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Kinetic Model of Pectin Extraction

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ABSTRACT

A model describing the kinetics of pectin extraction is presented The effect of degradation on the yield of pectin has been taken into account It is applied to extraction experiments with apple pressings and 0 5% nitric acid at temperatures of 60°C, 70°C and 80°C in laboratory extraction equipment The suggested theoretical model provides an opportunity to predict the yield of pectin, the quantity of depolymerized pectic substances and the optimum duration of extraction

INTRODUCTION

Pectic substances are widespread as building components in the tissue structure of higher plants They have an increasing significance in modern technology It has been established that pectic substances can be successfully used for the treatment of gastric and intestinal disease and in cases of heavy metal poisoning. Great hope in the prevention and treatment of arteriosclerosis is also laid on the use of pectin-enriched foods

Therefore, the applications of pectic substances in people's lives are constantly increasing. Of special importance here is the problem of expanding the production of pectin A key issue in pectin technology is the process of extracting the pectin from the plant raw material Despite the great variety of research in this direction, a complete theoretical model of this complex physicochemical process has not so far been given in the literature (Kertezs, 1951, Doesburg, 1965, Kratchanov *et al*, 1986, King, 1987, Sheluhina *et al*, 1987) On the other hand, the insufficient knowledge about the influence of temperature and acidity on

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the pectin yield during a continuous extraction has misled some authors in designing the methods for studying the process For instance, El-Nawawi & Shehata (1987) carried out 120-min extraction of pectin from orange peels to achieve the optimum temperature and acidity, overlooking the fact that at the extreme values of these parameters (e g temperature 90–110°C and pH < 1 5) the degradation of pectin becomes a very rapid process This certainly makes the validity of the optimal values found by them for the quoted parameters rather doubtful A knowledge of the extraction process kinetics would allow us to prognosticate this process and optimize the yield and quality of the obtained pectin. Besides, it would give quantitative information as to the effect of temperature, pH, duration, type of extractant and other factors on the values of the thermodynamic parameters of the process The present work is an attempt to create a model of pectin extraction

THEORETICAL DEVELOPMENT

The extraction process takes place in two stages. transformation of the insoluble pectin from the plant tissue (conditionally called 'protopectin') into soluble pectin and diffusion of the pectin from the plant tissue into the solution (Kertezs, 1951) In these two stages, part of the obtained pectin is degraded to low molecular components which is undesirable in practice

Taking this into account the extraction process can be discussed from the point of view of mathematical formalism in the following way. Let A_0 be the initial polyuronic acid content of the raw material. The transformation of the 'protopectin' into soluble pectin is done with a rate constant K_1 (including also the diffusion constant). As a result of acid–thermal hydrolysis the dissolved pectin could degrade and a low molecular product be obtained, the process of degradation taking place with a rate constant K_2. If by $y(t)$ we mark the quantity of dissolved pectin that will be obtained as a result of precipitation with alcohol after a time t (this process will be called 'obtaining the pectin') and by $z(t)$ the quantity of protopectin in the plant tissue at a time t, then the transition of the 'protopectin' into soluble pectin can be described by the differential equation

$$\frac{dz(t)}{dt} = -K_1 . z(t) \tag{1}$$

The quantity of dissolved pectin $y(t)$ is regarded as a process of accumulation of $y(t)$ and simultaneous degradation. This can be described by the differential equation

$$\frac{dy(t)}{dt} = K_1\ z(t) - K_2\ y(t) \tag{2}$$

Since the processes described by eqns (1) and (2) take place simultaneously and are the basis of the extraction process, it is necessary to solve them jointly as a system of differential equations

$$\begin{aligned} \frac{dz(t)}{dt} &= -K_1\ z(t) \\ \frac{dy(t)}{dt} &= K_1\ z(t) - K_2\ y(t) \end{aligned} \tag{3}$$

After solving the system (3) by the classical methods (the first equation by separation of the variables and the second, after replacing $z(t)$, are solved using an integrating multiplier $\mu = e^{K_2 t}$) we get the following dependences describing the changes with time of the 'protopectin' $z(t)$, the obtained pectin $y(t)$ and the degraded quantity of pectin $q(t)$

$$z(t) = A_0\ e^{-K_1 t} \tag{4}$$

$$y(t) = A_0\ \frac{K_1}{K_2 - K_1}\ (e^{-K_1 t} - e^{-K_2 t}) \tag{5}$$

$$q(t) = A_0 \left(1 + \frac{K_2}{K_1 - K_2}\ e^{-K_1 t} + \frac{K_1}{K_2 - K_1}\ e^{-K_2 t}\right) \tag{6}$$

As a consequence, from eqn (5) we get eqn (7) describing the kinetic process where the process of degradation has been stopped, i e such extraction conditions are at hand under which the pectin macromolecule is not depolymerized ($K_2 = 0$)

$$y(t) = A_0\ (1 - e^{-K_1 t}) \tag{7}$$

It is of practical interest to find out at what moment of time, t_{max}, the concentration, y_{max}, reaches its maximum value That is why we seek the maximum of $y(t)$ from eqn (5) following the classical mathematical procedure and we get

$$t_{\max} = \frac{\ln(K_1/K_2)}{K_1 - K_2} \tag{8}$$

$$y_{\max} = A_0 \cdot \left(\frac{K_2}{K_1}\right)^{(K_2/K_1)/(1-K_2/K_1)} \tag{9}$$

MATERIALS AND ANALYTICAL METHODS

Apple pressings (1988 crop) prepared by the Pectin Plant in Pernik were used in the experiments They had the following parameters· anhydrouronic acid content (AUA), 14 1%, degree of esterification (DE) of pectin, 74·8%, laboratory yield of pectin, 7 5% with 55 6% AUA, gel strength (GS), 225°TB. The AUA content and the DE were determined titrimetrically by the Owens *et al* (1952) method and the gel strength of the pectin was determined using standard 65% sugar jellies by the classical method of Tarr–Baker (Bender, 1949). The laboratory yield of pectin was determined after twofold extraction of 100 g apple pressings with 2 liters of 0 5% nitric acid at 85°C for 30 min. The collected filtrates were coagulated with an equal volume of 95% ethanol and the coagulate was filtered, washed with 70% ethanol and dried *in vacuo* at 40°C to a constant weight The extraction kinetics was carried out with 0 5% nitric acid at 60°C, 70°C and 80°C up to 120 min, determining the pectin yield (Kirtchev & Kratchanov, 1980) every 10 min.

DETERMINATION OF THE APPLICABILITY OF THE SUGGESTED THEORETICAL MODEL FOR PECTIN EXTRACTION

On the basis of the experimental data from Table 1, the rate constants K_1 and K_2 were determined from eqn (5) using the classical algorithm of Newton–Rhaffson for finding the parameters of nonlinear regressional dependence described by eqn (5) in accordance with Brandt (1970)

The realization of the numerical method was done using the NONLIN program compiled in FORTRAN IV by Johnson (1980) in which the sub-program FUNCTION was adapted from the specific functional dependence (5) The NONLIN program was tested and run on a CM-4 computer. The initial approximations of the rate constants K_1 and K_2 in the different examples were determined graphically in accordance with

TABLE 1
Experimental Data from the Kinetics of Pectin Extraction from Apple Pressings at Various Temperatures

No	*Duration of extraction (min)*	*60°C*			*70°C*			*80°C*		
		Yield of pectin (%)	*Degree of esterification (%)*	*AUA (%)*	*Yield of pectin (%)*	*Degree of esterification (%)*	*AUA (%)*	*Yield of pectin (%)*	*Degree of esterification (%)*	*AUA (%)*
1	10	2.15	74.4	56.8	2.84	74.1	56.3	4.04	74.0	56.7
2	20	3.66	74.0	57.0	4.71	73.0	56.8	6.84	72.6	56.8
3	30	4.64	73.8	57.0	6.17	72.8	56.8	8.20	72.1	57.4
4	40	5.44	73.4	57.5	7.21	72.0	57.6	8.66	71.6	57.8
5	50	5.96	73.0	57.6	7.71	71.6	57.8	8.88	71.0	58.5
6	60	6.38	72.8	57.9	8.01	71.3	58.5	8.90	70.4	59.0
7	70	6.53	72.4	58.5	8.05	70.6	58.8	8.90	69.4	59.3
8	80	6.66	72.1	58.5	8.00	70.1	59.0	8.85	69.0	60.2
9	90	6.72	71.7	58.9	7.95	69.5	59.5	8.63	68.5	60.2
10	100	6.78	72.4	59.0	7.87	69.4	59.5	8.32	68.1	60.5
11	110	6.75	71.3	59.0	7.66	69.1	60.0	7.91	68.0	60.5
12	120	6.64	71.0	59.0	7.38	69.4	60.0	7.50	67.7	60.9

Brandt (1970). The calculated values of the rate constants K_1 and K_2, $t_{\max}$, $y_{\max}$, Q_{10} are presented in Table 2.

The statistical dispersion analysis of the regressional dependence (5) and the adequacy check of the obtained analytical dependences were done in accordance with the classical procedures described by Brandt (1970). The respective data are given in Tables 3, 4 and 5 The adequacy check of the regressional equations was done using the statistical criterion of Fisher. The data in Table 3 indicate that $F_{\text{experimental}} > F_{\text{theoretical}}$ with a probability of $p = 99\%$ which gives us grounds to accept the adequacy estimate of the model for the kinetic process at 60°C The coefficient of regressional dependence $R = 0\ 9954$

TABLE 2

Parameters of Pectin Extraction from Apple Pressings

Temperature (°C)	*$K_1 \times 10^4\ s^{-1}$*	Q_{10}	*$K_2 \times 10^4\ s^{-1}$*	*$t_{\max}$ (min)*	*$y_{\max}$ (%)*
60	2 57	—	1 39	86 8	6 83
70	3 75	1 459	1 23	73 8	8 19
80	5 63	1 502	1 19	58 4	9 31

TABLE 3

Statistical Dispersion Analysis of the Kinetic Model of Pectin Extraction from Apple Pressings at 60°C

No	*Duration (min)*	*Yield y_i (%)*	*Theoretical y_i (%)*	*Differences between the measured and theoretical yields (%)*	
1	10	2 15	1 93	0 219	$SS =$ 24 2803
2	20	3 66	3 43	0 228	$SS_R =$ 0 2213
3	30	4 64	4 58	$0\ 642 \times 10^{-1}$	$SS_D =$ 24 059
4	40	5 44	5 43	$0\ 147 \times 10^{-1}$	$MS_R =$ 0 0264
5	50	5 96	6 03	$-0\ 731 \times 10^{-1}$	$MS_D =$ 12 0294
6	60	6 38	6 44	$-0\ 632 \times 10^{-1}$	$R =$ 0 9954
7	70	6 53	6 69	−0 163	$F_e = 489$
8	80	6 66	6 81	−0 153	$\nu_D =$ 2
9	90	6 72	6 83	−0 11	$\nu_R =$ 9
10	100	6 78	6 76	$0\ 151 \times 10^{-1}$	
11	110	6 75	6 64	0 114	$F_T(\nu_D, \nu_R, \alpha = 0\ 04) = F_T(2\ 9, 0\ 01)$
12	120	6 64	6 46	0 181	$= 8\ 02$

TABLE 4
Statistical Dispersion Analysis of the Kinetic Model of Pectin Extraction from Apple Pressings at 70°C

No	*Duration (min)*	*Yield y_i (%)*	*Theoretical y_i (%)*	*Differences between the measured and theoretical yields (%)*	
1	10	2.84	2.73	0.106	$SS = 29.1321$
2	20	4.71	4.72	-0.131×10^{-1}	$SS_R = 0.126$
3	30	6.17	6.13	0.387×10^{-1}	$SS_D = 29.0061$
4	40	7.21	7.09	0.122	$MS_R = 0.014$
5	50	7.71	7.70	0.126×10^{-1}	$MS_D = 14.50305$
6	60	8.01	8.04	-0.288×10^{-1}	$R = 0.9978$
7	70	8.05	8.18	-0.127	$F_e = 1035.93$
8	80	7.95	8.16	-0.213	$\nu_D = 2$
9	90	7.95	8.04	-0.858×10^{-1}	$\nu_R = 9$
10	100	7.87	7.83	0.435×10^{-1}	
11	110	7.66	7.56	0.101	$F_T(\nu_D, \nu_R, \alpha) = F_T(2, 9, 0.01)$
12	120	7.38	7.25	0.127	$= 8.02$

TABLE 5
Statistical Dispersion Analysis of the Kinetic Model of Pectin Extraction from Apple Pressings at 80°C

No	*Duration (min)*	*Yield y_i (%)*	*Theoretical y_i (%)*	*Differences between the measured and theoretical yields (%)*	
1	10	4.02	3.89	0.128	$SS = 21.3831$
2	20	6.84	6.40	0.438	$SS_R = 0.1808$
3	30	8.20	7.94	0.267	$SS_D = 21.2023$
4	40	8.66	8.81	-0.151	$MS_D = 10.60115$
5	50	8.80	9.21	-0.415	$MS_R = 0.0904$
6	60	8.90	9.30	-0.402	$R = 0.9958$
7	70	8.90	9.18	-0.276	$F_e = 117.27$
8	80	8.85	8.91	-0.624×10^{-1}	$\nu_D = 2$
9	90	8.63	8.56	0.683×10^{-1}	$\nu_R = 9$
10	100	8.32	8.16	0.160	
11	110	7.91	7.73	0.177	$F_T(\nu_D, \nu_R, \alpha = 0.01) = 8.02$
12	120	7.50	7.30	0.203	

shows that 99% of the experimental dispersion data are described by eqn (5).

The data in Table 4 show that $F_{\text{experimental}} > F_{\text{theoretical}}$ when $p = 99\%$, while $R = 0\ 9978$ indicates that 99·56% of the experimental dispersion values are described by eqn (5) at 70°C. The data in Table 5 also show that $F_{\text{experimental}} > F_{\text{theoretical}}$ when $p = 99\%$ while $R = 0{\cdot}9958$ indicates that 99·58% of the experimental dispersion values are described by eqn (5) at 80°C.

The results from the statistical analysis presented in Tables 3, 4 and 5 give grounds to the claim that the kinetic model (5) of pectin extraction suggested here is a reliable one and can be used for the description and optimization of the process. On the basis of the rate constants K_1 and K_2 determined by the above methods, we calculated also the change in the quantity of unextracted 'protopectin' $z(t)$ as well as in the quantity of the degraded pectin $q(t)$ for the different extraction temperatures. Figures 1, 2 and 3 give graphical presentations of the values of $y(t)$, $z(t)$ and $q(t)$ obtained using eqns (4), (5) and (6).

The analytical calculations and the graphical drawings were done using the KIN program with the PLOT sub-program borrowed from

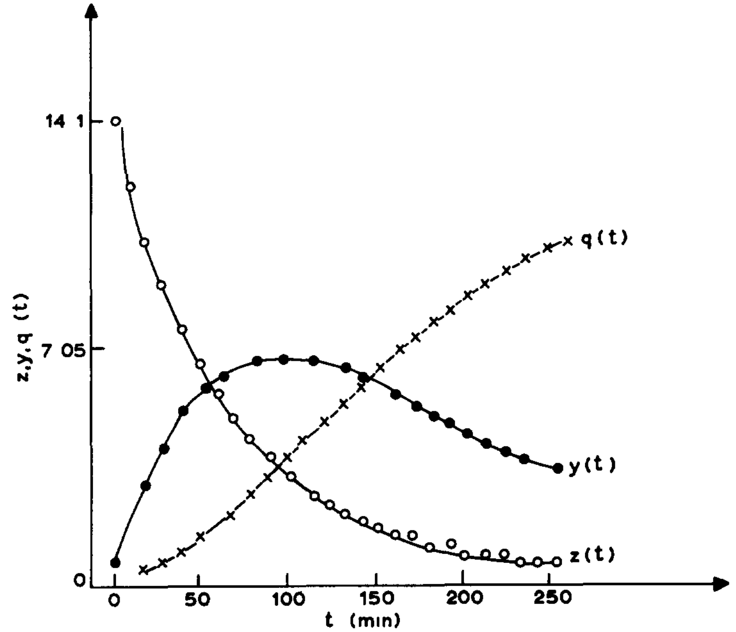

Fig. 1. Changes in quantity of extracted pectin, $y(t)$, of remaining 'protopectin', $z(t)$, and of depolymerized pectin, $q(t)$, at 60°C

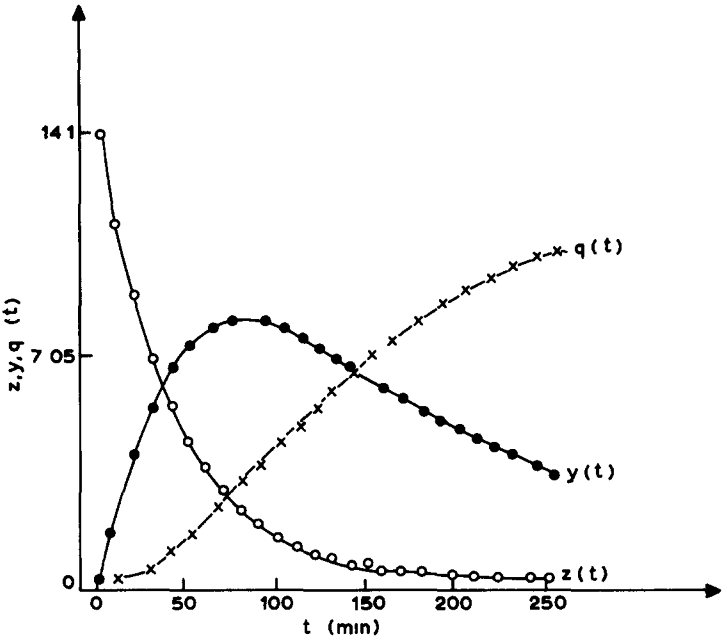

Fig. 2. Changes in quantity of extracted pectin, $y(t)$, of remaining 'protopectin', $z(t)$, and of depolymerized pectin, $q(t)$, at 70°C

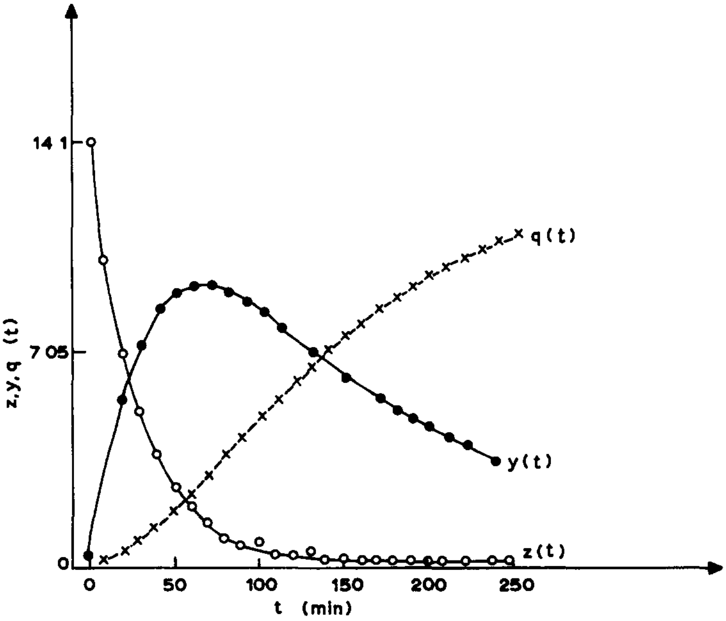

Fig. 3. Changes in quantity of extracted pectin, $y(t)$, of remaining 'protopectin', $z(t)$, and of depolymerized pectin, $q(t)$ at 80°C

Johnson (1980) The data in Table 2 indicate that in the temperature interval investigated (60–80°C) the values of K_2 decrease slowly with the increase in temperature The temperature coefficient, however, is close to unity while in other cases the hydrolysis of heteropolysaccharides is accelerated with an increase in temperature This seeming anomaly in the change of K_2 is connected with its indirect determination, i e by the pectin yield In practice it is rather difficult to study the depolymerization of pectin in the extraction mixture directly On the other hand, the molecular heterogeneity of extracted pectin, which also depends in a specific but so far unknown way on the temperature, also has an impact on the value of K_2 Checking this hypothesis requires that fractional extraction of the pectin macromolecules be carried out and that their molecular characteristics and quantity be determined during the extraction process It would also be useful to develop a new direct method for determining K_2 Despite all this, the results quoted above indicate that the suggested theoretical model describes adequately the process of pectin extraction and could be used in studying the optimal conditions for obtaining pectin from various raw materials

Our results provide an acceptable explanation of the unexpected observation made by El-Nawawi & Shehata (1987) that at pH $<1\ 5$ and a temperature of over 90°C the yield of extracted pectin drops sharply Under these extreme conditions the extraction of pectin should obviously take place for a considerably shorter time than 120 min The shape of the curves in Figs 1–3 leads to the conclusion that at a temperature of over 90°C the maximum yield would be obtained in a time of 20–40 min. The effect of pH could be predicted in the same way. Therefore, the optimal values of the parameters of pectin extraction deduced from El-Nawawi & Shehata (1987) are not sufficiently proven.

In relation to using the model suggested in this article for predetermining the yield of pectin during industrial extraction processes, some measurements were made of the gel strength of pectic preparations obtained at an extraction temperature of 80°C (described in Table 1) The results are shown in Fig 4 It can be seen that prolonged pectin extraction at 80°C results in a 10% change in the gel strength of the obtained pectic preparations The function (curve 1) passes through a maximum in relation to time which coincides with the maximum value of the yield. This coincidence is more clearly expressed by curve 2 which represents the pectin yield indicated as 200°TB pectin. The increase in the gel strength with time is due to the decrease in the DE of the pectin and probably to the fact that highly molecular pectin is slowly extracted. A similar observation of a slight effect of the extraction time on pectin gel strength was described in a previous publication (Kratchanov *et al*,

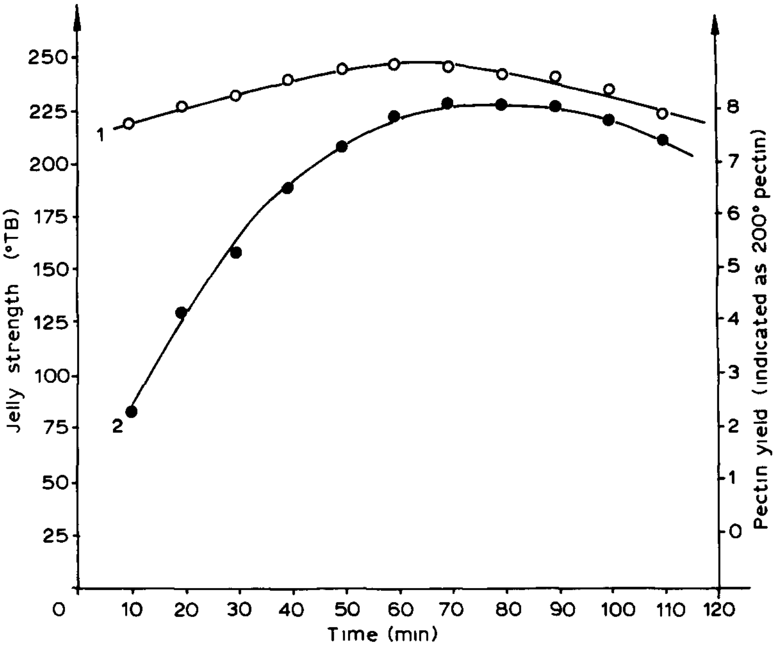

Fig. 4. Effect of the extraction duration at 80°C on the gel strength (curve 1) and pectin yield (curve 2)

1986) Compared with the curve in Fig 3 indicating a relatively intensive depolymerization of the pectin during extraction, these data require the assumption that the rate of depolymerization of pectin molecules depends on their molecular weight — the low molecular pectin fractions are more quickly depolymerized than the high molecular pectin

CONCLUSIONS

A kinetic model of pectin extraction is proposed taking into account the impact of dissolved pectin molecule degradation. The maximum yield and the optimal extraction time were determined using mathematical methods

The applicability of the model for describing the acid extraction of apple pectin with 0 5% nitric acid was tested under laboratory conditions It was established that the rate constant of extraction varied from 2 57 $\times 10^{-4}$ s^{-1} at 60°C to 5 63 $\times 10^{-4}$ s^{-1} at 80°C, while the maximum yield (9 31%) was obtained at 80°C over a period of 68 min. The proposed theoretical model describes adequately the pectin extraction process in an acid medium and offers opportunities for optimizing the extraction conditions

REFERENCES

Bender, W A (1949). *Analyt Chem*, **21**(3), 408–11.

Brandt, Z (1970) *Statistical and Computational Method in Data Analysis*, American Elsevier, New York

Doesburg, J J (1965) Pectic Substances in Fresh and Preserved Fruits and Vegetables Communication No 25 Wageningen, The Netherlands.

El-Nawawi, S A. & Shehata, F R (1987) *Biol Wastes*, **20**, 281–90.

Johnson, H. (1980) *Numerical Methods in Chemistry*, Marcel Dekker, Inc, New York

Kertezs, Z. I. (1951). *The Pectic Substances*, Interscience Publishers, New York, p 415

King, K. (1987) *Food Chem*, **26**, 109–18

Kirtchev, N. A & Kratchanov, Chr (1980) *Zeitschrift fur Lebensmittel Untersunchung und Forschung*, **170**, 31–3.

Kratchanov, Chr, Marev, K, Kirtchev, N & Bratanoff, A (1986) *J Food Technol*, **21**, 751–61

Owens, H. S, McCready, R M, Shepherd, A D, Schultz, I H, Pippen, E L, Swenson, H A, Miers, J. C, Erlandsen, R F. & Maclay, W D. (1952) Methods Used at Western Regional Research Laboratory for Extraction and Analysis of Pectin Materials AIC Report no 340, Western Regional Research Laboratory, Albany, Calif

Sheluhina, N P, Abaeva, R Ch & Aimuhamedova, J B (1987) Pectin and Parameters of its Production, Isd Ilim, Frunze, USSR