputten and Horisberger (1974) studied the activity of trypsin immobilized on partially oxidized cellulose toward 1% casein solution. The hydrolysis rates (as measured by the percentage of peptides soluble in 12% trichloroacetic acid) of soluble trypsin were compared to the rates of the insoluble trypsin. The initial hydrolysis rate of the insoluble trypsin was 3% of the initial soluble trypsin rate.

MATERIALS AND METHODS

Materials

Crystallized and lyophilized bovine serum albumin and lyophilized trypsin were obtained from the Sigma Chemical Company and were used without further purification. The porous phenol-formaldehyde resin, Duolite[3] DS-9737, was donated by the Diamond Shamrock Company, Redwood City, Cal. Analytical grade reagents and double-distilled water were used throughout the experimentation. Sephadex[4] G-75 was obtained from Pharmacia Fine Chemicals, Inc.

Gel Permeation Chromatography

Gel permeation chromatography can help separate the reaction products of protein digestions. To assist in the determination of peak area for quantitative analysis of protein concentration, a PDP 15 computer was used to digitize, store and analyze the chromatographic data.

A schematic drawing of the GPC apparatus is shown in Fig. 1. A known volume of sample was injected into the top of the column using a syringe in combination with the four-way valve. Immediately after injecting the sample, solvent flow was started and the computer began taking data. The syringe pump maintained a constant solvent flow throughout the elution with no pressure buildup. The ultraviolet absorbance of the column effluent relative to a reference was measured by an Ultraviolet Monitor[5]. The millivolt output of the Monitor was digitized by the computer and stored on magnetic tape every 10 sec during the chromatography run. The column was maintained at a constant temperature of 20 °C. The column packing was 40 × 1.6 cm of Sephadex G-75. The eluant was a 0.1 N $CaCl_2$-HCl buffer prepared at a pH of 2. The low pH reduced microorganism growth and trypsin autolysis in the column. At this normality, no proteins could be detected adsorbing to the column packing. When the column was stored for long periods of time, it was backwashed with 10 ml of 0.01% sodium azide solution. No microorganism growth was noted under these conditions.

Three to four data points, not including zero, were used for calibration curves. For BSA, plots of peak area versus concentration were linear to 8 g BSA/1. The calibration points were taken at different times during the study to check for column fouling. When the column was at 20 °C,

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[3]Registered trademark, Diamond Shamrock Company
[4]Registered trademark, Pharmacia Fine Chemicals, Inc.
[5]Registered trademark, Pharmacia Fine Chemicals, Inc.

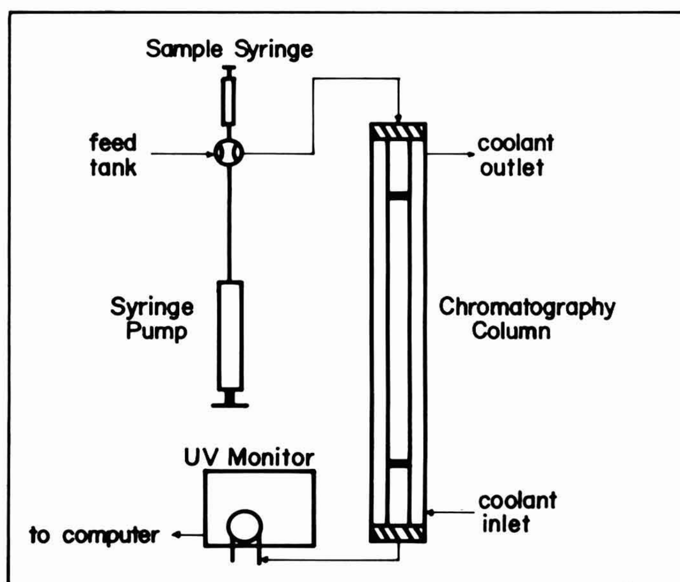

FIG. 1 SCHEMATIC DRAWING OF THE GEL PERMEATION CHROMATOGRAPHY EQUIPMENT

variations in peak area were less than 4% for replicate samples.

Computation of Peak Area

In many chromatographic techniques, the parameter which gives the best linear response with sample concentration is peak area. Each peak on a GPC chromatogram may not represent a pure component. As a first step toward evaluating peak spreading and multiple peaks, the higher order moments of the chromatogram were computed. These parameters were useful in determining the degree of separation.

The absorbance of the UV monitor was computed relative to the baseline by averaging 6 to 40 data points on each side of the peak. Area was computed in units of millivolt-minutes. The monitor signal was in the range of 0 to 10 millivolts, although negative values were also accurate. The volume of sample to be injected in the column was chosen after comparing the elution characteristics of several different sample sizes. A volume of 0.4 ml seemed to give the best separation. Peak areas determined for one setting of the UV monitor attenuation corresponded linearly with peak areas determined at different attenutations. Figure 2

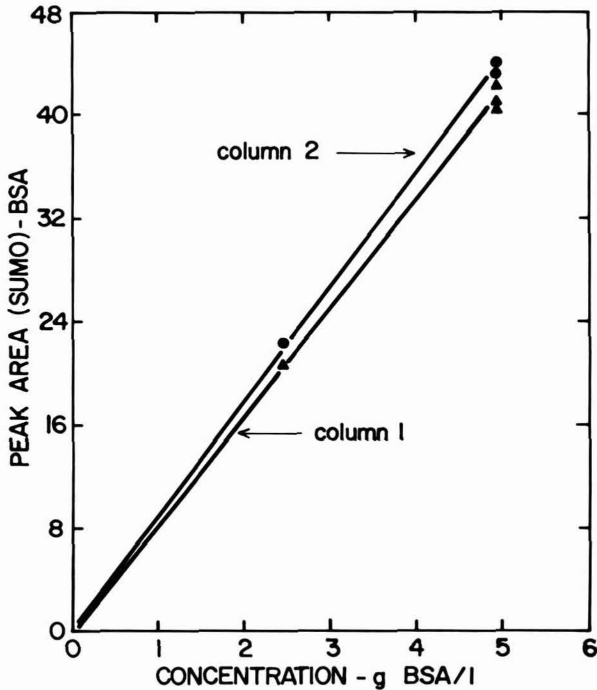

FIG. 2. BOVINE SERUM ALBUMIN CALIBRATION CURVES SHOWING PEAK AREA (MV-MIN) VERSUS BSA CONCENTRATION (g BSA/1)

shows two typical calibration curves for BSA taken with two different columns.

Figure 3 shows the chromatogram of a 5.0 g BSA/1 sample. This peak had significant skewing on the trailing edge compared to other pure component samples. Other samples had much less skewing. The peak was assumed to occur between 35 and 60 min (most other BSA samples were eluted in this interval with this column). None of the protein peaks were Gaussian, therefore the 0th, 1st and 2nd order moments were used to describe the curves. The zeroth order moment is given by

$$m_0 = \int_0^\infty c(t)\, dt \tag{1}$$

The first order, normalized moment is

$$u_1 = \frac{1}{m_0} \int_0^\infty t\, c(t)\, dt \tag{2}$$

The second order, normalized moment is

$$u_2 = \frac{1}{m_0} \int_0^\infty t^2\, c(t)\, dt \tag{3}$$

The leading and trailing baseline values were computed by a 10 point average. The baseline during elution was assumed to be linear between these two values.

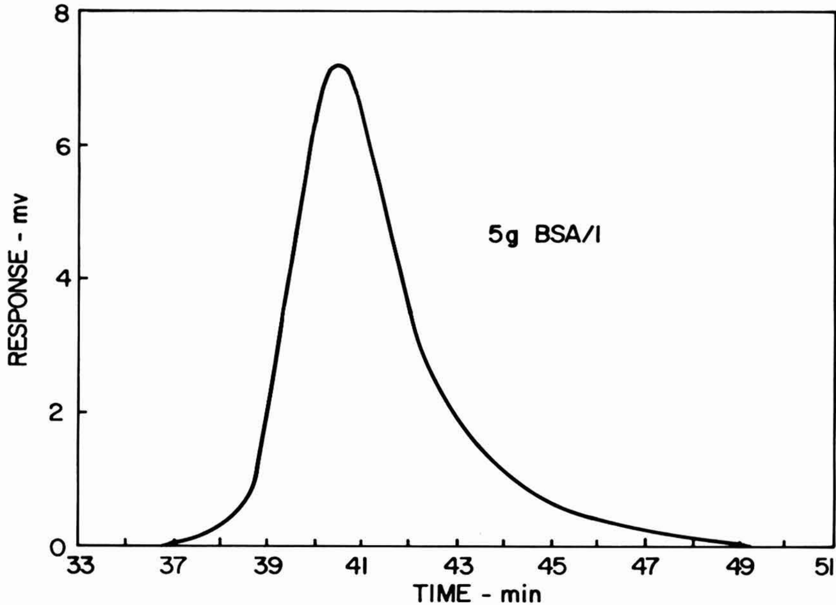

FIG. 3. CHROMATOGRAM OF A 5 g BSA/1 SOLUTION

Two-component samples were routinely analyzed in a similar manner. Figure 4 shows chromatograms of two concentration levels of trypsin and benzamidine. Table 1 gives the solute concentrations, areas under the peaks, mean elution times and the second moments of the curves. Both samples were acidified to pH 2.0 before elution to minimize autolysis. Changes in the curve parameters were used as an aid for detecting changes in protein composition due to autolysis or hydrolysis.

Samples containing autolysis or hydrolysis products were analyzed routinely for protein composition by the same chromatographic technique. Figure 5 shows a chromatogram of a sample of BSA solution which had been hydrolyzed at 40 °C at pH 8.5 for 1.3 hr. For the samples examined in this study, BSA hydrolysates produced using a heterogeneous catalyst exhibited two major fragments—high molecular weight materials of a size similar to the starting material and low

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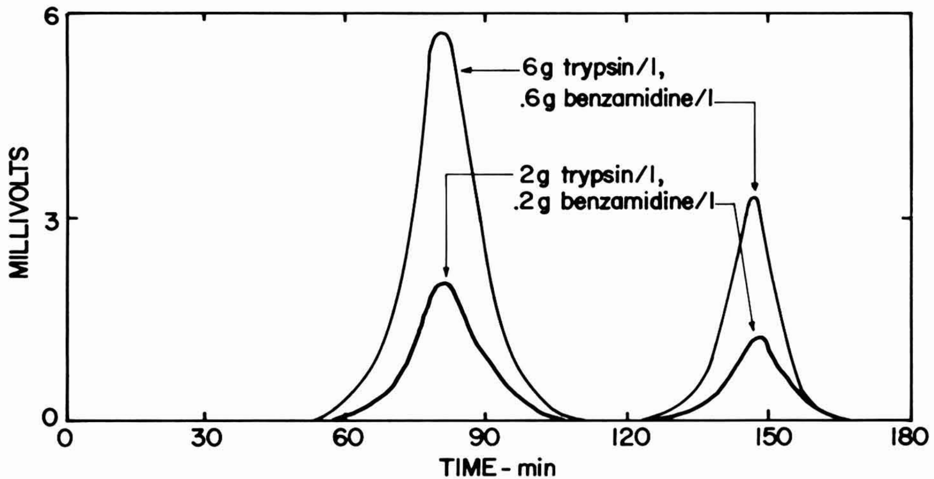

FIG. 4. CHROMATOGRAMS OF TWO-COMPONENT SAMPLES OF TRYPSIN AND BENZAMIDINE

Table 1. Calculated parameters for chromatograms

	Sample 2	Sample 6
Trypsin Peak		
Concentration	1.95 g/1	6.08g/1
Area	33.9 mv-min	99.2 mv-min
Mean elution time	80.2 min	80.3 min
Second moment	45.6 min²	45.9 min²
Benzamidine Peak		
Concentration	.195 g/1	.616 g/1
Area	16.9 mv-min	47.4 mv-min
Mean elution time	146.0 min	146.0 min
Second moment	25.6 min²	26.6 min²

molecular weight fragments of less than 2000 molecular weight. BSA hydrolysates consistently had a skewed trailing edge on the high molecular weight peak. This peak probably consists of a range of materials. From a kinetic and analytical point of view, it was not clear what area of this curve would represent unreacted BSA. The interval taken to represent the unreacted BSA peak was arbitrarily chosen to be

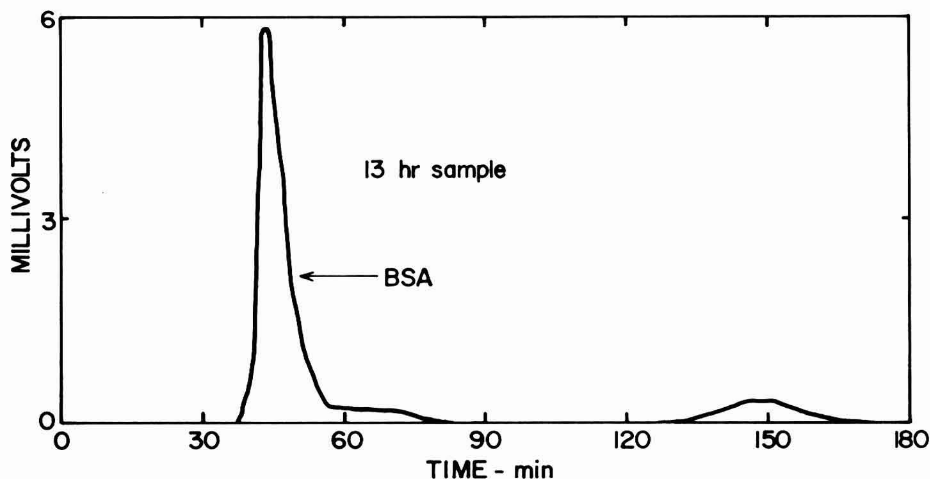

FIG. 5. CHROMATOGRAM OF IMMOBILIZED TRYPSIN BSA HYDROLYSATES

the same as the BSA peak interval of a pure component sample. The average of 10 points was used as the value for the leading baseline. Since the material causing the trailing edge was assumed to be a reaction product, the trailing baseline was taken as the value of the curve at the normal endpoint. The straight line connecting the baselines at 35 and 60 min was used as the baseline for the peak. On this basis, the value calculated for the BSA peak probably can be taken as a minimum value. However, it was felt that this was a fair approximation to the separation problem in the absence of more sophisticated mathematical and analytical tools.

Trypsin Adsorption on a Phenol-Formaldehyde Resin

Several different catalysts were made in this laboratory by adsorbing trypsin on ion exchange resins and by covalent coupling to various supports. However, many of these catalysts could not be analyzed for active sites spectrophotometrically, by the pH-stat or by the quick-burst method. Benzoylarginine ethyl ester (a standard low molecular weight substrate) and benzoylarginine (its reaction product) were found to adsorb to the resin, altering the mass balance. When using titration techniques, the supports often reacted with the base, causing high blank values and loss of accuracy. Therefore, only hydrolysis of proteins were studied.

A major problem with many of the experimental catalysts prepared in

this laboratory was trypsin autolysis during adsorption. Crosslinking the enzyme in place with glutaraldehyde did not improve catalyst stability. A solution to the autolysis problem was based on a technique of Beaven and Gratzer (1973). They experienced oligomer formation and autolysis when crosslinking soluble trypsin with glutaraldehyde for binding studies. The inhibitor benzamidine significantly decreased oligomer formation and autolysis. During catalyst preparation, 15 moles of benzamidine per mole of trypsin were added to the adsorption solution to reduce autolysis.

A phenol-formaldehyde resin was used as the support for trypsin in this study. The enzyme, b-galactosidase, and other enzymes had been successfully immobilized to this support (Okos 1975; Olson and Stanley 1973; Grulke 1975). The resin is rigid and is not comminuted in a stirred tank reactor.

Most adsorption data for trypsin adsorbing on Duolite DS-9737 were taken with batch experiments. One gram of wet resin was weighed and cleaned. Cleaning was done by washing the resin with 0.1 N NaOH and then 0.1 N HCl solutions at room temperature for 10 min each. The resin was equilibrated with buffer solution at the temperature and pH for the adsorption experiment for at least ½ hr.

For the adsorption experiment, 10 ml of buffer were placed in a dry polyethylene tube. Benzamidine was added and the solution was well mixed. Trypsin was added in the powder form. A batch of resin was decanted over a glass suction funnel and added quantitatively to the trypsin-benzamidine solution. The tube was stoppered and placed in a water bath at the appropriate temperature. The test tube was shaken periodically during the 4- to 6-hr adsorption period. The order of component addition did not affect the steady-state adsorption of trypsin.

At the end of the adsorption period, part of the supernatant liquid was pipetted from the test tube. Exactly 3.0 ml of this adsorption solution was acidified with 0.3 ml of 0.10 N HCl and stored in polyethylene bottles at 5 °C. Under these conditions, no tryptic hydrolysis could be detected by the chromatograph (detectable to less than 0.1 g trypsin/l).

Stirred Tank Reactor

A 500 ml stirred tank reactor was used for kinetic and adsorption experiments. Baffles were made from 16 gauge stainless steel cut in strips of 1/10 of the tank diameter. The baffles were silver-soldered to two rings of heavy stainless steel wire. A miniature pH probe could be clamped and grounded to the baffles. The impeller was fashioned of Pyrex glass and

the total impeller diameter was 1/3 of the tank diameter.

Catalyst Preparation

The catalysts used for BSA hydrolysis were made in the stirred tank reactor. The resin was cleaned by the same procedure employed for the adsorption experiments. Lyophilized trypsin was slowly added to the stirred solution when both the resin and the solution were at 40 °C. Trypsin addition was complete in 2 min. The reactor was then sealed and stirring was continued for the entire adsorption period. Trypsin concentration in the solution was measured by using the GPC column. Conventional active assays of BAEE could not be used with this support since the resin could sorb arginine.

BSA Hydrolysis by Immobilized Trypsin

All kinetic data for the heterogeneous catalysis runs were taken in the stirred tank reactor. About 10 to 20 g of wet catalyst were used to react with 250 to 500 ml of protein solution in order to keep the catalyst volume to reactor volume ratio less than 0.10 (Lewis and Paynter 1971). The catalyst particles were injected into the reaction solution to start a run. Stray particles were washed back into the slurry with reaction fluid and the reactor was then sealed. The entire catalyst charging operation was completed in 60 sec. Samples of the reaction fluid were taken using a syringe. Reaction samples were acidified and stored by the same procedure used for the adsorption samples. Repeated washings of this catalyst with buffer solution did not leach trypsin from the support. No low molecular weight polypeptides were detected in the chromatograms of these subsequent washes.

RESULTS

Trypsin-Benzamidine Adsorption

An unsteady-state adsorption of trypsin and benzamidine on the resin was run at 30 °C, pH 10 to determine the time required for equilibrium adsorption. Trypsin adsorption was completed in about 2 hr. At this time, no trypsin was detectable in the adsorption solution by the GPC column. About 30% of the benzamidine in solution absorbed on the resin. Since benzamidine adsorption was completed at the same time as trypsin adsorption despite the great differences in their diffusivities,

benzamidine was probably associated with the trypsin during this process.

Desorption and subsequent autolysis had been problems with other catalysts. When benzamidine was used, desorption of trypsin from the support could be studied with only minimal autolysis occurring. Figure 6 shows a batch adsorption and desorption. For the desorption experiment, only buffer solution was added to the decanted resin. No trypsin desorbed from the resin (as detectable by the GPC column) although benzamidine did desorb. Some trypsin autolysis may have occurred during adsorption as evidenced by the slight skewing in the low molecular weight peak. The moments of the low molecular weight peak of the first wash were slightly different from those of benzamidine. The amount of trypsin adsorbed on this catalyst sample was 0.115 g trypsin/g dry resin.

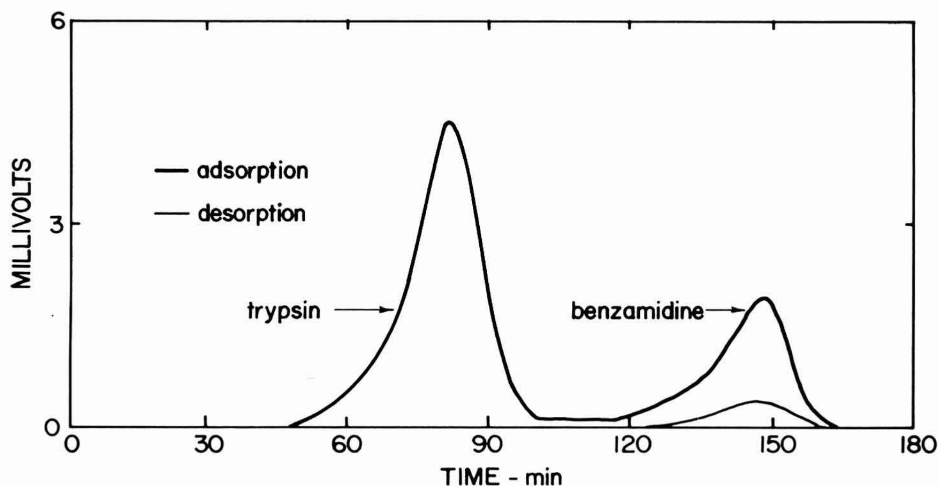

FIG. 6. CHROMATOGRAMS OF AN ADSORPTION RUN FOLLOWED BY A DESORPTION RUN

A series of adsorption isotherms were taken at 20 °C. Phosphate buffer was used for pH 6 and pH 8.4. Borate buffer was used for pH 8.55 and pH 10. Figure 7 shows these adsorption isotherms. Trypsin adsorption increased with pH. It is not known whether the high adsorption of trypsin at pH 10 is related to its isoelectric point (pH 10.8). There is a significant difference between the isotherm at pH 8.4 and the isotherm at pH 8.55. Not all this difference may be attributable to the different buffers

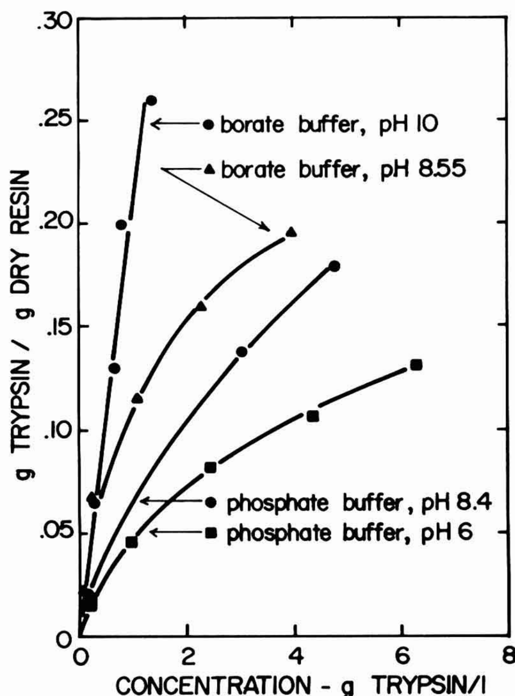

FIG. 7. EFFECT OF pH ON TRYPSIN ADSORPTION ISOTHERMS

0.10 N buffers, 20 °C, 15 moles benzamidine/mole trypsin

used. According to the manufacturer's description of the resin, salts are dissociated from the resin above pH 8.5. The difference between these isotherms may be due in part to this dissociation phenomenon.

A series of adsorption runs was done at pH 10 at 3 temperatures. Figure 8 shows that adsorption increased with temperature in the range 0 to 40 °C. The adsorption done at 40 °C shows extremely high loadings. The GPC column showed that some autolysis occurred in these adsorption solutions, with the most autolysis occurring at the highest enzyme concentrations. The curve for the adsorption at 40 °C has arbitrarily been drawn through the points, although the points with high loadings (0.8 g trypsin/g dry resin) may have had as much as 30% error in the concentration values. None of the traditional adsorption isotherms describe these data. The 40 °C isotherm may represent a saturation of the support.

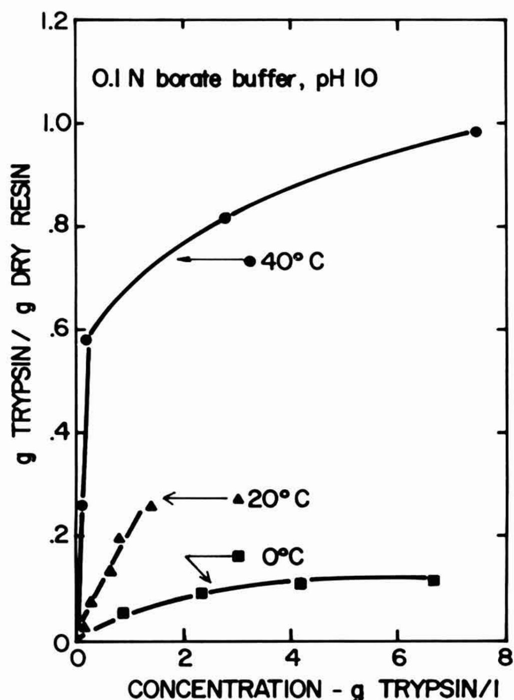

FIG. 8. EFFECT OF TEMPERATURE ON TRYPSIN ADSORPTION ISOTHERMS

0.10 N borate buffer, pH 10, 15 moles benzamidine/mole trypsin.

BSA Hydrolysis

All of the catalysts were tested in 5 g BSA/1 solutions at 40 °C and pH 8.5 with 0.1 N borate buffer. A comparison of typical initial solution and 24-hr hydrolysate chromatograms is shown in Fig. 9. There are two major peaks in the hydrolysate chromatogram. The first peak is the BSA peak. The 24-hr hydrolysate sample shows the presence of products a little smaller than BSA, implying that some BSA has been only slightly altered. The peak appearing at long elution times represents polypeptides. The size of the low molecular weight peak always increased as the size of the BSA peak decreased. The initial protein solution and the hydrolysis solution were analyzed for free α-amino groups. The large increase in free α-amino groups in the hydrolysis solution indicated that a reaction had taken place. The appearance of mostly low molecular weight

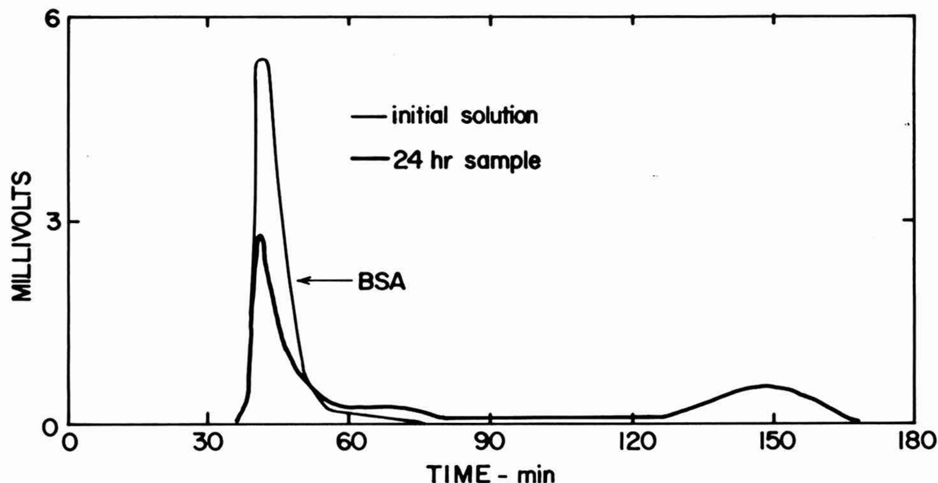

FIG. 9. COMPARISON OF INITIAL SOLUTION AND 24-HR HYDROLYSATES
pH 8.5, 0.1 N borate buffer, 10 g wet catalyst/250 ml solution, 5 g BSA/1 in initial solution.

polypeptides as reaction products implies that once it diffuses to an active site in the support, the BSA reacts almost completely to low molecular weight products before large protein fragments can diffuse back to bulk solution.

Catalyst life is important in evaluating the usefulness of a particular catalyst. The first batch of catalyst made by the adsorption technique was assayed 31 days after it was made, by which time it had been hydrolyzing BSA for 14 days and had been stored for 17 days in pH 8.5 buffer at room temperature. Figure 10 shows that the 24-hr hydrolysates from the aged catalyst contained 5% more BSA, indicating a slight drop in activity. This drop in activity includes any trypsin autolysis, catalyst pore fouling and denaturation that resulted from the catalyst's treatment in addition to any losses incurred during transfer operations.

For the first 24 hr of hydrolysis, no significant levels of products were observed between the BSA peak and the low molecular weight peak. However, after 24 hr, reaction products were observed in this range (see Fig. 11). During this same time, the rate of disappearance of BSA had slowed considerably. The reaction may be sterically hindered by reaction products slowing substrate diffusion to active sites or may be chemically inhibited by reaction products.

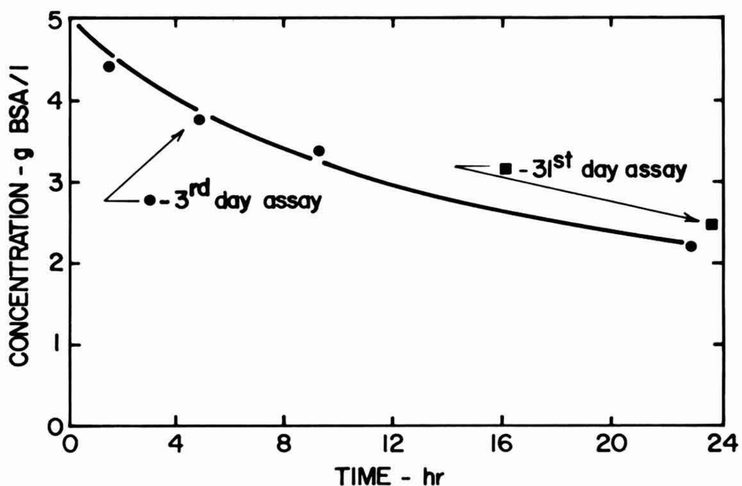

FIG. 10. CATALYST ACTIVITY AFTER AGEING

pH 8.5, 0.1 N borate buffer 10 g wet catalyst/250 ml solution, 5 g BSA/1 in initial solution.

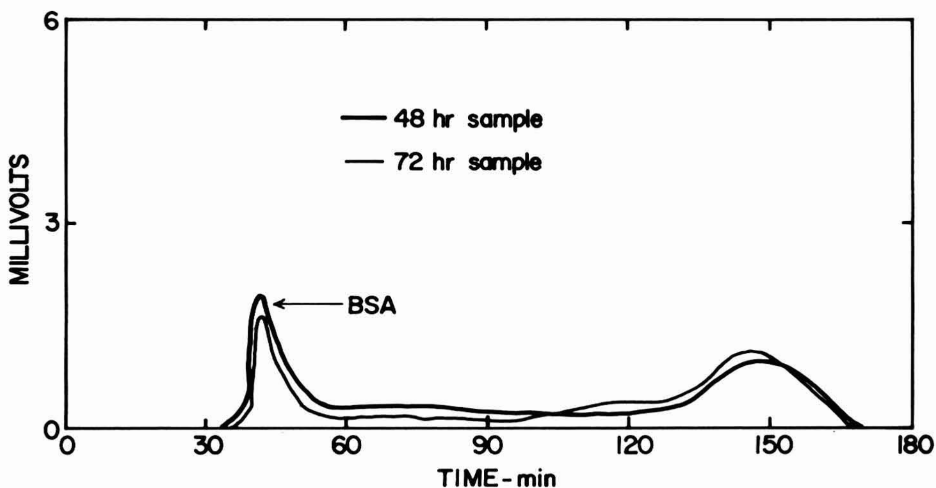

FIG. 11. CHROMATOGRAMS OF HIGHER CONVERSION BATCH HYDROLYSIS RUNS

The BSA hydrolysates produced by the immobilized trypsin were distinctly different from the reaction products made by trypsin in solution. Figure 12 shows two typical chromatograms of soluble trypsin-BSA hydrolysates. Every chromatogram of these materials showed reaction products throughout the molecular weight rage of the GPC column. In contrast, the immobilized trypsin generated no medium molecular weight materials until after 24 hr of reaction (Fig. 9, 10). At similar levels of BSA reduction, the immobilized enzyme made more low molecular weight polypeptides. The immobilized trypsin hydrolysates also seemed different from the soluble trypsin hydrolysates reported by King and Spencer (1970) and Markus *et al.* (1967). Large hydrolysis fragments were not observed in the same yields as reported by these authors.

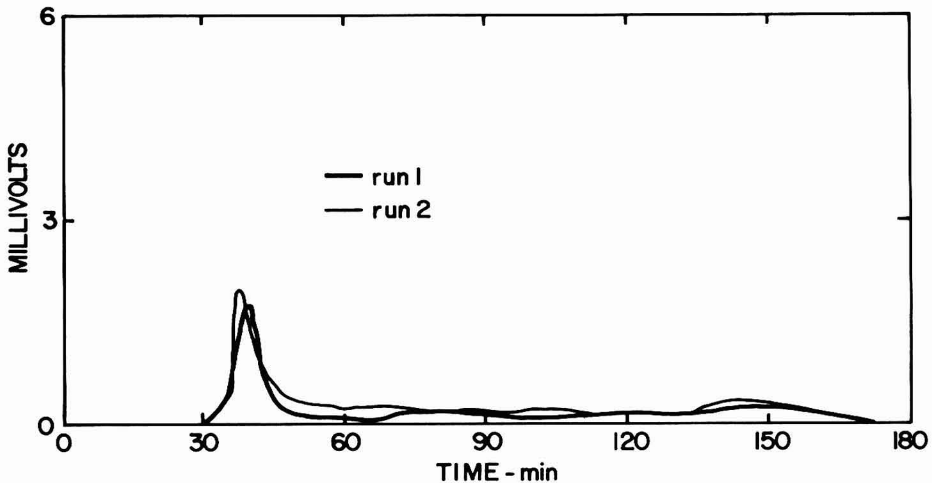

FIG. 12. CHROMATOGRAMS OF SOLUBLE TRYPSIN HYDROLYSATES

The immobilized trypsin seems to give a different product distribution from the soluble enzyme. This product distribution may be affected by enzyme loading. A second catalyst batch was made with one-half the amount of trypsin on the resin as the first batch. As shown in Fig. 13, both of these catalysts showed the same amount of disappearance of BSA for a 24-hr hydrolysis period. However, the amount of low molecular weight materials generated by the second catalyst was less than that produced by the first catalyst (see Fig. 14). The remainder of the reacted BSA may have been of intermediate molecular weight. (The UV detector

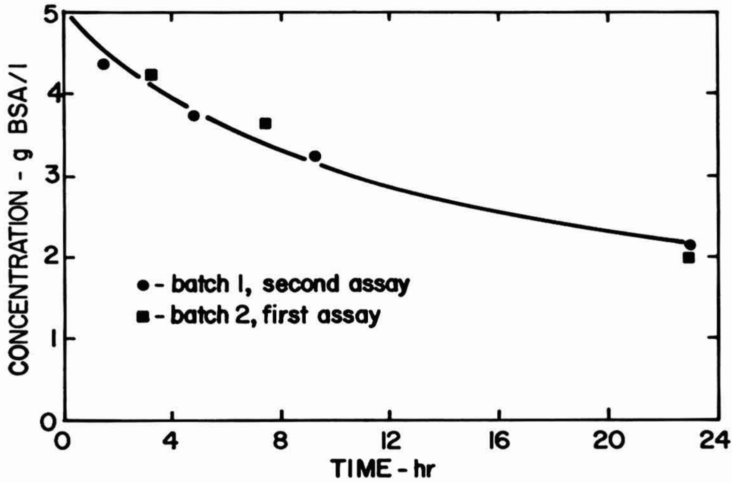

FIG. 13. COMPARISON OF TWO CATALYSTS; BSA HYDROLYZED

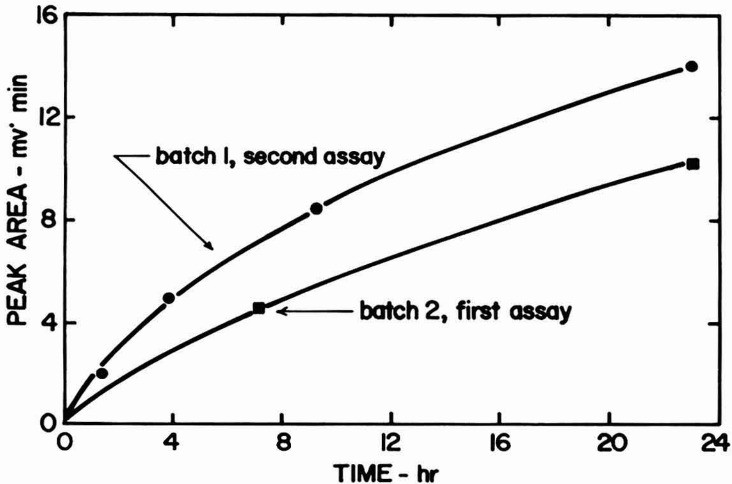

FIG. 14. COMPARISON OF TWO CATALYSTS; LOW MOLECULAR WEIGHT POLYPEPTIDES PRODUCED

had a higher response during the middle of the elution of the reaction products from the second catalyst, but it was not resolved into a distinct peak). At the lower enzyme loading, there would be less enzyme and less steric hindrance to diffusion at a reactive site. The probability that large fragments could diffuse from the catalyst before extensive hydrolysis was higher for the lower enzyme loading.

The hydrolysis of BSA by the immobilized trypsin catalyst resulted in a bimodal product distribution. However, low molecular weight polypeptides can contribute a bitter taste to foods. Another protein, β-lactoglobulin (35,000 MW), was hydrolyzed to determine whether it would also yield mainly low molecular weight polypeptides. Figures 15 and 16 show hydrolysates at various times during the run. Qualitatively, β-lactoglobulin reacted faster than BSA and yielded products with a range of molecular weights. The β-lactoglobulin peak area decreased to 55% of the original area in the 7-hr sample. An interesting feature of the 24-hr sample is the appearance of a high molecular weight peak which is probably precipitated protein.

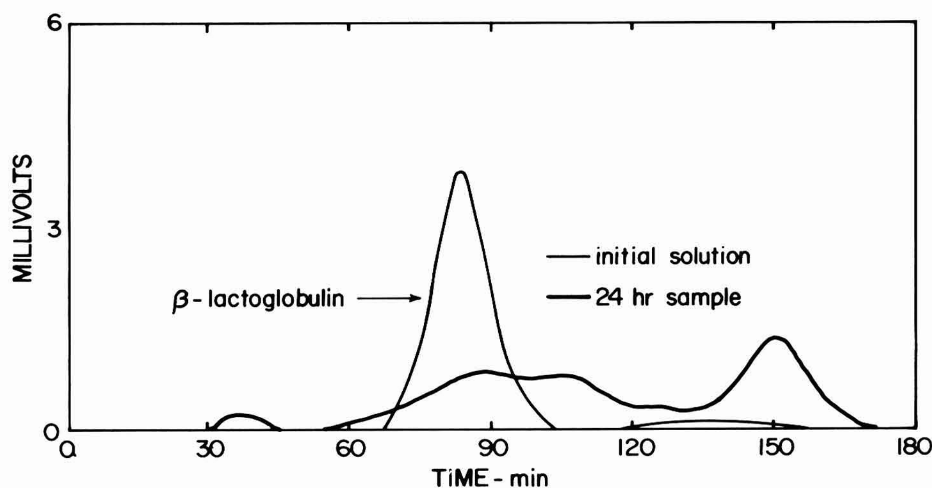

FIG. 15. HYDROLYSIS OF β-LACTOGLOBULIN

4 g β-lactoglobulin/l, pH 8.5, 40 °C, initial solution and 24 hr hydrolysates.

CONCLUSIONS

Gel permeation chromatography was a useful tool for measuring trypsin coupling to a phenol-formaldehyde resin. Automation of the column allowed quantitative determination of protein concentration. The column could be used to follow both adsorption and desorption of materials from the catalyst. Trypsin adsorption with benzamidine present in the solution greatly reduced autolysis during coupling. Trypsin adsorption on the support increased with temperature in the range 0 to 40 °C and increased with pH in the range pH 6 to 10 using 0.1 N buffers. The column

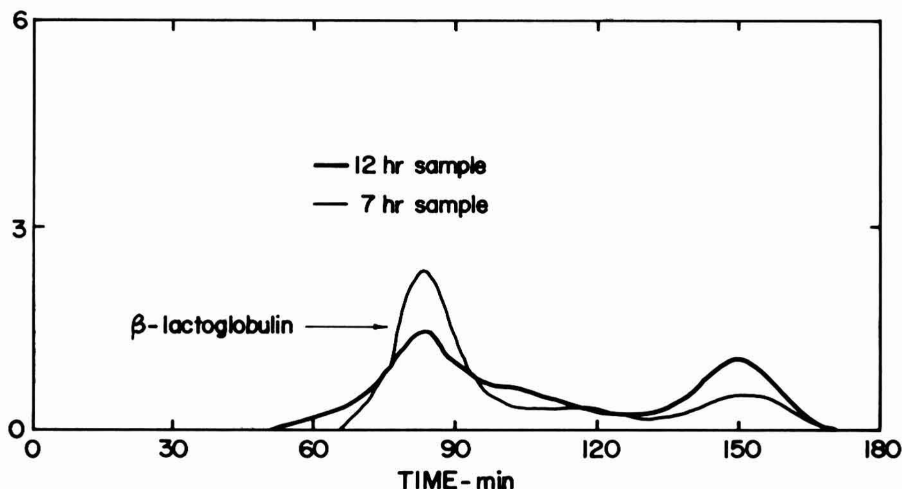

FIG. 16. HYDROLYSIS OF β-LACTOGLOBULIN
4 g β-lactoglobulin/1, pH 8.5, 40 °C, 7 and 12 hr hydrolysates.

could not detect any trypsin leaching from the resin, indicating that the coupling was stable. One catalyst showed only a slight loss (5%) in BSA proteolysis activity after 31 days, also indicating a stable coupling.

BSA hydrolyzed by the immobilized trypsin catalyst gave two major fragments—large molecular weight materials and small molecular weight polypeptides. Gel permeation chromatography of soluble trypsin hydrolysates of BSA showed reaction products throughout the molecular weight range of the column. Heterogeneous trypsin hydrolysates of BSA seemed to be distinctly different from soluble trypsin hydrolysates. Varying trypsin loading on the support changed in the amount of products produced but still resulted in a large low molecular weight polypeptide peak.

The use of an inhibitor during coupling can greatly reduce autolysis when immobilizing a proteolytic enzyme. Gel permeation chromatography can be useful for describing changes in enzyme proteolysis after coupling. It can help identify autolysis and it constitutes a first step in analyzing reaction products. Changes in reaction products due to changes in enzyme loading may be a significant way of achieving the desired protein modification.

ACKNOWLEDGMENTS

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INDIRECT ENERGY REQUIREMENTS FOR VEGETABLE CANNING

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ABSTRACT

Energy embedded in materials employed for vegetable canning was studied. The materials studied were vegetables, packaging materials, water treatment chemicals, and processing equipment. Data on energy use for vegetables, packaging, and water treatment chemicals were derived from published sources. For process equipment a new method, based on data of the Bureau of the Census, was devised. It is more specific and reflects recent energy use data. Its results compare favorably with those of Herendeen. For the one cannery's inventory of the various materials, the indirect energy (k cal) inputs per case of 1-lb cans (24/303) were: 8,157; 36,466; 641; *and* 207, *for vegetables, packaging materials, water treatment chemicals, and processing machinery, respectively. Earlier, the direct energy use in the cannery was determined to be* 17,589 *k cal per case of* 1-*lb cans.*

INTRODUCTION

In the U.S. total energy usage for food processing exceeds that for production. For example, in 1971 the total energy for production was 502 trillion k cal while that for processing was 829 trillion k cal (Anon. 1976). Total energy requirements can be divided into direct and indirect energy inputs. Direct energy sources for vegetable canning include fuels for thermal energy, and electricity for lighting and motors. Studies related to direct energy consumption in canneries have been presented (Elkins 1976; Farrow 1975; Rao *et al.* 1976a,b; Vergara *et al.* 1978).

For indirect energy sources, energy is sequestered outside the

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boundaries of a system. In this study, the system boundary was the cannery. The energy sequestered in several materials was estimated: vegetables, packaging materials, water treatment chemicals, and process equipment. These materials play a direct role in the canning of vegetables.

According to the guidelines of the International Federation of Institutes for Advanced Study (IFIAS) (Anon. 1974a), energy for transportation must be included in the indirect energy inputs. For example, if the system considered was canned vegetables then the energy used in the complex distribution system must be included. Even with the simpler system as cannery, determination of energy use for transportation of all the materials and workers was not possible due to the lack of reliable data. Energy sequestered for the construction of the cannery buildings, i.e. in the construction materials such as cement, steel, and bricks, was also not undertaken.

METHODS EMPLOYED

Data on the materials and machinery used were obtained from a vegetable cannery in western New York. This cannery was referred to as Plant A in our previous studies (Rao *et al.* 1976b; Vergara *et al.* 1978). The cannery, about 15 years old, was located in western New York and produced 2.75 million cases of 1-lb cans in 1977; other data on the cannery were given in our previous studies.

Vegetable Production

The vegetables processed in the cannery were peas, beets, sweet corn (whole kernel and cream style), peas and carrots, dry beans, and lima beans. Peas, beets, and corn constituted 91.5% of the production.

Data on the consumption of tractor fuel and fertilizers were available for the production of peas, beets, corn, and carrots in New York (Gunkel *et al.* 1974, 1976). Pesticide use data were taken from Terhune (1977). Sources of energy coefficients were: Terhune (1977) for agricultural machinery, seeds, and pesticides, and Pimentel *et al.* (1973) for fertilizers. No data were available for the production of dry beans and lima beans in New York. For the former the estimate of Pimentel (1976) was used, while for the later the magnitude was taken as equal to that for snap beans; the energy for the production of snap beans was calculated with the aid of Gunkel *et al.*'s data (1974, 1976). Quantity of each vegetable harvested

was calculated from the quantity canned, drained weights (Anon. 1977), and the solid waste data of Katsuyama *et al.* (1973).

Packaging Materials

Packaging materials used in the cannery included cans, glass jars, and cardboard boxes. Data on the sizes and quantities used were noted. Energy use for packaging materials has been reported in a number of studies. The guidelines of IFIAS (Anon. 1974a) were used to select the "best" data; i.e. data based on most number of inputs in the total cycle were considered to be superior to others.

Energy values for cans were cited by Berry and Makino (1974); Brown and Batty (1976); Hoddinott (1975); Seehafer (1976); and Payne (1975). The magnitude reported by Payne of American Can Co., is higher than those of others indicating that more inputs were considered in the energy cycle of a can and also access to reliable data. Also, it is in good agreement with the estimate of Seehafer (1976) of U.S. Steel Corporation. For these reasons, Payne's magnitude was used in this study. The mass of steel in different sized cans and their lids was determined by either weighing or from the weight data in the literature (Anon. 1977).

Energy data for glass jars were cited by Hannon (1972) as well as the sources mentioned for cans. The estimate of Berry and Makino (1974) was employed in this study because it was based on more careful analysis; also, it agrees well with the estimate of Hannon (1972). For cardboard boxes also, the magnitude cited by Berry and Makino (1974) was employed. The necessary weights of jars and boxes were determined by weighing.

Chemicals and Water Treatment

The chemicals used in the cannery were chlorine for disinfection, salt, soda ash, aluminum sulfate, clay and a coagulant for water softening and treatment, sodium phosphates for treating boiler feed water and water for cooling cans, and caustic soda and sulfuric acid for wastewater disposal.

Chlorine and caustic soda are produced together in electrolytic cells. Data presented by The Conference Board (Anon. 1974b) were used to estimate energy per 1-kg mix of chlorine and caustic soda. The concept of chlorine-caustic soda mix was used because both the products were used in the plant and to avoid double accounting the energy use. For soda ash also data of The Conference Board (Anon. 1974b) were used.

For aluminum sulfate, sulfuric acid, and sodium phosphates, specific

energy data were not available. Instead, data were available for a large group of inorganic chemicals (Anon. 1974b) per 1967 dollar transaction. Value of (k cal/kg) of each chemical was derived from the cost data (Dryden 1966) and updating the cost to 1967 using cost indexes (Perry *et al.* 1963; Perry and Chilton 1973).

Energy for Process Equipment

A new method (Vergara 1977) was used for estimating energy consumed for the manufacture of process equipment. It takes into account the direct energy for the manufacture of the equipment and the energy embedded in the raw materials used to build the equipment. In general terms, machinery requires the following classes of raw materials: mill shapes and forms, primary metals, castings, engines, bearings, and electronic components. In the present analysis, the energy for raw materials was taken as the direct energy for their manufacture. The sources of data for this method were those published by the Bureau of the Census (1973, 1976).

The energy cost of equipment can be represented by Equation (1):

$$e_t = \frac{e_D V_M + \Sigma\, e_j x_j}{V_T} \quad (1)$$

Where e_t is the energy (k cal) for an equipment per dollar cost; e_D is the direct energy for the manufacture of the equipment per dollar value added during the manufacture (k cal/$); V_M is the total value added to the raw materials when the equipment is manufactured; e_j is the direct energy of manufacture for raw material j per dollar of delivered cost; x_j is the quantity of raw material j used for the equipment and is measured in delivered cost of the material; and V_T is the total cost of the equipment manufactured.

To facilitate the computations and presentation of results, the following definitions are introduced:

$$\bar{e}_j = \frac{\Sigma e_j x_j}{\Sigma\, x_j} \quad (2)$$

$$V_T = V_M + \Sigma\, x_j \quad (3)$$

$$e_D = \frac{E_D}{V_M} \quad (4)$$

and

$$e_j = \frac{E_{Dj}}{V_{Mj}} \quad (5)$$

Where, e_j is an average energy coefficient for the manufacture of raw materials; E_D and E_{Dj} are the direct energies used by the manufacturer of the equipment and the supplier of the raw material j, respectively; and V_{Mj} is the value added due to raw material j. It is noted that E_D and E_{Dj} were given in kwh equivalents (Bureau of the Census 1973, 1976) and their magnitudes were recalculated taking into account fossil fuel equivalence.

In order to use the method to estimate energy consumed for process equipment, their costs in 1974 must be known. The method was applied to processing equipment. The needed costs were obtained from food equipment manufacturers and studies on engineering economics (Peters and Timmerhaus 1968; Mills 1964). All costs were reduced to base 1974 using the Marshall and Stevens index of *Chemical Engineering* magazine. It is emphasized that equipment not required for processing but which support plant activities such as maintenance, fire prevention, and office furniture were not considered.

RESULTS AND DISCUSSION

Energy use for vegetables and packaging materials was calculated from data of 1974. For water treatment chemicals, reliable inventories were not available for 1974 and for this reason data of 1977 were used. Equipment inventory was also conducted in 1977.

Vegetables

Energy use (k cal/kg) for the production of beets, carrots, peas, snap beans, and sweet corn was estimated as 196, 195, 1,772, 1,142, and 700, respectively. It is noted that the average for these 5 vegetables is 800 k cal/kg. This figure is in reasonable agreement with the value 667 k cal/kg of Terhune (1977) for all processed vegetables in the U.S. The

energy consumed for producing all the vegetables canned in the plant was calculated to be 22.40 $\times$ 10^9 k cal. Because a case of 1-lb cans (24/303) is used as a measure of production in the industry, we note that the energy for growing vegetables translates to 8,157 k cal per case.

Packaging Materials

For packaging materials, the magnitudes of energy coefficients used were 18,650 k cal/kg for steel cans; 4,812 k cal/kg for glass jars; and 8,740 k cal/kg for paperboard. While the energy per kg for cans may seem much higher than for glass jars, we note that glass jars are heavier than cans. For example, a 1-lb can weighs 65.8 g while a jar of the same capacity weighs 204.3 g. The total energy embedded in packaging used in the plant was 100.28 $\times$ 10^9 k cal. Per case of 1-lb cans, this translates to 36,466 k cal.

Water Treatment Chemicals

For water treatment chemicals, the following energy coefficients were used: 7,773 k cal/kg for chlorine-caustic soda mix; 3,027 k cal/kg for soda ash; 3,355 k cal/kg for aluminum sulfate; 888 k cal/kg for sulfuric acid; and 7,497 k cal/kg for tripoly sodium phosphates. No energy data were found for salt and clay; for both the value 900 k cal/kg was assumed, arbitrarily. The total energy for water treatment chemicals used in the plant was 1.36 $\times$ 10^9 k cal or 641 k cal per case of 1-lb cans.

Process Equipment

Besides the method described in this study for estimating energy use for equipment, the only other method is that of Herendeen (1973) for computing the energy cost of goods and services in the U.S. economy. Herendeen's method (1973) is based on an input-output analysis using a series of linear equations which are solved for any particular sector or activity of the economy. The results based on data of 1963 and 1967 (Herendeen and Bullard 1974) can be interpreted as the energy equivalent of any economic activity and permit estimation of energy used for a large class of equipment such as food processing machinery in general. The present method (Vergara 1977) follows the guidelines of IFIAS (Anon. 1974a), and is more specific for a given sector of the economy. Further, it utilizes more recent data (1972—1974) and thus reflects more recent energy use.

As an example, Table A-1 and the appendix show a detailed list of the elements included, the calculation of the energy cost of pumps and pumping equipment, and the results. Table 1 summarizes the results for

Table 1. Energy expended for the manufacture of equipment related to food processing

Equipment	e_t K cal Dollars of 1972	e_t^{1} K cal Dollars of 1974
Food products machinery	11,473	9,404
Ball and roller bearings	11,456	5,910
Air and gas compressors	7,326	6,005
Industrial furnaces and ovens	14,927	12,235
Motors and generators	9,597	7,866
Valves and pipe fittings	11,540	9,459
Conveyors and conveyor equipment	12,734	10,438
Industrial trucks and tractors	11,283	9,248
Measuring and controlling devices	5,500	4,582
Pumps and pumping equipment	7,211	5,910
Commercial food products machinery	11,716	9,603
Food packaging machinery	10,857	8,678
Industrial pumps	7,485	6,135
Fractional HP motors	16,284	13,347
Integral HP motors	9,687	7,940
Automotive control valves	10,721	8,788
Neumatic and hydraulic valves	9,949	8,155
Flanges and metal fittings	12,414	10,175

[1]Translation to cost in 1974 was done taking into account the change in costs from 1972 to 1974 as reported by *Chemical Engineering* and the increase in GNP by Grosvenor (1976).

several categories of equipment. It was thought that the categories included would cover most, if not all, of the equipment in a typical vegetable cannery.

We note that the calculated direct energy cost (or energy value of a dollar added during manufacture) is in general, one order of magnitude smaller than the corresponding energy value of the raw materials. As a consequence, the energy cost of the equipment changes drastically depending on whether or not the energy cost of the raw materials is included. The explanation lies in the fact that an important fraction of the raw materials is represented by primary metals, mill shapes, forms, and castings which are known to be highly energy intensive (Berry and Fels 1973). It should also be noted that a higher degree of assembly (e.g. motors, pumps and measuring devices), generally leads to a smaller energy equivalent of the dollar value as more labor than fuel energy is invested in the equipment.

The results in Table 1 also include data on subsectors like "fractional

HP motors" and "automatic control valves" which were possible using the data provided by the Bureau of the Census (1973). It is emphasized that the information and method given in this section can be used to estimate energy for most equipment if their components and their cost are known.

The equipment inventoried and their energy values are summarized in Table 2. The total energy was found to be 12.908×10^9 k cal. If the useful life of the equipment is 25 years, the annual energy "depreciation" would be 516.3×10^6 k cal. Based on an average annual production of 2.5 million cases of 1-lb cans in Plant A, the energy for machinery can be apportioned as 207 k cal per case for the studied cannery.

Table 2. Energy expended for inventoried equipment in the cannery

Equipment	Estimated 1974 Cost (Dollars)	Estimated 1974 Energy Cost (k cal)
Receiver tanks (2)	3,460	32.53×10^6
Blowers (2)	1,590	9.55×10^6
Shakers (2)	3,880	37.43×10^6
Sieve size separators (8)	95,550	898.55×10^6
Inspection shakers (7)	15,680	147.45×10^6
Grading tables (7)	230	2.16×10^6
Hopper carts (4)	2,570	23.77×10^6
Blanchers (4)	6,968	65.52×10^6
Quality graders (4)	4,780	41.48×10^6
Fillers (4)	135,540	$1{,}176.21 \times 10^6$
Sterilizers (3)	800,000	$7{,}523.00 \times 10^6$
Retorts (5)	44,790	421.20×10^6
Motors (74)	67,900	534.10×10^6
Pumps (10)	6,740	39.83×10^6
Conveyors (350 feet)	31,350	327.23×10^6
Pipes (5,100 feet)	45,020	425.84×10^6
Boilers (2)	79,130	968.15×10^6
Lift trucks (5)	13,410	124.02×10^6
Air compressors (2)	29,860	17.90×10^6
Control panels (3)	6,615	30.31×10^6
Automatic valves (48)	7,065	62.09×10^6
Total		$12{,}908.32 \times 10^6$

Comparison with Herendeen's Data

Prior to comparing the present results with Herendeen's data (1973) the following facts must be noted: (1) Some of the sectors of the economy

reported in the census of the sixties have changed; some have been divided into several more specific sectors while others have been included within the definition of a new sector. Even the coding of the sectors have changed radically between the census of the sixties and the more recent census. (2) The real value of the dollar has changed, decreasing sharply during the past few years, therefore the amount of energy per dollar ten years ago will appear higher than the value today if all other parameters remain identical. (3) Changes in technology and practice tend to reduce the amount of energy per dollar spent as energy becomes more expensive, and (4) the rising costs of energy alone helps to decrease the amount of energy per dollar of manufacture.

Table 3 shows for selected equipment the energy coefficients as reported by Herendeen (1973) and from the present analysis. It is observed that the general trend is towards lower energy coefficients in 1974 as compared to those of 1963.

Table 3. Comparison of the results reported by Herendeen with the results of this analysis (k cal/dollar)

	Herendeen (1973)		New Method
Equipment	Dollars of 1963	Dollars of 1974	Dollars of 1974
Conveyors	18,721	12,398	10,438
Industrial trucks	18,676	12,368	9,248
Food processing machinery	16,392	10,855	9,404
Bearings	25,086	16,613	9,390
Furnaces	18,216	12,063	12,235

CONCLUDING REMARKS

Significant quantities of energy are embedded in the indirect energy sources for vegetable canning. Packaging and raw vegetables are the most energy intensive elements. Chemicals for water treatment and energy for machinery are, relatively, of lower intensity. For comparative purposes we note that the direct energy consumption in the cannery per case of 1-lb cans was 17,859 k cal (Vergara *et al.* 1978). The energy embedded for the indirect energy sources was estimated in this study to be 8,157 k cal, 36,466 k cal, 641 k cal, and 207 k cal, for the vegetables, packaging materials, water treatment chemicals, and processing machinery, respectively.

A special effort of this study was a new method for estimating the energy expenditure for food processing machinery. The method is based on a two level analysis of direct energy for manufacturing the equipment and the raw materials of the equipment. It allows estimating of energy use for specific pieces of equipment hitherto not possible with other methods. The results compare favorably with those of Herendeen for specific equipment.

APPENDIX

Calculation of the Energy Expended for Pumps and Pumping Equipment

The following direct energy data were derived from the compilations of the Bureau of the Census (1973, 1976): purchased fuels, $E_D = 2{,}064 \times 10^9$ k cal; value added by manufacture, $V_M = 1{,}095.7 \times 10^6$ dollars; and cost of materials, $\Sigma\, x_j = 852.7 \times 10^6$ dollars.

For the energy embedded in the raw materials, the data tabulated in Table A-1 was utilized:

$$\bar{e}_j = \frac{\Sigma\, e_j x_j}{\Sigma\, x_j} = \frac{4{,}491.7 \times 10^9 \text{ k cal}}{319.5 \times 10^6 \text{ dollars}} = 14{,}058 \text{ k cal/dollar}$$

The total energy coefficient, e_t, was obtained from:

$$e_t = \frac{\bar{e}_j\ x_j + E_D}{V_T}$$

$$= \frac{14{,}058 \text{ k cal/dollar} \times \$852.7 \times 10^6 + 2{,}064 \times 10^9 \text{ k cal}}{\$1{,}095.7 \times 10^6 + \$852.7 \times 10^6}$$

$$= 7{,}211 \text{ k cal/dollar}$$

Table A-1. Calculation of the energy embedded in raw materials of pumps and pumping equipment

Supply of Materials	Delivered Cost, x_j 10^6 Dollars[1]	Fuel and Electrical Energy, E_{Dj} 10^9 kwh Equivalent[2]	Value Added by Manufacturer, V_{Mj} 10^6 Dollars[1]	Energy Coefficient, e_j k cal/Dollar[3]	Total Energy, $e_j x_j$ 10^9 k cal[4]
Mill Shapes and Forms					
Carbon and alloy steel	62.9	484.2	12,116	34,370	2,162
Copper insulated wire and cable	3.2	7.9	1,447	4,693	15
Copper reel, brass plates, pipes and tubes	7.2	9.5	799	10,227	74
All other aluminum mill shapes	0.3	51.2	3,799	11,600	3.5
Aluminum extended shapes	0.8	6.7	427.6	13,500	10.8
Primary Metals					
Pig iron	7.7	484.2	12,116	34,370	264.6
Copper and copper alloy refinery shapes	2.5	22.9	487.8	40,372	101.0
Iron and steel scrap castings	0.9			34,370	31
Iron (gray)	77.3	51.8	3,481	12,800	989
Aluminum castings	11.2	7.9	718.3	15,810	177
Copper castings	19.9	1.6	236.9	5,808	115.6
Iron forgings	6.3	15.5	661.8	20,142	127
Engines					
Diesel	4.2	5.9	1.677	3,024	12.7
Electric motors	100.0	5.8	1,484	3,361	336
Bearings					
Roller and ball	15.1	5.2	931	4,803	72.5

[1] Bureau of the Census (1973)
[2] Bureau of the Census (1976)
[3] Calculated by dividing purchased fuels by the value added in manufacturing
[4] Calculated by multiplying the delivered cost of materials and the energy coefficient

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RETENTION OF SPARINGLY SOLUBLE VOLATILE COMPOUNDS DURING THE FREEZE DRYING OF MODEL SOLUTIONS

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ABSTRACT

The retentions of terpenic essential oil components (carvone, pulegone and piperitone) and non-terpenic essential oil components (eugenol and m-anisaldehyde) were measured during the freeze drying of model aqueous solutions. Model solutions contained sucrose, glucose, sodium chloride or gum arabic which are all common food components. The percent retentions of these slightly soluble flavoring compounds were found to increase with increased initial solids concentration, decreased initial volatile content, increased sample thickness, increased freezing rate and the absence of an additional sparingly soluble volatile.

INTRODUCTION

During the past few years many investigators have studied the retention of volatile flavoring compounds during the freeze drying of liquid food systems. Most noteworthy are the contributions of Flink and Karel (1970a,b), King and coworkers (King and Chrandrasekaran 1973; Massaldi and King 1974) and Thijssen and coworkers (Rulkens and Thijssen 1972). Flink (1975) has recently reviewed many of the important process conditions associated with achieving maximum volatile retention during freeze drying.

Flink and Gejl-Hansen (1972) have shown that the retention of very slightly soluble volatiles was significantly less than the retentions of

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very soluble volatiles in freeze-dried maltodextrin solutions. On the basis of microscopic observations, Flink and Gejl-Hansen (1972) concluded that the slightly soluble volatiles separated out as a pure organic phase as their solubility limits were exceeded during the freezing process. Massaldi and King (1974) studied the retention of d-limonene and n-hexyl acetate, two relatively insoluble volatiles (Massaldi and King 1973). These authors postulated that the volatile could be distributed throughout the frozen sample in three different locations: droplets in contact with the ice phase, droplets embedded within the concentrated amorphous solution (CAS) and volatile homogeneously dissolved in the CAS. The retention studies of Massaldi and King (1974) were directed more to emulsified systems in which initial volatile concentration exceeded its solubility limit in the aqueous sucrose solutions employed.

The main objective of this work was to evaluate the behavior of several sparingly soluble essential oil components of which the solubility parameters are well known in the solution to be freeze dried. Particular attention was paid to systems in which the sparingly soluble volatiles were initially present at levels below the solubility limit.

MATERIALS AND METHODS

Dissolved solids or substrates were sucrose, glucose, gum arabic or sodium chloride. All were reagent grade and used as received. Carvone (Kand K), piperitone (ICN), pulegone (Fluka), eugenol (ICN) and m-anisaldehyde (ICN) were found to be at least 95% pure by gas chromatographic analysis and were used without further purification.

Aqueous solutions of the substrate were prepared on a weight percent basis. Volatile concentrations are expressed on a volumetric basis (ppm). Volatile containing solutions were prepared by one of two methods. Individual samples were prepared by injecting a desired volume of volatiles, using a 10 μl Hamilton syringe, into a known volume of solution in a 50-ml Erlenmeyer flask. After the volatile was injected it was necessary to vigorously shake the flask contents for at least several minutes to effect total solubilization of the volatile as evidenced by the absence of a separate organic phase. Such a mixing procedure was required even for volatiles well below their solubility limit. Numerous analyses have shown that this technique of volatile addition is reproducible to $\pm 1.5\%$. When volatile containing solutions were made in this manner 4 replicates were prepared, 3 for freeze drying and 1 as a reference. Bulk volatile containing samples were prepared by introducing weighed portions of volatile into volumetric flasks. When necessary, solu-

tions were stored in stoppered flasks at 40 °C. To avoid possible interaction between the volatile and stopper, the stoppers were wrapped in aluminum foil. All bulk solutions were prepared on a regular basis to minimize possible effects of microbial growth.

Each of the triplicate samples was frozen on a different shelf of the freeze-dryer (Model 42 RePP Sublimator) which had been previously cooled to −40 °C. A condenser temperature of −70 °C was maintained for all freeze-drying experiments. Immediately after freeze-drying the samples were rehydrated to their original weight and the absorbance was determined, after appropriate dilution, spectrophotometrically (Unicam SP1800 Ultraviolet Spectrophotometer). The fourth member or reference was diluted similarly and the absorbance also recorded. Percent retention was calculated as the ratio of the absorbance of the rehydrated freeze-dried samples to the absorbance of the reference. In cases where samples initially contained volatile in excess of its solubility, both the freeze-dried and reference samples were diluted to such an extent that all the volatile was homogeneously dissolved and then the dilutions for spectrophotometric analyses were performed. All volatiles were proven to follow the Lambert-Beer law in the concentration ranges employed.

RESULTS AND DISCUSSION

Effect of Dissolved Solids Content

The retentions of the essential oil components were monitored as a function of the initial dissolved solids content. Figures 1, 2 and 3 show the respective retentions of carvone, eugenol and m-anisaldehyde as a function of increasing sucrose content. The vertical bars represent standard deviations calculated on the basis of triplicate measurements. The fractional retention of the three essential oil components (initially present at 500 ppm) appears to increase in a linear fashion with increased sucrose levels up to a dissolved solids content of 20 to 25%. In all three cases the volatile retention appears to level off when the initial sucrose content reaches 20%. Previous investigations have shown that volatile retention is critically dependent upon initial dissolved solids content (Thijssen and Rulkens 1969; Bartholomai *et al.* 1975; Sugisawa *et al.* 1973). In addition Chirife *et al.* (1973) and Thijssen (1972) have shown that at low solids concentration (10—20%), increases in solids concentration greatly increases the volatile retention, while at higher initial solids concentraiton (greater than 25%) there is little influence on volatile retention. Figures 1, 2 and 3 show that the essential oil components behave similarly.

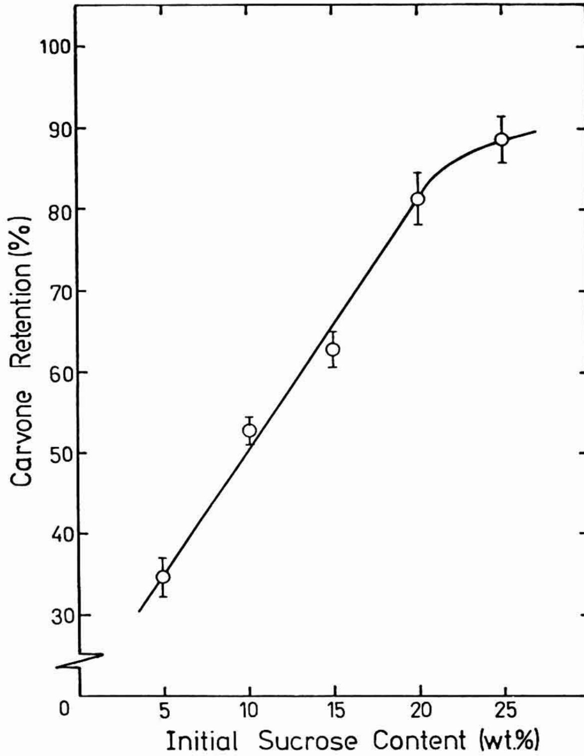

FIG. 1. RETENTION OF CARVONE AS A FUNCTION OF INITIAL SUCROSE CONTENT

Figure 4 illustrates the retention of the above 3 essential oil components (500 ppm) in gum arabic solutions of 1 to 4 wt %. Carvone and m-anisaldehyde retentions increase linearly and exhibit very similar retentions whereas the retention of eugenol is significantly higher than that of the other two species. Kayaert *et al.* (1975) have reported retention studies involving acetone and n-propanol in a mixture of 4 carbohydrate gums. The retentions of these 2 infinitely water soluble volatiles were found to increase linearly with increasing gum concentrations to 3%. This study and that of Kayaert *et al.* (1975) indicate that the gums are well suited for retaining substantial amounts of volatile when incorporated into a freeze-dried solution. Comparison of Fig. 4 with Fig. 1, 2 or 3 shows that a 1% gum arabic solution retains a significantly greater proportion of volatile than a 5% sucrose solution. The ability of gum arabic to lock in flavoring compounds is very well known and has been used to

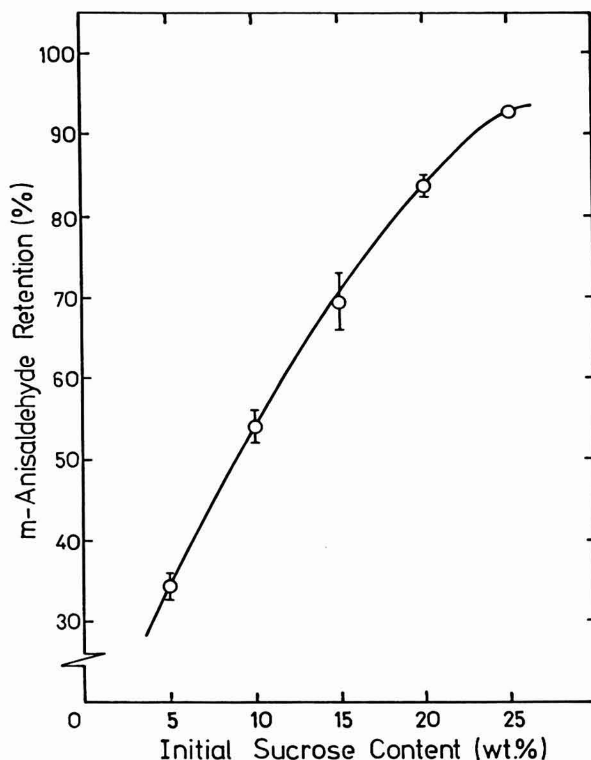

FIG. 2. RETENTION OF M-ANISALDEHYDE AS A FUNCTION OF INITIAL SUCROSE CONTENT

great advantage in spray-drying operations (Glicksman 1969). Thus it appears that the gums, in contrast to other polymeric species, give a higher volatile retention than the simpler sugars. Chirife and Karel (1973) have provided information that the volatile retention in solutions containing other polymeric species (starch, cellulose and dextran 10) is generally much lower than for solutions containing either a mono or disaccharide. The ability of the gums to retain volatiles to such a high degree is likely due to their ability to form a crosslinked network.

Table 1 is of particular interest in that it shows that the essential oil components, carvone (300 ppm) and m-anisaldehyde (500 ppm), are retained to a significant extent in freeze-dried solutions of sodium chloride. At these concentrations, both carvone and m-anisaldehyde are below their solubility limits in the sodium chloride solution (Smyrl 1977). Previously, Flink and Karel (1970b) had shown that the retentions of

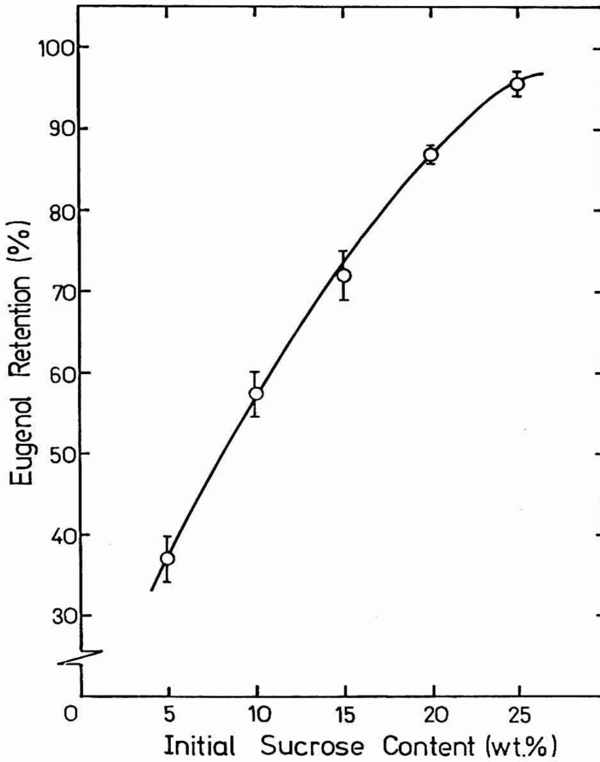

FIG. 3. RETENTION OF EUGENOL AS A FUNCTION OF INITIAL SUCROSE CONTENT

several volatile species in freeze-dried sodium chloride were very low. Gal (1975) has recently shown that under favorable freeze-drying conditions, an amorphous sodium chloride phase may be obtained. Our results showing significant volatile retentions in freeze-dried sodium chloride solutions suggest that in the present case, an amorphous form of sodium chloride may be responsible for entrapping the volatiles. Retentions of eugenol in sodium chloride were not studied since ultraviolet analysis showed that eugenol in aqueous sodium chloride solutions was chemically unstable. The nature of the interaction between sodium chloride and eugenol was not investigated.

Effect of Initial Volatile Concentration

Figures 5 to 9 illustrate the retention of the essential oil components in

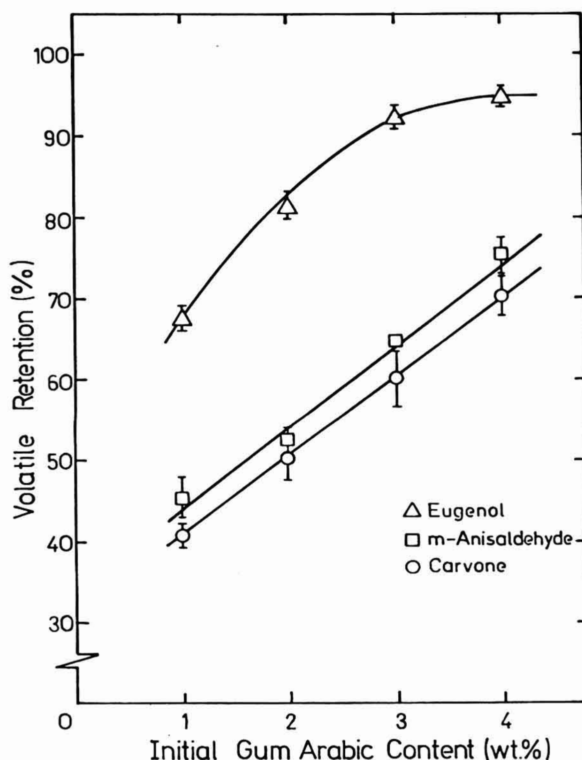

FIG. 4. RETENTION OF CARVONE, M-ANISALDEHYDE AND EUGENOL AS A FUNCTION OF INITIAL GUM ARABIC CONTENT

Table 1. Retention of carvone and m-anisaldehyde as a function of initial sodium chloride content

Sodium Chloride (wt%)	Volatile Retention (%)	
	Carvone[a]	m-Anisaldehyde[b]
3	4.1 ± 0.9	13.7 ± 0.9
5	7.8 ± 0.8	23.5 ± 1.6
7.5	13.4 ± 1.6	31.4 ± 2.1
10	18.0 ± 1.4	36.3 ± 1.5

[a]Initial carvone content, 300 ppm
[b]Initial m-anisaldehyde content, 500 ppm

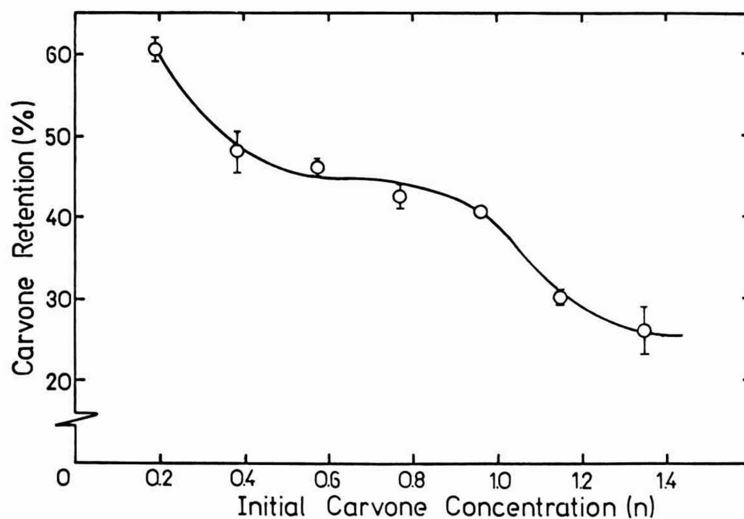

FIG. 5. CARVONE RETENTION AS A FUNCTION OF INITIAL CARVONE CONCENTRATION IN 10% SUCROSE

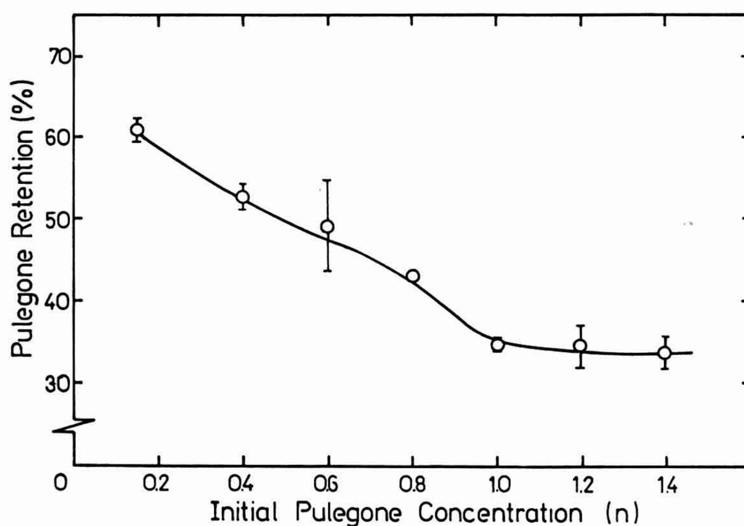

FIG. 6. PULEGONE RETENTION AS A FUNCTION OF INITIAL PULEGONE CONCENTRATION IN 10% SUCROSE

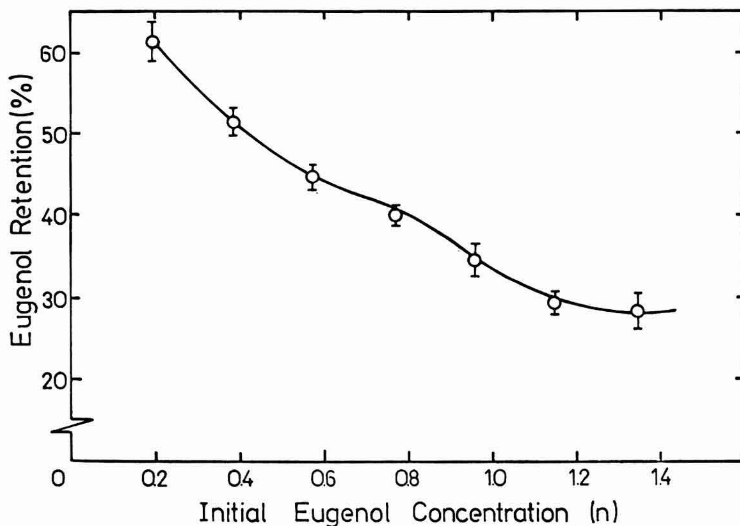

FIG. 7. EUGENOL RETENTION AS A FUNCTION OF INITIAL EUGENOL RETENTION IN 10% SUCROSE

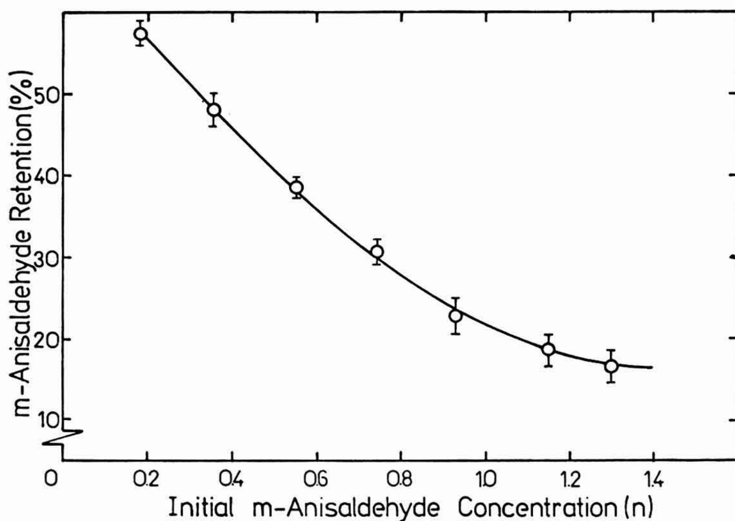

FIG. 8. M-ANISALDEHYDE RETENTION AS A FUNCTION OF INITIAL M-ANISALDEHYDE CONCENTRATION IN 10% SUCROSE

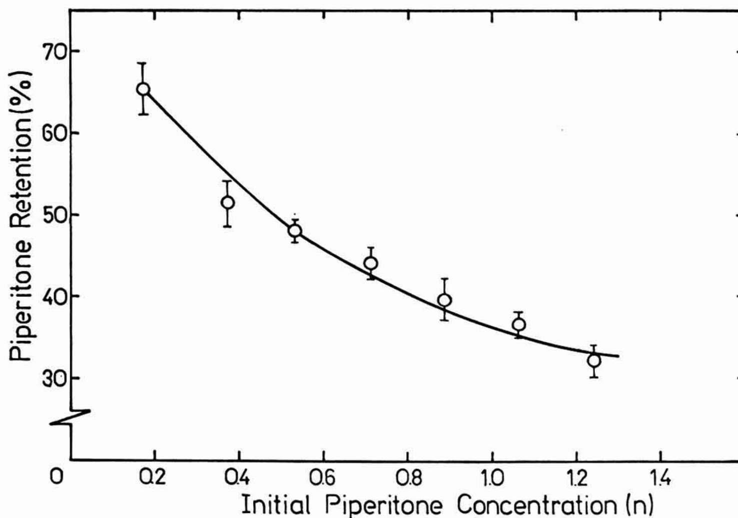

FIG. 9. PIPERITONE RETENTION AS A FUNCTION OF INITIAL PIPERITONE CONCENTRATION IN 10% SUCROSE

a 10% sucrose solution as a function of initial volatile concentration. Following the convention of Massaldi and King (1974) initial volatile content is expressed by the parameter n, where when n represents the ratio of the initial volatile concentration to the volatile solubility in 10% sucrose as measured at 10 °C. We have studied the solubilities of the essential oil components in aqueous solutions of sucrose, glucose, and sodium chloride (Smyrl 1977) and the solubilities in 10% sucrose are tabulated in Table 2. Generally all volatiles, as evidenced in Fig. 5 through 9, are seen to exhibit a decrease in retention with increasing values of n. For values of $n < 1$ volatile retention appears to decrease in a fairly regular fashion. Apart from the work of Voilley *et al.* (1973), other workers have observed the same trend of volatile retention with increasing initial volatile content (Bartholomai *et al.* 1975). It is interesting to note that carvone and pulegone, the least soluble of the volatiles studied (Table 2), exhibit a very pronounced decrease in retention at n near 1 as shown in Fig. 5 and 6 respectively. Inspection of Fig. 5 and 6 also shows that at $n > 1$ (emulsified systems), the retention appears to level out. Eugenol, which has a solubility greater than that of carvone or pulegone, has a much less pronounced dip in the retention curve at n near 1 (Fig. 7). Figures 8 and 9 show that the most soluble of the essential oil components, m-anisaldehyde and piperitone, do not exhibit this pronounced

Table 2. Solubilities of the essential oil components in 10% sucrose at 10 °C

Essential Oil Component	Solubility (ppm)
carvone	1560
pulegone	1490
eugenol	2050
m-anisaldehyde	2690
piperitone	2820

decrease in retention at n values near 1. In all cases (Fig. 5 to 9) the retention stabilizes for values of $n > 1$.

Massaldi and King (1974) have studied the retention of d-limonene and n-hexyl acetate in sucrose as a function of initial volatile concentration. These authors were able to calculate theoretical retention curves in emulsified systems ($n > 1$) which predicted experimental results very well. In the development of their theoretical model, the authors assumed that the retentions of the volatile initially present below the saturation limit would be constant since the volatiles would be homogeneously dissolved. Figures 5 through 9, however, do show that some additional loss of volatile does occur with increasing volatile content even below the saturation limit. This decrease in sparingly soluble volatile retention for initial volatile contents $n < 1$, in comparison to soluble volatiles, may be attributed to the solubility limit of the volatile being exceeded during the freezing process and thus giving rise to droplets of pure volatile. If these droplets are in close proximity to the free surface or the vapor phase after sublimation of ice, they will be lost by evaporation when exposed to the vacuum. The droplets entrapped within the CAS and not in contact with the free surface or vapor phase will be largely retained as will that portion of the volatile which remains homogeneously dissolved within the CAS (Massaldi and King 1974). Although the study of emulsified systems was not emphasized in this work, Fig. 5 through 9 show them at $n > 1$, the volatile retentions appear to level out which is in accordance with the emulsion studies of Massaldi and King (1974).

The work of Flink and Gejl-Hansen (1972) and Massaldi and King (1974) and the results of this study show that the solubility characteristics of the volatile compounds are very important in determining the overall retentions of the volatile during freeze-drying. It has generally been assumed that the volatile will separate out as a pure organic phase

during the low temperatures and high solutes concentrations involved with the freezing process (Flink and Gejl-Hansen 1972). However, an inspection of the literature shows that numerous organic compounds, many of which may be classified as flavoring volatiles, exhibit increased solubilities in aqueous solutions with lower temperatures. Ketones (Gross *et al.* 1939), butane (Rice *et al.* 1976), ethyl ether and isoamyl alcohol (Kablukov and Malischeva 1925), ethyl acetate (Glasstone and Pound 1925), isomeric hexanols (Ginnings and Webb 1938) and aliphatic ethers (Bennett and Phillip 1928) serve as examples. In a sense the solubilities of many sparingly soluble liquid organics appear to parallel the temperature dependence of gases in aqueous solution. We have similarly shown that the solubilities of pulegone and piperitone increase with decreasing temperature in water and aqueous solutions of sucrose, glucose and sodium chloride. The solubilities of carvone in the same aqueous media were found to increase for temperatures greater and less than 20 °C. Thus it appears that for many sparingly soluble volatile compounds in an aqueous solution which is being frozen, two opposing effects are operative. These correspond to an increase in solubility due to decreasing temperature and a decrease in solubility as a result of increased dissolved solids concentration (salting out). The photographic results presented by Flink and Gejl-Hansen (1972) and Flink *et al.* (1973) illustrate that the concentrating of dissolved solids exerts the major influence since volatile droplets were observed in freeze-dried solutions which were initially homogeneous.

Flink and Gejl-Hansen (1972) have also shown that generally the degree of retention of a particular volatile is dependent on the solubility of the volatile in the solution to be freeze dried. In particular the more water soluble volatiles are retained to a greater extent than sparingly soluble volatiles. The question arises as to whether the retention of sparingly soluble volatiles may be enhanced by the incorporation of a low temperature equilibration process. Such a low temperature equilibration process (at a temperature barely exceeding the solution freezing point) would have the effect of increasing the amount of sparingly soluble volatile homogeneously dissolved if the volatile is in fact initially present as an emulsion. As an example, we have found that the solubility of pulegone in a 40% sucrose solution at 10 °C is 27% greater than its solubility at 30 °C. This prefreezing equilibration step would be necessary since increased solubilization of the volatile would not occur during the relatively short time span involved with freezing of the solutions.

Effect of Sample Dimensions

Figure 10 shows that the degree of volatile (carvone, initially at 500

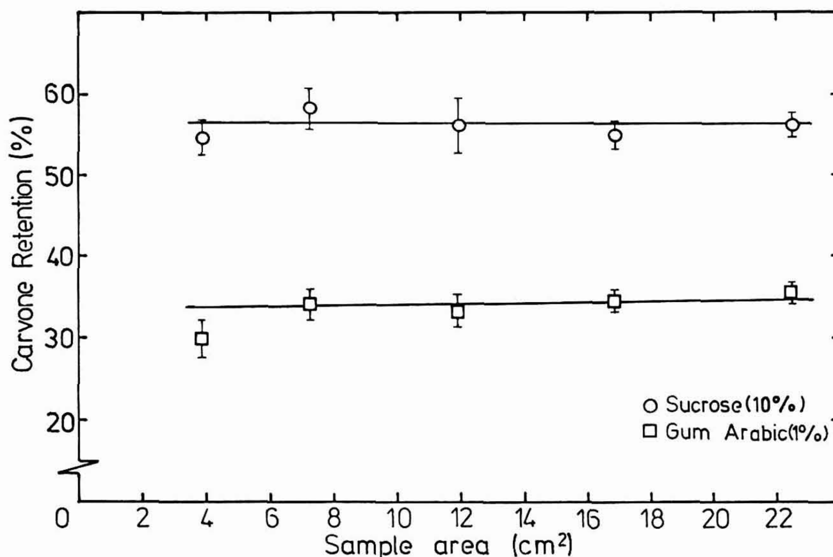

FIG. 10. RETENTION OF CARVONE AS A FUNCTION OF SURFACE AREA IN 10% SUCROSE AND 1% GUM ARABIC AT CONSTANT SAMPLE THICKNESS

ppm) retention in 1% gum arabic and 10% sucrose solution is independent of sample area when sample thickness is kept constant. These findings are in accordance with the results of Flink and Karel (1970b) who found that water soluble 2-propanol retention was independent of surface area in a variety of freeze-dried solutions. Figure 11 illustrates carvone retention in 1% gum arabic and 10% sucrose solutions as a function of sample thickness. In both cases volatile retention is seen to increase with increasing sample thickness to approximately 8 mm. At greater sample thicknesses carvone retention becomes independent of sample thickness. These findings of increased volatile retention with increased sample thickness appear to conflict with results presented by several other investigators (Flink and Karel 1970b; Kayaert *et al.* 1975; Chirife *et al.* 1973) who studied volatile retention using volatiles much more soluble than the essential oil components.

At the present time the reason why retention of the essential oil components increases with sample thickness must remain open to question. Ettrup-Petersen *et al.* (1973), who reported increased volatile retentions with increased thicknesses of freeze-dried coffee samples, attributed the higher retentions to a slower freezing rate within the thicker samples. If this freezing rate phenomenon were indeed operative, it would be

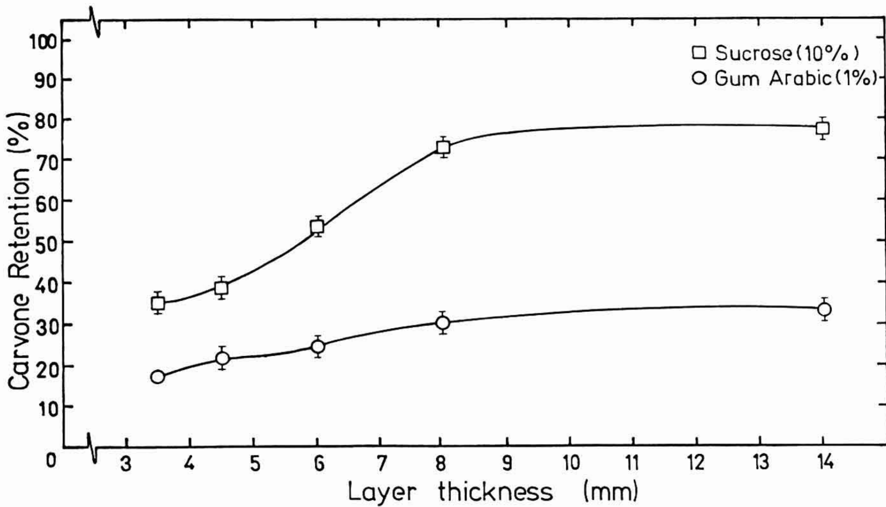

FIG. 11. INFLUENCE OF LAYER THICKNESS ON THE RETENTION OF CARVONE IN 10% SUCROSE AND 1% GUM ARABIC AT CONSTANT SAMPLE VOLUME

expected that all thinner samples should freeze more quickly than the thicker samples with the result being lower volatile retention in all thin samples. However, as stated previously, in thickness studies involving the more water soluble volatiles, this has not been found to be the case. In addition, we have shown that no volatile was lost from the samples during sample preparation or during freezing. This was verified by analysis of volatile-containing samples after the freezing treatment and prior to vacuum treatment. In samples of all thicknesses volatile content after freezing was found to be equal to the volatile content of the freshly prepared sample. Thus it was concluded that volatile loss takes place only during the vacuum treatment.

A possible explanation for the observed increase in retention with increased sample thickness arises from consideration of the studies of Lambert *et al.* (1973a). These investigators showed that in frozen solutions containing the sparingly soluble volatile, butanol, a lower percentage of butanol was present at the free surface in frozen thicker samples than in frozen thinner samples. Several authors have shown that during ascending freezing of an aqueous solution, an elevated concentration of dissolved solids is formed at the top of the frozen sample (Quast and Karel 1968; Ito 1970). Similarly during ascending freezing of volatile-

containing solutions, the dissolved volatiles would be pushed to the top of the freezing sample in a manner analogous to the movement of the dissolved solids. At the elevated solids concentrations developing during freezing, the sparingly soluble volatiles may separate out as a pure phase. In the thin samples the droplets of pure volatile would have a greater tendency to be in contact with the free surface than in thicker samples since the thickness of the concentrated surface layer in thicker samples would be greater. Under these conditions the droplets formed below the free surface of thick samples would be inhibited from reaching the free surface since they would have to travel a greater distance through this very viscous medium. Thus, as the concentrated layer freezes in the thicker samples, the volatile droplets present below the free surface are entrapped within the CAS regions and less prone to loss during vacuum treatment (Massaldi and King 1974). The droplets of pure volatile in contact with the free surface in the thin samples would be easily lost when the vacuum is applied in much the same manner as described by Lambert *et al.* (1973a) in their equilibration studies.

Effect of Freezing Rate

Chirife and Karel (1974) and Flink and Karel (1970b) have shown that the retention of soluble volatile decreases as the freezing rate of the sample is increased. As evidenced in Table 3, the sparingly soluble essential oil components exhibit the opposite behavior, i.e. increased volatile retention with increased freezing rate. Slow freezing was accomplished by freezing the samples on the shelf of the freeze dryer previously cooled to −40 °C whereas the fast freezing treatment was performed by immersion of sample flasks in liquid nitrogen. Once again the retention characteristics of the sparingly soluble volatile compounds appear to conflict with the retention characteristics of the water soluble volatiles. According to the microregion entrapment theory, slow freezing is more conducive to microregion formation than is rapid freezing, although the explanation of why this is so is speculative (Bartholomai *et al.* 1975). The diffusion theory predicts decreased retentions with increased freezing rates due to elevated values of Dt/L^2 (King 1970).

The apparently conflicting results concerning the retention of soluble and insoluble volatile may again be rationalized by considering the effect that freezing rate has on the degree of solute concentration during the freezing stages. Slow freezing treatments yield higher or greater degree of solute concentration than fast freezing treatments (Fennema and Powrie 1964). During slow freezing more of the dissolved solids are rejected from the ice-liquid interface hence a greater concentration of

Table 3. Retention of carvone and piperitone as a function of freezing rate

Volatile[a]	Solution	Volatile Retention (%)	
		Fast Freezing	Slow Freezing
carvone	10% sucrose	79.9 ± 1.1	54.7 ± 2.2
piperitone	10% sucrose	88.1 ± 0.5	65.9 ± 4.2
carvone	10% glucose	84.9 ± 0.6	78.1 ± 8.4
carvone	1% gum arabic	37.0 ± 0.9	36.2 ± 0.3
carvone	5% sodium chloride	10.8 ± 0.8	12.9 ± 1.2

[a] Initial volatile content, 500 ppm

dissolved solids forms at the sample surface during the last stages of freezing. Fast freezing, on the other hand, promotes entrapment of dissolved solids by the ice phase and the tendency for an elevated solids content at the surface of the frozen sample would be considerably diminished. Volatile solutes, in a slow freezing process, are rejected from the growing ice phase along with dissolved solids. When this surface layer solidifies, the soluble volatiles are entrapped in a region of high dissolved solids concentration leading to increased retention. Soluble volatiles in a fast-frozen sample, however, would not be associated with a condition of such high solids content simply because this region of high solids content does not form during fast freezing. Therefore in fast frozen samples soluble volatiles would be retained to a lesser extent since the beneficial effect of increased solids content will not exist in this case.

The sparingly soluble volatiles will behave in a similar manner during freezing. However, in the slowly frozen samples, where solute migration is promoted, the volatile droplets present in the surface layer will be in contact with the air phase and hence will not be incorporated into the concentrated solution at the surface as it is frozen. The result will be increased volatile loss. Fast-frozen samples containing sparingly soluble volatile are expected to have higher retentions since volatile droplets would be entrapped within the matrix away from the air phase. Lambert *et al.* (1973b) have studied the redistribution of butanol in a water-butanol system and have shown that fast freezing results in a lower butanol concentration in the surface layer in comparison to slow freezing.

Table 3 shows that the carvone retention in 1% gum arabic appears to be relatively independent of the freezing rate. Chirife *et al.* (1973) have pointed out that such polymeric materials will have a reduced mobility during freezing. Thus on the basis of the results of Table 3 it is expected that the degree of gum arabic redistribution, during both slow and fast

freezing of solutes, will be equal since even at the low temperature the concentration effect is small compared to that experienced by the lower molecular weight saccharides.

Thijssen (1972) had previously predicted that systems containing partially soluble volatile compounds would exhibit a decreased volatile retention during freeze drying when the sample was frozen with lower freezing rate.

Effect of Additional Volatiles

Massaldi and King (1974) have suggested that the presence of an additional immiscible liquid phase, in a product that is to be freeze dried, may adversely effect the retention of important flavoring volatiles. An additional immiscible phase would extract useful volatile components from the aqueous mixture and thus the useful volatile would be more susceptible to loss during the drying stage. The results presented in Table 4 indicate that the presence of immiscible octanol does indeed cause a marked decrease in the retentions of carvone, eugenol and m-anisaldehyde. The solutions with initial octanol concentrations of 600 ppm and 800 ppm were not homogeneous since the solubility limit of octanol in the 10% sucrose solution was exceeded. It is apparent that increasing amounts of initial octanol above the solubility limit cause increased losses of the volatile being monitored. It is also apparent that increasing amounts of initial octanol, initially present at levels below the solubility limit, decrease the retention of the volatile under consideration. In all probability this homogeneously dissolved octanol separates out as a pure phase as its solubility limit is exceeded during freezing. These

Table 4. Retention of carvone, eugenol and m-anisaldehyde as a function of initial octanol concentration in 10% sucrose

Initial Octanol Concentration (ppm)	Volatile Retention (%)		
	Carvone[a]	Eugenol[a]	m-Anisaldehyde[a]
0	53.0 ± 1.3	58.3 ± 1.4	56.8 ± 1.1
200	43.5 ± 4.3	54.7 ± 2.0	46.3 ± 3.1
400	42.5 ± 3.1	47.3 ± 1.0	51.7 ± 0.7
600	41.0 ± 2.9	42.5 ± 1.0	53.9 ± 0.9
800	34.3 ± 2.1	41.2 ± 1.6	48.9 ± 0.6

[a]Initial volatile content, 500 ppm

droplets are then able to extract the other volatiles in much the same manner as the initially immiscible octanol. King and Massaldi (1974) have discussed the implications of having an immiscible phase present in a liquid food that is to be freeze dried.

Table 5 illustrates that the retentions of carvone, eugenol and m-anisaldehyde in 10% sucrose are not adversely affected by the presence of varying amounts of ethanol, an infinitely water soluble volatile.

Table 5. Retention of carvone, eugenol and m-anisaldehyde as a function of initial ethanol concentration in 10% sucrose

Initial Ethanol Concentration (ppm)	Volatile Retention (%)		
	Carvone[a]	Eugenol[a]	m-Anisaldehyde[a]
0	53.0 ± 1.3	58.3 ± 1.4	56.8 ± 1.1
300	54.4 ± 2.8	59.3 ± 2.4	56.2 ± 2.2
600	53.9 ± 2.2	61.7 ± 1.2	58.3 ± 0.6
900	52.5 ± 4.6	58.9 ± 2.4	57.6 ± 1.3
1200	54.6 ± 2.9	60.1 ± 2.0	56.7 ± 1.5

[a]Initial volatile content, 500 ppm

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PASTEURIZATION OF CHERRY BRINE IN A HELICALLY COILED HEAT EXCHANGER

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ABSTRACT

Spent cherry brine was pasteurized in a helically coiled heat exchanger. The brine contained polygalacturonase enzyme at a concentration of 1 *mg of enzyme per* 1 *ml of brine. Two methods were used to predict the amount of polygalacturonase inactivation. Predicted and measured values varied less than* 2.34%. *A pasteurization process with a constant temperature of* 81 °*C throughout the holding coil of the heat exchanger for* 9 *sec resulted in* 99.8% *inactivation.*

INTRODUCTION

Spent cherry brine is difficult to handle in conventional waste treatment systems since it contains several thousand ppm SO_2, color, and a considerable amount of solids. The brine also has low pH. Recycling of the spent brine has been proposed as a solution to the pollution problem. Reclamation of spent brine by using activated carbon was studied by Beavers *et al.* 1970. Athanasopoulos and Heldman (1976) investigated possible commercialization of the reclamation process based upon the work of other investigators (Soderquist 1971; Panasiuk *et al.* 1977).

Polygalacturonase enzyme (PG) which might be present in spent brine,

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adversely affects product quality if the brine is reused, by softening the tissues of the brined cherries. Possible sources of PG in brined cherries may be from microbial growth, certain cherry diseases, or the fruit itself might synthesize the enzyme during ripening (Steele *et al.* 1960). A safe method to prevent enzymatic softening would be the inactivation of PG by heat.

Research was initiated by the USDA and Michigan State University to determine the feasibility of reusing cherry brine. The primary objective of this study was to determine the amount of inactivation of polygalacturonase in spent cherry brine after heat treatment in a helically coiled heat exchanger. An analytical method developed by Deindoerfer and Humphrey (1959) and the general method described by Ball *et al.* (1957) were used to predict the percent inactivation of polygalacturonase.

MATERIALS AND METHODS

Cherry brine from the Napoleon variety was chosen for the experimental trials. The brine was obtained from a processing plant located in Traverse City, Michigan. Extraneous matter including color, stems, leaves and seeds was removed using a reclamation system developed by Athanasopoulos and Heldman (1976). Purified commercial polygalacturonase from *Aspergillus niger* was used at a concentration of 1 mg of the enzyme per 1 ml of brine.

The brine was pasteurized in a helically coiled heat exchanger which consisted of heating, holding and cooling sections. The specifications of the unit are given in Table 1. Hot and cold water were used for the heating and cooling medium respectively. A steam heated water bath was used to maintain the heating medium at a constant and controlled temperature. The flow rate of the brine was kept constant during the pasteurization process by using 2 pumps of different flow rates and a supply tank positioned 4 ft above the pumps. Figure 1 represents a schematic diagram of the heating and cooling systems. Counter-flow arrangement was used in both heating and cooling sections; the brine flowing upward in the heater and downward in the cooler. The flow rate of the liquids was as follows: hot water 3.8 Kg/min, cold water 5.6 Kg/min and brine 1 Kg/min.

The over-all heat transfer coefficient (U) was calculated by the equation:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{x}{kw} + \frac{1}{h_o} \quad (1)$$

Equation (1) is valid in situations where the tube wall is very thin and the resistance due to scale deposit is negligible. In this study the various heat transfer equations related to the helically coiled heat exchanger were derived from previous studies concerning heat transfer in helices and coils (Mintzias 1977). Experimentally determined values of the overall heat transfer coefficient under several experimental conditions are given in Table 2.

Table 1. Specifications of experimental heat exchanger

Specification	Heater	Cooler
Shell diameter	22 cm	22 cm
Shell height	43 cm	43 cm
Helix diameter	19.05 cm	19.05 cm
Number of turns	10	7
Tube length	580 cm	397 cm
Pitch	3.18 cm	3.81 cm
Tube I.D	0.635 cm	0.635 cm
Tube O.D	0.7937 cm	0.7937 cm

Length of tube in holding section: 488 cm

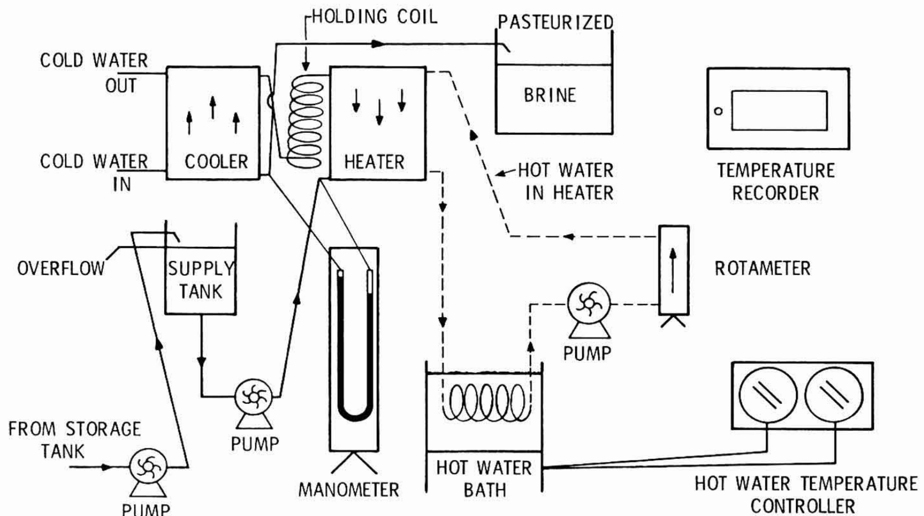

FIG. 1. SCHEMATIC DIAGRAM OF HEATING AND COOLING SYSTEM FOR PASTEURIZATION OF CHERRY BRINE

Table 2. Experimentally determined values of the over-all heat transfer coefficient

Fluid temperature, °C				U, W/m² °C
T_{bi}	T_{bo}	T_{wi}	T_{wo}	
23.3	70.0	87.8	72.2	1056
69.7	33.3	11.7	25.6	977
22.2	72.0	86.1	74.4	1062
77.7	32.2	13.0	19.5	999
22.2	76.7	93.9	77.5	1085
76.1	34.0	13.0	22.0	1011
22.2	81.0	98.9	79.4	1096
80.5	34.5	11.1	19.2	1016

T_{bi} = Brine inlet temperature T_{wi} = Water inlet temperature
T_{bo} = Brine outlet temperature T_{wo} = Water outlet temperature

The agar cup plate diffusion procedure (Dingle *et al.* 1953) was used to measure the degree of inactivation of polygalacturonase enzyme. To apply the cup plate diffusion procedure a standard curve was constructed.

In order to apply the general and analytical methods for polygalacturonase inactivation, the brine temperature at several points in the apparatus had to be determined. Copper-constantan thermocouples were attached to the coils as shown in Fig. 2. Temperatures were recorded using a multi-point recording potentiometer. Measurements of the wall temperature of the coil in both the heater and cooler indicated that the temperature varied exponentially with distance along each coil. It was assumed that the fluid temperature in the coils also varied exponentially with distance. The average velocity of the brine in the coils was determined by measuring the flow rate of the brine and considering the cross sectional area of the pipe. Thus, a residence time, t, of the brine within the coils can easily be determined. Furthermore, the fluid temperature in the coils of the heater and cooler is given by Deindoerfer and Humphrey (1959):

$$T = J\,(1 + be^{-Kt}) \qquad (2)$$

where T = stream temperature at any time, t (°K).

The analytical method (Deindoerfer and Humphrey 1959) is based on calculating the design criterion in a sterilization process. The design criterion (∇) is a measure of the size of the task to be accomplished or the degree of inactivation. In a continuous sterilization process, where the medium flows through heating, holding, and cooling sections:

$$\nabla_{total} = \nabla_{heating} + \nabla_{holding} + \nabla_{cooling} \quad (3)$$

For heating and cooling:

$$\nabla = A \int_{o}^{t} \exp\,(-Ea/RT)\,dt \quad (4)$$

For the holding section where the process is isothermal:

$$\nabla = AT \exp\,(-Ea/RT) = -kt \quad (5)$$

Equation (2) for the temperature-time profiles in the experimental heat exchanger can be combined with Equation (4) and the result integrated. Thus, for the heating and cooling sections:

$$\nabla = \frac{A}{K}\left[E_1\left(\frac{a}{1+b}\right) - E_1\left(\frac{a}{1+b} - Kt\right)\right] - \frac{Ae^{-a}}{k}\left[E_1\left(\frac{a}{1+b} - a\right)\right.$$
$$\left. - E_1\left(\frac{a}{1+be} - kt - a\right)\right] \quad (6)$$

and by definition:

$$E_1(z) = \int_{z}^{\infty} \frac{e^{-x}}{x}\,dx \quad (7)$$

A requirement for process calculation by the general method is knowledge of the temperature variation with time of the sterilized medium during heat treatment. In this study the temperature of the treated brine was measured at several points. These measurements were used to determine b and K equation (2). Time temperature profiles of the brine as it passes through the heat exchanger were constructed using Equation (1). Thus, the method is a modification of the general method as described by Ball *et al.* (1957). Application of the equation,

$$L = 10^{(T - Tp)/z} \quad (8)$$

where z, (°C), is the negative reciprocal of the "thermal death time" curve, gives the lethal rate, L, of the heat treated enzyme at temperature T. The lethal effect (or lethality") during a given time interval at ∇t for

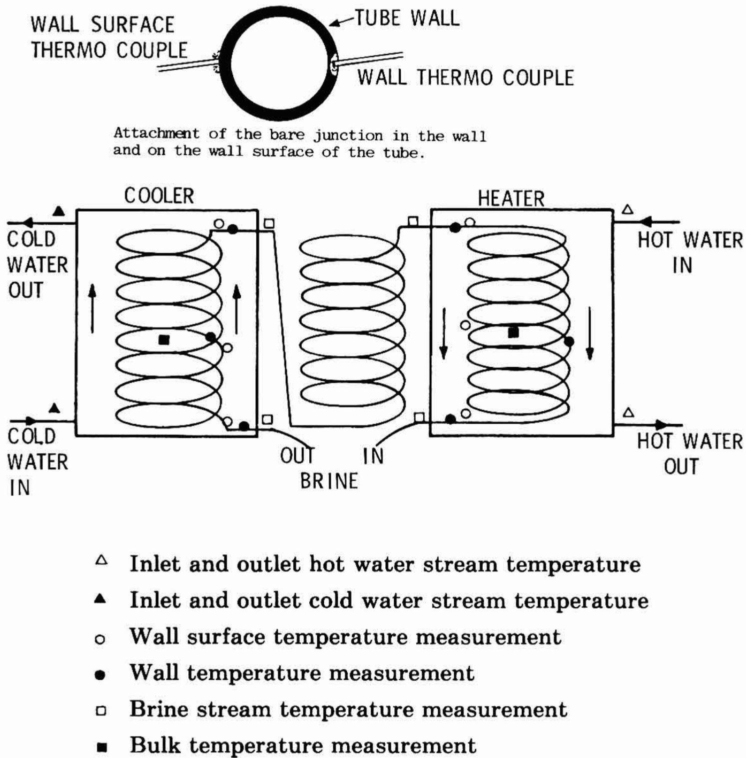

FIG. 2. THERMOCOUPLE STATIONS FOR WALL, WALL SURFACE AND FLUID STREAM TEMPERATURE MEASUREMENT

which T is considered a constant, is the product $L \times \nabla t$. The cumulative lethality for a certain period of time can be calculated as the summation of the lethalities for each time increment.

Rate constants for polygalacturonase taken from Athanasopoulos (1976) are presented in Table 3.

RESULTS AND DISCUSSION

Figure 3 shows temperature-time profiles as they were measured and predicted by Equation (2). These profiles were used for calculating polygalacturonase inactivation at several process temperatures. The constant temperature along the holding coil was considered to be the process temperature, (Tp), during each experimental trial. Because of the exponential

Table 3. Rate constants of polygalacturonase at pH = 3.0[1]

Temperature, °C	D, Value, Sec	K × 100 Sec^{-1}
70	46.76	4.925
72	29.26	7.870
74	15.62	14.743
76	9.02	25.532
78	5.20	44.288
80	3.01	76.511

Z = 8.45 °C
E = 64668 Cal/mole

[1]Ahanasopoulos (1976)

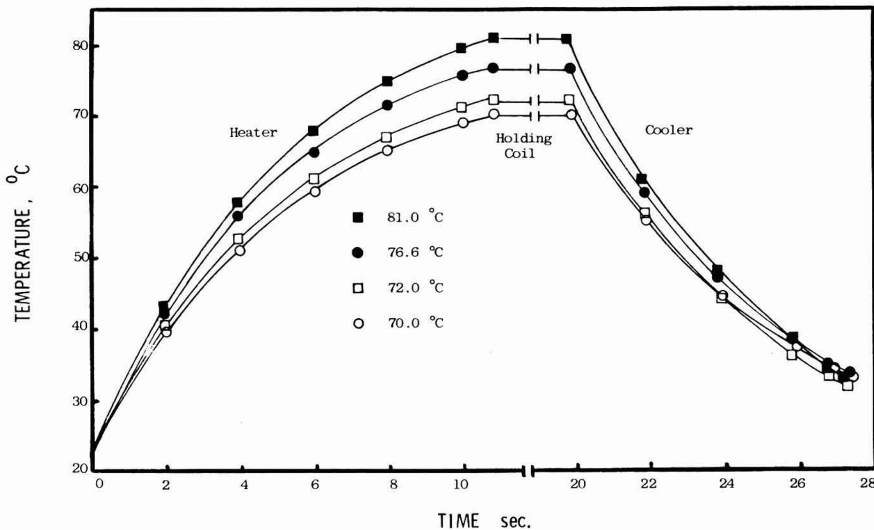

FIG. 3. PREDICTED TIME TEMPERATURE PROFILES AT FOUR CONSTANT TEMPERATURES ALONG THE HOLDING COIL

nature of the heating and cooling portions, the enzyme was subjected to higher temperatures for a longer period of time in the heater than in the cooler for the same temperature range. Thus the heating section contributed more to the total inactivation than the cooling section, as shown in Table 4. While the contribution of the cooler to the total inactivation was not of great importance (1.44 to 2.16%), the heater contributed from 9.84 to 18.01% (Table 4). This indicates that a considerable amount of inactivation occurs during the heating period.

Table 4. Polygalacturonase inactivation occurring in each section of the experimental heat exchanger, calculated by the analytical method, using a constant temperature along the holding coil

Temperature °C	Total Percent	Heater Percent	Cooler Percent	Holding Coil Percent
70.0	45.00(100)	9.84(22)	1.44(3.2)	33.7(74.8)[1]
72.0	64.23(100)	14.14(22)	1.83(2.8)	48.22(75.2)
76.7	96.16(100)	16.53(17.2)	3.36(3.5)	76.24(79.3)
81.0	99.998(100)	18.01(18)	2.16(2.2)	79.81(79.8)

[1]The numbers in parentheses represent the percentage of the total percent

Calculation of the inactivation under conditions of varying temperature by any of the existing methods is a tedious and time consuming procedure. It is also obvious from Equations (2) and (6) that application of the analytical method requires accurate information regarding the heat transfer within a heat exchanger. Thus, a lack of heat transfer data might make the analytical method useless in process calculation.

In practice, where the amount of time required for process calculation is of great importance, the analytical and general methods do not satisfy this requirement. During the course of this study it was found that at process temperatures higher than 76 °C where the total inactivation exceeds 96% (Table 4) addition of 20% to the inactivation achieved in the holding coil gives a satisfactory estimation of the total inactivation. The inactivation in the holding coil is relatively easy to determine since the process in isothermal (Equation 5). The above described procedure is considerably faster than the general or analytical method but less accurate.

The three methods which were used for determining inactivation, namely plating, analytical and general, gave results in close agreement with each other as shown in Table 5. The analytical and general methods resulted in inactivation which varied from those of plating by −1.9 to +2.3%. Therefore, either the general or the analytical method may give a satisfactory estimation of polygalacturonase inactivation. The analytical method may be more advantageous since it is faster than the general method. It should also be noted that the variation becomes smaller as the degree of inactivation increases.

A temperature of 81 °C along the holding coil resulted in 99.998% inactivation or a 4.8 D process (Table 2). This inactivation is considered adequate to prevent softening of cherries treated with recycled heat treated brine.

With the pasteurization unit used in these experiments a 4.8 D process

Table 5. Percent inactivation determined by the three methods, and percent deviation of the general and analytical methods from plating

Temperature °C	Plating	% Inactivation Analytical	% Inactivation General	% Deviation Analytical	% Deviation General
70.00	44.00	45.03	43.16	+2.34	−1.9
72.00	63.00	64.23	62.00	+1.92	−1.58
76.66	95.40	96.91	96.86	+1.58	+1.53
81.00	99.985	99.998	99.997	+0.013	+0.012

will currently cost about $3.92 per 1000 gallons of cherry brine. The cost may be reduced as much as 50 percent if the system includes a regenerative section where untreated brine replaces the cold water as the cooling medium. The heat gained by the untreated brine substantially reduces the operating cost of the heating section.

CONCLUSION

Pasteurization of spent cherry brine can be accomplished in a helically coiled heat exchanger. A process temperature of 81 °C for 9 sec will inactivate as much as 99.998% of the polygalacturonase.

The amount of inactivation can be satisfactorily determined by either the general or the analytical method. Plating can be used to check the results of the two methods.

NOMENCLATURE

A = Proportionality constant in Arrhenius equation, Sec^{-1}
Aa = Area, m^2
a = Ea/RJ, dimensionless
b = (To — TH)/TH for heating
  = (To — Tc)/Tc for cooling
c = Specific heat, KJ/Kg — °C
Ea = Activation Energy, cal/mole
E_1 = First order exponential function
h_i = Inside heat transfer coefficient, W/m^2 — °C
h_o = Outside heat transfer coefficient, W/m^2 — °C
J = TH for heating
  = Tc for cooling

K = UAa/Wc
kw = Thermal conductivity, W/m °C (Eq. 1)
K = Velocity constant of enzyme activity
R = Universal gas constant, cal/g-mol-°K
T = Temperature, °C or °K
Tc = Cold stream temperature, °K
TH = Hot stream temperature, °K
To = Brine initial temperature, °K
Tp = Process temperature, °K
t = Time, sec
U = Over-all heat transfer coefficient, W/m^2 °C
W = Mass of brine in contact with the area of the heat exchanger, kg
x = Wall thickness, m

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LITERATURE ABSTRACTS

ABSTRACTS FROM THE JOURNAL OF FOOD SCIENCE

Each of the following abstracts has been reprinted with permission from the *Journal of Food Science.*

MATHEMATICAL APPROACH FOR THE DETERMINATION OF DYES CONCENTRATION IN MIXTURES. I. Saguy, S. Mizrahi, and I. J. Kopelman, J. Food Sci. *43*, 121–123.

A method is proposed whereby pigments content (in a two or more components admixture) can be determined accurately and directly from the spectra, thus dispensing the time consuming initial step of pigments separation. The procedure is based upon a nonlinear curve fitting of the visible spectrum of the pigments with a predicted function of the individual dyes. The logarithmic normal distribution function showed a remarkable fitting with the pigments tested (Amaranth—Red #2, Tartrazine—Yellow #5 and Yellow 2G) thus, used as the mathematical model for the curve fitting process.

COMPUTER-AIDED DETERMINATION OF BEET PIGMENTS. I. Saguy, I. J. Kopelman, and S. Mizrahi, J. Food Sci. *43*, 124–127.

A quick and accurate method is proposed for determining all major beet pigments (betanin, vulgaxathin-I, betalamic acid) and browning substances, from the visible spectrum of the mixture. The procedure is based on nonlinear curve fitting of the spectrum with a predicted function of the individual pigments, and obviates the need for laborious and time-consuming separation. The approach is extremely useful in continuous monitoring of time- and temperature-related processes, such as drying and storage.

ON THE APPLICATION OF FICK'S LAW FOR THE KINETIC ANALYSIS OF AIR DRYING OF FOODS. L. M. Vaccarezza and J. Cherife, J. Food Sci. *43*, 236–238.

Analysis of literature data on air drying of foods during the first falling rate period, showed that the thickness dependence of drying rate is somewhat lower than is predicted by Fick's law. An explanation based on heat transfer effects is proposed to explain this "anomaly" and a quantitative model was accordingly developed. The model was tested with experimental data on sugar beet root drying and an excellent agreement was now found between theoretical (Fick's law) and experimental thickness dependence of drying rate.

FINITE ELEMENT ANALYSIS OF FREEZING PROCESS IN FOOD STUFFS. L. Rebellato, S. Del Giudice and G. Comine, J. Food Sci. *43*, 239–243.

Finite element analysis concerning freezing processes of interest to food engineering allows the solution of practically any phase-change problem described in terms of

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two-dimensional geometries. Special features of the program used include isoparametric elements, control of numerical oscillations and an accurate procedure for the estimation of thermal properties. In the examples of applications presented in the paper, reference is made to air-blast freezing of foodstuffs having irregular shapes.

VISCOMETRIC BEHAVIOR OF GUAVA PUREES AND CONCENTRATES. J. E. Brekke, C. R. N. De Aquino, and A. L. Myers, J. Food Sci. *43*, 272–273.

Guava purees and concentrates had flow characteristics of pseudoplastic fluids as determined with a tube viscometer. Puree treated with a pectinolytic enzyme could be concentrated significantly more than untreated puree.

ABSTRACTS FROM THE AICHE JOURNAL

Each of the following has been reprinted with permission from the *AICHE Journal.*

AERATION AND MIXING IN DEEP TANK FERMENTATION SYSTEMS. M. L. Jackson and C. C. Shen, AICHE J. *24*, 63.

Oxygen transfer characteristics for three sizes of equipment, from 76 mm to 7.6 m in diameter and for liquid depths from 4 to 21 m, correlate well and permit scaling of fermentation systems in size. Simple orifice inlets for gas flow, uniformly distributed over a tank bottom, effect rapid mixing and permit very high oxygen demands to be met. Supersaturation provides dissolved gases for the flotation and solids separation as an inherent processing procedure. Nearly uniform bulk liquid composition and a linear decrease of gas phase composition with depth permit a proper, integrated value of the oxygen saturation driving force to be employed. Results provide the design basis for large scale aeration systems which offer potential savings in both capital and energy.

REALTIME ESTIMATION OF AEROBIC BATCH FERMENTATION BIOMASS CONCENTRATION BY COMPONENT BALANCING. D. W. Zabriskie and A. E. Humphrey, AICHE J. *24*, 138.

Real-time estimates of biomass concentration and growth rate in fermentation processes were obtained by performing a material balance on oxygen and employing a kinetic model for molecular oxygen utilization. A model containing yield and maintenance terms was satisfactory in fermentations where only the EMP and TCA pathways were utilized for glucose metabolism. However, model alterations based on metabolic energetics were required before accurate estimates were obtained for a metabolically complex fermentation producing bakers yeast.

ABSTRACTS FROM THE INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER

Each of the following abstracts has been reprinted with permission from the *International Journal of Heat and Mass Transfer.*

UNSTEADY STATE MASS TRANSFER THROUGH THE INTERFACE OF SPHERICAL PARTICLES — I. H. Brauer, Int. J. Heat Mass Transfer *21*, 445.

Unsteady state mass transfer through the interface of spherical particles has been thoroughly investigated using numerical methods. The particles may be bubbles, drops and solids. Mass transfer may occur in a motionless system and in a system with either the surrounding fluid only or both fluids being in motion. Creeping flow conditions are assumed for the surrounding fluid, so that the equations presented by Hadamard and Rybczinski for the velocity field can be used for calculations of the concentration field. The first part of the paper is devoted to a comprehensive discussion of the various mass-transfer conditions. This discussion is the basis for an understanding of the differential equations governing the concentration field inside and outside the sphere and the pertaining initial, boundary and interfacial conditions. These conditions are given for the general case of mass-transfer resistance in both phases as well as for the two limiting cases, for which mass-transfer resistance occurs in one of the two phases only.

UNSTEADY STATE MASS TRANSFER THROUGH THE INTERFACE OF SPHERICAL PARTICLES — II. H. Brauer, Int. J. Heat Mass Transfer *21*, 445.

In the second part of the investigation the results obtained by numerical solution of the differential equations given in the first part are thoroughly discussed. The discussion starts with mass transfer through the particle interface when there is no movement in either phase. It is limited to the mean concentration in the sphere and the mean Sherwood numbers for both phases. Empirical equations are presented for the mean concentration in the sphere for the limiting cases of mass-transfer resistance in one of the two phases only. The last chapter of the paper contains the discussion pertaining to the influence of convection on mass transfer. With mass-transfer resistance in the sphere only there exists an upper limit for the mean Sherwood number which is due to the fact that the streamlines inside the sphere become lines of constant concentration. The instantaneous Sherwood number changes stepwise with time which may be explained by the movement of fluid elements in the sphere. For the second limiting case, mass transfer resistance in the surrounding fluid only, the mean Sherwood number is discussed as a function of the Fourier-, Henry-, and convection-number.

TRANSFER OF HEAT OR MASS TO PARTICLES IN FIXED AND FLUIDISED BEDS. D. J. Gunn, Int. J. Heat Mass Transfer *21*, 467.

Experimental measurements of heat transfer to particles in fixed beds show either a constant value of the Nusselt group as the Reynolds number is reduced or, if axial dispersion has been neglected, the Nusselt group decreases to zero. A quantitative analysis of particle to fluid heat transfer on the basis of a stochastic model of the fixed bed leads to a constant value of the Nusselt group at low Reynolds number. When the analytical equation is included as an asymptotic condition, an expression is derived that describes the dependence of Nusselt group upon Reynolds number. The expression is extended to describe mass and heat transfer to fixed and fluidised beds of particles within the porosity range of 0.35–1.0. Both gas and liquid phase transfer groups are correlated up to a Reynolds number of 10^5.

LOCAL HEAT TRANSFER FROM A SINGLE SPHERE TO A TURBULENT AIR STREAM. G. L. Hayward and D. C. T. Pei, Int. J. Heat Mass Transfer *21*, 35.

The local heat transfer between a sphere and a turbulent air stream was studied. The flow conditions covered Reynolds number between 2600 and 6100 and turbulence intensities from 0.45 to 6.0%. The results obtained show that the boundary layer over the leading surface becomes turbulent at the laminar separation point. This turbulent layer becomes reattached to the surface and separates further downstream, resulting in a turbulent wake. These phenomena occur at low Reynolds number through the interaction between the freestream turbulence and the boundary layer.

ABSTRACTS FROM ASHRAE TRANSACTIONS

Each of the following abstracts has been reprinted with permission from the American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

PASSIVE SOLAR HEATING AND COOLING SYSTEMS. J. I. Yellott, ASHRAE Trans. *83*, 429.

Passive solar systems use the sun's radiation for heating and natural processes (connection, radiation and evaporation) for cooling. Three passive heating systems and one natural cooling system have evolved which may be classified as follows: (I) Sun + Space + Building Mass Storage; (II) Sun + Storage Mass + Space; (III) Sun + Natural Convection + Storage. The first type is characterized by large south-facing windows, equipped with additional insulation which can be made effective when the sun is not shining. The second type uses glazed south-facing heat storage masses which also cause heat to enter the space when the sun is shining, or it uses shallow water ponds on the roof with movable insulation which can be moved to admit or reflect solar radiation. By a simple modification, the latter system can also accomplish natural cooling. The third system includes one of the oldest solar devices, the thermosyphon water heater, and one of the newest, a natural circulation air heater and rock bed thermal storage. All three systems have now had extensive testing and are in use in a rapidly growing number of residences in the U.S. and abroad.

ABSTRACTS FROM TRANSACTIONS OF THE ASAE

Each of the following abstracts has been reprinted with permission from the American Society of Agricultural Engineers.

MODELING CATFISH POND NIGHTTIME DISSOLVED OXYGEN LEVELS. C. D. Busch, C. A. Flood Jr., J. L. Koon and R. Allison, ASAE Trans. *20FE*, 394–396.

A computer simulation has been devised to account for fish and other fish pond nighttime oxygen demands. The model includes the capability for intermittently providing mechanical aeration to maintain more satisfactory dissolved oxygen levels. A comparison of the model with actual ponds has given promising results.

THERMAL DIFFUSIVITY OF SWEET POTATOES. W. R. Crumpton and E. D. Threadgill, ASAE Trans. *20FE*, 589–592.

The thermal diffusivities of 5 states of sweet potato materials were found experimentally for 3 processing temperatures using uniform size samples. The firmness of the processed samples were evaluated. The results show that the thermal diffusivity varies according to both the state of sweet potato material and processing temperature whereas the firmness of the processed samples vary only according to the state of the material.

TEACHING FOOD ENGINEERING FOR FOOD SCIENCE STUDENTS. D. R. Thompson. ASAE Trans. *20FE*, 598–600.

Opinions of food science graduates, employers and educators are utilized in the study of food engineering course objectives, topics, and teaching methods. The objectives of food engineering courses for food science students are not to educate them to be engineers or technicians, but to help them develop logical problem-solving abilities, converse intelligently with engineers, and develop a basic knowledge of food processing equipment and processes.

KINETICS OF FOOD UTILIZATION BY OYSTERS. P. N. Walker and J. W. Zahradnik, ASAE Trans. *20FE*, 795–799.

Oysters were grown in raceways for 121 days. Each raceway received water at a different combination of flow rate and food concentration. The weight growth data indicate that, for a given set of physical parameters, food concentration controls the growth rate. Using a chemical reaction model the rate of food uptake and the rate of growth were determined as a function of food concentration. These rates were used to predict conversion (ratio of growth to food) as a function space time (ratio of number of animals to flow rate).

DELAYED LIGHT EMISSION AS A MEANS OF AUTOMATIC SELECTION OF SATSUMA ORANGES. Y. Chuma, K. Sein, S. Kawano and K. Nakaji. ASAE Trans. *20FE*, 996–1000.

Conditions effecting the delayed light emission (DLE) intensity were investigated for the Satsuma orange.

DLE intensity indices were established for the fruit conditions such as peel temperature, chlorophyll content, peel treatment in the packing house line (such as brushing or waxing), and correlated to the storage period for the purpose of providing an automatic mechanization of selecting process.

PRODUCTION OF EDIBLE FOODS FROM SURF CLAM WASTES. R. R. Zall and I. J. Cho. ASAE Trans. *20FE*, 1170–1173.

This paper shows how to salvage food from discarded clam meat fractions in shellfish plants with manual shucking operations. The process suggested uses shell separation and retort heating of materials culled from an outgoing waste stream. Results show that about five percent of a shellfish plant's meat material can be captured as additional meat to increase commodity yield and profits.

FORCED-AIR COOLING OF BELL PEPPERS IN BULK. J. J. Gaffney and C. D. Baird, ASAE Trans. *20FE*, 1174–1179.

Temperature response, as a function of air velocity and position in load, was determined during cooling of bell peppers in bulk with 1.7°C (35°F) air. Data were analyzed to provide graphs and equations that can be used to predict mass average temperatures during cooling for any desired initial product temperature or cooling air temperature, and at any air velocity from 0.02 to 2.0 m/s (4 to 400 ft/min). Information is also presented on moisture loss during cooling and on static pressure drop through the load as a function of air flow.

INSTRUMENTATION FOR MEASUREMENT OF LATERAL AND VERTICAL PRESSURES IN POTATO STORAGE. E. C. Yaeger and G. L. Pratt. ASAE Trans. *20FE*, 1180–1184.

An engineer who designs a potato storage structure is concerned with the pressure exerted by the potatoes on the walls of the structure. The most recent design data available, before these tests, were developed from experiments on very narrow, deep bins, which are outmoded. The instrumentation used to measure bin pressures has been updated. A pressure panel was developed with which either strain gages or hermetically sealed load cells could be used. It was tested in modern, wide, shallow bins. The cantilevered-bar strain gage pressure transducers failed under long term tests. The load-cell pressure transducer proved to be a useful research tool for obtaining structural design data applicable to potato storages.

CONTINUUM THEORY FOR GAS-SOLID-LIQUID MEDIA — I. R. J. Gustafson, G. E. Mase and L. J. Segerlind. ASAE Trans. *20FE*, 1186–1189.

Principles of continuum theory are applied to a porous solid having two sets of interconnected pores, one filled with gas, one with liquid. The development of the governing constitutive equations follows closely the procedure of Biot (1962). Linear stress-strain relations are developed. Limits on material property coefficients are determined. Interpretation of elastic coefficients by defining a series of compressibility tests is given.

CONTINUUM THEORY FOR GAS-SOLID-LIQUID MEDIA — II. MODELING BY USE OF FINITE ELEMENT METHOD. R. J. Gustafson and L. J. Segerlind. ASAE Trans *20FE*, 1190–1200.

The finite element method is used in conjunction with the model developed in Part I. Variational equations are developed by minimization of total potential energy. Sample applications given for a body simulating a fruit include stress due in an unrestrained body due to internal liquid pressure and stress due to flat plate compression.

GUIDE FOR AUTHORS

Typewritten manuscripts in triplicate should be submitted to the editorial office. The typing should be double-spaced throughout with one-inch margins on all sides.

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Page two should contain an abstract of not more than 150 words. This abstract should be intelligible by itself.

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Introduction: This should be brief and state the reason for the work in relation to the field. It should indicate what new contribution is made by the work described.

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DEWALD, B., DULANEY, J. T. and TOUSTER, O. 1974. Solubilization and polyacrylamide gel electrophoresis of membrane enzymes with detergents. In *Methods in Enzymology*, Vol. xxxii, (S. Fleischer and L. Packer, eds.) pp. 82–91, Academic Press, New York.

HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. *57*, 142–147.

ZABORSKY, O. 1973. *Immobilized Enzymes*, pp. 28–46, CRC Press, Cleveland, Ohio.

Journal abbreviations should follow those used in *Chemical Abstracts*. Responsibility for the accuracy of citations rests entirely with the author(s). References to papers in press should indicate the name of the journal and should only be used for papers that have been accepted for publication. Submitted papers should be referred to by such terms as "unpublished observations" or "private communication." However, these last should be used only when absolutely necessary.

Tables should be numbered consecutively with Arabic numerals. The title of the table should appear as below:

Table 1. Activity of potato acyl-hydrolases on neutral lipids, galactolipids, and phospholipids

Description of experimental work or explanation of symbols should go below the table proper.

Figures should be listed in order in the text using Arabic numbers. Figure legends should be typed on a separate page. Figures and tables should be intelligible without reference to the text. Authors should indicate where the tables and figures should be placed in the text. Photographs must be supplied as glossy black and white prints. Line diagrams should be drawn with black waterproof ink on white paper or board. The lettering should be of such a size that it is easily legible after reduction. Each diagram and photograph should be clearly labeled on the reverse side with the name(s) of author(s), and title of paper. When not obvious, each photograph and diagram should be labeled on the back to show the top of the photograph or diagram.

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JOURNAL OF FOOD PROCESS ENGINEERING VOL. 2, NO. 2 1978

CONTENTS

Meetings vii

Proteolysis by Immobilized Trypsin
ERIC A. GRULKE, MARTIN R. OKOS and **ALDRICH SYVERSON,** The Ohio State University, Columbus, Ohio 115

Indirect Energy Requirements for Vegetable Canning
W. VERGARA and **M. A. RAO,** New York State Agricultural Experiment Station, Cornell University, Geneva, New York 137

Retention of Sparingly Soluble Volatile Compounds During the Freeze Drying of Model Solutions
T. G. SMYRL and **MARC LEMAGUER,** University of Alberta, Edmonton, Alberta, Canada 151

Pasteurization of Cherry Brine in a Helically Coiled Heat Exchanger
PETROS Z. MINTZIAS, ALVIN L. RIPPEN and **LLOYD E. LEREW,** Michigan State University, East Lansing, Michigan . 171

Literature Abstracts 181

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