

3-one. This product is reported to be formed in a yield of 70 % in the treatment of pinacolone with potassium-*t*-butoxide at 200°C for 4 h.¹¹

Fraction III crystallized in the receiver and was dissolved in carbon tetrachloride and subjected to the above-mentioned acid-washing procedure. After one recrystallization from methanol there remained 6.2 g (30 %) of 1,3,5-tri-*t*-butylbenzene, m.p. 72–73°C. Lit. 72.5–73°C,¹¹ 72–74°C.¹³

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Spectrophotometric Studies on a Humic Acid Fraction

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In a study of fractionation and separation of humic acids¹ it was suggested that physico-chemical studies should be preceded by a careful fractionation procedure. This paper reports spectrophotometric studies on a defined (but still probably not monodisperse) humic acid fraction. The application of differential spectrophotometry to the study of humic acids was recently reported² and the absorbancy variation with pH has therefore been studied in detail.

Experimental. The humic acid fraction was obtained from an iron humus podsol B₁₂ (from Lerbäck, Sweden) by extraction at pH 7 with sodium pyrophosphate in 2 M NaCl (after preceding extractions with benzene and with 2 M NaCl). The humic acid was precipitated with H₂SO₄ dissolved with NaOH to pH 7 and dialysed against distilled water. The remaining humic acid has been studied.

For the studies at different pH the following buffers (P.-H. Tamm) have been used: pH 2.00 (HCl-KCl), pH 7.00 (phosphate) and pH 11.5 (phosphate).

All spectrophotometric measurements have been made on a Zeiss PMQ II Spectrophotometer.

Results. Accurate determinations of the absorbancy of a humic acid solution cannot generally be obtained in the whole spectral range 13 000–40 000 cm⁻¹ from measurements on one solution, because of the steady increase of the absorbancy from low to high wave numbers. Especially at low wave numbers the shape of the absorption curve would be rather inaccurately determined. If the shape of the log *A* curve should be used as a characteristic it is further important to know that it is independent of the dilution. It is therefore suggested that absorption spectra are always measured at different dilutions in order to ascertain the constancy of the shape of the absorption curve. The same slit width should always be used for a given wave number.

In Fig. 1 the results of such measurements are given for three different pH. The

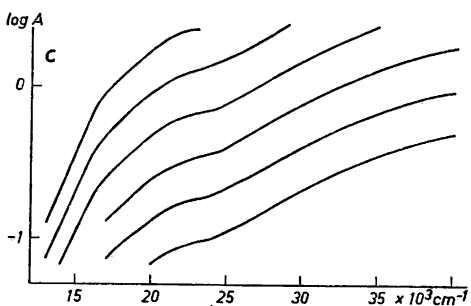
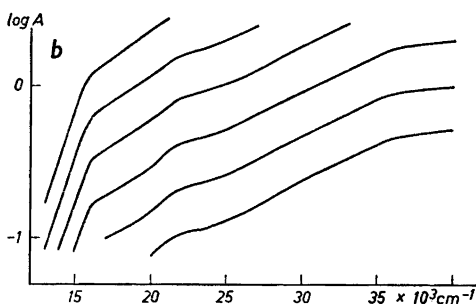
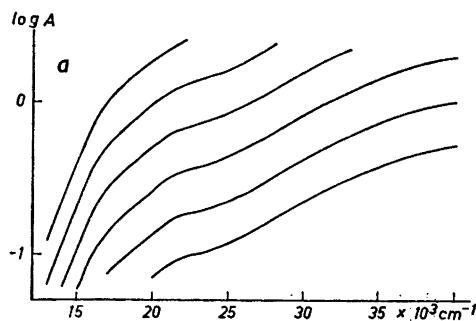


Fig. 1. The absorption spectra ($\log A$) for different dilutions and varying pH. a) pH 7.0. b) pH 11.5. c) pH 2.0.

constancy is very good (generally within 2–3 %) but small deviations are found in the visible range, particularly for the acid solution. The steepness of the absorption curve in this spectral range is very sensitive to errors of this type (and to pH variation) and is therefore not a safe characteristic for a humic acid fraction, whatever the reasons for the deviation might be. Much larger deviations have been found in

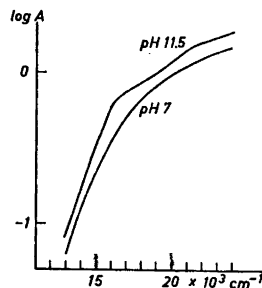


Fig. 2. Comparison between the absorption spectra at pH 7.0 and pH 11.5.

other cases, especially with some artificial humic acids (to be reported in future papers).¹

The pH variation influences the whole absorption spectrum, with higher absorbancy in basic solution and lower in acidic solution than in neutral solution. (At low wave numbers the differences between acidic and neutral solutions are small and might change sign.) This general effect of pH variation greatly diminishes the value of differential spectrophotometry, because maxima obtained need not correspond to the titration of specific functional groups of the humic acid molecules. The positions of the maxima might very well be arbitrarily fixed by the sum of a general and a specific effect of the pH changes and therefore not have a theoretical significance. Studies at intermediate pH also indicate that the absorbancy changes do not take place in narrow pH intervals but are obtained gradually.

The absorption curves indicate a very specific effect at $16\,000\text{ cm}^{-1}$ (Fig. 2) but the pH dependence of the absorbancy is gradual also in that case, the absorbancy rising strongly in the pH range from 7 to 11.5. Against this background it is obvious that difference spectra should not be given premature theoretical interpretations. On the other hand they might still have a diagnostic value. It is thus obvious that the difference spectra obtained for this humic acid fraction (Fig. 3) differ significantly from those reported in an earlier communication.² The humic acids studied in the latter were obtained by an extraction procedure with concentrated sodium hydroxide while the present humic acid was extracted with sodium pyro-

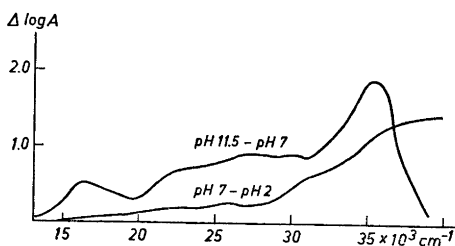


Fig. 3. Difference spectra. A is recalculated to a concentration corresponding to $A=1.00$ at $17\,000\text{ cm}^{-1}$ and pH 7.0.

phosphate at pH 7 and has further been carefully dialysed. Almost all the humic acid fractions obtained by pyrophosphate extraction¹ show similar difference spectra as the humic acid studied here, differing from those extracted with concentrated sodium hydroxide. The latter extraction thus seems to cause drastic chemical changes of the humic acids. This has been confirmed by treatment of the present humic acid with concentrated NaOH solutions. The resulting humic acid exhibits a strong ΔA maximum at $28\,500\text{ cm}^{-1}$ as reported earlier. The difference spectra are thus very sensitive to changes in the treatment of the soils and less suitable for characterization. The shape of the $\log A$ curves need not vary much to give such appreciable shifts in the difference spectra.

The change in shape with pH can be found from $\Delta \log A$ curves (Fig. 4). Such difference curves show the pronounced general effect and indicate that the most typical specific effect is obtained at $16\,000\text{ cm}^{-1}$ in basic solution (*vide supra*). They might be more valuable for characterization of humic acids than the common difference (ΔA) curves.

On the basis of this study it is suggested that the shape of the $\log A$ curve at dif-

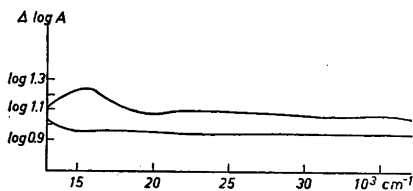


Fig. 4. $\log A$ for pH 11.5 (upper curve) and pH 2.0 (lower curve) relative to pH 7.0.

ferent pH can be safely used as a characteristic if its constancy is proved by measurements at different dilutions. Difference spectra can only have a diagnostic value at present. The general and specific effects of pH variation on the absorption spectra of humic acids should be further studied.

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The Protonation of Benzyl Alcohol in Aqueous Sulfuric Acid

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Branching of the hydrocarbon chain has very little effect on the basicity of aliphatic alcohols.¹ By Raman spectral,² extraction,^{1,3} and solubility⁴ studies, aliphatic alcohols, regardless of structural differences, have been found to be half-protonated in sulfuric acid solutions whose H_0 values lie within the very narrow range from -2.2 to -2.7 . We wish to report that even a phenyl substituent has very little influence on the basicity because extraction studies carried out with benzyl alcohol revealed that this alcohol is half-protonated in 44.6 wt. % sulfuric acid, the H_0 value of which is -2.81 .

The solvent extraction—GLC method⁵ used previously³ was employed. Values of the ratio

$$D = [\text{ROH}]_{\text{org.}} / ([\text{ROH}]_{\text{tot.}} - [\text{ROH}]_{\text{org.}})$$

where $[\text{ROH}]_{\text{tot.}}$ and $[\text{ROH}]_{\text{org.}}$ are the analytical concentrations of the alcohol in cyclohexane before and after shaking the solution with a sulfuric acid solution, were determined. The values of the ratio D for benzyl alcohol at different sulfuric acid concentrations are given in Table 1 and