

CONTRIBUTIONS OF SOIL ORGANIC MATTER  

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TO PRODUCTION POTENTIAL OF SOILS AND  

---

SOME PROPOSALS FOR PRACTICAL APPLICATION  

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Wolfgang FLAIG

Annex II

to the report of W. FLAIG

9 Lectures about: Contributions of soil organic matter to production potential of soils and some proposals for practical application.

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CONTRIBUTIONS OF SOIL ORGANIC MATTER

TO PRODUCTION POTENTIAL OF SOILS AND SOME PROPOSALS

FOR PRACTICAL APPLICATION

Wolfgang FLAIG

1973

## Preface

The increase of yield/ha is important for the food production of Indian Population. For this purpose firstly high yielding varieties of rice, wheat and other crops were bred. These demand a higher quantity of mineral fertilizers. Fertilization alone does not allow the realization of the full genetical potential of cereals. The inorganic ions of the fertilizers enhance also microbial activity. The microorganisms use the carbon from soil organic matter as source for energy and reproduction. As a consequence of decrease of soil organic matter unfavourable processes in soil, the substrate for production occur, which cause a reduction in plant production. Therefore an increase of yield by fertilization alone is limited.

Another way to overwhelm the biological border for the use of the genetical potential of cereals is to utilize the effect of bioregulators on plant metabolism, such as CCC, "Cycocel" to increase the resistance against lodging of wheat. There are some other substances in soil organic matter, which have bioregulating effects under unfavourable growth conditions. This influence of soil organic matter on yield is well known by the farmers as "humate-effect".

Therefore, it is evident, that special procedures for maintaining a critical status of soil organic matter should be followed. More research about humus is necessary. An intensive cereal production is then economical only, when yields are always maintained at a relatively high level. One should try to minimize the yield depressions by appropriate procedures.

The lectures are an introduction into the problems. The transfer of results of basic research into practice are mentioned and the experiences about the utilization of new findings are summarized.

I have to thank Mr. M.S. Sachdev (M.Sc.) for his indefatigable help, for the revision of the lectures and for compiling the references.

Wolfgang FLAIG

New Delhi, 29. September 1973

## Content

	Page
<u>Lecture - 1</u> Introductory lecture	
Introduction to some fields of soil organic matter studies in relation to soil productivity	1
 <u>References</u>	 31
 <u>Lecture - 2</u> Formation of humic substances from plant residues	 34
 <u>Lecture - 3</u> Slow releasing nitrogen fertilizer from lig- nosulfonates of pulp and paper industries - (N-lignin)-production and its effect on plant growth due to production conditions.	 71
 <u>Lecture - 4</u> N-lignin as nitrogen fertilizer and its special effects.	 95
 <u>Lecture - 5</u> Biosynthesis of humic substances especially participation of nitrogenous compounds.	 126
 <u>Lecture - 6</u> About the possible effect of fractions of humic substances on plant metabolism and yield.	 172
 <u>Lecture - 7</u> Chemistry and some physical properties of fractions of soil organic matter.	 218
 <u>Lecture - 8</u> Characterization of humic systems in different soils.	 251
 <u>Lecture - 9</u> General Lecture	
Modern aspects in humus research for plant production.	277
 <u>References</u> (Lecture 2-9)	 313

Lecture - 7

CHEMISTRY AND SOME PHYSICAL PROPERTIES OF FRACTIONS  
OF SOIL ORGANIC MATTER

1. Problems of isolation of fractions of humic substances.
2. Data about comparison of fractions of humic substances.
3. Fractionated precipitation of humic acids with neutral salts ("gray" and "brown" humic acid fractions).
4. Contribution to the problem of fractionation of humic acid.
5. An example for the characterization of humic acids and their fractions by IR-absorption.
6. Absorption in UV and visible range of light
  - 6.1 Principles of absorption spectroscopy of humic acids
  - 6.2 Structural units and light absorption of humic acids
    - 6.21 Phenols
    - 6.22 Radicals
    - 6.23 Heterocyclic ring systems
7. Electronic spectra of humic acids
8. Final remarks - About the efficiency of optical methods for characterization of humic acids.

CHEMISTRY AND SOME PHYSICAL PROPERTIES  
OF SOIL ORGANIC MATTER

In this lecture some special problems of chemistry and of some physical properties of fractions of soil organic matter will be mentioned. Some data will be a supplementation to the former lectures and some may serve as introduction to the problems of the next lecture about characterisation of humic systems. The first subject concerns the isolation of fractions of humic substances from the soil. This is one of the most severe problems of humus chemistry because by changing the method the properties of isolated fractions are no more the same. The conclusions of the different authors cannot be congruent.

1. Problems of isolation of fractions  
of humic substances.

The substances which are formed from plant material during humification consist of a mixture of various compounds. As these compounds have similar properties, the extraction of substances with a uniform composition is very difficult. Therefore, the separation procedures lead to very different results according to the physico-chemical properties of the materials to be extracted and also of the extractants.

A further difficulty is the fact, that the organic substances in the soil are bound by bi- and trivalent cations and possibly by hydrogen bridge linkages of phenolic or aliphatic hydroxyl groups or of carboxylic groups and also, to a smaller extent, of amino groups with silicic clay minerals. A maximum extraction excluding larger chemical alterations is obtained only by the use of polar solvents with high dielectric constants, which increase the dispersity of humic substances or which improve the conditions of solubility by disrupting the hydrogen bonds of the fixed metallic cations and immobilize them (WHITEHEAD and TINSLEY 1964).

Difficulties of separation of humic acids from inorganic soil constituents led mainly to the investigation of humic substances of B-horizons of podzolic soils; the extraction of these is less difficult than of other (BURGES and LATTER 1960, COFFIN and DELONG 1960, DUBACH, MEHTA and DEUEL 1961, JACQUIN 1960, MARTIN and REEVE 1955, MARTIN, DUBACH, MEHTA and DEUEL 1963, SCHNITZER, WRIGHT and DESJARDINS 1958, SOWDEN and DEUEL 1961, STEELINK, BERRY, HO and NORDBY 1960, WRIGHT AND SCHNITZER 1960, MARTIN and REEVE 1957 a,b).



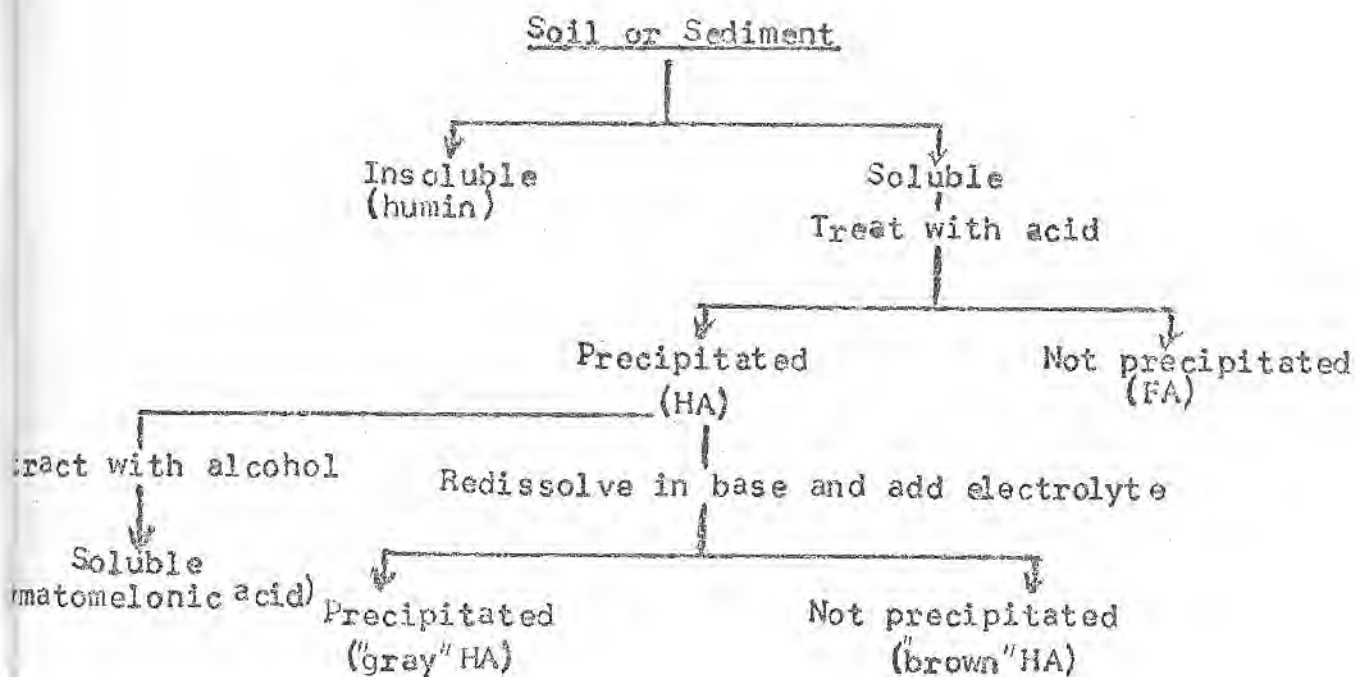


Fig. 1: Fractionation of Humic Substances.

In this scheme the classical methods for extraction and fractionation of humic substances is mentioned.

Many extractants were used for separation of organic soil substance (see SCHEFEER and ULRICH 1960, TINSLEY and SALAM 1961, DUBACH and MEHTA 1963). With regard to the mentioned point of view, the solvents can be divided according to their chemical and physical efficiency in several groups: 1. acids, 2. strong alkali, 3. weak alkali, 4. complexing agents and 5. organic solvents.

A pretreatment with hydrochloric acid and/or a mixture of hydrochloric acid with hydrofluoric acid is applied for desorption of humic substances which are fixed on sesquioxides, free silicic acid or clay minerals, and for removal of carbonates or exchangeable bases to increase the yield of extraction (BREMNER and HARDA 1959,

CHOUDRI and STEVENSON 1957, DUBACH, MEHTA and DEUEL 1963, POSNER 1966).

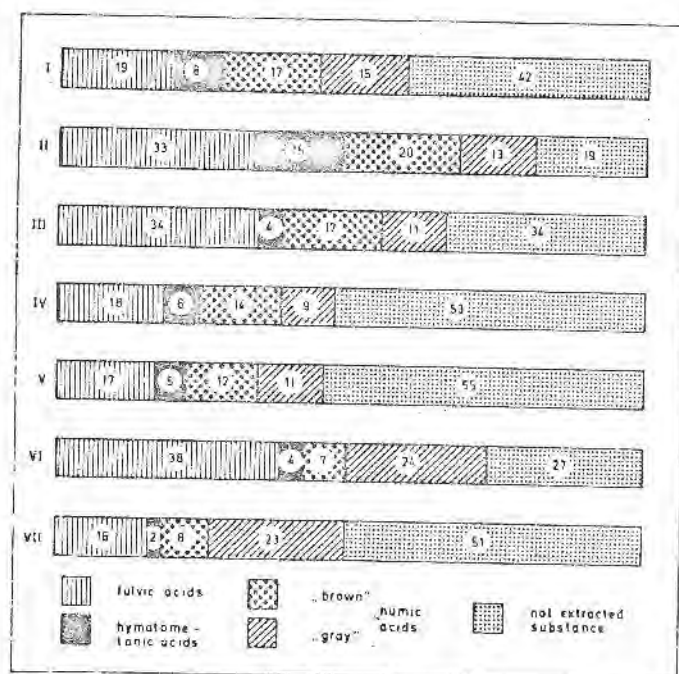
The method of isolation of humic fractions is at first of principle importance for their characterization.

Therefore a summary of extractants of different efficiencies, is shown for extraction of total organic soil substance of two horizons of a podzol profile (SCHNITZER et al. 1958).

Table 1: Efficiency of different extractants for organic soil substance from two horizons of a podzol profile (SCHNITZER, WRIGHT and DESJARDINS 1958).

Solvent	Percentage of carbon extracts from	
	A <sub>0</sub> -horizon	B <sub>21</sub> -horizon
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> · 1 OH <sub>2</sub> O	6.1	91.7
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> · 1 OH <sub>2</sub> O	5.5	82.6
Na <sub>3</sub> PO <sub>4</sub> · 12 H <sub>2</sub> O	9.1	93.6
(NaPO <sub>3</sub> ) <sub>6</sub>	1.2	37.0
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 1 OH <sub>2</sub> O	7.7	80.8
NaF	6.6	88.4
NaF	4.4	88.7
NaCl	2.5	2.2
NaBr	T*	2.7
NaI	T*	3.2
Na <sub>2</sub> CO <sub>3</sub>	8.8	92.3
NaOH	24.8	96.3
HCl	T*	11.2
HF	T*	83.1
EDTA-Na <sub>2</sub>	T*	97.0
T* 3 Traces		

Only some of them extract soil carbon up to 90% or more from the B-horizon. The selection of the solvent has a decisive influence on the result of fractionation. In the next figure different procedures of extraction are summarized in the case of chernozem (WIESENMULLER 1965).



- I. = 2 % HCl cold, 1 % NaOH, cold: NEHRING (1955), TYURIN (1937)  
 II. = 5 % HCl, 70°C, 0,5 % NaOH, boiling: SPRINGER(1938)  
 III. = 5 % HCl, 70°C, 1 % NaOH, cold  
 IV. = 0,1 M  $\text{Na}_4\text{P}_2\text{O}_7$ , 0,1 N NaOH, 16 hours, cold: KONONOVA and BELCHIKOVA (1961)  
 V. = 0,1 N  $\text{Na}_4\text{P}_2\text{O}_7$ , 0,1 N NaOH, 16 hours, cold  
 VI. = 0,1 N  $\text{Na}_4\text{P}_2\text{O}_7$ , 8 hours, boiling: WELTE (1956)  
 VII. = 0,1 N  $\text{Na}_4\text{P}_2\text{O}_7$ , 5 % hydrazinehydrate, 16 hours, cold

Fig. 2: Comparison of different extractants (data in % of total C from chernozem) (WIESENMULLER 1965).

Several facts are remarkable:

1. By the solvents less soil organic carbon is extracted in the case of chernozem in comparison to this of podzol B-horizon,

as mentioned in the Fig. before. This is due to the quantity and type of inorganic parts of the chernozem.

2. The ratio of fulvic acids to the sum of "brown" and "gray" humic acids varies according to the procedure of extraction.
3. The ratio of "brown" to "gray" humic acids depends upon the method of extraction.

These facts should lead to the conclusion that all authors should use a standardized, conventional method, it is possible to compare the results of different investigations. We work according to the method of KONONOVA and BELSCHIKOWA, because with this method the most comparing work of isolation of humic substances from many soils in different climates have been made.

2. Some data about the composition of fractions of humic substances.

In the next slide some data will be presented which concern the chemical composition of humic fractions.

For further applications of properties of humic fractions some remarks will be made about the aromaticity of humic acids.

According to the method of Mazumdar et al. (1957)

the aromaticity was determined by air oxidation at 170 °C during approximately 500 hrs. The side chains of aromatic compounds are oxidized to CO<sub>2</sub>. Some of the carbon atoms remain at the aromatic network in the form of carboxyl groups. The percentage of aromatic carbon in humic acids is about 65 per cent, the aliphatic and or

Table 2 : Distribution of C and H in Humic Substances

(WRIGHT and SCHNITZER, 1961; KHAN, 1971; ISHIWATARI, 1969)

Origin of humic material	Carbon			Hydrogen		
	Aroma- tic	Alipha- tic and/ or ali- cyclic	in CO <sub>2</sub> H groups	Aroma- tic	Alipha- tic and/ or ali- cyclic	in CO <sub>2</sub> H groups
<u>HA's</u>						
Chernozem (Ah)	66	24	10	35	54	11
Solod (Ah)	67	25	8	31	61	8
Solonetz (Ah)	69	22	9	44	47	9
Lake Sediment	36	59	5	10	82	4
<u>Humins</u>						
Chernozem (Ah)	53	34	8	32	61	7
Solod (Ah)	59	34	7	33	62	5
Solonetz (Ah)	54	40	6	26	69	5
<u>FA</u>						
Podzol (Bh)	48	30	22	21	51	28

alicyclic carbon 24 per cent. In the COOH groups remain 8 per cent carbon. These numbers are interesting in connection with the spectroscopic investigations.

Table 3: Nitrogen distribution in HA, FA, and a HUMIN FRACTION  
(KHAN and SOWDEN, 1971, 1972).

Type of material	<u>N distribution after acid hydrolysis, % of total N in material</u>				
	N content, %	Amino acid N	Amino sugar N	Ammonia N	N accounted for
HA	4.07	28.3	1.3	19.8	49.4
FA	3.87	26.4	3.6	15.1	45.1
Humin	4.60	36.1	1.6	22.1	59.8

With this table the nitrogen distribution in the fractions of humic substances is remembered. The percentage of amino acids is nearly the same in humic and fulvic acids. The residual nitrogen which can not be hydrolysed differs also not very much. These data are interesting in connection with consideration concerning light absorption.

The meq/g of the major oxygen containing functional groups in humic substances differs in each fraction. This difference is not only caused by the isolation from different soils. They can also occur by isolation with different methods.

Table 4: Major Oxygen containing functional groups in humic substances (meg/g)

Total acidity	Carboxyl	Phenolic OH	Alcoholic OH	Carbonyl	Methoxyl	Ref.
<u>Soil HA's</u>						
6.6	4.5	2.1	2.8	4.4	0.3	(Khan, 1971)
8.7	3.0	5.7	3.5	1.8	- <sup>a</sup>	(Schnitzer and Gupta 1964)
5.7	1.5	4.2	2.8	0.9	- <sup>a</sup>	(Schnitzer and Desjardins, 1962)
10.2	4.7	5.5	0.2	5.2	- <sup>a</sup>	(Hansen and Schnitzer, 1968)
8.2	4.7	3.6	- <sup>a</sup>	3.1	0.3	(Riffaldi and Schnitzer, 1971)
<u>Coal HA'S</u>						
7.3	4.4	2.9	- <sup>a</sup>	- <sup>a</sup>	1.7	(Moschopedis, 1962)
<u>Soil FA's</u>						
14.2	8.5	5.7	3.4	1.7	- <sup>a</sup>	(Schnitzer and Gupta, 1964)
12.4	9.1	3.3	3.6	3.1	0.5	(Schnitzer and Desjardins, 1962).
11.8	9.1	2.7	4.9	1.1	0.3	(Wright and Schnitzer, 1960)
<u>Soil Humins</u>						
5.9	3.8	2.1	- <sup>a</sup>	4.8	0.4	(Khan, 1971)
5.0	2.6	2.4	- <sup>a</sup>	5.7	0.3	(Khan, 1971)

<sup>a</sup> Not determined

The distribution of the carbonyl content may belong to aliphatic keto groups or quinone groups.

Table 5 : Distribution of Oxygen in Humic Substances

Oxygen %	Carboxyl	Phenolic OH	Alcoholic OH	Carbonyl	Methoxyl	Oxygen accounted for	Ref.
<u>% of oxygen</u>							
<u>Soil HA's</u>							
32.9	43.8	10.2	13.6	21.4	1.5	90.5	(Khan, 1971)
36.8	26.1	24.9	15.2	7.8	- <sup>a</sup>	74.0	(Schnitzer and Gupta, 1964)
35.4	13.6	38.0	12.7	4.1	- <sup>a</sup>	68.4	(Schnitzer and Desjardins, 1962)
35.6	42.2	24.7	0.9	23.4	- <sup>a</sup>	91.2	(Hansen and Schnitzer, 1966)
33.6	44.8	17.1	- <sup>a</sup>	14.8	1.4	78.1	(Riffaldi and Schnitzer, 1972)
<u>Coal HA</u>							
28.7	49.1	16.2	- <sup>a</sup>	- <sup>a</sup>	9.4	74.4	(Maschopodis, 1962)
<u>Soil FA's</u>							
47.3	57.5	19.3	11.5	5.8	- <sup>a</sup>	94.1	(Schnitzer and Gupta, 1964)
44.8	65.0	11.8	12.9	11.1	1.7	102.5	(Schnitzer and Desjardins, 1962)
47.7	61.0	9.1	16.4	3.7	1.0	91.2	(Wright and Schnitzer, 1960)
<u>Soil Humins</u>							
33.8	36.0	9.9	- <sup>a</sup>	22.7	1.9	70.5	(Khan, 1971)
31.8	26.1	12.1	- <sup>a</sup>	28.7	1.5	68.4	(Khan, 1971)

<sup>a</sup>Not determined.



The oxygen content of humic acids can be distributed of oxygen containing functional groups in humic acids between 70-90% in fulvic acids between 90-100%.

The differences in the content of phenolic hydroxyl groups in humic and fulvic acids may be one of the the causes of different light absorption. The higher content of phenolic hydroxyl groups in humic acids may cause the stronger light absorption than by fulvic acids.

Also the carbonyl content is higher than in fulvic acids. As mentioned before at the moment no method exists to differentiate exactly between carbonyl groups in aliphatic parts or in form of quinones. The possibility exists that in humic acids is a higher percentage of quinonoid carbonyls than in fulvic acids. This would also be a cause for stronger light absorption for humic acids.

According to the results of different authors one can suppose that quinone groups in humic substances occurs in complex structures and not in simple compounds. Later on we have to refer to this data.

3. Fractionated precipitation of humic acids with neutral salts ("gray" and "brown" humic acids fractions).

By flocculation with sodium chloride at pH-values between 7 and 8 purified humic acids can be separated in two fractions. The precipitated fraction is called "gray" humic acid, the part, which remains in the solution and is precipitated with hydrochloric acid, is the "brown" humic acid fraction (comp. FLAIG, SCHEFFER and KLAIRORTH 1955).

By electrophoresis and by gel filtration similar fractions are obtained.

Table 6: Separation of humic acids in "gray" and "brown" humic acids fraction by precipitation with sodium chloride in percent of total humic acids (SCHARPENSEEL and KRAUSE 1962).

Chernozem, Hungary		Podzol, Germany B <sub>h</sub> -horizon	
"Gray"- humic acids fraction	"Brown"- humic acids fraction	"Gray"- humic acids fraction	"Brown"- humic acids fraction
68.5 %	31.5 %	28.1 %	71.9 %

The quantity of "gray" and "brown" humic acids fractions is different according to soil type from which the humic acids have been isolated. Both fractions differ in their properties remarkably.

Table 7: Differences in the chemical composition of "gray" and "brown" humic acids fractions (values of ash-free substances, oxygen separately determined) (Flaig, Scheffer and Klamroth 1955).

<u>Chernozem</u>	C %	H %	O %	N %	Sum	OCH <sub>3</sub>	Ash	
<u>Total-h.a.</u>	57,78	3,25	34,32	3,90	99,52	0,95	9,60	brown-red
G-Fraction	61,60	2,79	32,42	2,83	99,64	0,78	10,18	dark-brown
B-Fraction	56,97	4,25	33,66	4,19	99,07	1,60	3,42	carmine-red
<u>Podzol</u>								
G-Fraction	61,62	2,96	33,93	2,18	100,89	0,00	5,26	carmine-red
B-Fraction	59,40	3,07	36,34	1,89	101,10	0,27	2,38	gray

In the "gray" humic acids fraction

the carbon and the ash content is higher

the oxygen, the nitrogen and the methoxyl content is lower.

than in the "brown" humic acids fraction.

The distribution of the functions of the nitrogen is different in both fractions.

In this connection, it is mentioned that a methoxyl content of 1,5% would correspond to a lignin content of about 10% lignin. This fact is interesting for investigations of separations of humic acids by means of organic solvents. Later some data are given.

The ash content of "gray" humic acids fractions consists mainly of silicic clay minerals, this of "brown" humic acids of oxides of iron and aluminium.

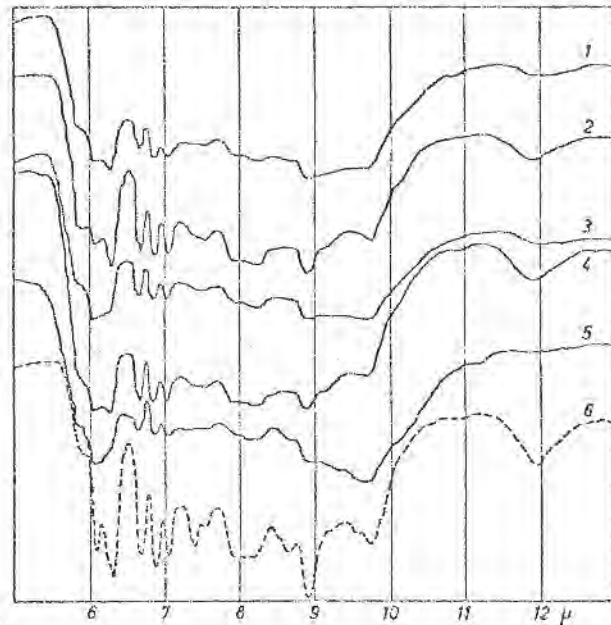
4. Contribution to the problem of fractionation of humic acids.

A summarizing review of the main methods of fractionation indicates that all so-called "humic substances" prepared by conventional methods in nearly no case lead to substances of chemical uniformity.

So for instance a fraction, defined as "humic acids" was isolated with a mixture of 0, 1 N sodium hydroxide and 0,2 N sodium fluoride from decomposed rye straw, which was extracted before with ether and water (FLAIG and TROJANOWSKI, unpublished).

After the usual purification by repeated precipitation a product (1) was obtained from which a fraction (2) was extracted with 95 % alcohol. The yield of this fraction decreased with increasing time of decomposition. This fraction was very similar in elemental

composition and light absorption properties to the original straw lignin (6), whereas the residue of the extraction (3) became more and more like humic acids isolated from soils. By treatment of the alcohol insoluble residue with aqueous acetone a fraction (4) was obtained whose properties are also more like lignin than those of the part remaining insoluble in acetone (5) (SALFELD 1964).

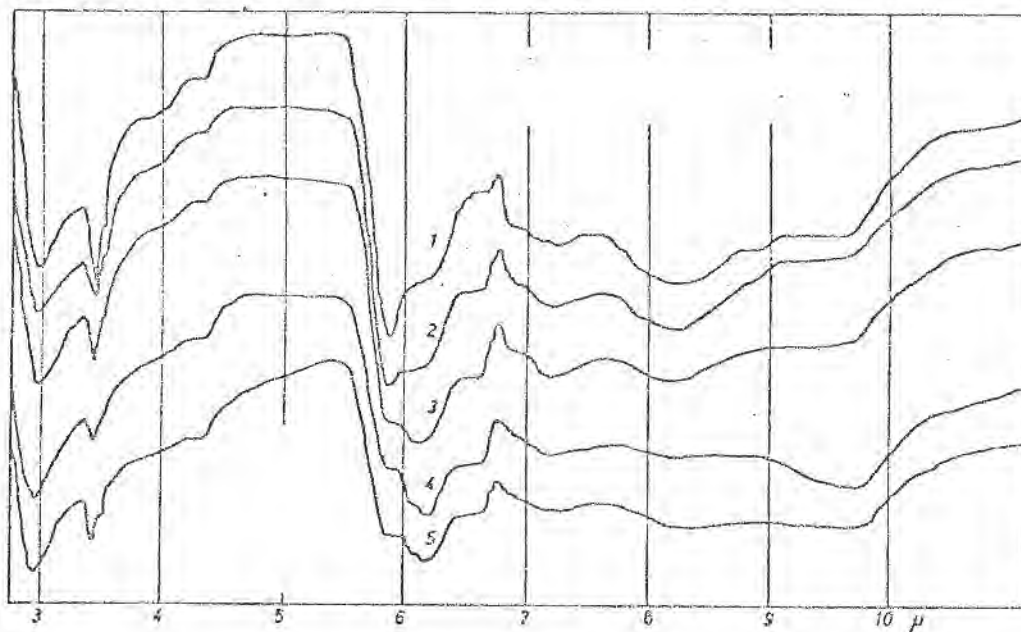


1. Total extract
2. Alcohol soluble fraction
3. Alcohol insoluble fraction
4. Acetone soluble fraction from (3)
5. Acetone insoluble fraction from (3)
6. Bjorkman lignin from straw

Fig. 3: Infrared spectra of humic acids fractions from decomposed rye straw prepared with different solvents (SALFELD 1964).

A comparison of the infrared spectrum of Bjorkman lignin (6) (Fig. 3) with the alcohol (2) and acetone soluble (4) fractions shows, that from the humic acids fraction a relative large portion can be isolated which is nearly unchanged lignin according to its spectrum. The spectra of the insoluble residues are somewhat similar to those of the humic acids.

Similar observations can be made also by separation of fractions of humic acids such as a "brown" humic acids fraction from chernozem by extraction with tetrahydrofuran (THF) of different water content (SALFELD 1964).



1. 5% H<sub>2</sub>O (39% soluble of initial material)
2. 10% " (10% " " " " )
3. 25% " (24% " " " " )
4. Residue (25% insoluble)
5. Initial material

Fig. 4: Infrared spectra of the subfractions from "brown" humic acids isolated from chernozem and extracted with tetrahydrofuran of different water content (SALFELD 1964).

The infrared spectra show a relative decrease of the carbonyl absorption at  $5,9\mu$  ( $1695\text{ cm}^{-1}$ ) followed by a reduction of the hydroxyl vibration, which means a decrease of the free carboxylic groups. On the other hand the C=C-vibration at  $6,2\mu$  ( $1610\text{ cm}^{-1}$ ) tends to strengthen and may be adjoined to increasing aromatic double bonds. The absorption of the carboxylic group at  $7,2\mu$  ( $1390\text{ cm}^{-1}$ )

with increasing water content similar to the decrease of the carbonyl function.

Table:8 Elemental composition of fractions of "brown"-humic acids of chernozem isolated with tetrahydrofuran (SALFELD 1964).

	ash in %	C <sup>+</sup>	O <sup>+</sup>	N <sup>+</sup>	OCH <sub>3</sub>	log ++ 400-600m $\mu$
1. Fraction 5% H <sub>2</sub> O/THF	1.29	58.81	33.20	2.79	3.00	0.82
2. Fraction 25%H <sub>2</sub> O/THF	3.72	55.65	33.02	5.89	2.08	0.68
3. Residue	6.73	53.17	34.59	5.50	1.49	0.58
5. Initial material	3.18	56.04	33.64	4.91	2.13	0.66

+ In % of ashfree substance (H no differences)

++ measured in 0.1 N NaOH

The elemental composition is in good agreement with the infrared analysis. The oxygen and nitrogen content increases, whilst the content decreases.

Not only the elemental analysis changes, but also the slope of the electronic spectra.

KYUMA (1964) obtained similar fractionation series by successive precipitation with alcohols in alkaline solution.

In comparison to the ratio of extinction (the  $E_4/E_6$ ) of other humic acids.

Table -9:  $E_4/E_6$  ratio of humic acids extracted from soils (KONONOVA, 1966).

Great Soil Group	$E_4/E_6$ ratio
Podzol	$\pm 5.0$
Dark Gray Forest	$\pm 3.5$
Chernozem	3.0 to 3.5
Chestnut	3.8 to 4.0
Serozem	4.0 to 4.5
Krasnozem	$\pm 5.0$
FA's	6.0 to 8.5

In this slide  $E_4/E_6$  of humic acids from different soil groups are presented. According to these numbers the fractions isolated with aqueous tetra hetro furane (THF) correspond more fulvic acids and the residue of the extraction of humic acids from chernozem.

These examples demonstrate, that the chemical and physical properties of the humic acids depend strongly on the methods of isolation.

In spite of this, any different isolated fractions are e.g. called "humic acids". Therefore it should be demanded, that a sample of used humic acids is isolated by a conventional standard method. This is the only way, whereby the various authors can draw conclusions from their results to the materials for comparison (FLAIG 1964 (2)).

KONONOVA 1964).

5. An example for the characterization of humic acids and their fractions by infrared absorption.

The infrared spectroscopy of humic acids preparations and their fractions is used by many authors for the purpose of characterizing humic substances from different soil origin (KASATOCHKIN and ZILBERBRAND 1956, KASATOCHKIN, KONONOVA and ZILBERBRAND 1958, KUMADA and AIZAWA 1958, 1959, ZIECHMANN 1958, 1959, 1964, SCHARPENSEEL and ALBERSMEYER 1960, ZIECHMANN and SCHOLZ 1960, ORLOV, ROZANOVA and MATYUKHINA 1962, SCHARPENSEEL, KONIG and MENTHE 1964, KONONOVA 1966, THENG and POSNER 1967, TOKUDOME and KANNO, 1968, POSNER, THENG and WAKE 1968).

It gives some information about the modification by chemical treatments (FARMER and MORRISON 1960, ORLOV, ROZANOVA and MATYUKHINA 1962, SCHNITZER 1965), such as methylation, acetylation, esterification, saponification and the formation of other derivatives (SCHNITZER and SKINNER 1965 (1), (2), SCHNITZER and DESJARDINE 1965). On the other hand, it is possible by this method to detect changes in the chemical structure of the investigated material during oxidation and pyrolysis (SCHNITZER and HOFFMANN 1964, SCHNITZER 1965). Furthermore metalhumate complexes were investigated, which may occur by organometallic interactions in soils (KASATOCHKIN, KONONOVA and ZILBERBRAND 1958, SCHNITZER, SHEARER and WRIGHT 1959, SCHNITZER and SKINNER 1964 1965, SCHNITZER 1965, LEVESQUE and SCHNITZER 1967b).



Unfortunately, the assignment of the specific absorption bands is limited by the fact that soil organic matter preparations represent in most cases mixtures of more or less complex molecules with different types of linkages and functional groups.

This fact leads to an overlapping of the characteristic absorption bands. The infrared absorption spectra of humic acids therefore show some bands, which are not particularly elucidative for the chemical nature of the molecule. The spectra indicate that some absorption bands do not originate from identical structural features, but probably from similar groups in different molecular surroundings. The infrared absorption properties of these samples are also strongly influenced by the different methods of sample preparation, different methods of soil extraction and the following fractionation. In cases where pellet techniques are used the time of grinding and evacuation is also an influential factor.

There are some difficulties in the real assignment of the infrared absorption bands of humic acids preparations. Some main absorption regions are found which appear in nearly all soil organic matter preparations with some differences in intensity or specific wavelengths of the absorption.

In order to give a general assignment of the main infrared absorption bands humic acids prepared according to (FLAIG, SCHEFFER and KLAMROTH 1955) from chernozem are chosen for comparison. The soil was pretreated with hydrochloric acid (0.5%) and extracted

with 0.5% sodium hydroxide. After centrifugation and several reprecipitations and dialysis these raw humic acids were sub-fractionated with 2N NaCl at neutral conditions. The "gray" humic acids fraction (G-fraction) was precipitated in sodium chloride, while the "brown" humic acids fraction (B-fraction) remained in solution. After dialysis the G-fraction shows an ash content of 10%, while the B-fractions has only 3,5 % of inorganic constituents.

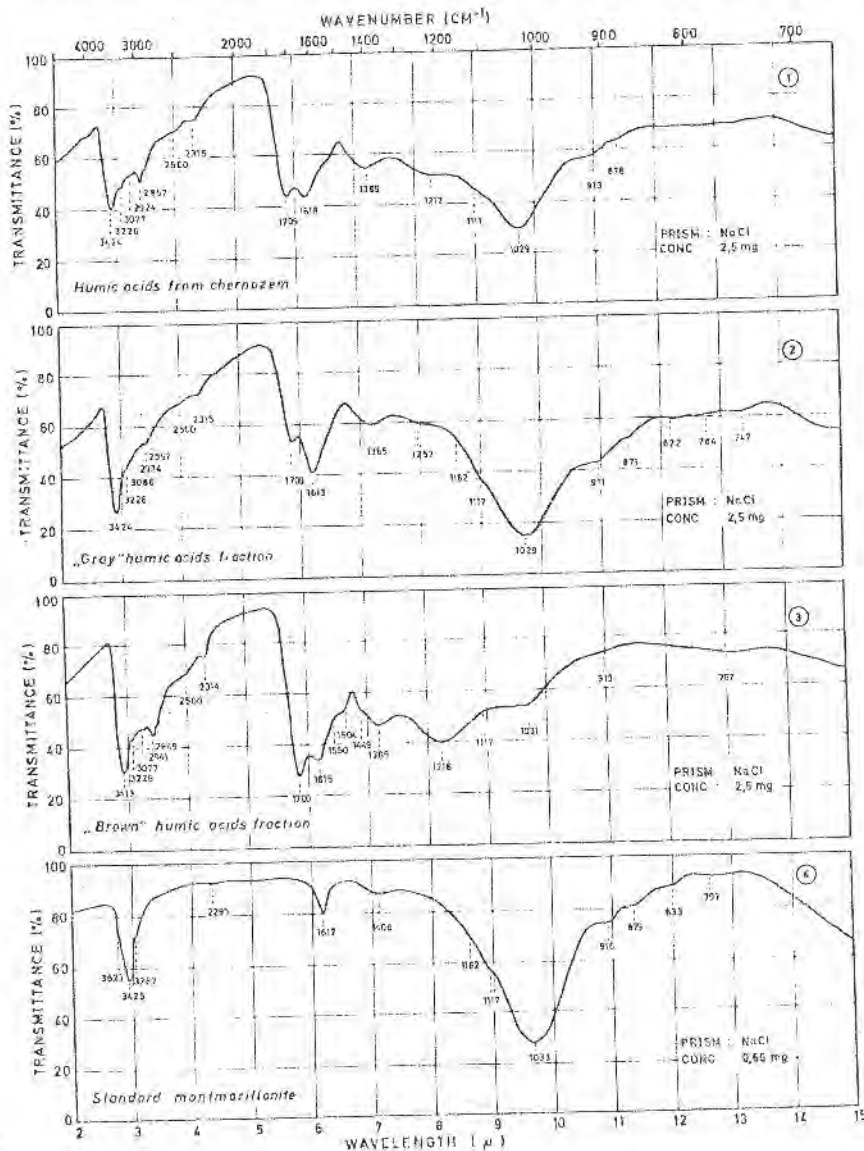


Fig. 5: Infrared spectra of humic acids from chernozem. (1) Original (2) "Gray" humic acids fraction (3) "Brown" humic acids fraction (4) Standard montmorillonite

A comparison of the infrared spectra of the raw humic acids (fig. 5 (1)), the gray humic acids fraction (fig. 5 (2)) and the brown humic acids fraction (fig. (3)) shows that the main differences in intensity of absorption bands are in the region at  $9.72 \mu$  ( $1029 \text{ cm}^{-1}$ ) which is assigned to the Si-O-Si-vibration frequencies of a complex silicate mineral component. Specific investigations of the "gray" humic acids fraction by infrared analysis and electron microscopy gave evidence of the occurrence of a smectite mineral of the montmorillonite type, as it is shown by the spectrum of standard montmorillonite (fig. 5 (4)) (RIETZ unpublished).

It shall not be reported about all details of the assignment of the infrared red absorption bands; this can be taken from publications. Only it should be demonstrated, that sometimes it is necessary to do basic research work to get methods for very practical use such as for the characterization of humic systems or to explain the properties of different fractions of humic acids, such as "gray" and "brown" humic acids fractions.

#### 6. Absorption in ultraviolet and visible range of light

The spectroscopic investigations of soil organic matter and its fractions in the ultraviolet and visible range of light has become more and more important for characterization and determination of genetic differences and also for transitions between the types of humic substances. So for instance contributions to characterization of humic systems or their fractions in dependence of environmental

conditions and soil management are very needed and of interest not only for soil chemistry and biochemistry but also for soil genesis and for agricultural management.

### 6.1 Principles of absorption spectroscopy of humic acids.

The concentration used for the analysis was of about 0.01 - 0.05 mg/100 ml. As chemical constitution is unknown the concentration can not be given in Mol/liter as in the case of chemical defined compounds. The absorption of humic substances in solution follows: the Lambert-Beer law:

$$(\text{absorbance} : A = E = \log P_0/P = \epsilon \cdot c \cdot d)$$

The extinction coefficient is  $K = \epsilon \cdot c$  if the length of the light path  $d$  in the cell is 1 cm. The extinction coefficient  $K$  is therefore directly proportional to the concentration  $c$  (mg/100 ml) whereby the proportionality constant  $\epsilon$  is specific for the investigated substance (molar extinction coefficient). As the value of  $\epsilon$  is dependent on the wavelength, the determination of concentration must be made at defined wavelength. Owing to the still undetermined molar absorptivity of the humic substances, due to their unknown chemical constitution, the absolute concentration of humic acids in Mol/liter cannot be determined. Therefore the spectroscopic measurements of absorption of soil organic matter or its fractions are used only for the determination of K-values.

The light absorption of a solution of humic substances of constant concentration is measured in the visible and ultraviolet range and

the logarithm of extinction ( $\log K$ ) is plotted against the wavelength ( $\log K = (\lambda)_c$ ). In contrast to many higher molecular weight substances, the electronic spectra of humic fractions show no distinct maxima but only more or less monotonously raising straight lines in the direction of shorter wavelengths with some deviations from linearity. On account of the applicability of the Lambert-Beer law, whereby  $\log \epsilon$  and  $\log c$  became additive ( $\log K = \log \epsilon + \log c$ ), spectra of solutions of the same humic substances measured at different concentrations are shifted parallel. The determination of relative concentrations by alterations of the absorbance are possible.

On the other hand this indicates that the slope of the curves is independent of variation in the concentration leading to the possibility of characterization of the colour type of humic substances by determination of the slope of the absorption curve. This characterization is based on the differences of the molar absorptivity of these substances.

More recently some other authors such as KUMADA (1955) and SALFELD (1965, 1968) characterized the slope of the colour curve by the difference of logarithmic extinction of at least two different wavelengths ( $\log K = \log K_{400} - \log K_{500}$ ).

## 6.2 Structural units and light absorption of humic acids.

The classification of humic acids with optical methods is the subject of many investigations. The spectroscopic and physico-chemical properties of the humic acids are caused primarily by the

different genetic conditions in soils and are furthermore varied by the methods of extraction and purification.

The multitude of molecular constituents of humic acids, which absorb in the ultraviolet and visible range, such as phenolic compounds and their oxidation products, amino acids and their condensation products with phenols in oxidizing medium, and the formation of heterocyclic components, leads to spectra of mixtures. These show no strongly marked differences in the absorption properties, when different types of humic acids are compared.

6.21 Contribution of phenols and their transformation products. The absorption of humic acid in the ultraviolet range may be caused by phenolic components and in the visible by chromophoric groups formed by oxidation. It could be demonstrated by oxidative or reductive cleavage of humic acids that these contain phenolic components.

FLAIG and SALFELD (1958) investigated especially the changes of the optical properties of differently substituted *o*- and *p*-benzoquinones as model substances. They demonstrated that the absorption curves of these compounds have two or three significant maxima according to their substitution. An *o*-substitution of the methoxyl group with a methyl group causes a stronger shift of the second maximum to longer wavelengths than a substitution in *p*-position. The kind and the position of the substituents cause changes of the absorption properties or shifts of specific absorption bands.

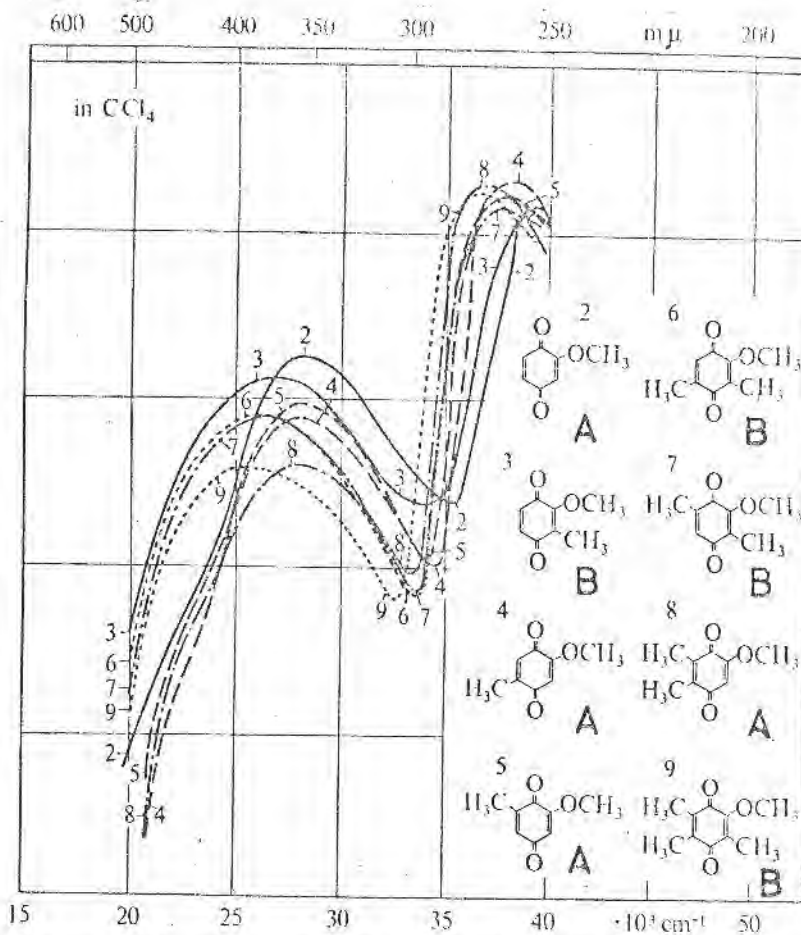
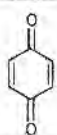
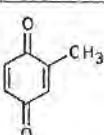
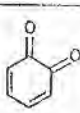

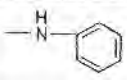


Fig. 6: Absorption curves of methylated 2-methoxy-p-benzoquinone.  
 A: p-substitution (methoxyl group more effective than methyl group).  
 B: o-substitution

Table: 10 Shift of the second maximum of absorption curve of benzoquinones by substitution with different groups.

								
	2. maximum in nm	shift in nm	2. maximum m-p-subst. in nm	shift in nm	2. maximum o-subst. in nm	shift in nm	2. maximum in nm	shift in nm
unsubstituted	262 (CCl <sub>4</sub> ) 288 (CHCl <sub>3</sub> )						375 (CCl <sub>4</sub> )	
-CH <sub>3</sub>	309 (CCl <sub>4</sub> )	27	310 (CCl <sub>4</sub> )	1	332 (CCl <sub>4</sub> )	23	328 (CCl <sub>4</sub> ) in 4-position	7 (CCl <sub>4</sub> )
-OCH <sub>3</sub>	351 (CCl <sub>4</sub> )	69	355 (CCl <sub>4</sub> )	46	374 (CCl <sub>4</sub> )	65	450 (CCl <sub>4</sub> ) in 3-position	75 (CCl <sub>4</sub> )
-OH	369 (CHCl <sub>3</sub> ) 372 (CCl <sub>4</sub> )	81 90	381 (CHCl <sub>3</sub> )	72	396 (CHCl <sub>3</sub> )	85	505 (CCl <sub>4</sub> ) in 3-position (3-hydroxy-4,6-di-tert butyl)	116 (CCl <sub>4</sub> )
	369 (CCl <sub>4</sub> )	67						
	550 (CHCl <sub>3</sub> )	262 minus benzene ring -175						

For instance substitution with an aliphatic group such as a methyl group results in a shift of the second maximum of p-benzoquinone at 282 nm (in carbon tetrachloride) for 27 nm, in the case of a methoxyl group for 69 nm and in the case of a hydroxyl group for 90 nm in direction of longer wavelengths.

Furthermore it could be established, that a shift of the second maximum to longer wavelengths depends less on the chain length of the aliphatic group, but much more on the kind of substitution at the ring with further alkyl-, alkoxyl- or hydroxyl groups. When the second substituent is on o-position to the other the shift is much larger, than by substitution in m- or p-position. It will be remembered that in the case of lignin degradation products and in the case of the transformations of microbial synthesized phenols there was often a substitution in o-position. o-Benzoquinones absorb light at longer wavelengths than the p-benzoquinones. Substitution in 3-position has a greater effect on the shift than in 4-position. Strongly effective chromophoric groups are also phenyl as well as aromatic or aliphatic (amino acids) amino groups.

It is unlikely that all phenolic units in the molecule of humic acids are present in the form of quinones, because these are not very stable against further oxidation. If quinonoid groups are present to a larger extent, they would presumably effect a broad maximum in the absorption curve in a range between 300 to 500nm. This is not observed; therefore other effects must exist.



## 6.22 Radicals

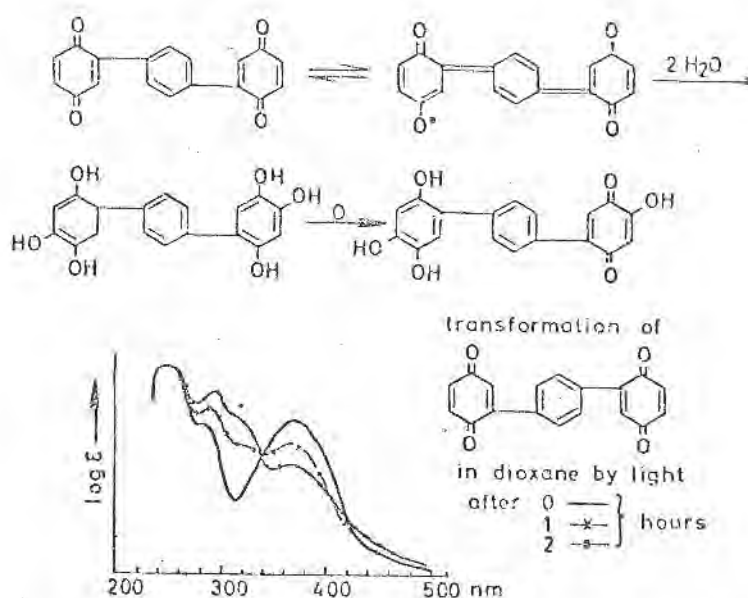


Fig. 7: Polymeric quinones as model substances of humic acids, 1, 4-diquinonyl-benzene.

Some model experiments were made to explain the absence of distinct maxima in the absorption curve of humic acids. According to the UV-spectrum 1,4-diquinonyl-benzene seems to be present in an o- and p-quinonoid configuration in solution (PLOETZ 1955). The o-configuration may be defined as a biradical and is very reactive. A corresponding hydroxylhydroquinone, which can be partially reoxidised to a hydroquinone, is formed by addition of water. A deeply coloured, intramolecular quinhydrone is formed. Diquinonyl-benzene is disproportionated in organic solvents. The formed mixture of substances show similar, nearly monoton increasing spectra as they are known from humic acids isolated from soils (FRÖMEL 1938 a,b, 1941 and later on many others).

STEELINK and TOLLIN (1962), STEELINK (1964) demonstrated by electron spin resonance, that humic acids contain radicals. This result agrees well with the assumption that the humic acids are intramolecular quinhydrone. Measurements by KLEIST and MÜCKE (1966), KLEIST (1967) established that the radicals (semiquinones) are

stabilized by mesomery and are responsible for the colour of humic acids. Thereby the humic acids would have the properties of electron exchanger. BAILEY, BRIGGS, LAWSON, SCRUTON and WARDS (1965) explain absorption in IR-spectra of browncoal humic acids by hydrogen bridge linkages between the hydrogen of phenolic hydroxyl groups and in the carbonyl groups of quinones. Hitherto no quinone group could be found by reducing acetylation (FARMER and MORRISON 1960). Otherwise MARTIN, DUBACH, MEHTA and DEUEL (1963) assume, that the carbonyl group of fulvic acids from podzol, which cannot be reduced by sodium boron hydride ( $\text{NaBH}_4$ ), may belong to quinone groups.

### 6.23 Heterocyclic ring systems.

A bathochromic effect can be caused by the oxygen, nitrogen or sulphur atoms in ring systems, which may occur in humic acids. The extent of a bathochromic effect of these elements is shown in the case of 4 dyestuffs with comparable chemical constitution.

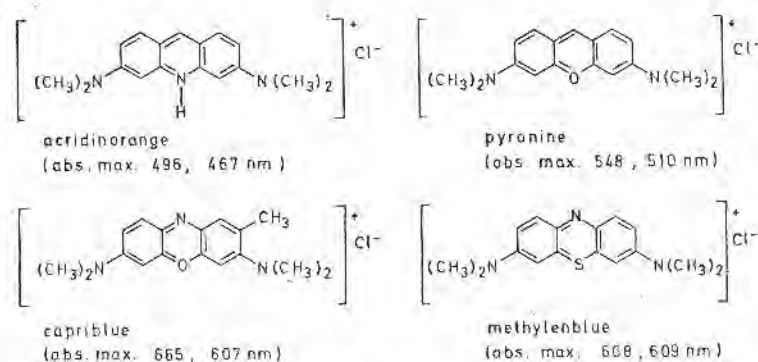


Fig. 8: Bathochromic effects of heteroatoms in dyestuffs with comparable chemical constitution.

The influence of the shift of the absorption maxima increases in order to nitrogen, oxygen, sulphur and corresponding combinations. The range of absorption of these compounds is at longer

wavelengths than that of the mentioned benzoquinone compounds.

### 7. Electronic spectra of humic acids.

In the following figure the absorption spectra of different humic acids and of fulvic acids are depicted schematically. The curves of absorption are not linear, as could be shown by more exact measurements (comp. SALFELD 1965).

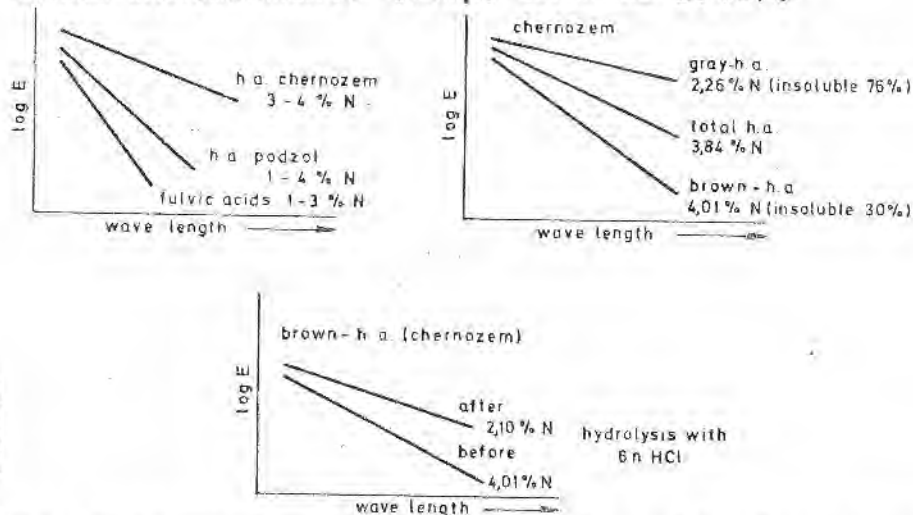


Fig. 9: Absorption spectra of humic acids from chernozem and podzol and fulvic acid (schematics).

As a rule, humic acids from chernozem rich in nitrogen have not only higher absorption, but also stronger absorption at longer wavelengths than the humic acids from podzols poor in nitrogen. The stronger absorption of humic acids from chernozems may be caused by the higher content of non-hydrolysable nitrogen, which may have a higher content of bathochromic heterocyclic compounds, than that in podzol humic acids. The total nitrogen content cannot play an important role in light absorption, since it is found largely in proteins, which do not absorb in the visible range.

The fraction of brown humic acids of chernozems has a higher nitrogen content than the fraction of gray humic acids. However, the absorption of the fraction of gray humic acids is stronger in the total range than that of the fraction of brown humic acids. There it may be that the residue of hydrolysis of the fraction of gray humic acids contains more heterocyclic, bathochromic components.

The absorption of the residue of hydrolysis of the fraction of brown humic acids is stronger in the total range than that of the fraction of the original brown humic acids, although the nitrogen content of this fraction (4.01 % N) is higher than that of the residue of hydrolysis (2.01 % N).

According to KLEIST and MUCKE (1966) the higher extinction of the fraction of gray humic acids is due to a higher content of radicals, measured by electron spin resonance.

It seems that the absorption of fulvic acids is more due to oxidised phenols than to heterocyclic components with properties of dyestuffs, since these bathochromic components would show stronger absorption at longer wavelengths. The absorption of fulvic acids is less in the range of longer wavelengths. The nitrogen content of fulvic acids is generally lower (KONONOWA 1966) and the carbonyl content higher (SCHNITZER 1965) than that of humic acids.

There is voluminous literature on light absorption of humic substances. KUMDA (1965), recently CRLOV and CRINDEL (1967) and Schnitzer and KHAN (1972) published summaries of work dealing with this problem.

The current thereby concerning the colour of humic substances has been developed according to results of chemical investigations, but it must be supplemented by further investigations and isolation of corresponding compounds.

About the efficiency of optical methods for  
characterization of humic fractions

A critical evaluation of the optical methods in the range of ultraviolet, visible and infrared range leadt to the following conclusions:

- 1) All these methods are not suited for exact determination of chemical structure.
- 2) It is only possible to show differences when the material is isolated in the same way by a conventional method. Preparations of humic acids for instance, isolated from the same soil but with different methods show differences, which are nearly so large as isolations from different soils.
- 3) Only some bands of infrared spectra can be assigned to special groups in the molecules of humic acids.
- 4) The differences in absorption in ultraviolet and visible range are large enough to determine characteristics of humic systems by statistical methods, which can be used for their classification.

A preposition is the isolation by well defined method, which must be used in every case. The needed number for statistical methods requires complete automatized procedures at least of spectroscopy and the evaluation of the measured data.

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