

# THE COPPER COMPLEXING PROPERTIES OF MELANOIDINS AND MARINE HUMIC MATERIAL

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## Abstract

Melanoidins, condensation products of sugar and amino acids may represent a key link in the transformation of polysaccharides to humic material in marine environment. Melanoidins prepared using a condensation time longer than two days exhibit complexation properties towards copper ions that appear to depend on the basicity of the amino acid precursor. Melanoidins of molecular mass <10000 and >10000 exhibit similar complexing properties. The copper complexing properties of humic material isolated from marine lagoon sediments were determined for a comparison.

*Key words: electrochemistry, organic matter, metals*

## Introduction

Recently, melanoidins, sugar- amino acid condensation products, have gained attention due to their chemical similarities to natural humic substances. Although humic substances are often thought to be formed from lignin polymers, in marine environments carbohydrates are more abundant and are thus more likely precursors of humic acids (1). Although, melanoidins are commonly prepared in laboratories by prolonged heating (1), they also may be formed under natural environmental conditions in soil as well as in sea water. For example, melanoidins have been identified in archeological plant remains from excavations in Egypt and thus must have been produced by reactions that occurred in buried organic matter (2). In the present work we examined and correlated the copper complexing capacity values of twelve differently prepared melanoidins and two humic acids (HA).

## Experimental

Voltammetric measurements were performed on  $\mu$  - Autolab (ECONCHEMIE), connected to a Metrohm VA 663 stand. Complexing capacity was determined as described in detail previously (3, 4, 5). Fulvic acid (FA) was isolated from Cannel lagoon sediments (France) at the University of Perpignan (6)(Table1). Aldrich HA is a commercially available, well characterized humic material (Table1). Melanoidins were prepared at SUNY (USA) from glucose and amino acids (glutamic acid, lysine or valine) which were added in 1:1 ratio and heated at 100°C for 2, 4, 16 or 32 days. The products of the reactions were soluble in water and were separated into two fractions: 1) molecular mass <10000 Da, and 2) molecular mass >10000 Da. For lysine and valine, only a 16-d reaction time with glucose was used. Thus 12 different melanoidins were obtained (Table 2). The copper complexing capacity was determined for 10 mg/L solutions of each melanoidin, FA or HA in 0.55mol/L NaCl at pH 6 and pH 8.5.

Table 1. The elemental composition of humic acids and melanoidins (1)

	C	H	N	O	S	Acidity (meq./g)	Mol. mass distr. (Da)
FA (Canet)	38.7	5.38	2.25	51.64	1.97	5.82	>1000-20 000
HA (Aldrich)	50.17	5.43	0.88	41.00	3.26	-	1000-5000
glu-glu (7 days)	46.0	3.6	3.5	46.9	-	5.3	not determined
glu-val (7 days)	53.3	3.7	3.8	39.2	-	3.4	not determined
glu-lys (7 days)	54.4	7.4	8.0	30.2	-	1.3	not determined

## Results and Discussion

The complexing capacity of the investigated melanoidins, HA and FA are presented in Table 2. Among the melanoidins higher complexing capacity values for copper ions are obtained for glu-lys, followed by glu-val and the lowest values are for glu-glu. Lysine contains more amino groups than glutamic acid or valine (1); basic amino acids (i.e., those containing more amino groups than carboxylic groups) preferentially condense with sugars to form nitrogen-rich polymers (1). These polymers are good complexing agents for copper ions. Glu-glu 1 and glu-glu 5 show no complexing capacity towards copper ions regardless of their large molecular masses, which shows that two days of heating is not enough to form structures capable of binding copper ions.

The complexing capacity for glu-glu 7 was determined at both pH 6 (shown in Table 2) and at pH 8.5. The complexing capacity at pH 8.5 is much higher with:  $L_T = 2.65 \times 10^{-7}$  mol/L and  $K_{app} = 9.8 \times 10^7$  L/mol. This higher value is obtained at pH 8.5 because additional binding sites for copper ions are available as more groups are dissociated. There was no difference in complexing capacity between melanoidins with molecular masses <10000 Da and >10000 Da (Table 2). FA iso-

lated from lagoon sediments has a complexing capacity in the same range as melanoidins while HA isolated from soil (containing more lignin type residues) has a complexing capacity four times higher than the highest one for melanoidins.

Table 2. The composition, molecular mass, time of reaction, complexing capacity and apparent stability constant determined at pH=6

Melanoidins; HA; FA [10 mg/L]	Reaction time (days)	Mol. mass (Da)	$L_T$ (mol Cu <sup>2+</sup> /L)	$K_{ML}$ (L/mol Cu <sup>2+</sup> )
glu-glu 1	2	<10 000	not detected	not detected
glu-glu 2	4	<10 000	$4.83 \diamond 10^{-8}$	$1.4 \diamond 10^7$
glu-glu 3	16	<10 000	$4.56 \diamond 10^{-8}$	$2.4 \diamond 10^8$
glu-glu 4	32	<10 000	$7.43 \diamond 10^{-8}$	$7.2 \diamond 10^7$
glu-glu 5	2	>10 000	not detected	not detected
glu-glu 6	4	>10 000	$2.03 \diamond 10^{-8}$	not determined
glu-glu 7	16	>10 000	$8.01 \diamond 10^{-8}$	$5.8 \diamond 10^7$
glu-glu 8	32	>10 000	$6.86 \diamond 10^{-8}$	not determined
glu-val 9	16	<10 000	$1.42 \diamond 10^{-7}$	$3.3 \diamond 10^7$
glu-val 10	16	>10 000	$1.98 \diamond 10^{-7}$	$4.6 \diamond 10^6$
glu-lys 11	16	<10 000	$9.92 \diamond 10^{-8}$	$7.6 \diamond 10^6$
glu-lys 12	16	>10 000	$2.14 \diamond 10^{-7}$	$1.4 \diamond 10^7$
FA	-	>1000-20000	$8.68 \diamond 10^{-8}$	$5.8 \diamond 10^7$
HA	-	1000-5000	$9.7 \diamond 10^{-7}$	$2.9 \diamond 10^6$

- glu = glucose; glu = glutamic acid; val = valine; lys = lysine

## Conclusion

Melanoidins complex copper ions, and the similarity in complexing properties with FA isolated from marine lagoon sediments is obvious. The extent of complexation depends on basicity of the amino acids used to make the melanoidin. A reaction time of two days was not enough to form structures capable of complexing copper ions. Complexing capacity values differed little between melanoidins with molecular mass <10000 Da and >10000 Da. As melanoidins have been found in nature (2), they may form under certain conditions (e.g., UV- light) and may represent a link in transformation of labile organic matter (polysaccharides, amino acids) into more recalcitrant humic material in seawater.

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