The three cadmium oxydiacetate hydrate structures can be compared with the structure of cadmium diacetate dihydrate, which has recently been determined.[1] In this compound the coordination about cadmium is also seven-fold although the coordination polyhedron is a square base-trigonal cap. Both acetate groups are bidentate forming carboxylate chelates and one oxygen is also in a bridging position in such a way that infinite cadmium-oxygen spirals are formed.

The cadmium oxydiacetate hydrate structures will be described in detail in forthcoming publications.

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Titrimetric Determination of Acidity and pK Values of Humic Acid

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COOH and phenolic OH groups in humic acid are responsible for the cation exchange capacity and complexing ability of soil humic acid. Therefore, several methods have been proposed for the determination of the amounts (expressed as mequiv./g humic acid) of each of these groups.[1,2] The COOH content is normally estimated by the calcium acetate method or by decarboxylation and the phenolic OH is estimated as the difference between total acidity (determined by the $Ba(OH)_2$ method) and the COOH content.[1,2] As humic acid is a polyelectrolyte the individual carboxylic acids and phenols have different acid dissociation constants. These dissociation constants fall, however, in groups each associated with an average dissociation constant (denoted $p\bar{K}$).[3,4]

This note presents a titrimetric method for the estimation of the amounts of COOH and phenolic OH and the $p\bar{K}$ values of these groups in humic acid.

It has been shown that the titration of humic acid ought to be carried out as fast as a normal acid-base titration.[5] Therefore, it seems possible
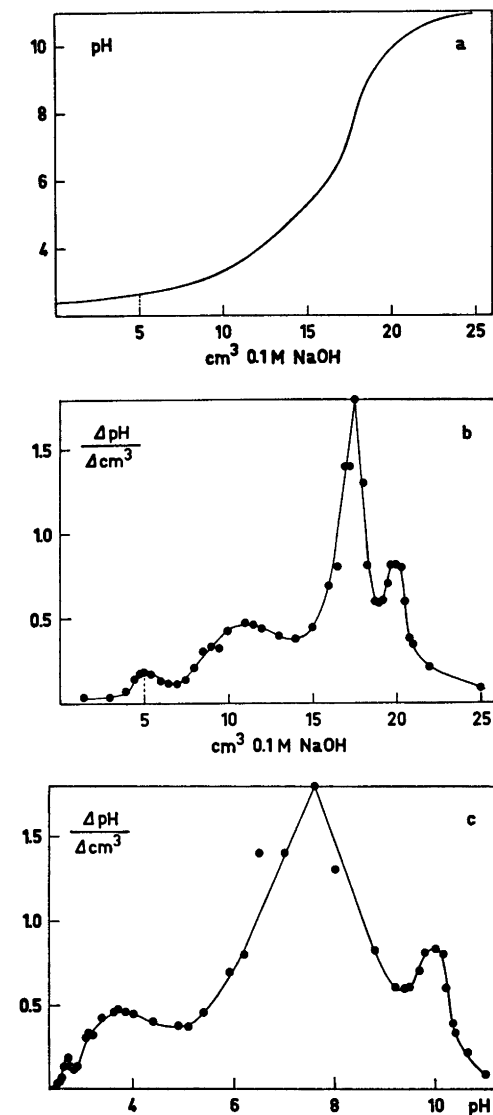

Fig. 1. The titration of 0.2 g Skarild A_1 humic acid. *a.* The original titration curve. *b.* $\Delta pH/\Delta cm^3$ plotted against cm^3 0.1 M NaOH. *c.* $\Delta pH/\Delta cm^3$ plotted against pH.

to determine the amounts of COOH and phenolic OH and the $p\bar{K}$ values from a simple titration. The inflection points of the titration curve are, however, blurred. This problem is overcome by differentiation of the titration curve.

Humic acid from four soil samples were tested. The soils are described elsewhere[5] as is the extraction procedure. The titrations were

Table 1. The amounts of COOH and phenolic OH expressed as mequiv./g humic acid and the $p\bar{K}$ values for the four humic acids. Ionic strength 0.1 (NaCl). Values in brackets determined by the calcium acetate and $Ba(OH)_2$ methods.

Humic acid	COOH Type I	COOH Type II	mequiv. per g humic acid			$p\bar{K}$ values	
			Total COOH Type 1 + Type II	Phenolic OH	$p\bar{K}_1$	$p\bar{K}_2$	$p\bar{K}_3$
Skarild A_1	2.8 ± 0.1^a	3.6 ± 0.1	6.4 (6.2)	1.2 ± 0.2 (1.4)	2.8 ± 0.2	5.1 ± 0.2	9.4 ± 0.3
Skarild B_h	2.6 ± 0.1	3.9 ± 0.1	6.5 (6.6)	1.4 ± 0.1 (1.3)	3.0 ± 0.3	5.1 ± 0.2	9.5 ± 0.3
Sdr. Vissing	3.0 ± 0.1	4.2 ± 0.1	7.2	1.7 ± 0.1	2.8 ± 0.2	5.0 ± 0.3	9.7 ± 0.4
Stavning	1.5 ± 0.1	2.7 ± 0.1	4.2 (4.4)	1.1 ± 0.1 1.2)	3.4 ± 0.2	4.9 ± 0.1	9.6 ± 0.2

^{a} The figures are the mean values and the standard deviations calculated from at least five titrations.

carried out in the following way: Dried humic acid was dissolved in NaOH solution under CO_2- and O_2-free N_2. This solution was either titrated with 0.1 M HCl or it was mixed with HCl in excess and titrated with 0.1 M NaOH. No hysteresis occurred between the titration curves. The titrations were carried out by means of an automatic titration equipment (Radiometer SBR 2, TTT 11, ABU 11, and PHM 26). From the titration curves the $\Delta pH/\Delta cm^3$ values were calculated. In order to check the accuracy of the method EDTA and a mixture of acetic acid and NH_4Cl were titrated. The number of milliequivalents calculated from the titration curves agreed within $\pm 0.5\%$ with the theoretical values and the pK_A values obtained agreed within ± 0.05 with the literature.[6]

Fig. 1 a shows the original titration curve of Skarild A_1 humic acid; part of the acidity (indicated by the dotted line) was due to free hydrochloric acid. In Fig. 1b $\Delta pH/\Delta cm^3$ is plotted against cm^3 0.1 M NaOH. In Fig. 1c $\Delta pH/\Delta cm^3$ is plotted against pH. The maxima correspond to equivalence points while the minima correspond to $p\bar{K}$ values. As seen from Fig. 1 there are three equivalence points and three $p\bar{K}$ values. The first two correspond to two types of carboxyl groups: Type I is probably COOH on aromatic rings *ortho* to phenolic OH groups and Type II more weakly acidic carboxyl.[4] The third equivalence point corresponds to phenolic OH. Table 1 gives the number of mequiv./g humic acid and the $p\bar{K}$ values of the three groups in the four humic acids. The figures in brackets are determined by the calcium acetate and the $Ba(OH)_2$ methods and they are in good agreement with the values found by the titration procedure proposed here.

The carboxyl content (mequiv. Type I + mequiv. Type II) is greater than normally found [1,7] but this is certainly due to the extraction procedure which gives more oxidized humic acid than the NaOH extraction procedure.[5] On the other hand the content of phenolic OH is less than the phenolic OH content in humic acid extracted by NaOH [1,7] but in good agreement with that found in pyrophosphate extracted humic acid.[8]

The $p\bar{K}$ values given in Table 1 agree with those presented in the literature.[4,8,9] In spite of the fact, that the $p\bar{K}$ values depend on the degree of dissociation,[4] they are important in the characterization of humic acids extracted from different soils and by different methods.

From the data presented it is concluded, that the proposed titration procedure is a simple and rapid method for the determination of the COOH and phenolic OH content and the average dissociation constants of humic acid. These data are valuable in the characterization of soil humic acid.

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