

milk exhibits a spontaneous lipolysis, since the only condition necessary to initiate the hydrolysis of fat is the cooling of milk (26). Tarassuk and Jack (25), using exclusively this type of milk, prepared a series of spray-dried whole milk and ice cream mix powders, varying preheating temperatures from 71° C. (160° F.) to 93° C. (200° F.) for 12 to 15 seconds. The powder was packed un-gassed and gassed and stored at 21° C. (70° F.) and 38° C. (100° F.). Their data show that relatively low moisture content of dehydrated milk is not a limiting factor of milk lipase activity. If a dehydrated product is made from naturally lipolytically active milk (requiring no other activation than cooling of milk), hydrolytic rancidity will develop in powder upon aging. The lipolytic activity in this case is not stopped by preheating the milk before drying as high as 93° C. (200° F.) for 15 seconds. How high it is necessary to heat milk before the lipase of naturally lipolytically active milk is completely inactivated has not been established.

It has been observed that the acid degree of fat in powder has to be about 4.0 or above before hydrolytic rancidity can be recognized organoleptically in reconstituted milk. In fluid milk hydrolytic rancidity can be organoleptically detected when acid degree of milk fat is about 1.0 or above. It is possible that an incipient hydrolytic rancidity of dry whole milk which is not recognized organoleptically may be criticized as stale.

Literature Cited

- (1) Coulter, S. T., Jenness, R., and Crowe, L. K., *J. Dairy Sci.*, **31**, 986-1003 (1948).
- (2) Coulter, S. T., Jenness, R., and Geddes, W. F., *Advances in Food Research*, **3**, 45-118 (1951).
- (3) Doog, H., Jr., Wilmann, A., and Sharp, P. F., *Ind. Eng. Chem.*, **34**, 1460-8 (1942).
- (4) Dörner, W., and Widmer, A., *Le Lait*, **11**, 545-64 (1931).
- (5) Greenbank, G. R., and Wright, P. A., *J. Dairy Sci.*, **31**, 698-9 (1948).
- (6) Harland, H. A., and Ashworth, U. S., *Ibid.*, **28**, 15-23 (1945).
- (7) Henry, K. M., Kon, S. K., Lea, C. H., and White, J. C. D., *J. Dairy Research*, **15**, 292-363 (1948).
- (8) Hollender, H. A., and Tracy, P. H., *J. Dairy Sci.*, **25**, 249-74 (1942).
- (9) Holm, G. E., Greenbank, G. R., and Deysher, E. F., *Ibid.*, **9**, 512-16 (1926).
- (10) Jack, E. L., and Henderson, J. L., *Food Inds.*, **14**, 50-1 (1942).
- (11) Krukovsky, V. N., and Herrington, B. L., *J. Dairy Sci.*, **22**, 137-47 (1939).
- (12) Krukovsky, V. N., and Sharp, P. F., *Ibid.*, **21**, 671-82 (1938).
- (13) Lea, C. H., *J. Dairy Research*, **15**, 369-76 (1948).
- (14) Lea, C. H., Moran, T., and Smith, J. A. B., *Ibid.*, **13**, 162-215 (1943).
- (15) Mattick, A. T. R., Hiscox, E. R., Crossley, E. L., Lea, C. H., Findlay, J. D., Smith, J. A. B., Thompson, S. Y., and Kon, S. K., *Ibid.*, **14**, 116-59 (1945).
- (16) Nair, J. H., *Ind. Eng. Chem.*, **22**, 4-25 (1930).
- (17) Schibsted, H., *Ind. Eng. Chem., Anal. Ed.*, **4**, 204-16 (1932).
- (18) Schibsted, H. (to Borden Co.), U. S. Patent 1,863,355 (1932).
- (19) Shipstead, H., University of California, unpublished data, 1952.
- (20) Supplee, G. C., *Proc. World's Dairy Congr.*, **2**, 1248-53 (1923).
- (21) Tarassuk, N. P., Intern. Assoc. Milk Dealers, *Bull. Lab. Sect.*, **6**, 153-60 (1939).
- (22) Tarassuk, N. P., and Henderson, J. L., *J. Dairy Sci.*, **25**, 801-6 (1942).
- (23) Tarassuk, N. P., and Jack, E. L., Division of Agricultural and Food Chemistry, 116th Meeting, AM. CHEM. SOC., Atlantic City, N. J., 1949.
- (24) Tarassuk, N. P., and Jack, E. L., *J. Dairy Sci.*, **31**, 255-68 (1948).
- (25) Tarassuk, N. P., and Jack, E. L., Terminal Report Quartermaster Food and Container Institute, 1946.
- (26) Tarassuk, N. P., and Richardson, G. A., *Science*, **93**, 310-11 (1941).
- (27) Whitnah, C. H., *J. Am. Chem. Soc.*, **53**, 300-4 (1931).
- (28) Whitney, R. M., and Tracy, P. H., *J. Dairy Sci.*, **32**, 383-90 (1949).
- (29) *Ibid.*, p. 701.

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PECTIN GRADING

Application of Intrinsic Viscosity

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A study was undertaken to provide further information on tests for pectin grading, as a poll of American preservers has shown 71% in favor of a breaking measurement of the plunger type and 24% in favor of a rigidity measurement. A balance-plunger apparatus was developed, by which both small deformations and breaking strengths can be measured. Grades obtained from these measurements generally differ, but curves of intrinsic viscosity vs. grade can be used to estimate grade by elasticity, if grade by breaking has been determined, or the reverse if grade by elastic modulus has been determined. The curves and viscosity measurement alone offer a rapid and fairly reliable means of obtaining pectin grade values that would be procured by gel measurements of both types.

IN A POLL OF AMERICAN PRESERVERS (70), undertaken to determine the type of test preferred for pectin grading, 71% favored a breaking measurement of the

plunger type while 24% preferred a rigidity measurement. The remainder (5%) considered both tests necessary. This paper reports a study undertaken

to provide further information about the two properties involved and their relationship to intrinsic viscosity. A balance-plunger apparatus is described, with

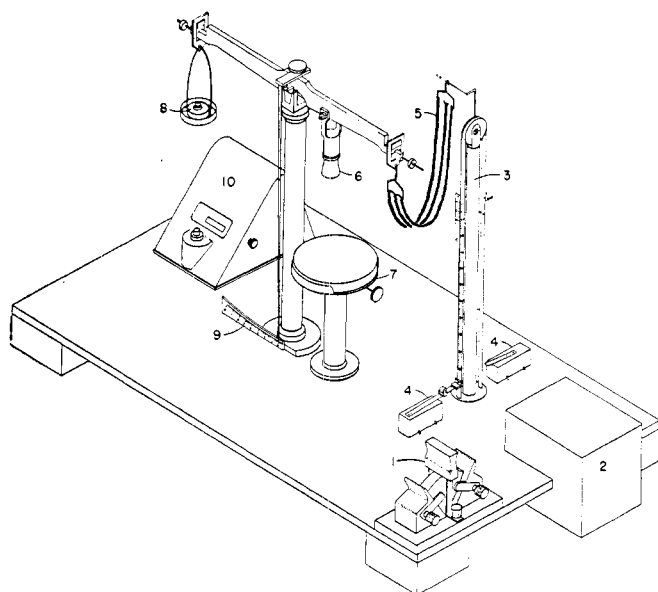


Figure 1. Chain balance tester

1. Throw switch
2. Motor
3. Chain support
4. Micro switches
5. Chain
6. Plunger
7. Gel platform
8. Counterweight
9. Scale in millimeters
10. Timer

which measurements of both small deformations and breaking strengths can be made.

A sensitive balance-and-chain assembly was adopted, which employs features used in a number of plunger testers (27). Both breaking-strength and elasticity can be measured with the one apparatus, thus avoiding the use of a combination of existing testers such as the Tarr-Baker (2, 23) or motor-driven plunger (4, 11, 27) for breaking and a precise shear tester like the Campbell (6) Säverborn (17) or Owens and Maclay (16) instruments for rigidity measurements. For comparative purposes the advantage of making both tests under like conditions is obvious. The easy removal of stress with a balance makes repeated rigidity tests possible within the elastic limit of the gel.

Preparation of Jellies

The acid-in-glass method (8, 9) was followed. Standard jelly glasses as well as dishes, 4.5 cm. deep by 7.0 cm. in diameter, were used. Three milliliters of jelly maker's acid (4.8 molal citric acid) was used per glass and an equivalent amount in the dishes. This resulted in a pH range of 2.2 to 2.6, depending on the pectins used. The jellies were prepared to 65% solids; the refractometer reading on the cold jellies ranged from 65.5 to 66.5%. Drafting tape extending 0.5 inch above the top of the glass was used. The jelly surface was covered with mineral oil an hour after pouring, and the tops of the leveled gels were sliced off with a sharpened jeweler's hack-saw blade after 18 to 24 hours' cooling and removal of the tape. The temperature of storage was $25^{\circ} \pm 1^{\circ} \text{C}$.

Chain Balance Tester

The apparatus shown in Figure 1 is composed of the center post, balance arm, and stirrup supports from a 1-kg. capac-

ity balance with 5-mg. sensitivity, in combination with the chain support from an analytical balance. A 1-r.p.m., reversible Telechron motor serves to move the chain support and an electric timer is wired in for greater ease and speed in reading than is possible if the calibrated tape is read directly.

The plunger support hangs 5 cm. to the right of the center knife-edge and is attached by means of two adjustable, tapered, steel pins fitted from each side into a hole bored through the brass beam. The plunger support is threaded on the inside, so that the plungers, cemented to a threaded bolt, can be changed easily.

A rack-and-pinion gear is used to adjust and support the gel platform in stationary position during the test, and a curved scale in millimeters is placed behind the pointer tip to follow deformations. A microswitch serves to

stop the pointer at the zero point after the motor is reversed. Three smooth-flowing silver chains, chosen for permanent use, are 24 cm. long, and weigh 19 grams each. They were calibrated by means of a platform balance pan under the plunger. A loading rate of 0.63 gram per second was found.

Operation of Balance Tester To make the measurement, the gel in the dish, freshly sliced off, is gently raised to engage the plunger and again raised or lowered to secure the zero point of the balance. After the motor is started, the pointer is followed by eye as compression proceeds, affording measurement of small strains within the elastic limit of the gel as well as complete stress-strain curves by interrupting the motor and quickly noting the timer reading at varying compression depths. The sudden release of the pointer marks the breaking of the gel, at which moment the switch to the motor and timer is thrown. A correction is necessary due to the apparent chain weight, which is ineffective because of the drop of the balance arm. This correction is not constant, as the gels break at different depths, as shown in Figure 2, which plots the variation in depth of compression at break as related to intrinsic viscosity.

Stress-strain curves to the breaking point with a plunger 8 mm. in diameter can be seen in Figure 3; they indicate that Hooke's law is obeyed in only a small portion of the total range of deformation. The curves agree with earlier ones (7, 15) in that the stress-strain relationship goes through an inflection. Figure 4 illustrates stress-strain curves obtained by use of a plunger 20 mm. in diameter, so that smaller loads in grams per square centimeter of plunger area could be used. In this

Figure 2. Variation in compression at break with intrinsic viscosity

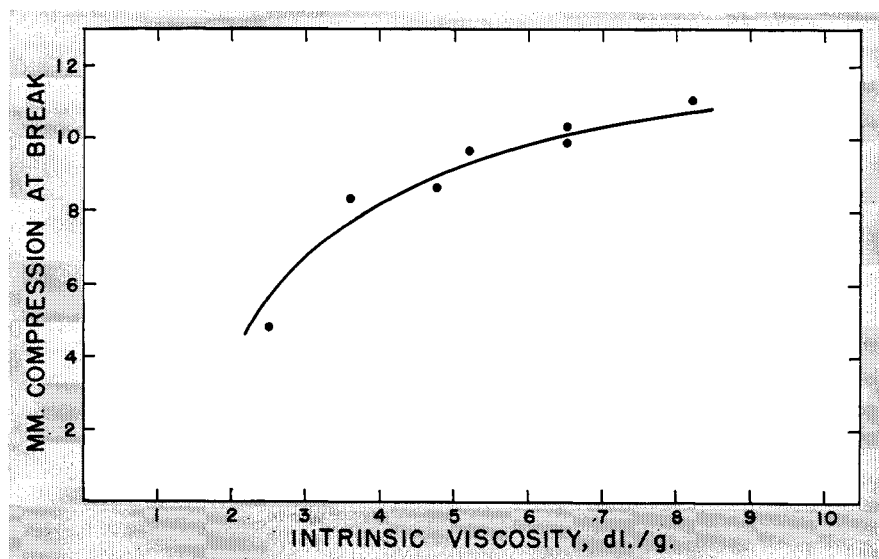


Table I. Effect of Plunger Size on Breaking

Pectin Sample No.	Breaking Stress ^a								
	Plunger 1 (15.5-Mm. Diameter)			Plunger 2 (10.0-Mm. Diameter)			Plunger 3 (5.0-Mm. Diameter)		
	Grams	Grams/ cm. circum.	Grams/ sq. cm. area	Grams	Grams/ cm. circum.	Grams/ sq. cm. area	Grams	Grams/ cm. circum.	Grams/ sq. cm. area
1	89.5	18.4	47.4	61.0	19.4	77.6	17.8	11.3	90.8
2	71.0	14.6	37.6	42.0	13.4	53.4	14.0	8.9	71.4
3	46.0	9.4	24.4	29.0	9.2	36.9	7.6	4.8	38.8
4	69.0	14.2	36.6	57.0	18.2	72.5	13.5	8.6	68.8

^a Tests with the three plungers were made on a number of jellies poured from a large batch prepared with each pectin sample.

case, the curves show that Hooke's law is obeyed by pectin gels and indicate that this region should be used for grading by elastic modulus measurements.

Several elasticity tests can be made on one gel, as the surface is not distorted, and four breaking tests can be made on one gel, as a small plunger is used. To avoid dehydration, the freshly cut surface should not be exposed to the atmosphere more than 30 minutes before measurement of the elasticity.

Wall and End Effects in Breaking

Jellies were tested in various dish sizes with the motor-driven plunger and scale, using an inverted rubber stopper as a plunger. No side wall effects were found when the ratio of gel diameter to plunger diameter was 3 or more, and no end effects in the range of depths studied which was 3.4 to 8.0 cm. Subsequent measurements were made above these limits, although in breaking tests the minimum jelly depth may only need to exceed the depth of the fracture cone

typically found after breaking the gel. Bender (4) and Meschter and Lataillade (11), for example, recommend slices 6 to 7 mm. in depth for breaking measurements.

Choice of Plunger

A rubber stopper is amply strong to resist distortion by the gel and was found preferable to metal for testing gelatin gels by Shepperd and Sweet (19). The degree to which the plunger edge should be rounded is important; if the edge is too sharp, discontinuous shear at the edge is likely to occur, while if the edge is too rounded a proportional stress-strain relation cannot be obtained with elastic gels (19).

To check on the degree of rounding, rubber plungers were tried which had sharp, medium, and rounded edges. The best reproducibility was found with a medium edge in conformity with the earlier work on gelatin gels. The edge used is similar to that on an ordinary rubber stopper.

To determine whether breaking strengths with different plunger sizes

can be equated through the plunger dimensions, jellies of like strength were tested with three plunger sizes. The results of the tests with the motor-driven plunger and scale (Table I) illustrate that stresses expressed as force per unit area have little meaning and that the plunger size must be specified. This unit has been retained throughout this paper because of common usage. It appears from Table I, however, that loads might be better expressed in terms of grams per centimeter of circumference, a probability suggested by Stoloff (27), in agreement with the assumption that the method measures primarily shear forces.

As the weight of chain which could be used on the balance was limited by the necessity for smooth flow and by the strength of the chain support, a plunger larger than 8 mm. in diameter could not be used and break the strongest gels which might be encountered in testing. The good agreement between the plungers, 15 mm. and 10 mm. in diameter, obtained by expressing load in terms of plunger circumference (Table I), was found in further tests to extend as well to the plunger 8 mm. in diameter. This size, used in the breaking tests, could be used in the elasticity measurement as well, except that the pointer moves more rapidly and precision is lower than with a large plunger. As a consequence, two plungers were interchanged and an inverted rubber stopper, 20 mm. in diameter, was used for the elasticity measurement. The smaller plunger was fashioned to a similar shape.

Pectin Grading by Breaking

For determining a standard breaking strength, a commercial lemon pectin,

Figure 3. Stress-strain relation to breaking limit

Gels from a citrus pectin with intrinsic viscosity 5.1, at varying concentrations

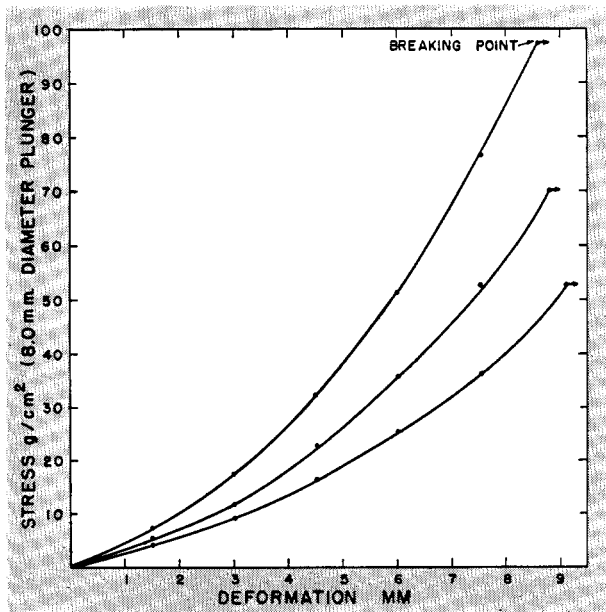
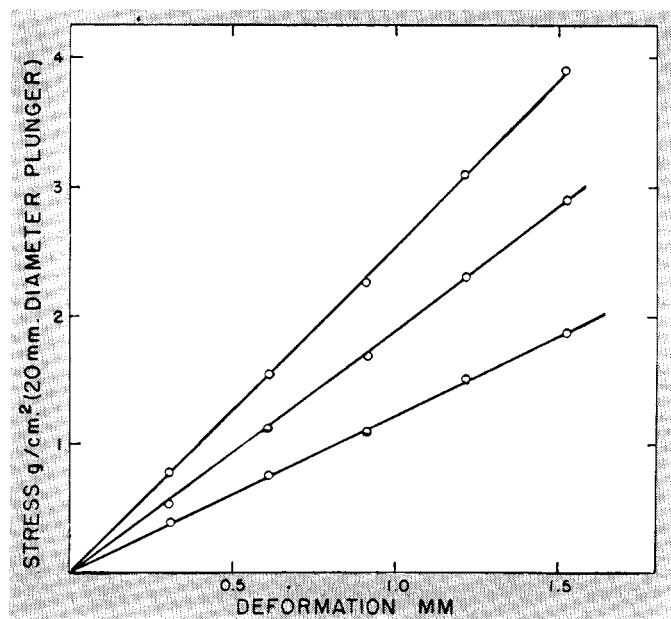


Figure 4. Linear stress-strain relation within elastic limit

Gels from a citrus pectin with intrinsic viscosity 6.9, at varying concentrations



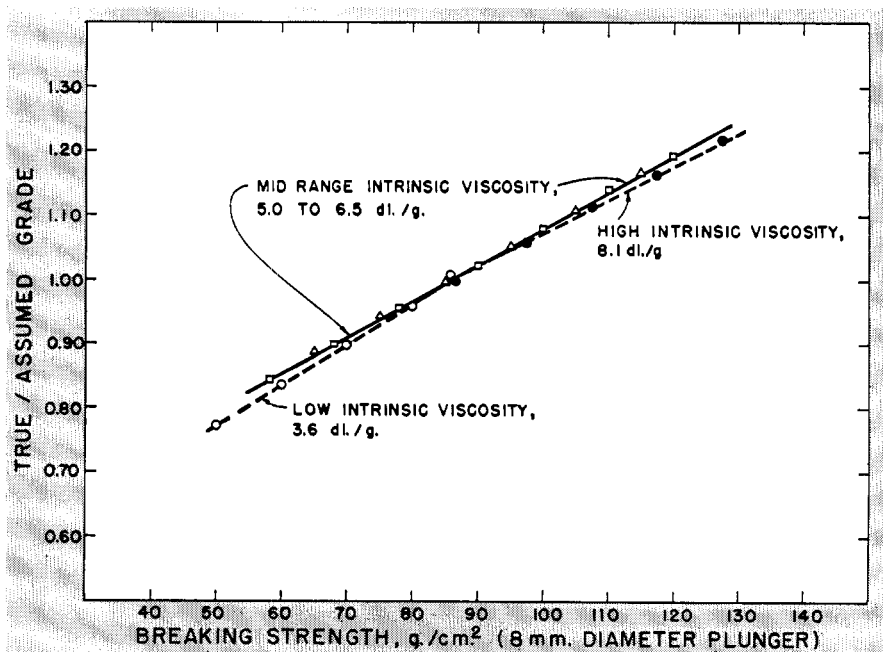


Figure 5. True/assumed grade vs. breaking strength

which had a like grade (250—i.e., 250 grams of soluble solids gelled by 1 gram of pectin) measured both by breaking with the motor-driven plunger and by sag measurement was chosen. The advantage of choosing a pectin of the same grade by breaking and rigidity measurement for this purpose is emphasized by reference to Figure 7, which relates grades by the two methods to intrinsic viscosity. A standard gel made to assumed grade of 250 with this pectin breaks with a stress of 86 grams per sq. cm. of the 8-mm.-diameter plunger surface.

To establish the method for grading with this standard, jellies from several citrus pectins and an apple pectin were prepared at varying pectin concentrations and the breaking strengths were measured. The methoxyl contents of these pectins, except in the case of a slow-set citrus pectin, all ran close to 10% and the intrinsic viscosities ranged from 3.6 to 8.1 deciliters per gram.

The assumed grades (per cent soluble solids in jelly divided by per cent of pectin) were plotted against breaking strength. True grades were then obtained by reference to the breaking standard, 86 grams per sq. cm., on the curves, and arbitrary breaking-strength values were chosen above and below the standard and related to assumed grade. The ratios of true to assumed grade obtained in this way were then plotted against breaking strength as shown in Figure 5. The influence of intrinsic viscosity on this relationship, as indicated in the figure, is small and in most cases can be neglected. The use of the solid line would result in an error of less than 2% in grade if jellies from pectins at the two extremes of intrinsic viscosity

number were prepared 20% below or above standard strength. The average standard deviation in grade (see footnote to Table II) from a large number of breaking measurements with the balance and use of the curve in Figure 5 was less than 5.

Grading by Elasticity

The elastic measurement depends on loading rate, as Cheftel and Mocquard (7) have shown, and irreversible distortion results if small strain is prolonged. However, at a loading rate of 0.2 gram per sq. cm. per second, with a plunger of 20-mm. diameter at deformations which lie within the Hookean portion of the stress-deformation curve, no apparent distortion of the gel results and the pointer returns immediately to the zero point when stress is removed within a minute or so. Gels prepared with a number of pectins, each at several concentrations, were compressed to a depth of 1.5 mm., equivalent to a pointer

deflection of 10 mm., which is within the elastic limit mentioned above. The relative standard deviation in grams of load required for a large number of these measurements averaged less than 2% (see footnote to Table II). Following a procedure similar to that used with the breaking-strength data, assumed grades were plotted against elasticity. For standard elasticity, a value of 7.3 grams per cm. of pointer deflection was chosen in order that grades would correspond with those obtained by the sag test, which was run concurrently on all jellies. The ratios of true to assumed grade were then taken from the curves of assumed grade vs. elasticity and plotted against elasticity in Figure 6. Table II illustrates the agreement in grades obtained by this means and by sag test.

Relation of Grade to Intrinsic Viscosity

The intrinsic viscosity, or limiting viscosity number, may be obtained by measuring the relative viscosity at varying low concentrations in the presence of salt and at pH 6 (5). The natural logarithm of the relative viscosity is divided by the concentration (grams per deciliter) and the quotient is plotted against concentration. Extrapolation of the line obtained to zero concentration gives the intrinsic viscosity, which has been shown to be related to the weight average molecular weight of the polymer (14). By use of a graph which relates relative viscosity at some given concentration to intrinsic viscosity (5), only one viscosity measurement need be made.

Curves showing the relation of grade by breaking and by elasticity to intrinsic viscosity are shown in Figure 7. It can be seen that grades differ on the same pectin, depending upon which test is used, and that the variation is related to the molecular weight or degree of polymerization of the pectin. Highly polymerized pectins have a much higher grade by breaking than by elasticity, whereas the converse is true, although to a lesser degree, where the weight average degree of polymerization is low.

Table II. Comparison of Grades by Sag and Elasticity Measurements

Pectin Sample No.	Sag Test			Elasticity Test		
	No. of tests	Grade	Standard deviation ^a (grade)	No. of tests	Grade	Standard deviation ^a (grade)
1	6	190	1.7	12	193	1.2
2	6	269	2.9	12	268	1.9
3 ^b	5	249	2.5	12	251	2.4
4	7	278	2.3	12	272	2.2

^a S.D. = $[\sum d^2 / (N - 1)]^{1/2}$ where d is the deviation from the average and N the number of measurements. Relative standard deviation referred to elsewhere in the paper is defined as S.D. \times 100 divided by the average.

^b Lemon pectin used for establishing standard breaking strength.

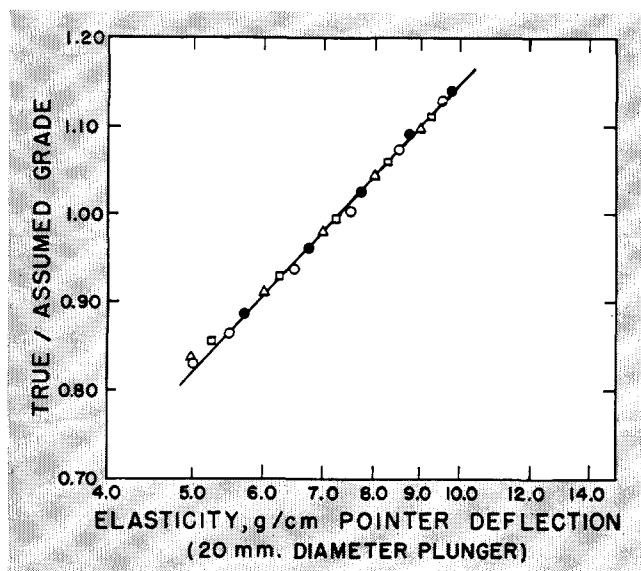


Figure 6. True/assumed grade vs. elasticity

The dependence of gelling ability and jelly strength on the molecular weight of pectins has been reported (18, 20). A relation between relative viscosity and grade by breaking strength, similar to the curve of intrinsic viscosity vs. grade by breaking strength in Figure 7, was shown by Myers and Baker (12) on a series of pectins of varying viscosities prepared by heat degradation.

From the standpoint of pectin grading by use of intrinsic viscosity values, some pectins fall from 5 to 8% from the general curves, indicating that a precise value cannot be obtained. Somewhat similar, though more restrictive, conclusions were reached by earlier investigators (1, 3, 12, 13, 24), who indicated that viscosity measurements should be used for grading only pectins of like source and like history. The deviations from the curves in Figure 7 may result from samples which consist of mixtures of pectins having markedly different molecular weights (22).

To summarize, the curves of intrinsic viscosity vs. grade can be used to estimate grade by elasticity if grade by breaking has been determined or the reverse when grade by elastic modulus has been determined. In addition, the curves and a viscosity measurement alone offer a rapid, fairly reliable means of obtaining the pectin grade values that would be procured by gel measurements of both types.

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References

- (1) Baker, G. L., *Food Inds.*, 6, 305 (1934).

- (2) Baker, G. L., *Ind. Eng. Chem.*, 18, 89 (1926).
- (3) Baker, G. L., and Woodmansee, C. W., *Del. Agr. Expt. Sta., Bull.* 272 (1948).
- (4) Bender, W. A., *Anal. Chem.*, 21, 408 (1949).
- (5) Bureau of Agricultural and Industrial Chemistry, U. S. Dept. Agriculture, "Methods Used at the Western Regional Research Laboratory for the Extraction and Analysis of Pectic Materials," *AIC-340* (1952).
- (6) Campbell, L. E., *J. Soc. Chem. Ind.*, 57, 413 (1938).
- (7) Chefel, H., and Mocquard, J., *Ibid.*, 66, 297 (1947).

- (8) Cox, R. E., and Higby, R. H., *Food Inds.*, 16, 441 (1944).
- (9) Joseph, G. H., and Baier, W. E., *Food Technol.*, 3, 18 (1949).
- (10) Kertesz, Z. I., "The Pectic Substances," New York, Interscience Publishers, 1951.
- (11) Meschter, E. E., and Lataillade, L. J., *Food Technol.*, 3, 28 (1949).
- (12) Myers, P. B., and Baker, G. L., *Del. Agr. Expt. Sta., Bull.* 149 (1927).
- (13) Ogg, W. G., dissertation, University of Cambridge, 1925.
- (14) Owens, H. S., Lotzkar, H., Schultz, T. H., and Maclay, W. D., *J. Am. Chem. Soc.*, 68, 1628 (1946).
- (15) Owens, H. S., McCready, R. M., and Maclay, W. D., *Food Technol.*, 3, 77 (1949).
- (16) Owens, H. S., Porter, O., and Maclay, W. D., *Food Inds.*, 19, 606 (1947).
- (17) Säverborn, S., dissertation, University of Uppsala, 1945.
- (18) Schneider, G. G., and Bock, H., *Ber.*, 71, 1353 (1938).
- (19) Sheppard, S. E., and Sweet, S. S., *Ind. Eng. Chem.*, 15, 571 (1923).
- (20) Speiser, R., Copley, M. J., and Nutting, G. C., *J. Phys. & Colloid Chem.*, 51, 117 (1947).
- (21) Stoloff, L. S., U. S. Dept. Interior, *Fishery Leaflet* 306 (April 1948).
- (22) Swenson, H. A., Schultz, T. H., and Owens, H. S., unpublished results.
- (23) Tarr, L. W., *Del. Agr. Expt. Sta., Bull.* 142 (1926).
- (24) Wendelmuth, G., *Kolloid Beih.*, 19, 115 (1924).

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Figure 7. Jelly grade vs. intrinsic viscosity

