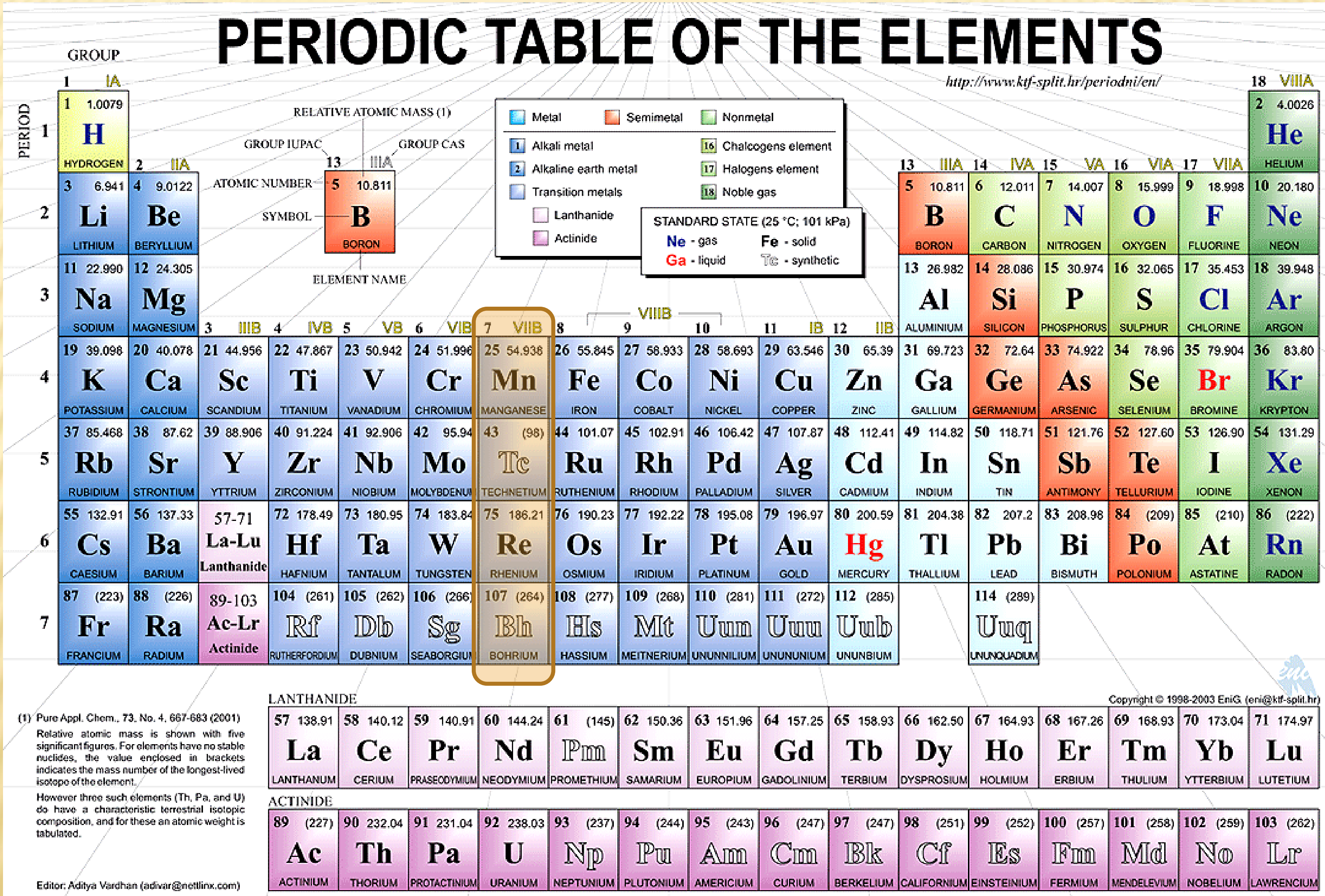
LECTURE 4

Chemical properties of elements from group VIIB

The plan of the lecture

1.Overall characteristic of d-elements from VIIB group
2.Natural resources
3.Physical and chemical properties
4.Compounds of manganese and their chemical properties
5.Biological role of manganese
6.The usage of $KMnO_4$ in pharmaceutical analysis


PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
Metal
Semimetal
Nonmetal
Alkali metal
Alkaline earth metal
Transition metals
Lanthanide
Actinide
Chalcogens element
Halogens element
Noble gas
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIIIB
10
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.007 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.974 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
19 39.098 K POTASSIUM
20 40.078 Ca CALCIUM
21 44.956 Sc SCANDIUM
22 47.867 Ti TITANIUM
23 50.942 V VANADIUM
24 51.996 Cr CHROMIUM
25 54.938 Mn MANGANESE
26 55.845 Fe IRON
27 58.933 Co COBALT
28 58.693 Ni NICKEL
29 63.546 Cu COPPER
30 65.39 Zn ZINC
31 69.723 Ga GALLIUM
32 72.64 Ge GERMANIUM
33 74.922 As ARSENIC
34 78.96 Se SELENIUM
35 79.904 Br BROMINE
36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
40 91.224 Zr ZIRCONIUM
41 92.906 Nb NIOBIUM
42 95.94 Mo MOLYBDENUM
43 (98) Tc TECHNETIUM
44 101.07 Ru RUTHENIUM
45 102.91 Rh RHODIUM
46 106.42 Pd PALLADIUM
47 107.87 Ag SILVER
48 112.41 Cd CADMIUM
49 114.82 In INDIUM
50 118.71 Sn TIN
51 121.76 Sb ANTIMONY
52 127.60 Te TELLURIUM
53 126.90 I IODINE
54 131.29 Xe XENON
55 132.91 Cs CAESIUM
56 137.33 Ba BARIUM
57-71 La-Lu Lanthanide
72 178.49 Hf HAFNIUM
73 180.95 Ta TANTALUM
74 183.84 W TUNGSTEN
75 186.21 Re RHENIUM
76 190.23 Os OSMIUM
77 192.22 Ir IRIDIUM
78 195.08 Pt PLATINUM
79 196.97 Au GOLD
80 200.59 Hg MERCURY
81 204.38 Tl THALLIUM
82 207.2 Pb LEAD
83 208.98 Bi BISMUTH
84 (209) Po POLONIUM
85 (210) At ASTATINE
86 (222) Rn RADON
87 (223) Fr FRANCIUM
88 (226) Ra RADIUM
89-103 Ac-Lr Actinide
104 (261) Rf RUTHERFORDIUM
105 (262) Db DUBNIUM
106 (266) Sg SEABORGIUM
107 (264) Bh BOHRIUM
108 (277) Hs HASSIUM
109 (268) Mt MEITNERIUM
110 (281) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
LANTHANIDE
57 138.91 La LANTHANUM
58 140.12 Ce CERIUM
59 140.91 Pr PRASEODYMIUM
60 144.24 Nd NEODYMIUM
61 (145) Pm PROMETHIUM
62 150.36 Sm SAMARIUM
63 151.96 Eu EUROPIUM
64 157.25 Gd GADOLINIUM
65 158.93 Tb TERBIUM
66 162.50 Dy DYSPROSIUM
67 164.93 Ho HOLMIUM
68 167.26 Er ERBIUM
69 168.93 Tm THULIUM
70 173.04 Yb YTTERBIUM
71 174.97 Lu LUTETIUM
ACTINIDE
89 (227) Ac ACTINIUM
90 232.04 Th THORIUM
91 231.04 Pa PROTACTINIUM
92 238.03 U URANIUM
93 (237) Np NEPTUNIUM
94 (244) Pu PLUTONIUM
95 (243) Am AMERICIUM
96 (247) Cm CURIUM
97 (247) Bk BERKELIUM
98 (251) Cf CALIFORNIUM
99 (252) Es EINSTEINIUM
100 (257) Fm FERMIUM
101 (258) Md MENDELEVIUM
102 (259) No NOBELIUM
103 (262) Lr LAWRENCIUM
(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
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The properties of elements from VIIB group

	Mn	Tc	Re
The content in the Earth crust (mass %)	$3.2 \cdot 10^{-2}$	traces	$8.5 \cdot 10^{-9}$
Electronic configuration	$[Ar]4s^2 3d^5$	$[Kr]5s^2 4d^5$	$[Xe]6s^2 5d^5$
Atomic radius, nm	0.127	0.136	0.137
Ionization energy, kJ/mol	717	702	756
Electronegativity	1.60	1.36	1.46
t of melting, ^0C	1245	≈2250	3190
Density, g/ml	7.44	11.5	21.0
Oxidation state in compounds	+2,+3,+4, +6, +7	+2,+4, +6, +7	+2,+3,+4, +6, +7

The elements from VIIB group: Mn, Tc, Re, Bh

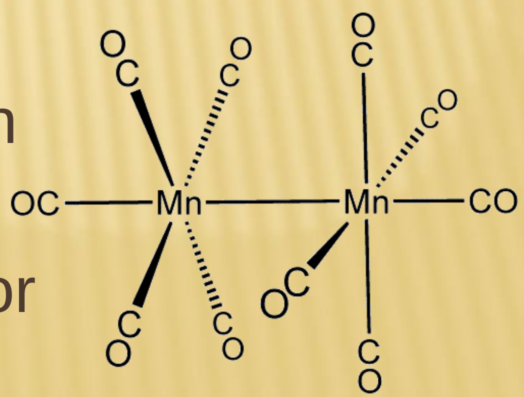
Mn is situated before H_2 in the electrochemical series of metals, while Tc and Re are situated after H_2.

In compounds Mn, Tc, Re demonstrate different oxidation states: 0, +2, +3, +4, +6, +7

Mn demonstartes 0 oxidation state in its carbonyl $Mn_2(CO)_{10}$.

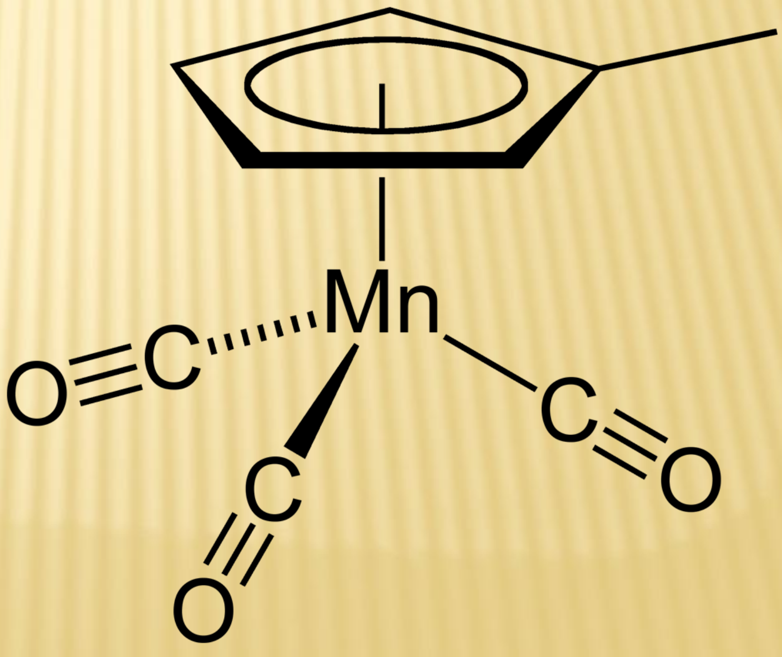
CARBONYLS

- The atom of a metal in carbonyl has an oxidation state of 0. There are mono-, di-, and polynucleic carbonyls. Bonds between two metal atoms are possible if an atom has an odd number of valence electrons.
- At high temperature and pressure carbon monoxide (CO) reacts with metals and their salts, and form carbonyls.
- Thermal decomposition of carbonyls is used for the coating of surfaces by a thin layer of a metal.
- Some carbonyls are used as catalysts for important chemical processes, such as



GASOLINE ADDITIVE

Manganese methylcyclopentadienyl tricarbonyl



The most stable oxidation state of manganese in salts is +2

Mn^{+2} ($MnSO_4$);

in oxides the most stable oxidation state is +4

Mn^{+4} (MnO_2).

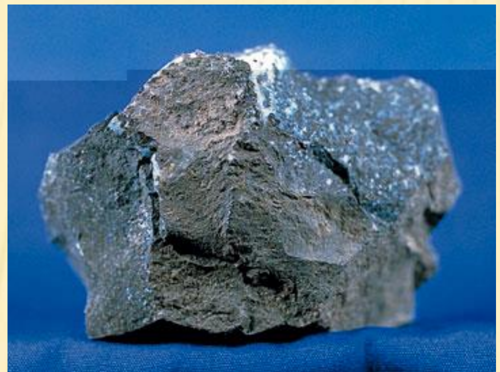
The most stable compounds of Tc and Re contain these elements in the oxidation state of +7.

The nature of the bonds of Mn, Tc, Re in compounds with other atoms depends on their oxidation state. Compounds with low oxidation state (+2) usually form ionic bonds; compounds with high oxidation state (+7) usually form covalent bonds (namely, with oxygen).

2. NATURAL RESOURCES

Just Mn and Re can be found in nature; Tc is the synthetic unstable element.

Pyrolusite MnO_2,



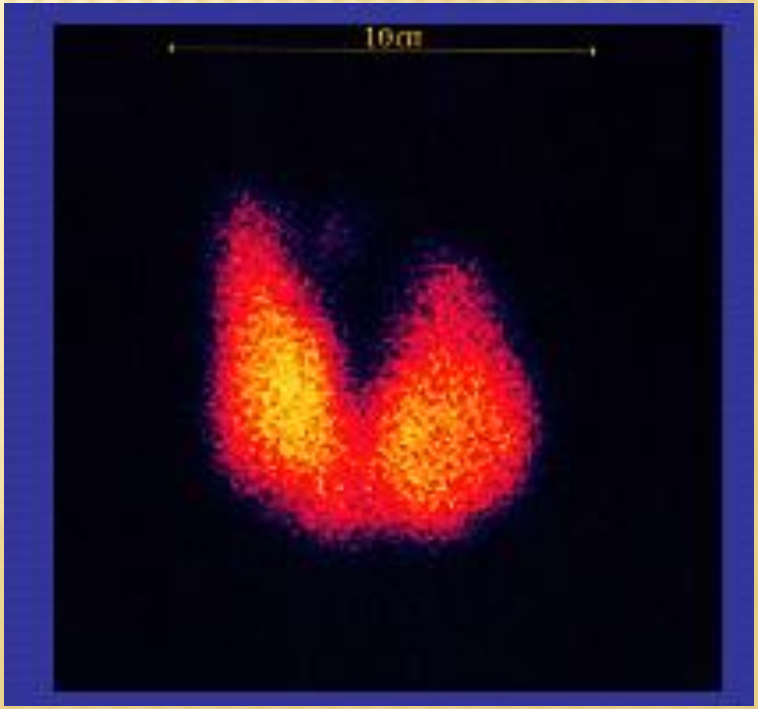
Rodochrosite $MnCO_3$

Iron-manganese concretions

Rhenium can be found in molibdenite as an impurity (up to 1,88% of Re).

TECHNECIUM – IS A SYNTHETIC ELEMENT

Technecium has no stable isotopes.
It is used in nuclear medicine as ^{99}Tc that is a metastable gamma-emmitter. The highest levels of technecium are accumulated in thyroid and stomach. This feature is used for diagnostics of thyroid tumors.



3. PHYSICAL AND CHEMICAL PROPERTIES OF MANGANESE

- **Manganese is silver-white, hard metal that is stable in the open air. Pure manganese is very plastic. At normal temperature it is inert, but at high temperature it reacts with the most nonmetals.**

$Mn + Cl_2 \xrightarrow{t} MnCl_2$

$Mn + F_2 \xrightarrow{t} MnF_2$ or $2Mn + 3F_2 \xrightarrow{t} 2MnF_3$

$3Mn + N_2 \xrightarrow{t} Mn_3N_2$ $3Mn + 2P \xrightarrow{t} Mn_3P_2$

$3Mn + C \xrightarrow{t} Mn_3C$ $Mn + S \rightarrow MnS$

$2Mn + O_2 \xrightarrow{t}$ ($2MnO$, and traces of Mn_2O_3, Mn_3O_4, MnO_2)

Manganese cannot react with hydrogen.

$Mn + H_2O \rightarrow MnO + H_2$

At room temperature Mn reacts slowly with H_2O; with the growth of temperature the rate of this reaction increases.

$Mn + 2HCl_{(dilute)} = MnCl_2 + H_2$

$Mn + H_2SO_{4\ (dilute)} = MnSO_4 + H_2$

Cold concentrated H_2SO_4 and HNO_3 cannot react with Mn, but at higher temperature they do react.

$3Mn + 8HNO_{3(conc.)} \longrightarrow 3Mn(NO_3)_2 + 2NO + 4H_2O$

$Mn + 2H_2SO_{4(conc.)} \longrightarrow MnSO_4 + SO_2 + 2H_2O$

Mn reduces ions of less active metals from water solutions of their salts

$Mn + CuSO_4 \rightarrow Cu + MnSO_4$

Complex compounds of Mn(II) are usually instable in water solutions.

$$MnCl_2 + 6NH_3 \leftrightarrow [Mn(NH_3)_6]Cl_2$$

Stable complexes exist for cyanides:

$$MnCl_2 + 2KCN \rightarrow Mn(CN)_2 + 2KCl$$

$$Mn(CN)_2 + 4KCN \rightarrow K_4[Mn(CN)_6]$$

4. COMPOUNDS OF MANGANESE. MANGANESE (II) COMPOUNDS

MANGANESE (II) OXIDE **– MnO is a green solid substance that is insolube in water. It demonstrates basic properties.**

$$MnO + 2HCl \rightarrow MnCl_2 + H_2O$$

MANGANESE (II) HYDROXIDE **– $Mn(OH)_2$ (white)**

On the open air:

$$4Mn(OH)_2 + O_2 \rightarrow 4MnO(OH)\downarrow + 2H_2O$$

brown metahydroxide

$$4Mn(OH)_2 + 2O_2 \rightarrow 4MnO_2 + 4H_2O$$

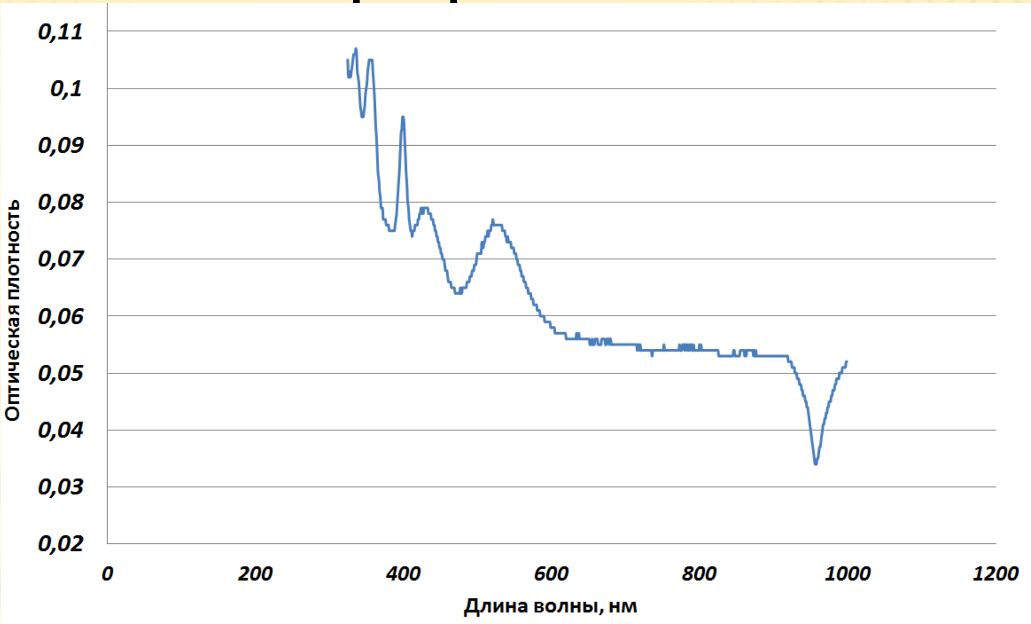
black-brown Mn(IV) oxide

It is soluble in acids:

$$Mn(OH)_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O$$

Hydrated Mn^{2+} – $[Mn(H_2O)_6]^{2+}$

pale pink color



Strong oxidizers turn Mn(II) compounds in manganates or permanganates

$MnSO_4 + 2KClO_3 + 12KOH \rightarrow K_2MnO_4 + 2KCl + 3K_2SO_4 + 6H_2O$

$2MnSO_4 + 5PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 3Pb(NO_3)_2 + 2PbSO_4 + 2H_2O$

Salts of Mn^{2+} are very hydroscopic

$MnCl_2$ anhydrous

$MnCl_2 \cdot 4H_2O$

MANGANESE (III) COMPOUNDS

Manganese (III) oxide **– is a solid brown substance. It is insoluble in water. The oxidation state of +3 is instable for manganese. Manganese (III) oxide corresponds to manganese metahydroxide MnO(OH). Their acidic and basic properties are weak. However, they can oxidize acids with reductive properties.**

$$Mn_2O_3 + 6HCl \rightarrow 2MnCl_2 + Cl_2\uparrow + 3H_2O$$

Reactions with oxidizing acids:

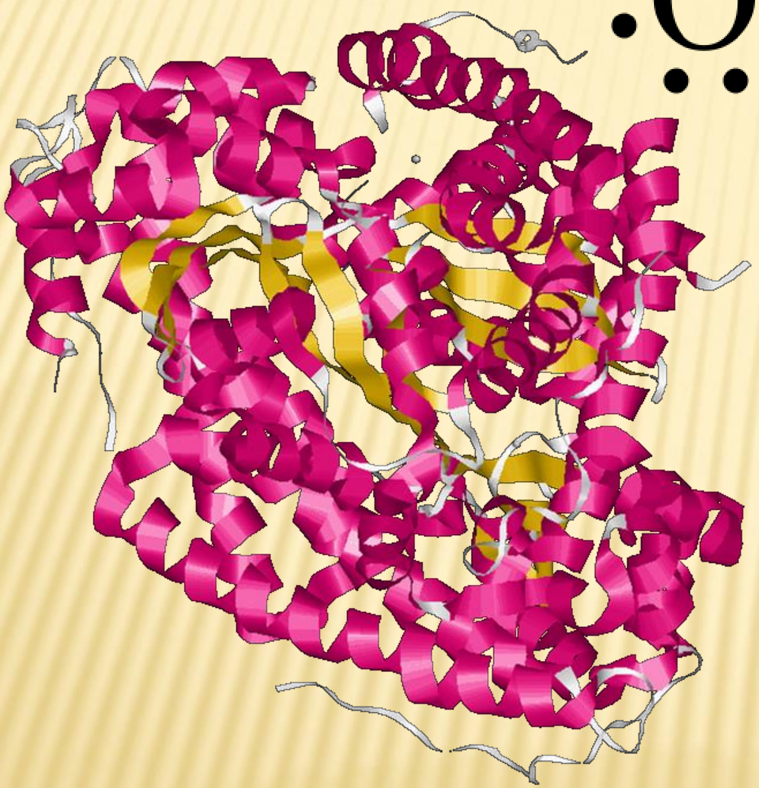
$$2MnO(OH) + H_2SO_{4\,dilute.} \rightarrow MnSO_4 + MnO_2\downarrow + 2H_2O$$

disproportioning

$$2Mn_2O_3 + 8HNO_{3(к)} \rightarrow 4Mn(NO_3)_2 + O_2 + 4H_2O$$

«intramolecular» redox process

IN COMPLEXES WITH PROTEINS MANGANESE (II) IONS CAN BE OXIDIZED TO MANGANESE (III) IONS



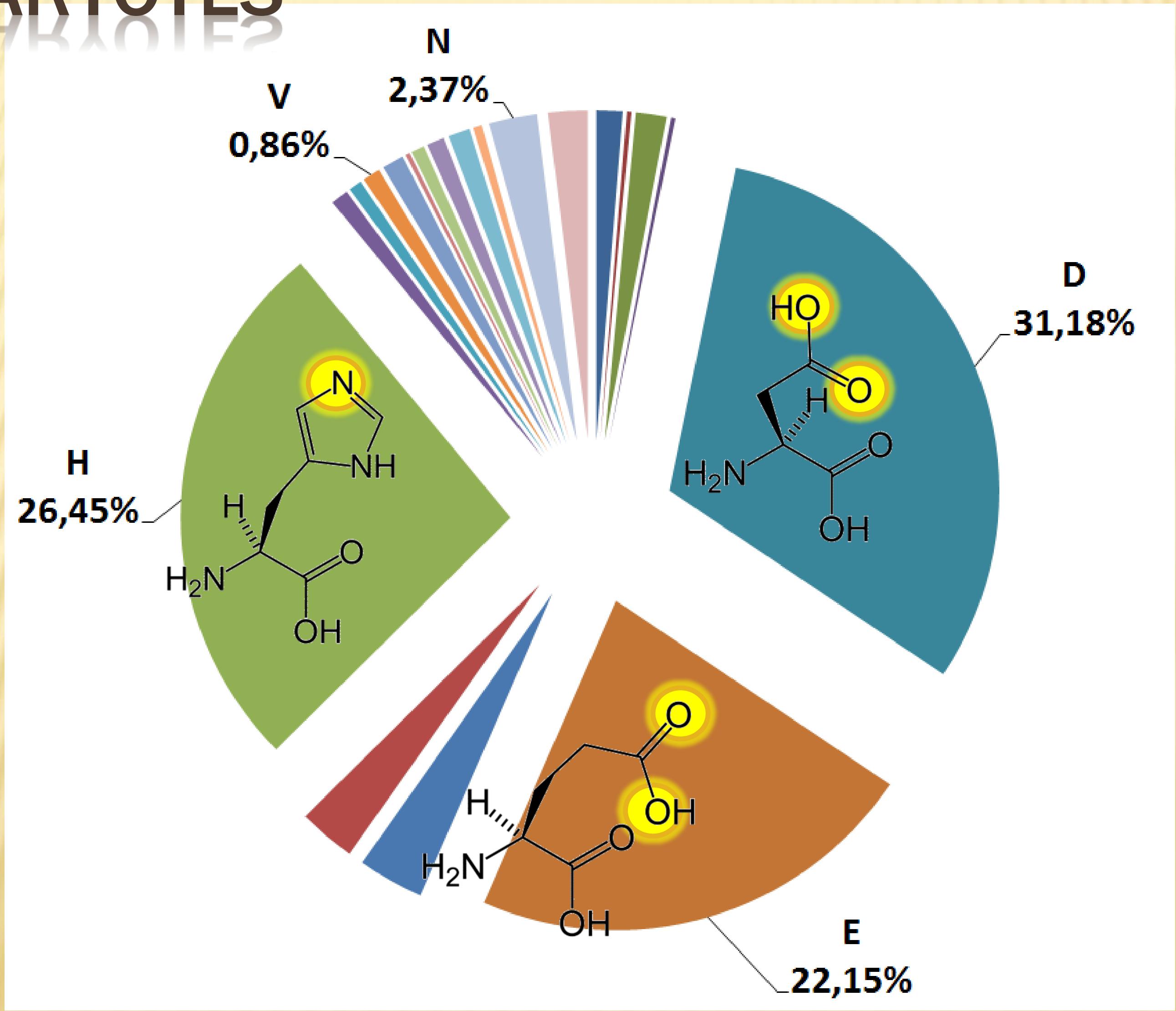
Mitochondrial superoxide dismutase of human
(tetrameric)

$Mn^{3+} - SOD + O_2^{-} \rightarrow Mn^{2+} - SOD + O_2$

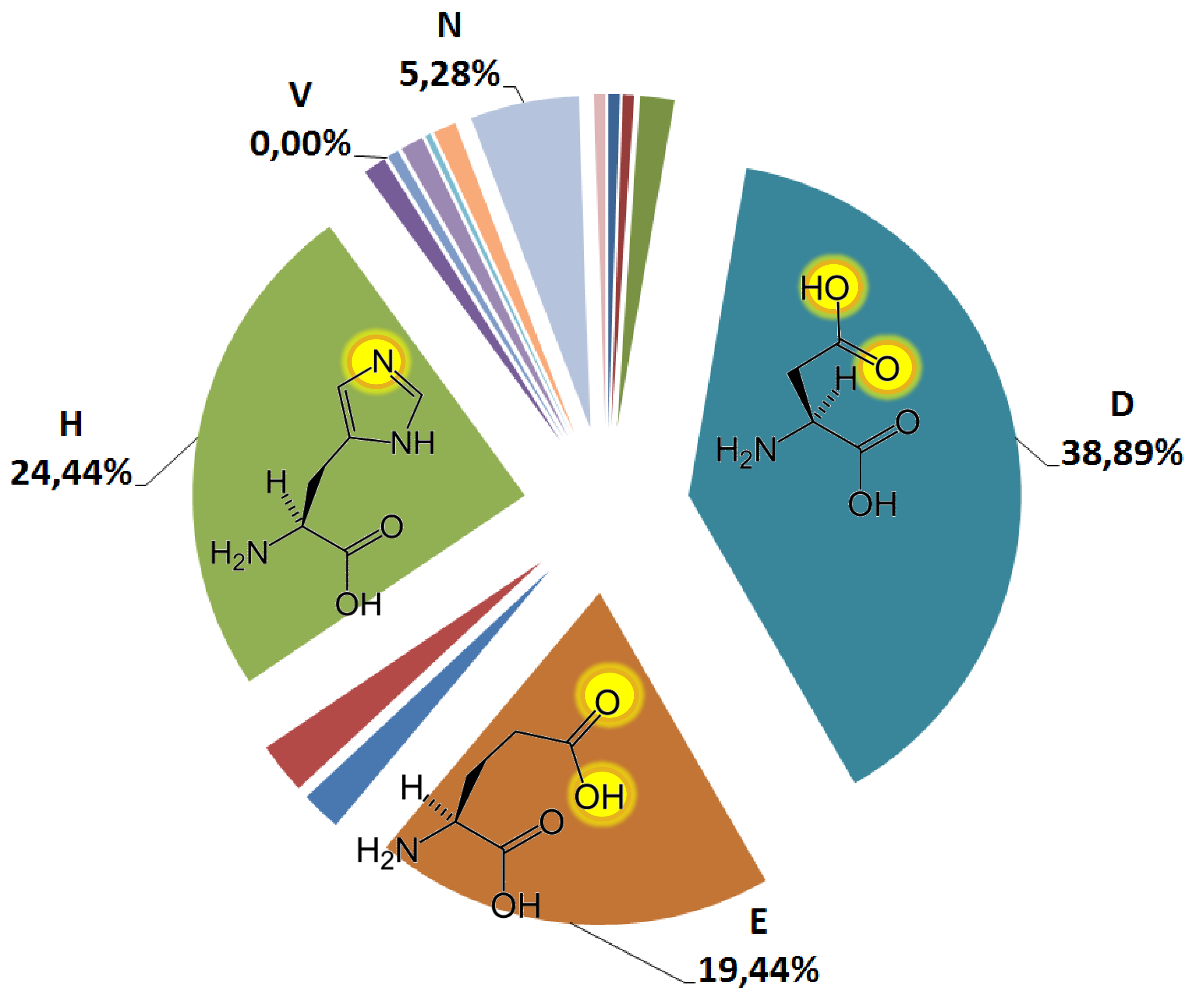
$Mn^{2+} - SOD + O_2^{-} + 2H^{+} \rightarrow Mn^{3+} - SOD + H_2O_2$.

Mitochondrial superoxide dismutase of human
(dimeric)

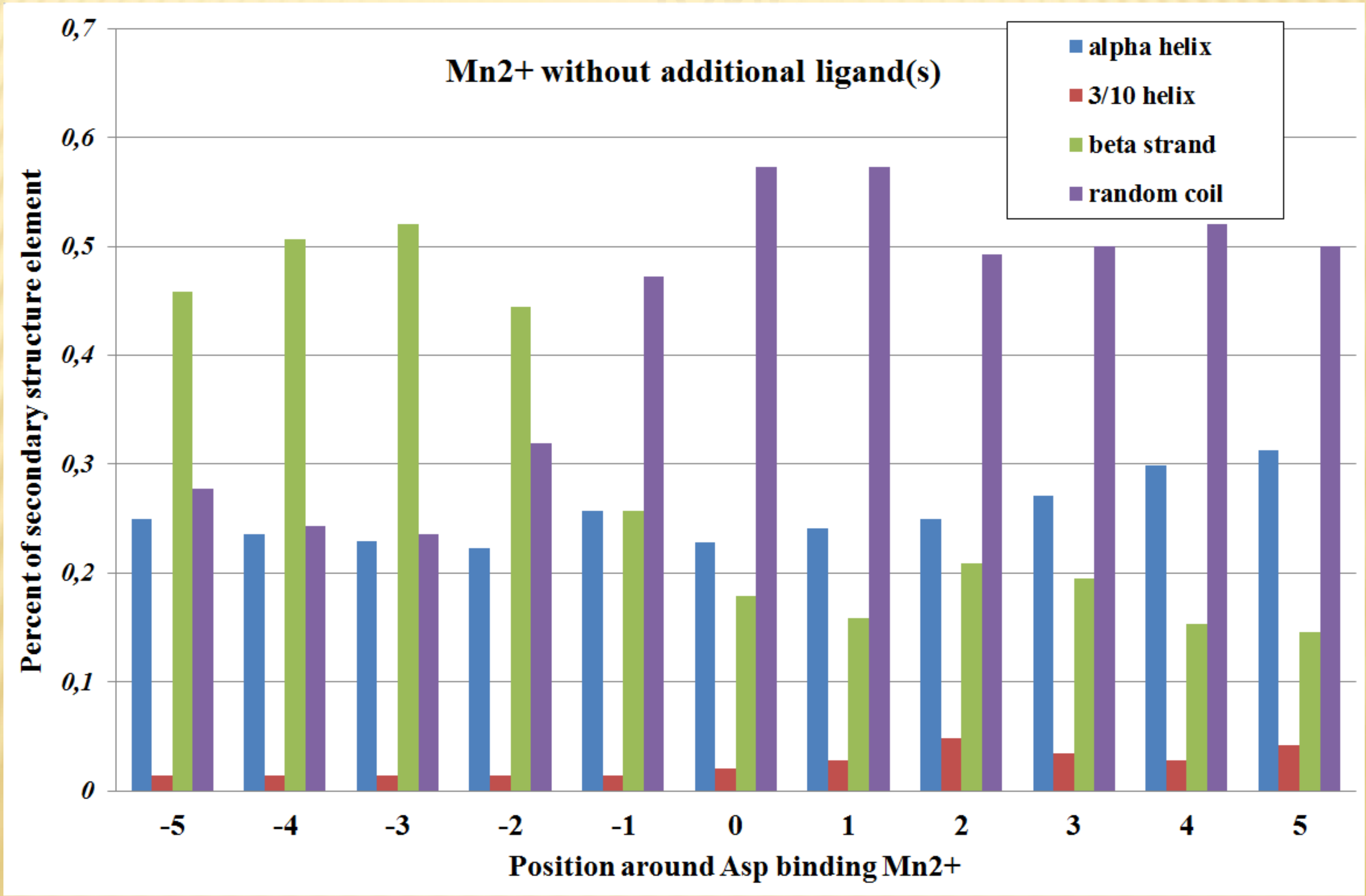
AMINO ACID RESIDUES BINDING MANGANESE (II) IONS IN PROTEINS OF BACTERIA AND EUKARYOTES



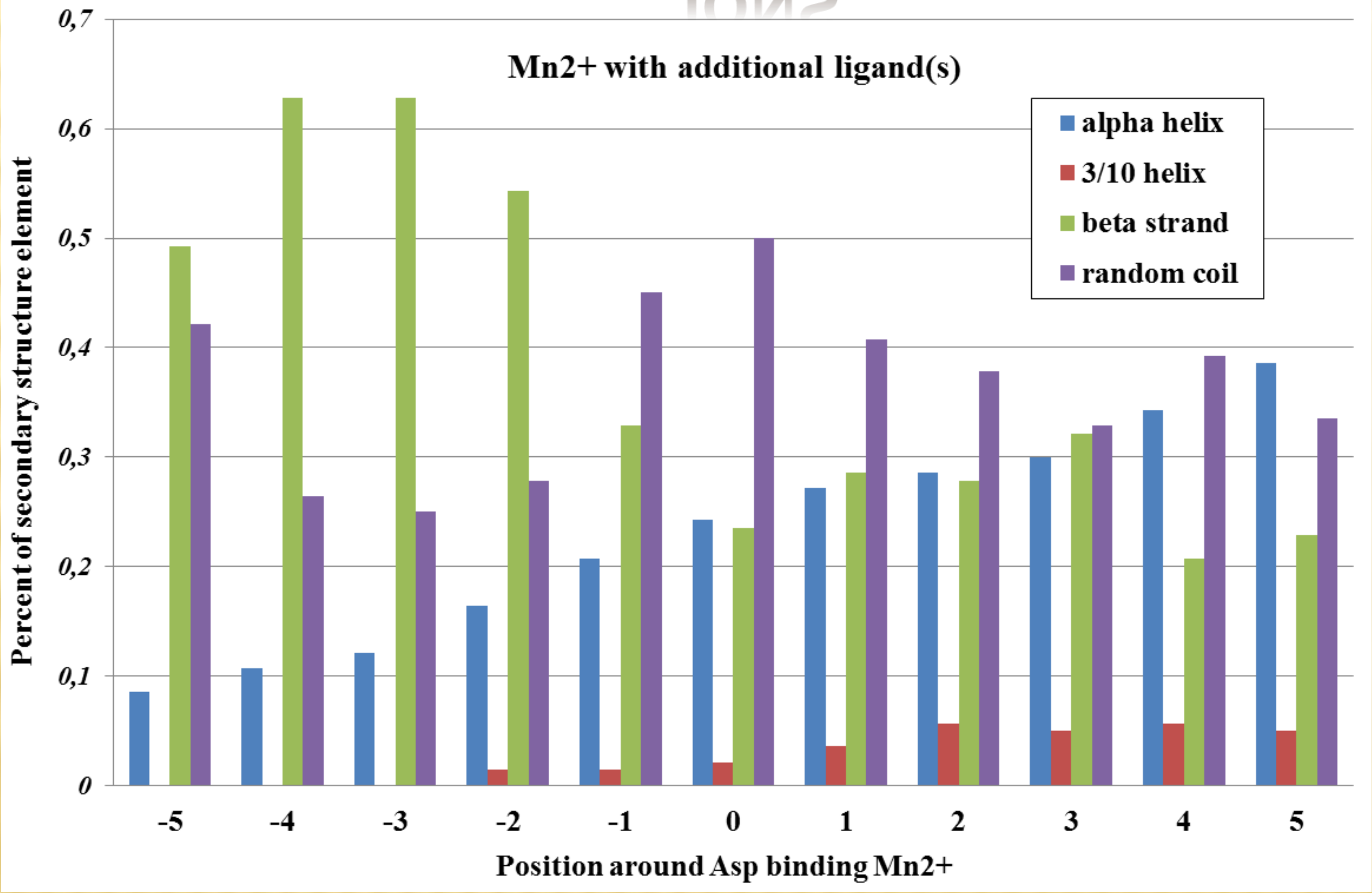
AMINO ACID RESIDUES BINDING MANGANESE (II) IONS IN PROTEINS OF BACTERIA AND EUKARYOTES TOGETHER WITH AN ADDITIONAL LIGAND



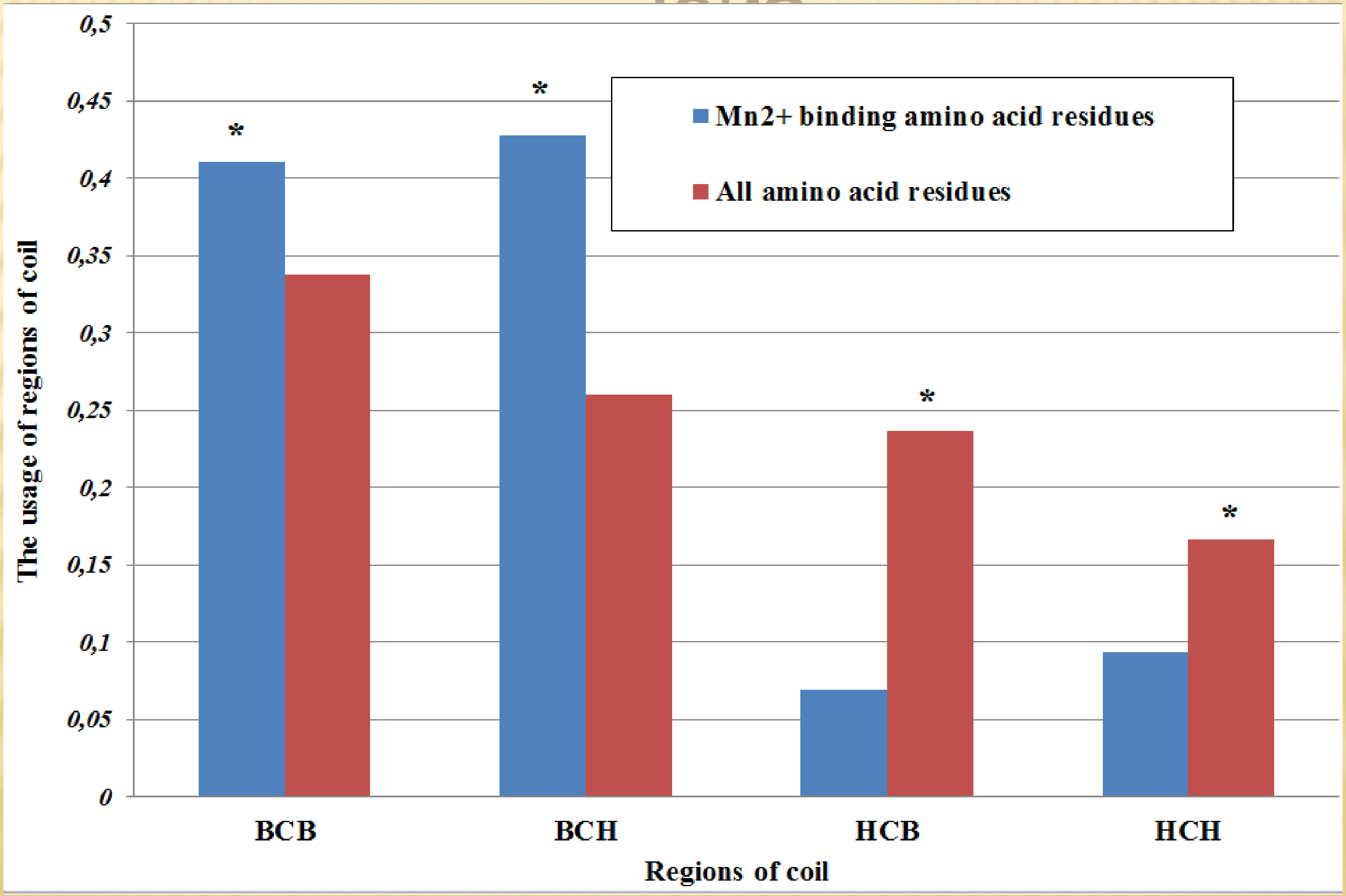
THE MOTIFS OF SECONDARY STRUCTURE AROUND RESIDUES BINDING MANGANESE (II) IONS



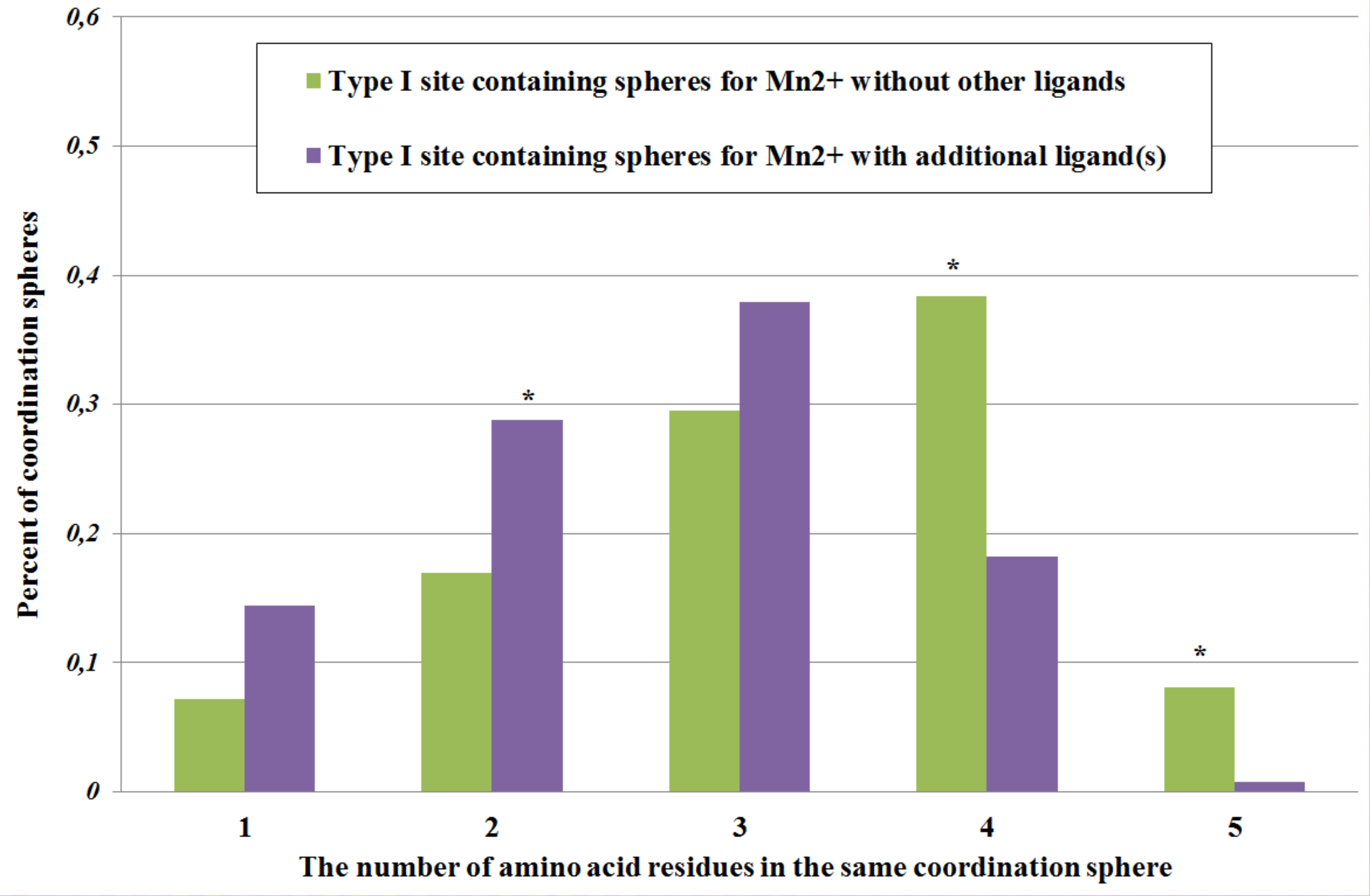
THE MOTIFS OF SECONDARY STRUCTURE AROUND RESIDUES BINDING MANGANESE (II) IONS



MOTIFS OF SUPERSECONDARY STRUCTURE AROUND RESIDUES BINDING MANGANESE (II) IONS



THE NUMBER OF AMINO ACID RESIDUES COORDINATING THE SAME MANGANESE (II) ION



MANGANESE (II) IONS CAN SUBSTITUTE MAGNESIUM (II) IONS IN ACTIVE CENTERS OF ENZYMES

- In 20% of cases the sites with Mn^{2+} ions in 3D structures of proteins from the Protein Data Bank are described as sites for Mg^{2+} binding in the Uniprot database.

MANGANESE (IV) COMPOUNDS

Stable compounds of manganese (IV) –

MnO_2, MnF_4, $Mn(SO_4)_2$

MnO_2 – **is a dark-brown or almost black substance. It is insoluble in water. This oxide is amphoteric.**

$$4NaOH + MnO_2 \xrightarrow[melt]{t} Na_4MnO_4 + 2H_2O$$

orthomanganate of sodium

$$MnO_2 + 4HCl(conc.) \rightarrow MnCl_4 + 2H_2O$$

$$MnCl_4 \rightarrow MnCl_2 \quad Cl_2$$

MnO_2 cannot react with dilute acids.

MnO_2 **can act as both reducer and oxidizer:**

a) $MnO_2 + 2NaCl + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + Cl_2\uparrow$

b) $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$

c) $3MnO_2 + KClO_3 + 6KOH \xrightarrow{melt} 3K_2MnO_4 + KCl + 3H_2O$

COMPOUNDS OF MANGANESE (VI)

MnO_3 – is unknown. MnO_3 corresponds to instable H_2MnO_4 that disproportionates in water solution

$$3H_2MnO_4 \rightarrow MnO_2 + 2HMnO_4 + 2H_2O$$

The color of manganates is green.

Production.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 2KOH + KNO_3 \rightarrow K_2MnO_4 + KNO_2 + H_2O$$

Manganates disproportionate in water.

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2\downarrow + 4KOH$$

Manganates are stable in basic solutions.

Manganates are strong oxidizers and weak reducers.

$$K_2MnO_4\text{(oxidizer)} + 8HCl\text{(conc.)} \rightarrow MnCl_2 + 2Cl_2 + 2KCl + 4H_2O$$

$$2K_2MnO_4\text{(reducer)} + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

COMPOUNDS OF MANGANESE (VII)

Mn_2O_7 – is an oily liquid of dark-green color. It forms $HMnO_4$ in water solutions. Permanganic acid is known to exist only in cold water solutions. At high concentration (>20%) it decomposes by the intramolecular mechanism.

$$4HMnO_4 \rightarrow 4MnO_2 + 3O_2 + 2H_2O$$

Mn_2O_7 – is an acidic oxide

$$2KOH + Mn_2O_7 \rightarrow 2KMnO_4 + H_2O$$

Salts of $HMnO_4$ are called permanganates. They are violet. Permanganates are strong oxidizers, especially, in acidic medium.

$KMnO_4$ cannot be hydrolyzed, since $HMnO_4$ is a strong acid

PERMANGANOMETRY

Standardization of a titrant ($KMnO_4$) by a primary standard ($H_2C_2O_4$)

$KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + К_2SO_4 + 10CO_2 + 8H_2O$

$MnO_4^- + 8H^+ + 5ē \rightarrow Mn^{2+} + 4H_2O$

$H_2C_2O_4 – 2ē \rightarrow 2CO_2 + 2H^+$

Sample 1 – determination of **iron (II) ions** concentration

$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

$MnO_4^- + 8H^+ + 5ē \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} – ē \rightarrow Fe^{3+}$

Sample 2 – determination of **hydrogen peroxide** concentration

$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$

$MnO_4^- + 8H^+ + 5ē \rightarrow Mn^{2+} 4H_2O$

$H_2O_2 – 2ē \rightarrow O_2 + 2H^+$

REDOX POTENTIAL OF POTASSIUM PERMANGANATE DEPENDS ON PH LEVEL

$2KMnO_4 + 5Na_2SO_3 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5Na_2SO_4 + 3H_2O + K_2SO_4$

$MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$
$SO_3^{2-} + H_2O - 2\bar{e} \rightarrow SO_4^{2-} + 2H^+$

$2KMnO_4 + 3Na_2SO_3 + H_2O \rightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH$

$MnO_4^- + 2H_2O + 3\bar{e} \rightarrow MnO_2 + 4OH^-$
$SO_3^{2-} + H_2O - 2\bar{e} \rightarrow SO_4^{2-} + 2H^+$

$2KMnO_4 + Na_2SO_3 + 2KOH \rightarrow 2K_2MnO_4 + Na_2SO_4 + H_2O$

$MnO_4^- + \bar{e} \rightarrow MnO_4^{2-}$
$SO_3^{2-} + 2OH^- - 2\bar{e} \rightarrow SO_4^{2-} + H_2O$

THE TEST FOR THE PRESENCE OF A DOUBLE BOND IN ORGANIC COMPOUNDS

$5CH_2{=}CH_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O \rightarrow 2MnSO_4 + K_2SO_4 + 5CH_2OH\text{-}CH_2OH$

THE TEST FOR THE PRESENCE OF ALDEHYDE GROUP IN ORGANIC COMPOUNDS

$2KMnO_4 + 5HCOOH + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5CO_2$

$KMnO_4 + CH_3COOH + H_2SO_4 \neq$

THE COLORS OF MANGANESE CONTAINING COMPOUNDS

MANGANESE IS AN ESSENTIAL MICROELEMENT

Blood level of manganese is around $2 \cdot 10^{-7}$ mol/L. every day we need about 3-8 mg of manganese. Mn^{2+} is an activator of numerous enzymes (both normally and as a replacer of Mg^{2+}).

Metalloenzymes: **arginase, DNA-polymerase iota, etc.**

Manganese intoxication. **This condition causes the weakness of memory, fatigue, permanent desire to sleep. «Manganese-induced parkinsonism» - develops after several years (or decades) of manganese intoxication.**

Insufficiency. **This condition is associated with the decrease of sex hormones synthesis. Since normally Mn^{2+} replaces Mg^{2+} in guanylate cyclase and increases its velocity leading to the production of gonadoliberin in hypothalamus.**

$MnSO_4$ neutralizes the poison of the European black widow

THE USAGE OF MANGANESE COMPOUNDS IN MEDICINE

- Solutions of $KMnO_4$ are used in medicine as disinfectants.
- For gastric lavage highly diluted solution of $KMnO_4$ is used (0.02-0.1%).

HOW DOES IT WORK?

- Atomic oxygen is released from $KMnO_4$ during the oxidation reaction, as well as during its spontaneous decomposition.
- MnO_2 is formed as a product of reduction in neutral medium. That oxide binds proteins of pathogenic bacteria and disturbs their structure.
- Aromatic amino acid residues are oxidized by MnO_2.

POTASSIUM PERMANGANATE AS A "PRECURSOR"

- $KMnO_4$ is used in organic synthesis as an oxidizer.
- The same reactions are used in the synthesis of narcotic drugs.
- Nowadays $KMnO_4$ cannot be sold without special permissions.

THANK YOU FOR LISTENING!