

# Characterization of humic and fulvic acids from Gorleben groundwater

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**Summary.** The humic material extracted from one of the Gorleben groundwaters is separated into humic and fulvic acids, and characterized, together with a commercial humic acid from Aldrich Co., for their chemical composition, size distribution, proton exchange capacity and spectroscopic characteristics. The results are compared with one another and with the literature data of other humic acids. The humic acid is fractionated by gel permeation chromatography into different size groups and the fractions are subjected to IR and <sup>1</sup>H-NMR spectroscopy. The high molecular weight fractions (>70000 Dalton) are poor in carboxylic groups, whereas the major fractions (approx. 10000 Dalton) contain organic acids of large molecular entities.

## 1 Introduction

The importance of complexation of radionuclides with natural organics is widely recognized [1–3], particularly, for the migration of heavy metal radionuclides of higher oxidation states ( $Z \geq 2+$ ) in natural aquifer systems. Among a wide variety of natural organics the preponderant species in groundwater are humic and fulvic acids, both of which are polyelectrolytes with a high complexation affinity [1–4]. These two acids are structurally similar but different in molecular weight and functional group content [5–9]. In groundwater, soluble humic substances, including humic and fulvic acids, are already complexed with metal ions of water constituents, e. g.  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ , REE-ions etc. and present as a humic colloid [10, 11]. This colloid behaves like a soluble ion exchanger and hence creates pseudocolloids of actinide ions [11]. Humic substances may thus cause an enhancement of migration or retention of some radionuclides depending on the filtration and sorption properties of aquifer systems concerned. For the quantification of each of these processes, a basic knowledge of the nature of humic acids and their complexation behaviour is indispensable.

This paper concentrates on the characterization of humic and fulvic acids from one of the groundwaters from the future repository site of nuclear waste in Gorleben, FRG. For the purpose of comparison, the easily available humic acid from Aldrich Co. is also investigated in parallel. Ana-

lytical data of humic substances provide an insight into their complexation behaviour with naturally occurring metal ions in groundwater. Such knowledge is useful for a better understanding of the humate complexation of radionuclides in a given groundwater. The assessment of the migration behaviour of radionuclides requires two important primary parameters, i. e. complexation constant and molecular size distribution. The evaluation of complexation constants requires knowledge of the chemical nature of proton exchanging groups and their exchange capacities. Therefore, a special emphasis is given to the determination of these parameters for the given humic and fulvic acids.

## 2 Experimental

The humic acid from the Gorleben groundwater, specified as Gohy-573, is isolated by precipitation after acidification with HCl to pH1. The fulvic acid remaining in the supernatant is separated by sorption on the XAD-8 resin. The Aldrich humic acid is originally the Na-salt form as available from Aldrich Co. The Gorleben humic acid thus isolated and Aldrich humic acid in its original form are dissolved in 0.1 mol/l NaOH with addition of 0.2 g NaF/g HA and left over night. The  $\text{F}^-$  ion is introduced to dissolve silicate impurities. After duplicate purification cycles, i. e. precipitation (pH 1), dissolution (0.1 mol/l NaOH) and precipitation, the humic acid precipitates are washed with 0.1 mol/l HCl until no  $\text{Na}^+$  ion is detected in the supernatant. The Gorleben fulvic acid is eluted from the XAD-8 resin with 0.1 mol/l NaOH and, after addition of NaF, left over night. After acidification to pH1 the fulvic acid is again sorbed on XAD-8, the column is washed with 0.1 mol/l HCl, the fulvic acid is then eluted with 0.1 mol/l NaOH and protonated by passing it through a cation-exchange column of Dowex 50X8 ( $\text{H}^+$ ). Finally the protonated products are freeze-dried. A precise description of the procedure is given elsewhere [12]. Humic acid is methylated with diazomethane according to the procedure known in literature [8]. Due to the hygroscopic properties of humic and fulvic acids [12], the samples are stored in a desiccator under vacuum. Experimentation on the proton exchange capacity is conducted in an inert gas box ( $\text{Ar}$ ,  $\text{O}_2 < 4$  ppb) with water and chemicals free from  $\text{O}_2$  and  $\text{CO}_2$  to prevent interferences due to oxidation by  $\text{O}_2$  and acidification by  $\text{CO}_2$  uptake [12].

**Table 1.** Elemental compositions of humic and fulvic acids normalized to 100% of organic components and the difference between total weight and the sum of the listed elements (Rest)

Element	Aldrich-HA	Gohy-573-		Lit. values [8]	
		HA	FA	HA	FA
C	55.23 ± 0.28	56.25 ± 0.28	57.18 ± 0.17	50–60	40–50
H	4.48 ± 0.02	4.52 ± 0.02	4.85 ± 0.01	4–6	4–6
N	0.32 ± 0.01	1.69 ± 0.01	1.14 ± 0.01	2–6	1–3
O	37.64 ± 0.19	35.80 ± 0.18	35.38 ± 0.11	30–35	44–50
S	2.33 ± 0.01	1.73 ± 0.01	1.44 ± 0.01	0–2	0–2
Rest	(3.35)	(0.82)	(~0)		

**Table 2.** H/C and O/C ratios of aquatic humic and fulvic acids

	Aldrich-HA	Gohy-573-		Lit. values [13]	
		HA	FA	HA	FA
H/C	0.97 ± 0.01	0.98 ± 0.01	1.02 ± 0.01	0.94 ± 0.12	1.02 ± 0.16
O/C	0.51 ± 0.01	0.48 ± 0.01	0.46 ± 0.01	0.50 ± 0.03	0.51 ± 0.10

### 3 Results and discussion

#### 3.1 Elemental composition

The elemental compositions (C, H, N, O and S) of the three humic substances normalized to 100 wt% are given in Table 1. The humic substances under investigation are named as Gohy-573-HA and Gohy-573-FA for the Gorleben humic acid and fulvic acid, respectively, and Aldrich-HA for the humic acid from Aldrich Co. In the bottom of Table 1, the difference between the total weight and the sum of each elemental weight is given as the rest, which represents the sum of all impurities. Whereas the rest weights for the two humic acids are 3.25 and 0.82%, the fulvic acid shows no measurable rest. The ranges of elemental composition known in literature [8] for humic and fulvic acids of different origins are given for comparison. The two humic acids under discussion (Gohy-573-HA and Aldrich-HA) show comparable elemental compositions for C, H and O, whereas the nitrogen and sulfur contents differ somewhat from one another. As a whole, the elemental compositions of Gohy-573-HA and Aldrich-HA are found to be within the literature ranges of each element. The elemental composition of Gohy-573-FA is close to that of Gohy-573-HA, but differs considerably from the literature values of fulvic acids, especially the C and O contents. The similarity between the Gorleben humic and fulvic acids in contrast to the different ranges of the elemental composition known in literature [8] may be explained by their origin. The literature values in Table 1 refer to humic and fulvic acids of various sources, humic acids being often extracted from hydrophobic materials (peat, coal, etc.) and fulvic acids from the aquatic phase. This is reflected by the higher oxygen and lower carbon contents of fulvic acids. However, the humic and fulvic acids from Gorleben are extracted from the same aquatic phase.

The O/C and H/C ratios can be useful to indicate the presence of various structures [13]. The H/C ratio approaching unity implies that the chemical structure predominantly consists of aromatic bodies containing carboxyl and quinone groups. Aliphatic structures including primary amino groups increase the H/C ratio to greater than unity. The O/C ratio reflects the carbohydrate content: the larger

the ratio, the higher the amount of carbohydrate that might be involved. The atomic ratios of H/C and O/C for the investigated humic and fulvic acids together with the data for aquatic humic and fulvic acids in literature [13] are shown in Table 2. The H/C as well as O/C ratios of Aldrich-HA, Gohy-573-HA and Gohy-573-FA are nearly identical to the literature data for aquatic humic and fulvic acids.

#### 3.2 Inorganic impurities

The major inorganic impurities as well as a number of trace elements determined in the purified humic and fulvic acids under investigation are given in Table 3. Impurity concentrations of the unpurified Aldrich-HA are also given in this table in order to demonstrate the effectiveness of the purification procedure applied in this experiment. The comparison of each elemental concentration in Aldrich-HA before and after purification illustrates that the major elements are substantially reduced in their concentration to less than 3% and the trace impurities, except Th, to 10–40% of the original concentrations. The lower extent of concentration reduction of trace elements, which are present as higher oxidation states in solution ( $Z \geq 3+$ ), infers their strong complexation affinity towards humic acid. The inorganic metal impurities remained in the purified humic and fulvic acids are very small compared with the known proton exchange capacities of each humic or fulvic acid, i.e. less than 1% for Gohy-573-HA and Aldrich-HA and less than 2% for Gohy-573-FA. Such amounts of remained impurities will not affect the complexation study of metal ions with the humic and fulvic acids.

#### 3.3 Spectroscopic characteristics

Various spectroscopic methods provide segmentary information on the structure of humic and fulvic acids but do not allow identification of their total structure [14]. The UV spectrum of humic acid shows an absorption continuum without recognizable peaks, increasing with decreasing wavelength. The E4/E6 value widely used to characterize humic acid is the ratio of absorption intensities at 465 and

**Table 3.** Inorganic impurities of humic and fulvic acids (in  $\mu\text{g/g}$ )

Element	Aldrich-HA (unpurified)	Aldrich-HA	Gohy-573-HA	Gohy-573-FA
Major impurities:				
Al	2950 $\pm$ 60	(35)	39.3 $\pm$ 8.3	—
Ca	9931 $\pm$ 89	31.7 $\pm$ 6.7	22.6 $\pm$ 5.6	437 $\pm$ 5
Cr	15.2 $\pm$ 0.1	12.1 $\pm$ 0.1	106 $\pm$ 1.4	—
Fe	12207 $\pm$ 651	360 $\pm$ 13	277 $\pm$ 6	52.9 $\pm$ 1.8
Mg	698 $\pm$ 25	5.6 $\pm$ 2.0	4.0 $\pm$ 1.0	44 $\pm$ 5
Na	75116 $\pm$ 140	270 $\pm$ 2	19.0 $\pm$ 0.1	2196 $\pm$ 200
Si	3333 $\pm$ 185	15 $\pm$ 8	68 $\pm$ 19	1196 $\pm$ 69
Trace impurities:				
Ce	23.0 $\pm$ 0.2	4.1 $\pm$ 0.3	1.1 $\pm$ 0.2	0.1
Co	2.5 $\pm$ 0.1	0.33 $\pm$ 0.01	2.5 $\pm$ 0.1	0.24 $\pm$ 0.01
Eu	0.66 $\pm$ 0.02	0.24 $\pm$ 0.01	0.05 $\pm$ 0.001	0.01 $\pm$ 0.01
Hf	0.38 $\pm$ 0.01	0.06 $\pm$ 0.01	1.53 $\pm$ 0.01	0.85 $\pm$ 0.01
La	8.8 $\pm$ 0.1	0.90 $\pm$ 0.01	0.39 $\pm$ 0.01	—
Nd	11.5 $\pm$ 0.3	4.1 $\pm$ 0.1	0.69 $\pm$ 0.01	—
Sm	2.3 $\pm$ 0.1	0.98 $\pm$ 0.03	0.13 $\pm$ 0.01	—
Tb	0.26 $\pm$ 0.01	0.060 $\pm$ 0.001	0.05 $\pm$ 0.002	—
Th	2.0 $\pm$ 0.1	1.53 $\pm$ 0.01	7.4 $\pm$ 0.1	0.23 $\pm$ 0.01
U	0.65 $\pm$ 0.01	0.23 $\pm$ 0.01	2.2 $\pm$ 0.1	—
Yb	0.49 $\pm$ 0.01	0.10 $\pm$ 0.01	0.50 $\pm$ 0.02	—
Zr	21 $\pm$ 2	4.6 $\pm$ 0.1	119 $\pm$ 3	97.47 $\pm$ 1.7

665 nm. However, its interpretation is not straightforward. The E4/E6 ratio is supposed to decrease with increasing humification [15] or increasing condensation of aromatic humic constituents [16]. On the other hand, the E4/E6 ratio is governed by the molecular size, which is again dependent on pH [17]. Therefore, its relation to the relative concentration of condensed rings is difficult to confirm. Due to the complex nature of humic acid, UV spectroscopy is of limited use for its characterization. The experimental data for the humic and fulvic acids are given as follows:

Aldrich-HA	E4/E6	= 8.6 $\pm$ 0.3
Gohy-573-HA	E4/E6	= 6.3 $\pm$ 0.3
Gohy-573-FA	E4/E6	= 7.1 $\pm$ 0.6

The relative differences between these data are biased by either molecular composition or size and cannot be correlated to the elemental compositions shown in Tables 1 and 2.

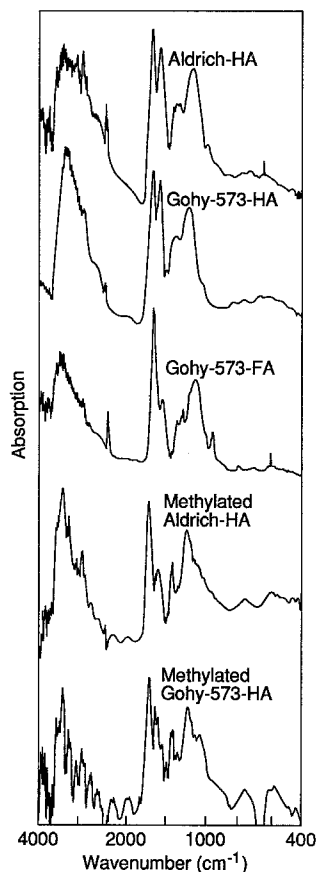
IR and  $^{13}\text{C}$ -NMR spectroscopy allow identification of various functional groups and provide information on differences among humic acids of different origins as well as changes introduced by chemical modification (e.g. methylation).

In Fig. 1, IR spectra of the investigated humic and fulvic acids as well as their methylated samples are shown. According to the literature database [4, 8, 18, 19], the identification of the observed peaks can be realized by the following qualitative information:

— 3450  $\text{cm}^{-1}$  region: In this region OH-stretching occurs from numerous sources, including water.

— 3150  $\text{cm}^{-1}$  region: OH-stretching from hydrogen bonds especially in carboxylic acids. Upon methylation the absorption in this region decreases substantially.

— 2900 and 1450  $\text{cm}^{-1}$  bands: These bands are attributed to aliphatic C—H bonds. The 2900  $\text{cm}^{-1}$  band is situated on the shoulder of the broad band from OH-stretching. Upon methylation the band at 1450  $\text{cm}^{-1}$  becomes clearly pronounced.



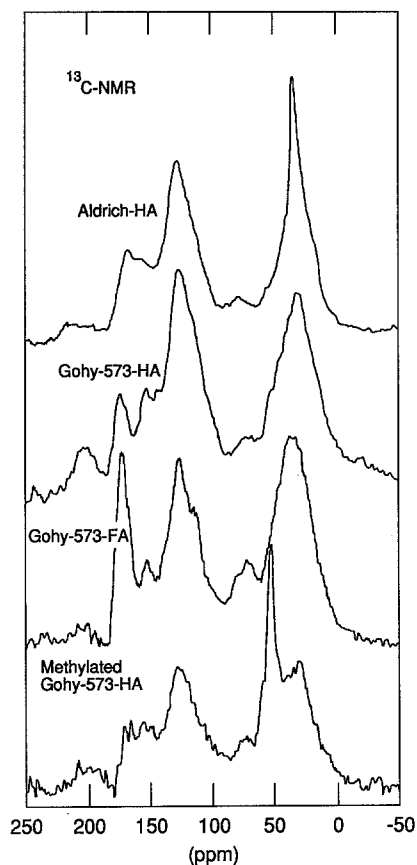
**Fig. 1.** IR spectra of humic and fulvic acids as well as methylated samples of the humic acids

— 1680–1750  $\text{cm}^{-1}$  region: This region is generally attributed to C=O stretching vibrations, mainly due to carboxylic groups. In the protonated samples the maximum appears at 1680–1725  $\text{cm}^{-1}$ . Upon methylation the

**Table 4.** Relative  $^{13}\text{C}$ -NMR peak areas (in percent) of various groups in the humic acids

Sample	Aliphatic 0–50 ppm	Ether, alcohol, carbo- hydrate, amine 50–96 ppm	Aromatic, olefin 108–165 ppm	Carboxylate, carbonyl 165–190 ppm
Aldrich-HA	41	5	40	14
Gohy-573-HA	38	8	41	13
Gohy-573-FA	48	13	23	16
Methylated Gohy-573-HA	50 (37)	8 (10)	31 (39)	11 (14)

( ): Values corrected for methyl groups added by methylation: These values are to be compared with those of non-methylated Gohy-573-HA



**Fig. 2.**  $^{13}\text{C}$ -NMR spectra of humic and fulvic acids as well as the methylated form of the Gorleben humic acid

carboxylic groups are transformed to ester groups and the maximum is shifted to  $1730\text{--}1750\text{ cm}^{-1}$ .

–  $1600\text{--}1650\text{ cm}^{-1}$  region: Among others  $\text{C}=\text{C}$  bonds conjugated with  $\text{C}=\text{O}$  and  $\text{COO}^{-1}$  groups appear in this region. Fulvic acids show a reduced absorption at this region compared with humic acid. Upon methylation the intensity of this band decreases.

–  $1220\text{ cm}^{-1}$  region: This band is attributed to  $\text{C}-\text{O}$  stretching vibrations and  $\text{OH}$  bending deformations mainly due to carboxylic groups. Upon methylation the band becomes narrower and various absorptions become better distinguished on the shoulder towards lower wavenumbers.

Solid state  $^{13}\text{C}$ -NMR has been carried out in cooperation with Florida State University (G. R. Choppin) for all three

samples including the methylated form of Gohy-573-HA. In Fig. 2, the  $^{13}\text{C}$ -NMR spectra are shown and the relative peak areas of regions attributed to different functional groups [20] are listed in Table 4. As shown for the elemental composition (cf. Table 1),  $^{13}\text{C}$ -NMR of the two humic acids, Gohy-573-HA and Aldrich-HA, show very similar results. Upon methylation a sharp peak (at 55 ppm) appears in the region of aliphatic groups and the relative peak area of aliphatic structures increases from 38 to 50%, while the peak area for aromatic and olefin groups decreases from 41 to 31%. If this sharp peak at 55 ppm from methyl groups is subtracted, the spectrum of the methylated sample becomes equal to the spectrum of the original form. Therefore, it can be concluded that methylation introduces methyl groups but does not lead to major changes in the gross structure of humic acid.

Information attained by IR and  $^{13}\text{C}$ -NMR spectroscopy is at best qualitative. However, it allows to identify structural dissimilarities of the humic substances. Structurally Gohy-573-HA appears to be almost the same as Aldrich-HA, while Gohy-573-FA differs from either of the two humic acids. In the elemental compositions shown in Table 1 such a distinction is not observed.

### 3.4 Exchange capacity

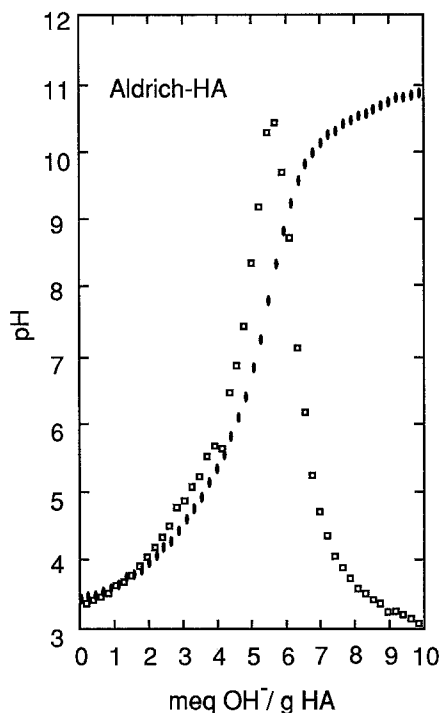
Of various functional groups associated with humic acids [7, 8] the most important ones for the complexation behaviour are carboxyl and phenol groups. The total proton exchange capacity is measured by the Baryta adsorption method [8], which allows the humic acid to react with excess  $\text{Ba}(\text{OH})_2$ , followed by titration of unused base with standard acid. The carboxyl group capacity is determined by the Ca-acetate exchange method where Ca exchanges in acetate medium [8]. The phenol group capacity (or acidic OH) is obtained from the difference between the total and the carboxyl group capacities. The results are shown in Table 5. The carboxyl group capacities of Gohy-573-HA and Aldrich-HA are very similar, whereas the total exchange capacity of Aldrich-HA is somewhat higher than that of Gohy-573-HA and consequently the phenol group capacities differ to the same extent.

By direct titration better information can be obtained for the proton exchange behaviour. Humic acid is dissolved in excess base (NaOH), back titrated with acid ( $\text{HClO}_4$ ) followed by forward titration with NaOH. With a humic acid concentration of 0.2 g/l in 0.1 mol/l  $\text{NaClO}_4$  at  $T = 20^\circ\text{C}$ , the back and forward titrations give nearly identical results. In Fig. 3 a typical example of a back titration is

**Table 5.** Proton exchange capacities of total, carboxyl and phenol groups as well as by direct titration (meq/g)

	Proton exchange capacity (meq/g)			
	Total (Ba(OH) <sub>2</sub> exchange)	Carboxyl groups (Ca-acetate exchange)	Phenol groups (Difference between total and carboxyl)	Direct titration
Aldrich-HA	7.06 ± 0.67	4.80 ± 0.21	2.26 ± 0.72	5.43 ± 0.16
Gohy-573-HA	6.61 ± 0.27	4.75 ± 0.29	1.86 ± 0.40	5.38 ± 0.20
Gohy-573-FA	n. m.	n. m.	n. m.	5.70 ± 0.09

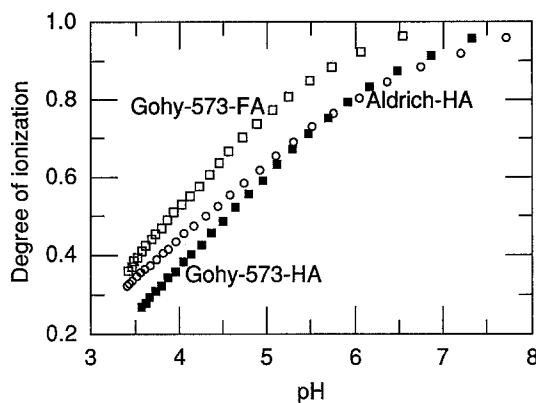
n. m.: not measured

**Fig. 3.** Titration curve as well as first derivative of the titration curve (dpH/dnOH<sup>-</sup>) of Aldrich humic acid: [HA] = 0.2 g/l, I = 0.1 (NaClO<sub>4</sub>) and T = 20°C

shown, plotting pH against the net amount of base added per gram humic acid. The acid capacity is determined by the amount of base added [21,22] up to neutralization. To evaluate the maximum slope, the derivative of the titration curve is produced as given in Fig. 3. The maximum slope of the titration curve appears at pH 7–8 which shows that the functional groups measured by direct titration are dissociated to the maximum at near neutral pH.

The proton exchange capacities determined by direct pH titration are also given in Table 5. The values of Gohy-573-HA and Aldrich-HA are nearly the same, whereas Gohy-573-FA shows a slightly higher value.

For better understanding of the complexation behaviour of humic acids, the variation of the degree of ionization of proton exchanging groups as a function of pH is useful. Such a variation is determined by the following procedure. Starting at the maximum slope of the titration curve, where the proton exchanging groups are ionized, with gradual addition of acid, the amount of undissociated functional groups is determined by the difference between the amount of pro-

**Fig. 4.** Degree of ionization of humic and fulvic acids as a function of pH by direct titration: humic/fulvic acid concentration = 0.2 g/l, I = 0.1 (NaClO<sub>4</sub>) and T = 20°C

tons added and free protons determined by pH-measurement. In Fig. 4 the degree of ionization is plotted against pH for the three humic substances. The last points to the left in Fig. 4 represent the degree of ionization where no strong base or acid is added. Here 30 ± 5% of the proton exchanging groups are ionized. The Gorleben fulvic acid appears somewhat more acidic than the Gorleben humic acid, whereas the acidity of the Gorleben humic acid does not differ much from that of the Aldrich humic acid, at least at pH > 5.

### 3.5 Size distribution

The size distribution of humic acids can be determined by a number of physical fractionation methods, such as Gel Permeation Chromatography (GPC), ultrafiltration, ultracentrifugation etc. [23]. Since humic acid is a polyelectrolyte, its molecular volume in aquatic solution varies with pH and ionic strength. The GPC method is used in the present experiment. A column with the gel Sephadex 100–120 was calibrated with globular proteins, which show a linear relationship between their molecular weight and hydrodynamic size [24]. Such a relationship is demonstrated in Fig. 5. The calibration is done with Dextrane blue for the exclusion volume of the column, globular proteins for the working range and benzyl alcohol for the total volume. The resulting calibration curve is shown in Fig. 6, in which the equivalent molecular size (Dalton) and hydrodynamic diameter (nm) are given as a function of the elution volume. The elution profiles of Gohy-573-HA, Aldrich-HA and Gohy-

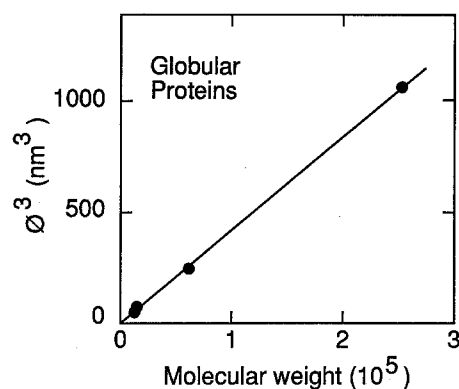


Fig. 5. Hydrodynamic diameter of globular proteins as a function of their molecular weight (from [24])

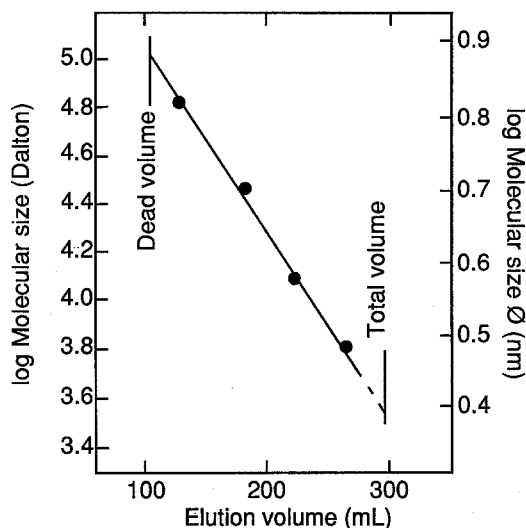


Fig. 6. Calibration curve of GPC column with the gel Sephadex 100–120 with the molecular size in Dalton (*left*) and hydrodynamic diameter (*right*) as a function of the elution volume. Calibration was done with Dextrane blue ( $2 \times 10^6$  Mwt) for the dead volume and benzyl alcohol (108 Mwt) for the total volume. The working range of the column was calibrated with globular proteins: albumin (66000 Mwt), carbonic anhydrase (24000 Mwt), cytochrome C (12400 Mwt) and aprotinin (6500 Mwt)

573-FA in 0.1 mol/l  $\text{NaClO}_4$  at pH 9.2 with  $10^{-3}$  mol/l borate buffer are shown in Fig. 7. The elution curves of the two humic acids show similar features with approximately 4% of Aldrich-HA and 2% of Gohy-573-HA on the exclusion limit of the column ( $\geq 100000$  Dalton). The rest is eluted over a broad range from approximately 70000 Dalton down to very low numbers. As this broad elution peak is relatively symmetric, its maximum represents a logarithmic average of the size distribution. The Gorleben fulvic acid shows an elution profile different from the two humic acids. The size distribution is relatively narrow and the elution peak on the exclusion limit of the column found for the humic acids is missing. The size distribution of the samples in hydrodynamic diameter (nm) as well as Dalton are summarized as:

Aldrich-HA            4.1%:  $\geq 7.4$  nm or  $\geq 100000$  Dalton  
                           95.9%: distribution maximum at  
                           3.25 nm or 8000 Dalton

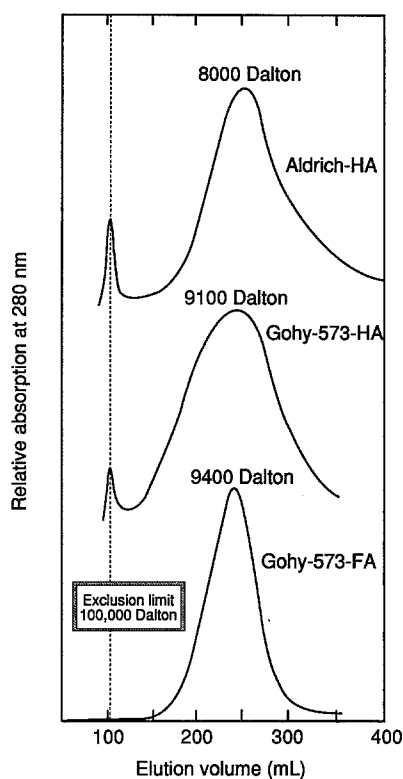


Fig. 7. GPC elution profiles of Aldrich and Gorleben humic acids as well as Gorleben fulvic acid at pH 9.2 ( $10^{-3}$  mol/l borate buffer) with  $I = 0.1$  ( $\text{NaClO}_4$ )

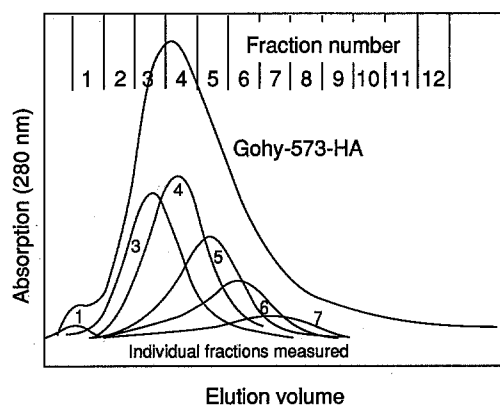


Fig. 8. Fractionation of Gorleben humic acid by GPC and elution profiles by remeasurement of individual fractions

Gohy-573-HA            1.6%:  $\geq 7.4$  nm or  $\geq 100000$  Dalton  
                           98.4%: distribution maximum at  
                           3.39 nm or 9100 Dalton  
 Gohy-573-FA            100%: distribution maximum at  
                           3.43 nm or 9400 Dalton

### 3.6 Characterization of size fractions

Various size fractions of Gohy-573-HA and Gohy-573-FA are isolated by GPC and characterized by IR and  $^1\text{H-NMR}$  spectroscopy. The elution of Gohy-573-HA is collected in 12 size fractions as shown in Fig. 8. The recycling of the

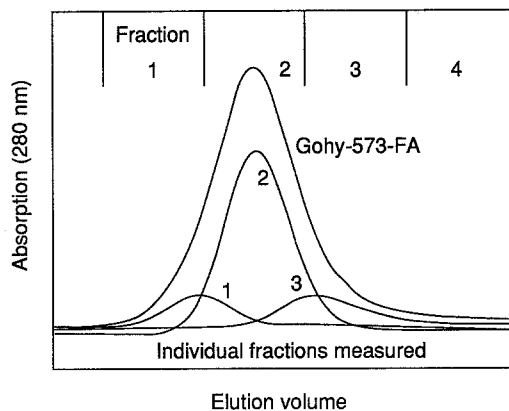


Fig. 9. Fractionation of Gorleben fulvic acid by GPC and elution profiles by remeasurement of individual fractions

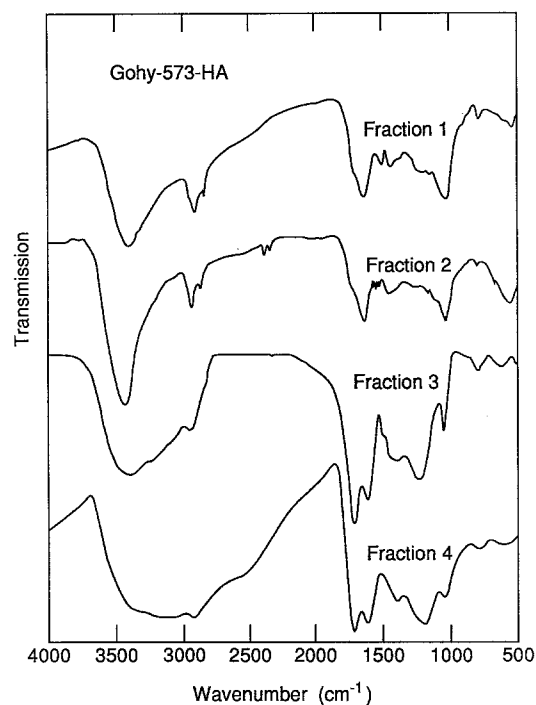


Fig. 10. IR spectra of individual fractions from Gorleben humic acid (cf. Fig. 8)

individual size fractions demonstrates that the maximum elution peak of each fraction reappears at the same elution position as previously collected. The fulvic acid fractionation is shown in Fig. 9. IR and  $^1\text{H-NMR}$  of selected humic acid fractions are shown in Figs. 10 and 11.

The IR spectra of the Gohy-573-HA fractions containing molecules of larger size (fractions 1 and 2) differ considerably from those of the main fractions (fractions 3 and 4) with molecules of smaller size and larger concentrations. The two bands from carboxylic groups at  $1220\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$  are missing. Also the OH-stretching from carboxylic groups at  $3150\text{ cm}^{-1}$  disappears and hence the band of aliphatic groups around  $2900\text{ cm}^{-1}$  becomes more distinguished. Based on the IR spectra in Fig. 10, it may be concluded that the fractions of larger molecular size contain a relatively low amount of carboxyl groups compared to those of smaller

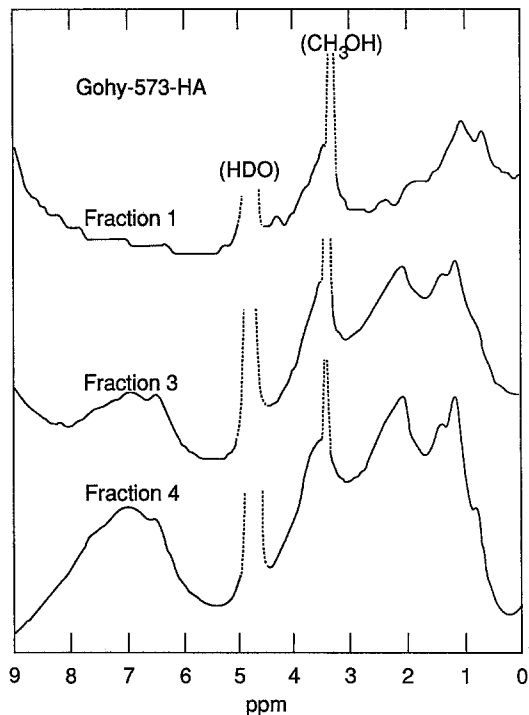


Fig. 11.  $^1\text{H-NMR}$  spectra of individual fractions from Gorleben humic acid (cf. Fig. 8)

molecular size. The  $^1\text{H-NMR}$  spectra of fraction 1, 3 and 4 of the Gorleben humic acid as shown in Fig. 11 are smeared out and interpretation of specific structures is, as discussed in literature [25], very difficult. Between approximately 0.5 and 2.5 ppm aliphatic structures appear, 2–4 ppm alcohols, 5–7 ppm phenol groups and 6–8 ppm aromatic structures [19]. In the main fractions (3 and 4), various peaks are found, some of which, however, are missing in fraction 1 (large molecules). Similar to the observation made in the IR spectra (Fig. 10), the  $^1\text{H-NMR}$  spectra also illustrate the structural differences between fraction 1 and fractions 3 and 4 of Gohy-573-HA.

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