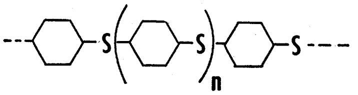
with stirring and cooling to maintain the temperature of the reaction mixture in the −5 to 0° C range. The mixture was allowed to stand for 1 hr at the same temperature, and the resulting clear solution was poured over crushed ice. The precipitated solid was removed by filtration, washed with water, and recrystallized from ethanol to yield 0.7 g (1.1%) of thianthrene-5,10-dioxide melting at 284–86° C. The literature reports the mp of this compound at 283–84° C (*5*). The 284–86° C melting product above was identical in mp and mixed mp with a sample prepared by oxidation in 80% yield of an authentic specimen of thianthrene by the same procedure used above. The thianthrene-5,10-dioxide was further characterized by its reduction with zinc dust and acetic acid to thianthrene according to the procedure of Krafft and Lyons (*5*). The thianthrene so produced was identical in mp and mixed mp with an authentic specimen.

A large amount of dark solid remaining in the reaction vessel after the distillation described above was ground to a fine powder and extracted repeatedly with carbon disulfide in order to remove occluded sulfur. The remaining solid was insoluble in all common solvents and melted above 300° C. This material was organic and possessed the properties of a polymer. A Parr bomb sulfur analysis on this product showed 35.95%. A polymer of the structure shown below would contain about 29.7% sulfur, as would other possible structures. The extra sulfur may be held in



$\overset{\overset{S}{\uparrow}}{—S—}$ type linkages or occluded mechanically. This product was formed in approximately 85% yield based on the assumption that it corresponded to the polymeric structure represented above.

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Acidimetric Titration of Alkali Chloride and Hydrochloride Salts

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Although chlorides, such as sodium and potassium chloride, are generally considered to be model examples of neutral salts, this is only relatively true. We have recently been able to titrate these, as well as hydrochlorides of amines, as bases with perchloric acid, using acetic acid as the solvent. In glacial acetic acid, which is considerably less protophilic than water, hydrochloric acid is largely unionized, being one of the relatively weaker inorganic acids, and is readily volatile. The titration of these salts in acetic acid would then be analogous in a sense to titration, for example, of alkali carbonates in water.

TABLE 1

Titration of Procaine and Procaine Hydrochloride in Glacial Acetic Acid

Sample	Equiv/mole found
Procaine	1.96
	1.96
	1.97
Procaine hydrochloride	1.92
	1.94
	1.94
	1.93
	1.95

Although acidimetric titration of bases in acetic acid with perchloric acid is a relatively well-established method (*1*), there appears to be no reference in the literature to the possibility of titrating chloride salts in this medium. We ourselves were led to this observation during a more or less routine application of the glacial acetic acid-perchloric acid method to the analysis of procaine and procaine hydrochloride. As expected, two equivalents of perchloric acid were required to neutralize the base. We were surprised to find, however, that the hydrochloride salt also required nearly two equivalents per mole. This seemed to indicate that hydrochloric acid was too weak an acid to affect the indicator, α-naphthobenzein, in the solvent employed. This conclusion pointed to the possibility of direct acidimetric determination of any chloride salt.

In order to test this possibility, the method has been applied to sodium, potassium, and ammonium chloride in addition to procaine hydrochloride.

The following procedure was employed in obtaining the data reported:

The weighed sample (0.1–0.5 g) was placed in a

TABLE 2

Acidimetric Titration of Sodium, Potassium, and Ammonium Chloride

Sample	Equiv/mole found	Indicator
Sodium chloride	0.997	α-Naphtholbenzein
	1.001	
	0.994	
	0.996	
Potassium chloride	1.016	Methyl violet
	1.018	
	1.024	
	1.020	
	1.020	
Ammonium chloride	1.000	α-Naphtholbenzein
	1.002	
	0.995	
	0.994	
	1.005	

250-ml Erlenmeyer flask with 50 ml of glacial acetic acid. The mixture was brought to a boil, and a few drops of an indicator (0.1% in benzene) was added. The solution was then titrated with a standardized perchloric acid-acetic acid solution (0.04–0.2 *M*), the solution being reheated near the end point to sharpen the indicator change. Where relatively insoluble salts —e.g., sodium chloride—were used, it was necessary to bring them gradually into solution by repeated heating and titrating.

In Table 1 are listed results obtained by titrating both procaine and procaine hydrochloride. The presence of the acidic group in the latter compound appeared to have no significant influence on the diacidic character of the original base.

In Table 2 the data obtained by titration of sodium, potassium, and ammonium chloride are presented. The titration of sodium chloride proved to be difficult because of its poor solubility in the solvent. In all cases, however, the salts behaved as monoacidic bases.

The observation that the titration end point faded on heating and that the stoichiometric end point was achieved best by bringing the solutions under titration to a boil appeared to indicate that the part of the apparent basicity of the chloride ion was due to the volatility of the acid formed; that is,

$$\mathrm{Cl^- + CH_3CO_2H_2^+ \rightleftharpoons \overset{\overset{\text{HCl (gas)}}{\uparrow}}{HCl} + CH_3CO_2H}.$$

The equilibrium in the above reaction appears to favor the right-hand side, permitting partial titration of the ion without loss of hydrogen chloride from the system. Near the end point, however, the reverse reaction becomes appreciable unless the gas is driven off by boiling.

This hypothesis was partly verified by applying the titration procedure to potassium bromide. In this case the indicator change occurred with only a slight addition of perchloric acid solution; however, it was possible to approach the stoichiometric end point by repeated boiling of the solution, the indicator reverting to the nonacid color after each heating up to the end point. Results obtained in this fashion are presented in Table 3.

TABLE 3

ACIDIMETRIC TITRATION OF POTASSIUM BROMIDE IN GLACIAL ACETIC ACID

Sample	Equiv/mole found	Indicator
Potassium bromide	0.969	α-Naphtholbenzein
	.973	
	.973	
	.984	
	0.976	

Since HBr is a much stronger acid than HCl, the former would be expected to be more highly ionized in acetic acid than the latter. This would explain the initial indicator change observed on addition of a small amount of the perchloric acid solution to potassium bromide. Because of the volatility of HBr, however, the indicator can be driven back to the basic form, permitting the titration to be carried through to the stoichiometric end point.

These observations have been further verified by results obtained by N. F. Hall and co-workers (*2*), using potentiometric means to follow the relative acidity of the acetic acid solutions.

References

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A Comparison of the Niacin and Pantothenic Acid Content of Certain Cereal Grains Grown under the Same Environmental Conditions

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For many years the emphasis in food production has been on higher yields, and the introduction of hybrid varieties of cereals has resulted in increased production per acre. Within recent years feeding experiments have shown that there is considerable variation in some of the quality factors—such as vitamins—among the different hybrids of any one cereal. Breeding programs have been undertaken to develop high-quality cereals. The work of Richey and Dawson (*1*), Burkholder (*2*), and Ditzler *et al.* (*3*) tends to show that the genetic factor may be the major influence in determining the niacin content of corn, and Hunt *et al.* (*4*) showed that the niacin content of corn is less subject to modification by environmental conditions than is pantothenic acid.

This report presents the data obtained with respect to the niacin and pantothenic acid content of several varieties of each of four different cereals grown under the same environmental conditions.

The cereals analyzed were two double-cross hybrids of corn (*Zea mays* L.), M20 and K24; four varieties of wheat (*Triticum aestivum* L.), Seneca, Trumbull, Butler and Thorne; two varieties of oats (*Avena sativa* L.), Clinton and Wayne; two varieties of soybeans (*Glycine soja* L.), Hawkeye and Lincoln. All are new, but well-established varieties and are used extensively in Ohio. They were all grown the same season on Wooster silt loam at the Ohio Agricultural Experiment Station on plots that were in a high state of fertility. Each sample of grain was ground in a Wiley mill through a 60-mesh sieve.

The niacin and pantothenic acid content was determined by the microbiological method as outlined in *Methods of Vitamin Assay* (*5*), based on the original method of Snell and Wright (*6*). The organism employed was *Lactobacillus arabinosus* 17-5. The results of the analysis are summarized in Table 1.