

# STUDIES ON THE DEGREE OF CONDENSATION OF HUMIC ACIDS AND HUMINS OF LOAMY SOILS, IN AN ATLANTIC CLIMATE

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The products of humification are studied in A<sub>1</sub> or Ap horizons of loamy soils distributed according to a sequence including successively :

Rendzina → Calcic cambisol → Brunic luvisol → Glossic luvisol

Different fractions of humic substances are successively extracted from soil samples after specific treatments :

I. Humic acids (H.A) extractable by 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>

II. H.A extractable by 0.1 N NaOH

II.a. Without treatment

II.b. After a NHCl treatment (H.A bound to Fe or Ca)

II.c. After a NHCl-N HF treatment (H.A bound to clay minerals)

Humin of insolubilization extractable after treatments

III. Humin of insolubilization non extractable, separated of plant residues by an acetyl bromide treatment and of mineral matter by an hot 6N HF treatment.

The different fractions are demineralized by dialysis and hydrolysed by 6N HCl.

The fractions of H.A successively extracted from the same soil after specific treatments are very similar in regard to the molecular size and the proportion of aromatic structures (Tables 3 and 4).

**Table 3 : Infrared study : variation of the ratio O.D. 2920/O.D. 1510 cm<sup>-1</sup> (aliphatic C-H/aromatic C=C)**

Average of the results obtained for each soil type.

SOILS	H.A directly extractable		H.A extractable after treatment		Humin of insolubilization non extractable
	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	NaOH	NaOH after HCl	NaOH after HCl-HF	
Rendzina	1.30	1.30	1.30	1.60	1.40
Calcic cambisol	1.30	1.35	1.25	1.90	1.30
Brunic luvisol	1.20	1.05	1.20	1.40	1.20
Glossic luvisol	1.20	1.20	1.50	1.60	1.40

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**Table 4 : Fractionation of H.A. by Sephadex gels. Results in %.**

SOILS	H.A directly extractable		H.A extractable after treatment	
	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	NaOH	NaOH after HCl	NaOH after HCl-HF
<u>Rendzina</u>				
Included in G 50	44.0	46.0	45.0	52.0
Included in G 75	14.0	7.0	9.0	15.0
Non included in G 75	42.0	47.0	46.0	33.0
<u>Brunic luvisol</u>				
Included in G 50	43.0	36.0	38.0	47.0
Included in G 75	12.0	13.0	12.0	5.5
Non included in G 75	45.0	51.0	50.0	47.5
<u>Glossic luvisol</u>				
Included in G 50	29.0	27.5	25.0	48.0
Included in G 75	3.0	9.5	22.5	3.5
Non included in G 75	68.0	63.0	52.5	48.5

However, the H.A molecules extracted by NaOH after an HCl-HF treatment are more aliphatic and smaller than directly extractable H.A. molecules. Consequently they would have been dispersed without treatment in NaOH solutions, but it is not the case because they are strongly bound to clay minerals.

On the other hand, for all the different fractions of H.A extracted from the soil with NaOH the carboxylic acidity ratio is the same, but this ratio is higher for the H.A extracted by Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (Table 5).

**Table 5 : Infrared study : variations of the ratio O.D. 1720/O.D. 1510 cm<sup>-1</sup>  
(C = O of acid/aromatic C = C)  
for the different fractions of H.A and humins  
(Average of the results obtained for each soil type)**

SOILS	H.A directly extractable		H.A extractable after treatment		Humins of insolubilization non extractable
	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	NaOH	NaOH after HCl	NaOH after HCl-HF	
Rendzina	2.0	1.5	1.5	1.4	1.2
Calcic cambisol	2.1	1.7	1.6	1.6	1.2
Brunic luvisol	1.8	1.7	1.4	1.3	1.1
Glossic luvisol	1.5	1.4	1.3	1.3	1.2

From a soil to another, the humification ratio and insolubilization ratio of humic substances are decreasing with the soil pH :

Rendzina	Calcic cambisol	Brunic luvisol	Glossic luvisol
59.5 %	55.9 %	44.2 %	28.7 %

In calcareous soils the flocculation of humic substances is premature ; it affects the humic molecules having a little size, an important aliphatic fraction and numerous carboxylic groups.

On the contrary, in acid soils such as glossic luvisols where flocculation of the humic substances is reduced, the humic acids having a large size, and few carboxylic groups are persisting in a dispersable state.

The irreversibly insoluble humin is not necessarily formed of larger molecules than those of humic acids. The insolubility in alkaline solutions of this humin would be related to its low carboxylic acidity ratio. It seems that iron participates to humin formation by decarboxylation of humic acids.