combined uncertainty in the inflection point determination and the  $H_o$  value indicate an uncertainty on the order of  $\pm 0.1 \log$  units.

The observed  $pK_a$  values of -2.24for *p*-fluorobenzamide and -6.20 for *p*-fluoroacetophenone agree quite well with the values of -2.24 and -6.06, respectively, reported by Stewart and coworkers (3, 8) from ultraviolet studies in aqueous sulfuric acid. The agreement is important for it provides convincing new evidence for the general assumption of the discretely protonated acid form of weak bases. The evidence comes from a measurement (NMR) which is on an enormously expanded time scale compared to the classical ultraviolet measurement.

#### **ACKNOWLEDGMENT**

The authors acknowledge support of the present work by the National Science Foundation. We also thank W. A. Steele and Ross Stewart for helpful discussions.

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# Detection of Ferric lons with 4,4'-Dicarboxydicyclohexylamine

SIR: The catalytic hydrogenation of p-aminobenzoic acid, affords as a byproduct, a small yield of the amine 4,4' - dicarboxydicyclohexylamine (3). The formation of this compound takes place by a mechanism analogous to the formation of dicyclohexylamine from the catalytic hydrogenation of aniline (1), and the reaction may be represented thus



Because dicyclohexylamine is more basic than cyclohexylamine (1), 4,4'dicarboxydicyclohexylamine contains a nitrogen atom which is more basic than the one of cyclohexylamine, as well as two free carboxyl groups. Therefore it would be expected to combine with transition metal ions. This is the case with ferric ions, and this reaction can be used for the qualitative detection of this ion. This reaction is indicated by the development of a deep red color in the solution.

# EXPERIMENTAL

4,4' - Dicarboxydicyclohexylamine. Ten grams of *p*-aminobenzoic acid were hydrogenated according to the procedure described in (3). After filtration and evaporation of the solution to dryness, the residue was extracted with 75 ml. of an equivolume mixture of ethyl alcohol and ether. This extract was evaporated to dryness, and resulted in 0.8 gram of yellow-brown needles. The crude product was washed twice with 5-ml. portions of distilled water, dissolved in 5 ml. of absolute ethyl

alcohol, heated for 1 minute with 0.5 gram of activated charcoal and filtered. To this were added 40 ml. of cold distilled water, and the mixture was cooled at 0° C. for 1 hour. Small white needles were obtained: Yield 0.5 g. (5%), m.p. 188° to 190° C. (decomposed).

For use as an analytical reagent 0.5 gram of 4,4' - dicarboxydicyclohexylamine was dissolved in 20 ml. of absolute ethyl alcohol.

Test for Ferric Ions. To 1 ml. of each solution of FeCl<sub>3</sub>.6H<sub>2</sub>O shown in Table I, was added 1 ml. of the alcoholic solution of 4,4'-dicarboxydicyclohexylamine. A red color developed in the solution immediately and lasted from 2 to 8 days depending on the concentration.

The detection of a minimum concentration of 0.0206 mg. of ferric ions per milliliter was possible. At this concentration the solution was a light yellow-brown.

Influence of pH. The ferric complex forms in the pH range of 1 to 3. Acidification with hydrochloric acid causes decolorization, and ferric ions are released. When the pH is raised above 3 with sodium hydroxide, ferric hydroxide precipitates out and the color of the solution disappears. The process was carried out reversibly from higher to lower pH, the red color being the transition stage.

Cation Interference Tests. Tests were carried out to determine which common cations would interfere with the determination of ferric ions. One tenth molar solutions were prepared, their pH's were adjusted with hydrochloric acid, and 1 ml. of the reagent was added. The results are summarized in Table II.

When concentrations of cupric ions higher than 10 mg. per ml. are used in the presence of ferric ions, the red

color of the ferric-4,4'-dicarboxydicyclohexylamine complex fails to appear.

#### RESULTS AND DISCUSSION

The above experiments show a method of detecting ferric ions qualitatively. In concentrations of 0.340 mg. of ferric ions per milliliter the test is excellent. In the range of 0.206 to 0.340 mg. of ferric ions per milliliter results are very good. In pure solutions the test works in concentrations as low as 0.0206 mg. of ferric ions per milliliter.

In evaluating the results of Table II, the nature of the cations must be

Table	I.	Ef	fect of	Fer	ric Ion	Concen-
tration		on	Color	of	Ferrio	:-4,4'-Di-
carbo	oх	vdia	vclohe	kyla	mine C	omplex

${ m FeCl}_{3.6{ m H}_2{ m O}},~M$	Color Test
0.0370	Deep red
$0.0185 \\ 0.0123$	
0.0092	
$0.0074 \\ 0.00615$	₽ed
0.00527	Red-brown
0.00462 0.00411	i i
0.00370	Light red-brown

# Table II. Qualitative Tests of Common Cations with 4,4'-Dicarboxydicyclohexylamine

Cation	$_{\rm pH}$	Observation
Al <sup>+3</sup> , Ba <sup>+2</sup> , Ca <sup>+2</sup> Cd <sup>+2</sup> , K <sup>+</sup> , Li <sup>+</sup>	2.0	Clear soln.
$Mg^{+2}$ , $Mn^{+2}$ , $Na^+$ NH, +, Sr^{+2}		
$Cu^{+2}$ Ag <sup>+</sup> , Hg <sub>2</sub> <sup>+2</sup> , Pb <sup>+2</sup> Bi <sup>+3</sup> , Sb <sup>+3</sup>	$2.0 \\ 2.0 \\ 1.0$	Light green soln. White ppt. White ppt.

Table	Ш.	Limit	of	Det	ection	of	Ferric
	lons	by D	iffei	rent	Reage	ents	

•	•	
Reagent	Limit of Detection	Ref- erence
4,4'-Dicarboxydi- cyclohexylamine	$1:0.87 \times 10^{5}$	
cyanate	$1:16 \times 10^{5}$	(2)
cinol 7-Iodo-8-hvdroxy-	$1:2.85 \times 10^{5}$	(6)
quinoline-5- sulfonic acid Thiodiacetic acid	$1:100 \times 10^{5}$ $1:100 \times 10^{5}$	(7) (4)

considered. For instance, in the case of Ag<sup>+</sup>, Hg<sub>2</sub><sup>+2</sup>, and Pb<sup>+2</sup>, the white precipitates are the insoluble chlorides, which can be separated from the solution. The phenomena observed with Bi<sup>+3</sup> and Sb<sup>+3</sup> are due to the formation of the oxychlorides. Antimony oxychloride will form when hydrochloric acid is added to a solution of the trichloride, while any bismuth salt in the presence of hydrochloric acid will precipitate as bismuth oxychloride. On the other hand cupric ions must complex to some extent with the reagent. That is why high concentrations of this ion interfere with the test for ferric ions.

The results obtained with the present method are compared with those employing different reagents. Table III gives the limits of detection of ferric ions in parts of ferric ions per parts of solution, using different reagents.

4,4' - Dicarboxydicyclohexylamine is a tridentate chelating agent and the coordination number of six of the ferric ion suggest that the coloring ion has the structure



The formation of the ferric complex with 4,4'-dicarboxydicyclohexylamine, depends greatly on the pH of the solution. Thus the species formed at different pH's are products of reversible reactions depending on the hydrogen concentration,

$$Fe^{+3} + 2C_{14}H_{23}NO_4 \xrightarrow[H^+]{OH^-}$$

$$\operatorname{Fe}(C_{14}H_{22}NO_4)_2^+ \xrightarrow[]{OH^-}{H^+} \operatorname{Fe}(OH)_3 +$$

#### $2C_{14}H_{22}NO_{4}^{-}$

4,4'-Dicarboxydicyclohexylamine as obtained here must be a mixture of isomeric compounds. It is suggested that the isomer having the conformation ae-ea (5) is the main chelating agent, the other isomers contributing little or not at all, to the formation of the complex.

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# Gas Chromatographic Analysis of Fatty and Chlorinated Fatty Acids

SIR: Although separation of volatile fatty acids by gas chromatography was first reported by James and Martin in 1952 (4), this procedure or its modifications (1) have received little application until very recently. As noted by Hunter et al. (3), two factors contributing to this lack of progress were the need for strict maintenance of anhydrous conditions and the corrosiveness of acid vapors on metallic elements of the usual types of sensitive measuring equipment. Another important factor has been the pronounced tailing exhibited by the strongly adsorbed acids on most gas chromatographic substrates.

Recently, Hunter and coworkers (2) have described a column packing that performed very satisfactorily for the separation of organic acids encountered in food flavor analyses. An essential feature of this analytical procedure was the use of dichloroacetic acid to liberate the weaker organic acids from their sodium salts. An ionization detector cell was employed. and under the analysis conditions employed, the dichloroacetic acid yielded only minor peaks in the early portion These were of the chromatogram. presumed to be due to decomposition products and caused only minor interference with the proposed analytical method.

In this work, the authors were concerned with the development of a gas chromatographic analysis method for the chlorinated acid acids. They were able to obtain appreciable response for these acids on a variety of column packings using a thermistor detector. Since ionization gage detectors are known to be insensitive to highly chlorinated compounds, it was thought that the explanation of Hunter's failure to observe peaks for these acids might lie in the fact that he was using this type of detector. To test this hypothesis, a standard sample was prepared containing a known mixture of three fatty acids plus mono- and dichloroacetic acids. These acids were chosen to be easily separated on a 1-meter copper column packed with 10% LAC-296 and 5% phosphoric acid (85%) on

acid-washed Chromosorb W. The standard sample was analyzed under identical conditions on a Perkin-Elmer 154-C Vapor Fractometer (thermistor detector) and a Barber-Colman Model 20 gas chromatograph (Sr $^{90}$  and Ra $^{226}$ ionization detectors). The same column was used in both instruments. The Perkin-Elmer chromatograms were run first using the usual U-shaped column. and then the column was coiled for insertion in the Barber-Colman instrument. An appreciably higher pressure was required for the latter runs in order to obtain the same flow rate (60 cc. per minute), and both instruments were operated at 150° C. with a flash heater temperature of 240° C.

# RESULTS AND DISCUSSION

Figure 1 shows a typical chromatogram of the standard acid mixture on each of the gas chromatographic instruments. Table I summarizes the individual acid responses in terms of peak areas. As expected, the response for the dichloroacetic acid was much