

dissolved upon 90 days of storage at the same nitrate concentration.

The internal appearance of the cans was also examined. Control packs generally showed a gradual increase in tin-etch during storage, but no detinning. Cans with added nitrates showed progressive detinning, up to complete detinning in those with 250 ppm of nitrate.

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Polymetaphosphate and Oxalate Extraction of Sunflower Pectins

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The potential of sunflower heads as a commercial source of low methoxyl pectin was investigated using two solvent systems over a range of temperature, concentration, and pH. By raising the temperature of extraction from 60 to 90°C, the yields of oxalate- and Calgon-extracted pectins were increased from 9 to 17% and from 15 to 20%, respectively. Although the high temperatures adversely affected anhydrouronic acid and methoxyl group contents of oxalate-extracted pectins, the levels of these constituents exceeded those of Calgon-extracted pectin at each temperature level. Increasing the concentration of Calgon improved the pectin yields but there was a proportionate increase in ash content of the pectin and even lower anhydrouronic acid and methoxyl group levels were obtained. Sodium hexametaphosphate was a more efficient solvent than Calgon but ash level in the dried pectin was still 8% even after rewashing with acidic alcohol, and the gel power was only 39.0. Residual ash levels in the oxalate-extracted pectin were reduced to 2% by acidic alcohol washing and the gel power values averaged 118. High ash levels appeared to adversely affect the gel power of the pectin and improved methods for removal of polyphosphate are needed if the latter solvent is to be used for commercial sunflower pectin extraction.

Despite the high pectin content of sunflower heads, the commercial production of sunflower pectin has not been undertaken because of problems associated with extraction. Shewfelt and Worthington (1953) demonstrated that oxalic acid-ammonium oxalate was superior to hydrochloric acid or sodium polyphosphates in the extraction of pectin from sunflower heads. Hot dilute solutions of ammonium oxalate-oxalic acid were also used successfully for the

extraction of pectin from polysaccharides in sunflower heads by other workers (Bishop, 1955; Riaz and Uddin, 1972), and also in this laboratory (Sabir et al., 1975). However, ammonium oxalate-oxalic acid forms calcium oxalate in isolated pectin and the complex can only be removed by extensive washing with acidified alcohol at a low pH. The acid treatments would have adverse effects on pectin quality and the problem of oxalate residues in the final product has not been resolved.

Polyphosphates are widely used as solvents in the food industry and some workers have utilized polyphosphates for the extraction of pectin from other plant tissues than sunflower (Baker and Woodmansee, 1944; Maclay and Nielsen, 1945). Polyphosphate-calcium complexes are highly soluble in aqueous ethanol at low pH and, therefore,

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Table I. Effect of Extraction Temperature on the Yield and Anhydrouronic Acid (AUA) and Methoxyl (MeO) Contents of Pectins Extracted from Sundak Heads with Oxalate and Calgon Solutions

Solvent	60°C			70°C			80°C			90°C		
	Yield, %	AUA, %	MeO, %	Yield, %	AUA, %	MeO, %	Yield, %	AUA, %	MeO, %	Yield, %	AUA, %	MeO, %
0.5% oxalate	9.0	97.3	11.3	11.8	95.2	10.5	17.2	85.6	10.2	16.8	78.0	9.2
0.5% Calgon	15.0	77.3	8.1	16.2	79.7	8.5	17.2	79.4	8.4	20.0	73.6	7.9

polyphosphates were effectively removed from citrus peel pectin at pH 1.6–2.4 (McCready et al., 1947). However, Shewfelt and Worthington (1953) extracted pectins from sunflower heads with sodium polyphosphates at a pH range of 5.5–6.3 and obtained low yields. Preliminary experiments in the present laboratory showed that pectin yield with this solvent could be improved by using a lower pH for the extraction step. The objective of the present study was to compare the extraction efficiency of hot dilute ammonium oxalate–oxalic acid (pH 3.3) and Calgon or sodium hexametaphosphate (pH 4.5–1.0) under the same conditions of concentration, temperature, and extraction time. Pectin quality was evaluated by the determination of anhydrouronic acid (AUA), methoxyl (MeO) group, ash contents, and gel power of the pectins.

EXPERIMENTAL SECTION

Heads of the cultivar Sundak were harvested, threshed to remove the seeds, and freeze-dried before grinding to 64 mesh in a Waring blender followed by a Unimec grinder. Pectic enzymes were inactivated by stirring 5-g samples of sunflower heads with 80% aqueous ethanol (200 ml) at 90°C for 30 min. Ethanol solubles, containing mostly low molecular weight sugars and pigments, were separated by centrifugation and discarded. Total pectic substances were extracted from the residues with several concentrations of Calgon (0.25–1.50%) or 0.5% oxalate solution (0.25% ammonium oxalate–0.25% oxalic acid) at several temperatures or 0.5% sodium hexametaphosphate at 80°C. The dry Calgon (0.5 to 3.0 g) or sodium hexametaphosphate (1.0 g) was added to the residues after introducing 200 ml of water and adjusting to pH 4.5–1.0 with dilute hydrochloric acid before extraction for 1 hr and filtration through bolting cloth (McCready, 1970). The pH of the extraction was checked and adjusted twice at 15-min intervals in the first half of the extraction period. The oxalate solution was added to the residues in two 100-ml portions for two extractions of 30 min each, followed by filtration through bolting cloth.

Extracts obtained with sodium hexametaphosphate were mixed with 2 vol of chilled 95% ethanol while the other pectin extracts were poured into 2 vol of chilled 95% ethanol containing 2 ml of HCl/l. (pH 1.7). After thorough shaking, the pectins were gelled by storing in a refrigerator for 1 hr. Pectin gels were then isolated by filtration through bolting cloth. Acidified ethanol should remove most of the free salts from the polyphosphate- and oxalate-extracted pectins. However, a completely ash-free sample was required for the determination of AUA and MeO (American Pharmaceutical Association, 1965). Therefore, Calgon- and oxalate-extracted pectins were washed three times with acidified ethanol. Five milliliters of HCl/100 ml of ethanol–water (1:1) was used for the Calgon- and oxalate-extracted pectins (American Pharmaceutical Association, 1965). In addition, two samples of sodium hexametaphosphate extracted pectin (pH 4.5) were washed twice with ethanol–water (1:1) containing 1 and 2 N HCl to lower the ash levels. Free chloride ions from polyphosphate-, Calgon-, and oxalate-extracted pectins were removed by thorough washing with ethanol–water (1:1, v/v). Finally, the three types of pectin were

Table II. Effect of Calgon Concentrations on the Yield and Ash, AUA, and MeO Contents of Pectins Extracted from Sundak Heads

Calgon, %	Yield, %		Ash, % dry basis	AUA, % dry basis	MeO, % dry basis
	Dry basis	Ash-free basis			
0.25	12.8	10.6	16.9	71.4	7.7
0.50	17.2	13.4	21.1	79.4	8.4
0.75	24.2	17.8	26.3	73.5	7.6
1.00	26.2	19.3	26.5	73.3	7.8
1.25	29.4	20.9	28.9	69.6	7.0
1.50	33.0	22.3	32.3	64.4	5.2

washed with 95% ethanol and dried overnight (16 hr) in a vacuum oven at 40°C before weighing to obtain pectin yields.

Determination of AUA and MeO contents in the above ethanol-washed pectin samples was done according to the titration method of McCready (1970). Ash content in pectin samples was determined according to the method of McCready et al. (1947) using the Blue M muffle furnace. Gel powers of oxalate- and Calgon-extracted pectin samples were determined by the Food Chemicals Codex (National Research Council, 1972) procedure for low ester pectins using the Exchange Ridgelmeter.

RESULTS AND DISCUSSION

The yield of pectin from Sundak heads increased from 9 to 17% as the temperature of oxalate extraction (pH 3.3) was raised at 10°C intervals from 60 to 90°C (Table I). The yields of pectin varied from 15 to 20% over the same temperature increments using 0.5% Calgon at an extraction pH of 4.5. The highest pectin yields were obtained at 80°C for the oxalate solvent while 90°C gave maximum yields when Calgon was used.

Because of the selectivity of ammonium oxalate–oxalic acid medium for solubilizing pectin as opposed to other carbohydrates, the levels of AUA and MeO groups in oxalate-extracted pectin were higher than those extracted with Calgon (Table I). The differences in the contents of these constituents tended to decrease at higher temperatures of extraction. Since the 90°C treatment appeared to cause some lowering in pectin quality, the 80°C extraction procedure was selected for further extractions with Calgon and sodium hexametaphosphate. The ash contents of oxalate- and Calgon-extracted pectins after acidic ethanol washings were about 2 and 21%, respectively, in each treatment. Therefore, the average yields of ash-free pectin obtained with oxalate and Calgon solutions in the first experiment were nearly equal at the higher temperatures of extraction. Gel power was determined on 80°C extracted pectins and a value of 118 was obtained for the oxalate-extracted sample but the gel produced from the Calgon-soluble pectin was too weak to be measured on the Ridgelmeter. Apparently, the high proportion of ash contamination in the Calgon-extracted pectin seriously interfered with gel formation.

The yield of pectin in Sundak heads varied from 13 to 33% with increases in Calgon concentration from 0.25 to 1.50% at pH 4.5 (Table II). However, the higher yields of pectin were associated with high ash levels in the pectin so that the real gain in ash-free pectin was only from 11

Table III. Effect of pH on the Yield and Ash, AUA, and MeO Contents of Pectins Extracted from Sundak Heads Using 0.5% Sodium Hexametaphosphate

pH of pectin extract	Yield, %		Ash, % dry basis	AUA, % dry basis	MeO, % dry basis
	Dry basis	Ash-free basis			
4.5	29.3	17.8	39.1	61.1	6.4
3.0	25.4	16.6	34.6	63.9	6.7
2.0	20.4	15.2	30.6	66.9	7.0
1.5	20.5	15.6	23.8	72.4	7.3
1.0	21.9	16.9	22.8	76.6	7.6

to 22%. Since AUA and MeO contents also decreased in high ash samples it appeared that concentrations of Calgon should not exceed 0.75% for optimum yield and quality of product. The gel powers of these pectins were also near zero.

McCready et al. (1947) found that ash levels of sodium hexametaphosphate extracted pectins from citrus peel could be decreased from 16 to 2% by reducing the pH of extraction from 4.0 to 1.0. Therefore, the pH of pectin extraction from Sundak heads was adjusted from 4.5 to 1.0 using 0.5% sodium hexametaphosphate as the solvent instead of Calgon (Table III). At pH 4.5 the yield of unwashed pectin was 29.3% dry basis (Table III) as compared to 17.2% of acidic alcohol washed pectin in Table II. On an ash-free basis, 0.5% sodium hexametaphosphate was a more efficient solvent than 0.5% Calgon. At pH levels below 4.5, the yields of dry pectin were reduced substantially by the more acidic pH but, on an ash-free basis, the pectin yields were similar for all treatments. Ash levels in the pectin did, however, decrease with the pH of extraction and, at pH 1.0, the highest AUA and MeO percentages were obtained. Unfortunately, the 22.8% ash sample produced a relatively weak gel. Samples of pH 4.5 hexametaphosphate-extracted pectin were re-washed twice with ethanol-water (1:1) containing 1 or 2 N HCl and the ash levels were reduced further to 12 and 8%, respectively. While the gel power of the original pH 4.5 hexametaphosphate-extracted pectin was nil, the two re-washed samples showed values of 32.3 and 39.0, respectively, for the 1 and 2 N HCl treatments. It appeared that residual ash levels had a marked influence on the gel power of the pectin.

Shewfelt and Worthington (1953) obtained low pectin yield (9.2%) from sunflower heads using 0.5% sodium

hexametaphosphate at pH 5.5. In the present study, a higher pectin yield of 29.3% dry basis or 17.8% ash-free basis was obtained by using a lower extraction pH of 4.5. At pH levels below 4.5, the pectin yield was not increased but ash content was reduced considerably. McCready et al. (1947) reduced the ash content of citrus pectin to 2% by washing with acidic ethanol at pH 1.0. However, the low ester pectins of sunflower bound a significant proportion of metaphosphate even after rewashing with aqueous alcohol containing 1 or 2 N HCl. Apparently, the metaphosphate ions were strongly associated with low methoxyl pectin through hydrogen bonding, by complexing with endogenous divalent metallic ions like Ca^{2+} and Mg^{2+} , and by physical enmeshing.

While sodium hexametaphosphate appeared to give the highest yields of extracted sunflower pectin, the ash levels could not be reduced to the same levels as were obtained with ammonium oxalate-oxalic acid. It appeared that oxalate would be the preferred solvent unless more efficient procedures are developed for the removal of ash in the polyphosphate extraction procedure. Residual oxalate levels of nearly 2% may be objectionable from a nutritional standpoint. Studies are underway to measure residual oxalate levels in pectin and their implications in human nutrition.

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