Spectrophotometric Titration of Water in Acetic Acid

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▶ A direct spectrophotometric titration of water in glacial acetic acid based on the sulfuric acid–catalyzed hydrolysis of acetic anhydride has been applied to the determination of water in the concentration range 0.009 to 1.7%. The relative merits of sulfuric and perchloric acids as catalysts and the mechanism of the catalysis are discussed.

WATER has been determined in glacial acetic acid in a number of ways. Toennies and Elliott (8) developed a polarimetric method based upon the reaction of excess acetic anhydride with water in glacial acetic acid in the presence of perchloric acid as a catalyst. They reported an accuracy to about 1% for water contents in the range 0.1 to 0.6%.

Hoover and Hutchison (6) used sulfuric acid as a catalyst for the acetic anhydride–water reaction in the determination of water in fuming nitric acid. The solvent was glacial acetic acid, and the equivalence point was detected conductometrically, using a high quality conductance bridge. The over-all change in conductance from start to end point was small, usually about 10%.
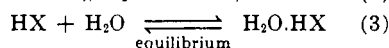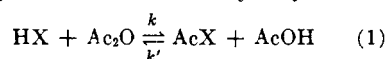
Greathouse, Janssen, and Haydel (5) determined the amount of water in acetic acid using perchloric acid as the catalyst for the acetic anhydride–water reaction. They determined the quantity of water by two thermometric methods. In the first, the rise in temperature on addition of perchloric acid to the mixture of acetic acid, water, and excess acetic anhydride was determined. In the second, the excess acetic anhydride was determined by back-titration with water. Both procedures compared favorably with the visual Karl Fischer method. Greathouse, Janssen, and Haydel (5) summarized other techniques that have been proposed for the determination of water in acetic acid.

A direct spectrophotometric titration procedure for water in glacial acetic acid is based upon the sulfuric acid-catalyzed reaction of acetic anhydride and water. The spectrum of acetic anhydride in acetic acid has been reported by Bruckenstein (1), who described a procedure for determining trace amounts of water in acetic acid. This technique is based on the reaction of excess acetic anhydride with the water at 100° C. for 90 minutes in a spectrophotometer cell fitted with a ground joint, and the determination of the unreacted acetic anhydride by ultraviolet spectrophotometry. This procedure, while extremely sensitive, is time-consuming. The accuracy of any procedure based on determining the excess acetic anhydride is impaired by the addition of too large an excess of acetic anhydride. As a consequence, it is not uncommon for several additions of acetic anhydride to be made before an excess is found. The direct titration technique does not suffer from this limitation.

The absorption of acetic anhydride obeys Beer's law in the range 250 to 260 mµ. Because mixtures of water, acetic acid, and sulfuric acid do not absorb appreciably in this wave length region, the absorbance of a water solution changes only slightly prior to the equivalence point on the addition of acetic anhydride, and then rises linearly with the concentration of excess acetic anhydride. Extrapolation of this line back to the blank absorbance yields the equivalence point.

Sulfuric, rather than perchloric, acid is the preferred catalyst for the hydrolysis of acetic anhydride in glacial acetic acid. Even though perchloric acid has a dissociation constant 234 times that of sulfuric acid (2) and appears 16 times stronger on the basis of indicator measurements (6), Yvernault (9) found sulfuric acid a more effective catalyst, provided the water concentration is less than $0.5M$. He postulated the following mechanism for the hydrolysis:

$$HX + Ac_2O \underset{k'}{\overset{k}{\rightleftharpoons}} AcX + AcOH \qquad (1)$$

$$AcX + H_2O \overset{k_2}{\rightarrow} HX + AcOH \qquad (2)$$

$$HX + H_2O \underset{\text{equilibrium}}{\rightleftharpoons} H_2O.HX \qquad (3)$$

which yields the following expression for the rate of hydrolysis $V' \left(-\dfrac{d \ Ac_2O}{dt} \right)$:

$$\frac{C_{HX} \ C_{Ac_2O}}{V'} = \frac{1}{k_2} \frac{C_{Ac_2O}}{C_{HX}} + \frac{k'}{kk_2} \frac{1}{C_{HX}} +$$
$$\left[\frac{Kk'}{kk_2} + \frac{1}{k} \right] + \frac{K}{k} C_{H_2O} \qquad (4)$$

where K is the equilibrium constant for Reaction 3 as written. At 25°, $k_2 \geq 10^4$ liters/mole/minute, $k' \geq 0, k = 141$ liters/mole/minute, and $K = 4.8$ for sulfuric acid; at 17° $k_2 = 10^4$ liters/mole/minute, $k'/k_2 = 0.16$, $k = 354$ liters/mole/minute, and $K = 26$ for perchloric acid. It is apparent that the apparent reversal of acid strength as shown by Yvernault's kinetic studies results from the more rapid reaction of acetyl perchlorate with acetic acid as compared to the reaction of acetyl bisulfate with acetic acid. Further evidence supporting Yvernault's mechanism is presented in the section on kinetic studies.

Besides being a better catalyst, sulfuric acid has a practical advantage. Concentrated sulfuric acid contains about 0.2 mole of water per mole of acid compared to 72% C.P. perchloric acid, which contains about 2 moles of water per mole of acid. If the concentrated C.P. acids are used as the catalyst, less water is introduced into the reaction mixture by sulfuric acid. Naturally, when extremely small amounts of water are determined, it is necessary to dehydrate the catalyst, using acetic anhydride equivalent to the water present in the acid.

REAGENTS

Acetic Acid. Acetic acid was purified according to the method of Eichelberger and LaMer (4), which involves preliminary treatment of a C.P. material with chromium trioxide, drying with triacetyl borate, and finally fractional distillation. On one occasion the triacetyl borate step was omitted, and the acetic acid dried by addition of C.P. benzene, followed by fractional distillation. The benzene technique gave results equal to the triacetyl borate method. The water content of the acetic acid was determined by the Karl Fischer method, the uncatalyzed spectrophotometric procedure (1), and the sulfuric acid-catalyzed spectrophotometric titration procedure. Usually the solvent contained no more than 0.02% water.

Acetic Anhydride. A C.P. product was used as titrant and standardized as described under "Experimental."

Perchloric Acid. A $1M$ stock solution in acetic acid was prepared by dissolving the required amount of 72% concentrated acid in acetic acid. Then 95% of the theoretical amount of acetic anhydride required to react with the water in this acid mixture was added to the chilled acid solution. The water content was determined and 99% of the quantity of acetic anhydride required to react with this residual water was added. This technique ensures that an excess of acetic anhydride is not present in the acid, and reduces the

Table I. Sulfuric Acid–Catalyzed Hydrolysis of Acetic Anhydride

Concentration of Water					
0.930M		0.470M		0.250M	
[H$_2$SO$_4$] × 10^3	[H$_2$SO$_4$]/k''^a	[H$_2$SO$_4$] × 10^3	[H$_2$SO$_4$]/k''^a	[H$_2$SO$_4$] × 10^3	[H$_2$SO$_4$]/k''^a
2.82	0.0319	3.57	0.0203	3.24	0.0114
2.85	0.0322	3.58	0.0197	3.64	0.0124
7.11	0.0358	7.14	0.0178	3.60	0.0135
7.11	0.0348	14.2	0.0185	7.26	0.0118
14.2	0.0343	14.4	0.0158	14.6	0.0116
15.2	0.0328	28.2	0.0160	14.5	0.0114
[H$_2$SO$_4$]/k''					
Mean	0.0336 ±		0.0180 ±		0.0122 ±
	0.0013		0.0016		0.0006
Calcd.^{b}	0.0341		0.0205		0.0141

^{a} $T = 24.7°$ C., $k'' = -\dfrac{d \ln [Ac_2O]}{dt}$, t in minutes. Initial concentration of acetic anhydride varied from 0.01 to 0.03M.

^{b} Calculated from Yvernault's (9) data at 25°.

water content to a negligible level. The acid was standardized against potassium acid phthalate in acetic acid as a solvent using p-naphtholbenzein as indicator.

Sulfuric Acid. A 2M stock solution of sulfuric acid in acetic acid was prepared by adding the required amount of concentrated sulfuric acid to acetic acid. A portion of this acid was then dehydrated as described for perchloric acid. Both the "wet" and dehydrated sulfuric acid solutions were standardized against potassium acid phthalate in acetic acid as a solvent using p-naphtholbenzein.

APPARATUS

A Beckman DU spectrophotometer equipped with a lead storage cell, photomultiplier attachment, and Beckman adapter for recording transmittance as a function of time at constant wave length was used. A Moseley Model 2 Autograph equipped with a mechanical time base was used to record the results of all the rapid kinetic studies. The cell compartment of the Beckman spectrophotometer was equipped with Thermospacers. The temperature of the compartment was controlled at 24.7° ± 0.2° unless otherwise stated.

One-centimeter square silica cells equipped with ground-glass joints functioned both as spectrophotometer cells and as reaction vessels of approximately 3-ml. capacity.

Gilmont ultramicroburets of 0.01-, 0.1-, and 1.0-ml. capacity were used as needed.

A dry box equipped with an entry port and two glove ports was used in performing the manipulations involved in the spectrophotometric titrations. A centrifugal blower circulated air from one corner of the dry box over silica gel and exhausted the dried air back into the dry box at the point most distant from the intake. The amount of atmospheric moisture introduced in the act of transferring the spectrophotometer cell in and out of the dry box was so small that it was unnecessary to wait for this trace of moisture to be removed before proceeding with the necessary manipulations. The box was large enough to hold three ultramicroburets comfortably.

EXPERIMENTAL PROCEDURE

Spectrophotometric Titrations. About 3 ml. of acetic acid was transferred to a weighed 1-cm. square silica cell in the dry box. The stoppered cell was then removed from the dry box, weighed, and replaced in the dry box. Then 0.1 ml. of 2M sulfuric acid catalyst was added to the cell using an ultramicroburet. The absorbance of this solution was determined with reference to pure acetic acid at some wave length in the range 250 to 260 mμ. The wave length chosen (usually 256 mμ) depended on the concentration of water in the acetic acid. The cell was returned to the dry box, and acetic anhydride added from a 0.1- or a 0.01-ml. ultramicroburet. The cell was again removed from the dry box and the absorbance was redetermined. This entire procedure was repeated until a complete titration line was obtained. Results were not reproducible unless a dry box was used. For example, unstoppering the silica cell for 30 seconds in the open laboratory after the equivalence point had been passed resulted in a decrease in the absorbance of acetic anhydride by an amount equivalent to 0.5 mg. of water. No such difficulties were observed when the dry box was used.

Kinetic Experiments. All kinetic experiments were carried out in the presence of a large excess of water over that of acetic anhydride, so that the use of a dry box was not necessary when addition to the spectrophotometer cell was made. The cell was filled with a known weight of acetic acid–water mixture and allowed to reach temperature equilibrium in the thermostated cell compartment. Acetic anhydride was then added, the recording adapter adjusted, and the acid catalyst added. The stoppered cell was shaken vigorously for 10 seconds and returned to the cell compartment and the transmittance-time curve was recorded. The 100% transmittance and the dark current were checked every 60 seconds in the first few experiments, but this was unnecessary when the instrument was operating properly. Ordinarily this check need be made only after about 3 minutes.

Standardization of Acetic Anhydride. A blank titration was performed on a sample of acetic acid containing 0.1 ml. of 2M sulfuric acid. A known amount of water was added to the cell from a 0.01-ml. microburet and the added water titrated at 256 mμ. The titer of the acetic anhydride was calculated from the difference in this end point and the blank end point. Usually a separate blank titration was not needed in the standardization of the acetic anhydride, because the end point obtained after titrating a routine water unknown served as the blank. A sample of c.p. acetic anhydride showed a negligible change in titer over 1 month when stored in a tightly stoppered bottle. The titer found for the acetic anhydride used in this work was 0.1798 ± 0.0003 ml. of water per ml. of acetic anhydride based on quadruplicate determinations.

Determination of Water Content of 2.0M Sulfuric Acid. A blank titration was performed as in the standardization of acetic anhydride and 0.2 ml. (or more, depending on water content) of 2M sulfuric acid added. This was titrated with acetic anhydride and the water content calculated from the difference between this end point and the blank end point.

EXPERIMENTAL RESULTS AND DISCUSSION

Kinetic Studies. The sulfuric acid-catalyzed hydrolysis of acetic anhydride was studied at 24.7° to verify the results of Yvernault (9) at 10 to about 100 times larger acid concentrations. The experimental results agree well with those calculated from Yvernault's data (Table I).

Sulfuric acid has been studied potentiometrically in a cell with liquid junction using the chloranil electrode as hydrogen ion indicator electrode (2). In the latter study it was found that sulfuric acid is only slightly dissociated with a pK equal to 7.24. If the acetic anhydride hydrolysis is hydrogen ion-catalyzed, the function [H$_2$SO$_4$]$^{1/2}$/k'' rather than [H$_2$SO$_4$]/k'' should be constant.

The latter function is constant, showing that the catalysis involves undissociated sulfuric acid, as was first proposed by Yvernault (Table I).

The perchloric acid-catalyzed hydrolysis of acetic anhydride was studied briefly at 30.0° (Table II). No quantitative comparison is possible with Yvernault's work, since he presents numerical results only at 17°. If the value of the equilibrium constant for Reaction 3, K, is assumed to be 34 (3), it is found using the data in Table II and Equation 4 that $k = 1360$ liters/mole/minute and $k'/k_2 = 0.09$. A brief study of the

temperature dependence of the over-all rate of hydrolysis of acetic anhydride indicates that the rate decreases about twofold for a 5° decrease in temperature.

In this case, as with sulfuric acid, potentiometric studies (2) of perchloric acid show it is a weakly dissociated compound in acetic acid, pK = 4.87, and support the view that undissociated perchloric acid is the principal acid catalyst.

This conclusion is also supported by the addition of sodium perchlorate to a perchloric acid solution and noting the change in rate of hydrolysis. Qualitatively, it is predicted that the concentration of hydrogen ion should decrease because of the repression of the dissociation of perchloric acid by perchlorate ion arising from the added sodium perchlorate. The actual decrease in hydrogen ion concentration on making a $3.27 \times 10^{-3}M$ perchloric acid and $0.0926M$ water solution $0.100M$ in sodium perchlorate is calculated using the methods described earlier (3). The calculated decrease in hydrogen ion concentration is 50%, while the observed rate increases by about 12%. The observed slight increase rules out a hydrogen ion mechanism and may be caused by changes in activity coefficients of ion pairs and undissociated molecules present.

Choice of Wave Length. As reported (1), a maximum is observed in the spectrum of acetic anhydride dissolved in glacial acetic acid. The molar absorptivity found using a Cary recording spectrophotometer was 36.6 liters/mole/cm. Because the slit width of the spectrophotometer was opening rapidly and was wide open at 250 mμ (2-cm. cell path), the accuracy of the reported molar absorptivity could not be high. By using the Beckman DU and a 1-cm. light path it was usually possible to make measurements at wave lengths as low as 248 mμ before the slit was wide open. No maximum absorbance for acetic anhydride was observed with the Beckman instrument; instead a continually increasing absorbance was found as the wave length was decreased. The difference in the observed spectrum may be associated with the recorder response and/or the rate at which the slit opens on the Cary instrument in the region where acetic anhydride starts to absorb strongly.

Beer's law was found to hold in the region investigated, 250 to 260 mμ. No absolute molar absorptivities are reported, as they are obviously dependent on the slit width of the instrument. For the purposes of a spectrophotometric titration this dependence is of no consequence, if wave length and slit are unchanged during the titration. In the experiment described below, it was necessary to change the wave length and slit settings. Care was taken to reset

both wave length dial and slit width accurately by approaching the setting from the same direction, in order to minimize backlash.

Figure 1 shows the spectrophotometric titration of an acetic acid solution containing anhydrous 0.1 ml. of sulfuric acid catalyst and 2.78 grams of acetic acid in a 1-cm. silica stoppered cell. The data were obtained by measuring the absorbance at 250, 254, and 260 mμ

Table II. Perchloric Acid–Catalyzed Hydrolysis of Acetic Anhydride

Concentration of Water

0.926M		0.463M		0.231M	
$C_{HClO_4} \times 10^3$	C_{HClO_4}/k'''^a	$C_{HClO_4} \times 10^3$	C_{HClO_4}/k'''^a	$C_{HClO_4} \times 10^3$	C_{HClO_4}/k'''^a
3.27	0.0263	3.27	0.0156	1.13	0.073
6.54	0.0263	6.54	0.0142	3.27	0.076
13.1	0.0260	13.1	0.0148	6.54	0.079
[HClO₄]/k''' Mean	0.0262 ± 0.0001		0.0149 ± 0.005		0.076 ± 0.003

^{a} $T = 30.0°$ C., $k''' = \dfrac{-d \ln [Ac_2O]}{dt}$, t in minutes. Initial concentration of acetic anhydride $\sim 0.01M$.

Table III. Determination of Water by Spectrophotometric Titration at 256 mμ

Expt.	Water, Vol. % Calcd.^{a}	Sample Vol., Ml.^{b}	Water, μl. Taken	Water, μl. Found^c	Water, μl. Difference
1	1.670	2.408	40.21	40.31	+0.10
2	1.670	2.426	40.52	40.73	+0.21
3	1.670	2.408	40.21	40.27	+0.06
4	0.836	2.991	25.00	24.96	−0.04
5	0.836	2.995	25.04	24.99	−0.05
6	0.836	3.001	25.09	24.97	−0.12
7	0.436	2.974	12.97	13.00	+0.03
8	0.436	2.971	12.95	13.04	+0.09
9	0.436	2.972	12.96	13.07	+0.11
10	0.177	3.000	5.31	5.23	−0.08
11	0.177	2.870	5.08	5.12	+0.04
12	0.018	2.749	0.495	0.495	0.000
13	0.018	2.900	0.522	0.530	+0.008
14	0.018	2.820	0.508	0.526	+0.018

^{a} Calculated from water content of "anhydrous" acetic acid and volume of water added to this acetic acid. Anhydrous acid used in preparing samples used in experiments 1–11 was analyzed by the Karl Fischer method with visual end point. The anhydrous acid was analyzed spectrophotometrically in experiments 12–14.
^{b} Volumes calculated from weights of acid taken.
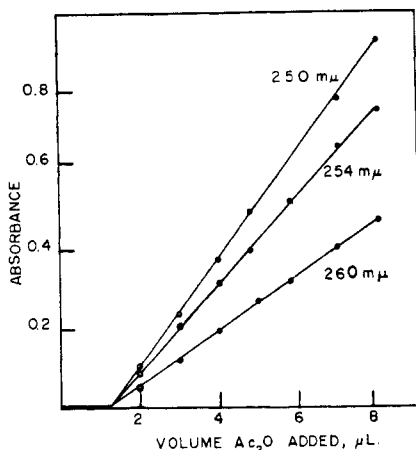^{c} Corrected for water added with sulfuric acid catalyst.

Figure 1. Spectrophotometric titration of 0.009% water in glacial acetic acid as solvent

after each addition of acetic anhydride. The lower the wave length used, the higher the slope of the excess reagent line. The observed end points at 250, 254, and 260 mμ were 0.00131, 0.00130, and 0.00130 ml. of acetic anhydride, respectively. Data at 256 and 258 mμ yielded lines with slopes which followed the expected trend and gave end points of 0.00137 and 0.00125 ml., respectively, but are omitted from Figure 1 for the sake of clarity. The water content of this sample of acetic acid was 0.236 ± 0.004 μl. per 2.67 ml. of acetic acid. It is concluded that any wave length in the range 250 to 260 mμ may be used for this titration. As a matter of convenience, $\lambda = 256$ mμ was used for the remainder of the titrations described, as it provides adequate sensitivity and permits the addition of larger increments of acetic anhydride than is possible at $\lambda = 250$ mμ.

Titration of Water. The results obtained in the spectrophotometric titration of glacial acetic acid samples containing 0.018 to 1.67 (v./v.) % water are shown in Table III.

In all cases agreement between the observed and calculated water content of the samples was satisfactory (Table III). The precision obtained in the spectrophotometric titrations was good.

The mean water contents found for the samples listed in Table III are 1.675 ± 0.003% (experiments 1 to 3), 0.834 ± 0.001% (experiments 4 to 6), 0.439 ± 0.001% (experiments 7 to 9), and 0.176 ± 0.001% (experiments 10 and 11). Direct analysis by visual Karl Fischer titration of three 1-ml. portions of the sample of acetic acid used in experiments 1 to 3 gave 1.674 ± 0.009%. The Karl Fischer reagent used had a titer of about 3 mg. of water per ml. of reagent.

Experiments 13 and 14 indicate that the spectrophotometric titration can be used at lower water contents than the visual Karl Fischer method when only 2 or 3 ml. of sample is available. This point is shown more clearly by Figure 1, which represents the titration of 2.670 ml. of acetic acid. The volume of water found is 0.236 μ. or 0.00884%. Such a sensitivity can be obtained using the visual Karl Fischer method only with much larger samples.

The demonstrated lower limit of the spectrophotometric titration method is still about six times larger than the demonstrated range of applicability of the uncatalyzed spectrophotometric procedure (1). The differences between the two methods are due mainly to cell length and volume. In this work a 1-cm. cell of about 3-ml. volume was used; in the previous work (1) a 2-cm. cell of about 6-ml. volume was used. Doubling the cell length doubles the absorbance due to excess acetic anhydride and also doubles the amount of water determined. The end result of doubling the cell length is a four times increase in sensitivity of the method. This reasoning suggests that the use of a 5-ml. cell of about 15-ml. capacity would permit the determination of water in the 0.01-μl. range.

Application of the spectrophotometric titration procedure to water contents much larger than 1.67% would require a special 1-cm. spectrophotometer cell with a volume much larger than 3 ml., to give sufficient capacity to hold the added acetic anhydride.

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Mass Spectrometric Determination of Hydroformylation Products of Ethyl Sorbate

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▶ Chemical methods of analysis are often inadequate for distinguishing the position of functional groups of organic compounds. The mass spectrometer, however, can be used to determine the position of various groups—e.g., that of the formyl group in an analysis of the products from the hydroformylation of ethyl sorbate. The technique involves oxidation of the refined formyl esters followed by esterification to form the diethyl esters of the dibasic acids. The mass spectra of the esters then are used to calculate the amount of each component. Mixtures containing the diesters of these 7-carbon diacids of a known composition have been analyzed with an average deviation of ±5 to ±8% of the known value of the contained ester.

THE USEFULNESS of the mass spectrometer as a tool for the analysis of gaseous mixtures is well known. Recent advances in the introductory system of the instrument, such as the heated inlet system, have extended the usefulness to the analysis of higher boiling materials. However, the material under investigation often undergoes thermal decomposition when introduced into the inlet system, and it is necessary to convert the material quantitatively to a compound which is thermally stable.

One of the more difficult problems has been the analysis of higher aldehydes, particularly those obtained from the hydroformylation of unsaturated compounds (1), such as the products from the hydroformylation of ethyl sorbate. In these products there are possible five different formyl esters—namely, ethyl 2-, 3-, 4-, 5-, and 6-formyl hexanoate.

EXPERIMENTAL

Preparation of Esters of Ethyl Formyl Hexanoates. Ethyl sorbate was reacted at elevated temperatures and pressures with carbon monoxide and hydrogen in the presence of cobalt carbonyl to yield ethyl formyl hexanoates (1). The crude hydroformulation product was refined to yield a fraction of the mixed formyl esters having a purity of >99% by weight as ethyl formyl hexanoate.

A sample of the material obtained from the hydroformylation of ethyl sorbate was examined with the mass spectrometer. Preliminary investigations of the crude hydroformylation product showed that resolution was not possible because of the similarity of the mass spectra of the various formyl isomers in the mixture. Aldehydes heavier than hexaldehydes are generally more difficult to resolve mass spectrometrically.

The formyl esters were susceptible also to oxidation by air and thermal decomposition; hence, they were converted to the mixed diesters of the dibasic acids by oxidation of the formyl group followed by esterification. The acids, which are solids, were not handled conveniently mass spectrometrically, but the esters could be handled easily and their mass spectra are unique.

The oxidation of the formyl group was carried out by the following procedure (2). The formyl ester, air, and a sodium hydroxide solution were continuously added to a reaction vessel containing finely divided silver dispersed in water. The product, which was a mixture of monoesters of dibasic acids, was filtered, crystallized, and finally refined. The total yield of diacid was always at least 97%, based on the amount of formyl acid added.

The refined acids were esterified by refluxing the mixture with ethyl alcohol. After distillation of ethyl alcohol, the acidity of the esters was less than 0.1% calculated as pimelic acid.

Procedure and Analysis. The spec-