Minerals

content - result of the natural distribution in the biosphere

composition : substances **x** **elemental**

represented by individual compounds ($FeSO_4$, hemoglobin)

represented by elements (Fe)

organogenic elements: C, O, H, N, P, S

minerals: P, S, other (ash) elements

rough content: ash (0,5 – 3%)

content in the body of an adult (70 kg body weight)

element	amount	unit
Ca	1000-1500	g
Mg	25-40	g
K	140-180	g
Na	70-100	g
P	420-840	g
S	~ 140	g
Cl	70-110	g
Fe	3-5	g
Zn	1,4-3	g
F	0,8-2,5	g
Si	1,4	g
Cu	100-180	mg
Mn	10-20	mg
Mo	5-10	mg
Co	1-1,5	mg
Ni	10	mg
Cr	5	mg
V	< 1-20	mg
I	10-30	mg
Se	10-20	mg

clasification

- **according to quantity** (very variable viewpoint)

majority (macro) elements >100 mg/kg (ppm) = 0,01%

Na, K, Mg, Ca, Cl, P, S

minority elements 10 – 100 mg/kg

Fe, Zn

trace (micro) elements < 10 mg/kg

Al, As, B, Cd, Co, Cr, Cu, F, Hg, I, Mn, Mo, Ni, Pb, Se, Sn

ultra trace elements < 1 μg/kg (ppb)

V

- **according to physiological importance**

essential (indispensable), functionally beneficial

Na, K, Mg, Ca, Cl, P, S

Fe, Zn, Mn, Cu, Ni, Co, Mo, Cr, Se, I, F, B, Si

as additives (recommended daily intake in mg)

Ca 800 mg	**P 800 mg**	**Fe 14 mg**
Mg 300 mg	**Zn 15 mg**	**I 150 μg**

non-essential (physiologically indifferent)

Li, Rb, Cs, Ti, Au, Sn, Bi, Te, Br, Al

toxic

Pb, Cd, As, Hg

Fe, Zn, Cr, Cu, Ni, Se, Al, Sn (legislation)

toxic anions: NO_3^-, NO_2^- **(legislation)**

CN^-, SCN^-

radionuclides: nuclides with an unstable nucleus, subject to radioactive decay

Vodka Gold Symphony
- 24karat gold flakes

chemical forms of elements in foods

Metals

- cations
- complex compounds (LMW, HMW)
- poorly soluble salts
- organometalic compounds

Nonmetals and semimetals

- anions
- covalent and organoelement compounds (LMW, HMW)

form	example
elemental form	Fe in fortified foods
Ions (free, hydrated)	Cu^{2+}, $Cu(H_2O)_4^{2+}$ $Fe(H_2O)_6^{3+}$, AsO_3^{3-}, Cl^-
little soluble inorg. and org.compounds	sulfides, sulfates, phosphates, oxalates
complex compounds with inorg. ligands	$CuCl_4^{2-}$, $Cu(NH_3)_4^{2+}$
complex compounds with org. ligands	complexes with aminoacids, proteins, saccharides, phytic acid, polyphenols, porfyrins
covalent compounds (non-metals and semi-metal)	sulphur aminoacids, selenocysteine, phytic acid
organokovové sl.	methylmercury, tetraethyl lead

example for Fe

heme enzymes:

cytochromes, catalase, peroxidase

non-heme enzymes :

succindehydrogenase, xanthinoxidase, flavin oxidoreductase, aconitase

transport proteins:

hemoglobin (erythrocytes), myoglobin (muscles) O_2

transferrin (plasma) **Fe**

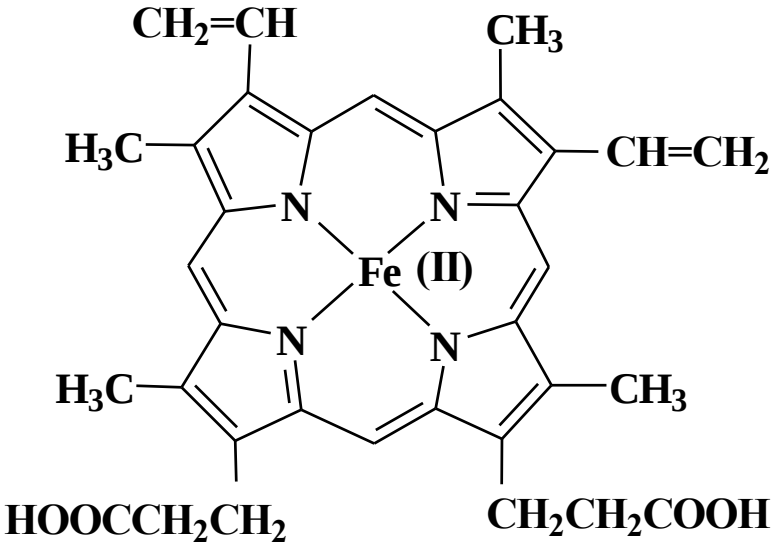
storage proteins:

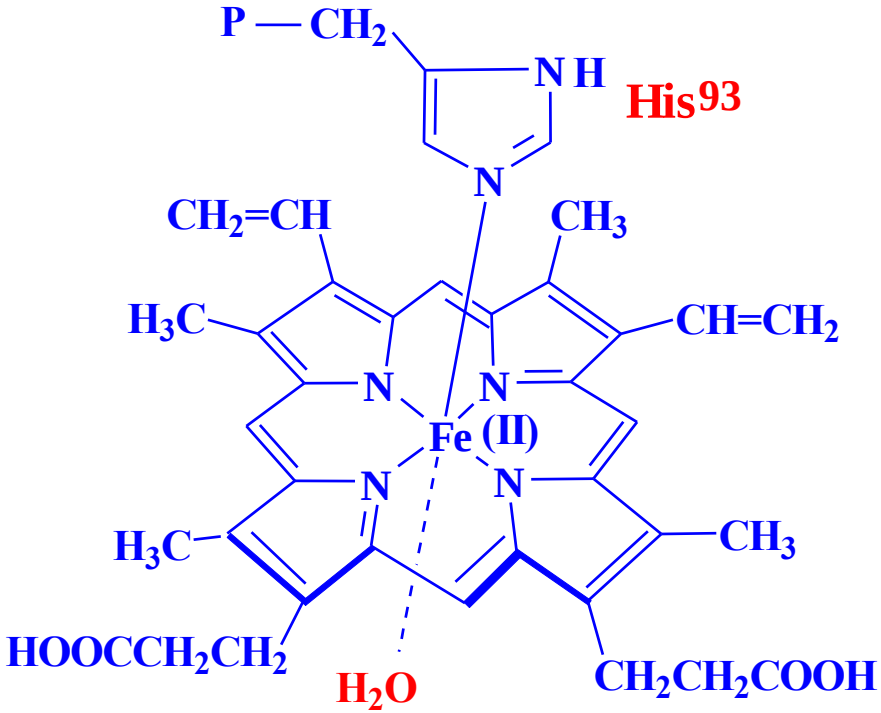
ferritin, homosiderin (spleen, liver, bones) **Fe**

Complexes

heme pigments

meat, meat products



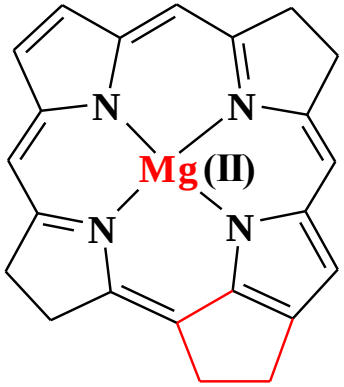


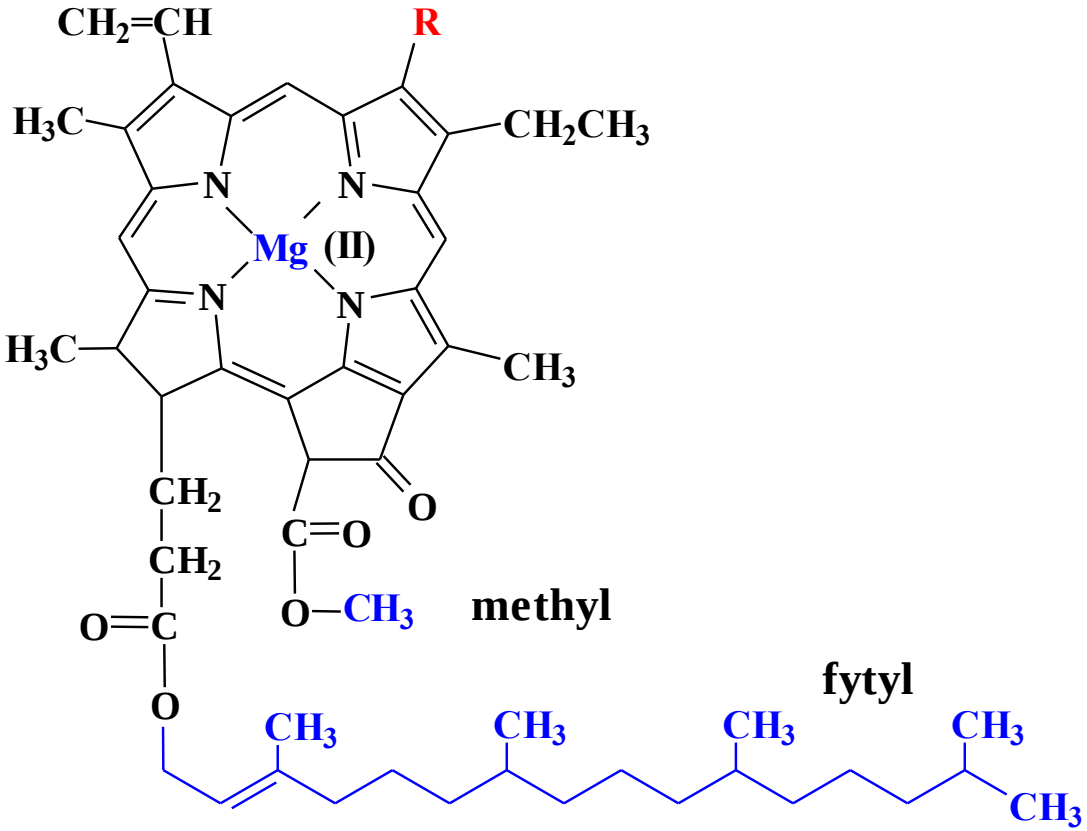
heme (Fe^{2+})
haematin (Fe^{3+})

haemoglobin
myoglobin (P=rest of globin 16,8 kDa)

Chlorophyll pigments

green parts of fruits and vegetables





tetrahydro porphyrin pigments

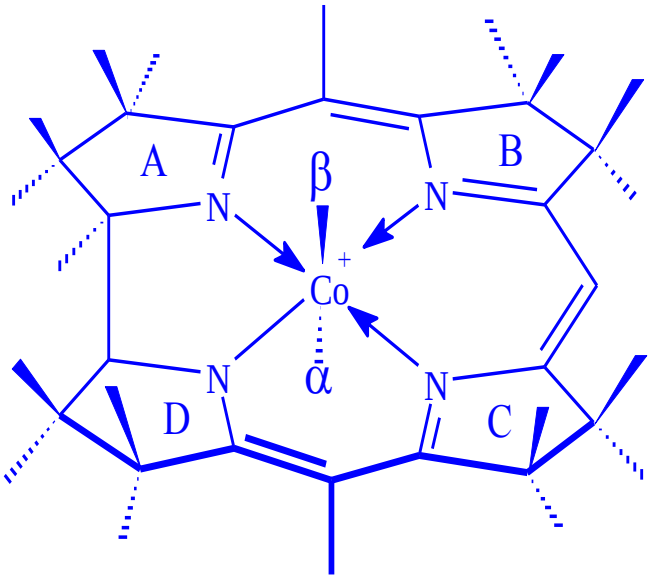
complex Mg (II) **chlorophylls**

without Mg (II) **pheophytins**

chlorophylles

R = CH_3 **chlorophyll a** **yellow-green**

R = CH=O **chlorophyll b** **blue-green**



Corrinoids

central atom Co 6 coordination bonds

α = 5,6-dimethylbenzimidazol cobalamins

β = OH hydroxycobalamin

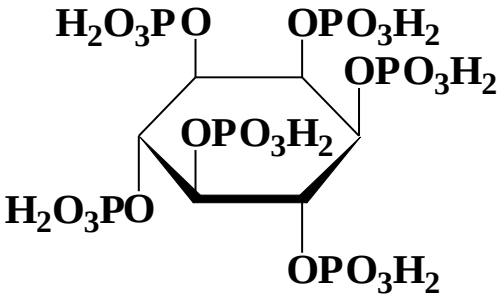
H_2O aquacobalamin

CH_3 methylcobalamin

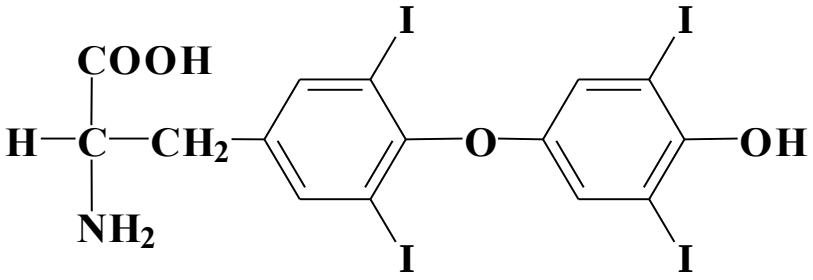
CN cyanocobalamin

deoxyadenosylcobalamin coenzyme B_{12}

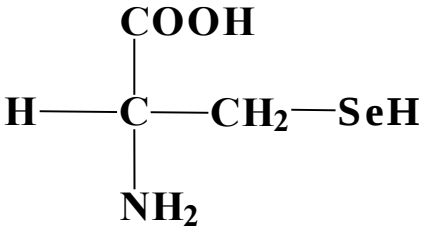
covalent compounds



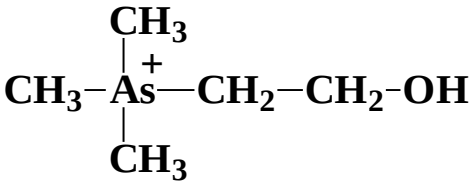
phytic acid



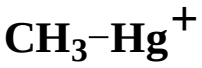
thyroxin



selenocystein



arsenocholine



methylmercury

biochemical function of essential elements

majority elements

Na

osmotic pressure, acid-basic equilibrium, enzymes activation

K

osmotic pressure, acid-basic equilibrium, enzymes activation, muscle activity

Cl

osmotic pressure, (combined with K+, Na+ /Cl-), digestion (HCl)

Mg

building function, muscle and neural activity, blood coagulation

P

building function, energetic metabolisms, enzymes activation, catalytic, regulative functions

S

biocatalysts (components of proteins/vitamins)

minority elements

Fe	catalytic, transport activity
Zn	catalytic

trace elements

Cu	catalytic, transport activity (O2 / invertebrates)
Mn	activation, catalytic activity
Ni	catalytic activity (plants, mikroorganisms))
Co	catalytic activity (vitamin B_{12})
Mo	catalytic activity (plants, microorganisms)
Cr	catalytic activity (glucose-tolerant factor)
V	activation
Se	catalytic activity (connection to vitamin E)
I	regulatory activity (hormones thyroid gland)
F	building function (bones and teeths)
B	activation, building function (plant, pectin)
Si	building function (collagen, mucopolysaccharides)

Nutrition

daily intake (mg) recommended by nutritionists

majority elements

Na	500 mg	Mg	350
K	2000	Ca	800
Cl	75	P	1200
S	not determined (100 – 600)*		

minority elements

Fe	10 – 15	Zn	10 – 15

trace elements

Se	0,01 (children)–0,07 (adults)	B	not determined (2 – 10) *
I	0,04 – 1,5	Sn	not determined (3) *
F	0,1 – 4	Si	not determined (20 – 50) *
Cu	1,5 – 3	Mn	2 – 5
Ni	not determined (0,15–0,7)*	Co	not determined (0,005–0,01)*
Mo	0,08 – 0,25	Cr	0,05–0,2

* = usual daily intake

Nutrition

Recommended Daily Intake (RDI) - the daily intake level of a nutrient that is considered to be sufficient to meet the requirements of 97–98% of healthy individuals ⇒ **legislation**

VYHLÁŠKA č. 225/2008 Sb., requirements for food supplements and the enrichment of foodstuffs (Czech Rep.)

	RDI (mg)		
majority elements			
K	2000	Ca	800
Cl	800	P	700
Mg	375	S, Na	not defined
minority elements			
Fe	14	Zn	10
trace elements			
Se	0,055	Mo	0,050
I	0,150	Cu	1
F	3,5	Mn	2
Cr	0,040		

biological availability and accesibility

The bioavailability of an element is defined as the fraction of ingested nutrient that is absorbed and subsequently utilised for normal physiological functions.

Fairweather-Tait S., Hurrell R.F.: Nutr. Res. Int. 9, 295, 1996
Fairweather-Tait S. et al. : Int. J. Vitam. Nutr. Res. 75, 371, 2005

bio-availability ≠ bio-accessibility = availability

- difficult to interpret the relationship of diet vs. biol. availability
- studies of bioavailability of elements
- impact of technology
- effect of combination of foods in the diet
- speciation analysis of elements

occurrence and important sources

majority elements

Na	NaCl (~ 75%), NaH-glutamate
K	tea, coffee, other plant foods
Cl	NaCl, contaminants (persistent pesticides, PCB, 3-MCPD), additives (including chlorinated water)
Mg	cereals, legumes, other plant foods
Ca	cheese, milk, fish, yolk, legumes
P	milk, cheese, yolk, legumes, nuts, additives (mostly phosphates)
S	eggs, meat, cereals, legumes

minority elements

Fe	meat, eggs, legumes, special cheeses, tea, cacao, additives and contaminants
Zn	meat, eggs, legumes, tea

trace elements

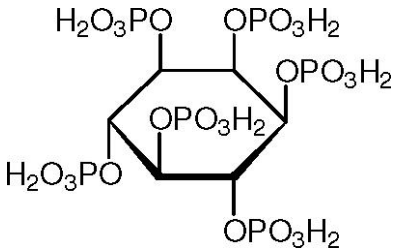
Cu	cheeses, cereals, legumes, tea, mushrooms, contaminants
Mn	cereals, legumes, forest fruits, tea, spices, meat
Ni	cereals, legumes, nuts, tea, cacao, contaminants
Co	cereals, cereals, nuts, tea
Mo	cereals
Cr	yeast, tea, cereals, contaminants
V	cereals
Se	fish, invertebrates, eggs, plants (fortification)
I	fish and algae, fortification
F	tea, fortification
B	cereals, nuts, fruits
Si	cereals, legumes

utilisation

forms, resorption

Ca	**generally from foods**	**5 – 15 %**	
	bread	**40 %**	**phytin**
	cabbage	**40 – 70 %**	**calcium lactate**
	oxalates	**2 – 5 %**	**oxalic acid**

P **cereals, legumes: phytic acid (phytin), partly hydrolyzed by phytases (endogenic, gut-microorganisms)**



phytic acid (phytates) → **partial esters + H_3PO_4**

additives: phytic acid, salts, H_3PO_4, polyphosphates (water binding)

Fe resorption 5 – 15%, Fe (II) > Fe (III), Fe in hem
phytates (Fe, Zn), phenolic compounds
additives: elementary Fe, inorg. a org. compounds (fumarate, baby foods)

I iodination of salt, foods,
antithyreoid compounds: natural (goitrin and other goitrogens), contaminants (PCB, pesticides, veterinary drugs)

toxic elements

contaminants, tolerable limits in legislation

natural sources of contamination

- disintegration of rocks
- fires
- volcanic activities
- floods

anthropogenic sources of contamination

- burning of fossil fuels
- transportation
- industry (especially production of metals)
- agriculture (fertilizers and other chemicals)
- wastes

Pb accumulators, sheet metal, pipes (metal packaging material), painting material and pigments, additives in gasoline: $Pb(CH_3)_4$, $Pb(C_2H_5)_4$

Cd anticorrosion protection (painting), painting material and pigments (CdS), PVC stabilizers (salts of fatty acids), phosphates as fertilizers, smoking

Hg volcanic activity, burning of coal, agrochemicals (phenylmercurichloride), wastes (bateries, switches, electrodes, thermometers, amalgams)

biochemical transformations:

biomethylation (organomercury compounds), microorganims, microscopic fungi

As metallurgy, burning of coal, agrochemicals, veterinary drugs, pigments

chemical transformations:

organoarsenic compounds - fishes

Vyhláška Ministerstva zdravotnictví č. 53/2002 - Decree of the Ministry of Health

Food	TDI in $mg.kg^{-1}$									
	As	Sn	Al [b), c)]	Cr	Cd	Cu	Ni	Pb	Hg	Zn	Fe [b), e)]
Meat	0,1		10,0		0,1 [a)]	5,0	0,5	0,1	0,05	50 [a)]	
Milk	0,05		1,0		0,01	0,4	0,1	0,02	0,01	10,0 [a)]	
Eggs	0,1				0,02 [a)]	3,0 [a)]		0,1 [a)]	0,03	25,0 [a)]	
Bread					0,07			0,1			
Sugar	1,0				0,02	1,0		1,0	0,01		
Fruits	0,5				0,05 [a)]	5,0		0,1	0,01	10,0 [a)]	
Vegetables	0,5				0,1 [d)]	10,0 [a)]	2,5	0,3	0,03	25,0 [a)]	
Non-alcoholic beverages	0,1		5,0		0,05	3,0		0,02	0,003	5,0 [a)]	
Beer	0,2		5,0		0,01	5,0		0,05 [a)]			
Food A	0,5 [a)]	100,0 [a)]		0,2 [a)]	0,1 [a)]	20,0 [a)]	2,0 [a)]		0,05 [a)]	50,0 [a)]	
Drinks A	0,5 [a)]	100,0 [a)]		0,1 [a)]		20,0 [a)]	1,0 [a)]				
Food B	3,0 [a)]	200,0 [a)]		4,0 [a)]	0,5 [a)]	80,0 [a)]	6,0 [a)]	8,0 [a)]	0,5 [a)]	80,0 [a)]	
Drinks B	3,0 [a)]	200,0 [a)]		1,0 [a)]		20,0 [a)]	6,0 [a)]				

A = baby food, most of the basic food
B = other food (not consumed frequently)

nitrates and nitrites

content

high: **vegetables**

low: **fruits (melon, banana)**

food classification

- **with high content (> 1000 mg.kg^{-1})**

  lettuces, endive, spinach, spinach beet, Chinese cabbage, radish, celery, rhubarb, corn

- **with median content (250-1000 mg.kg^{-1})**

  cabbage, kale, cauliflower, eggplant, parsley, carrot, broccoli, garlic, potatoes

- **with low content (< 250 mg.kg^{-1})**

  Brussels sprouts, onion, tomato, pea, cucumber, artichoke, asparagus

ADI (NO_3^-) = 3,5 mg.kg^{-1}

ADI (NO_2^-) = 0,2 mg.kg^{-1} (lethal dosage 32 mg.kg^{-1})

methemoglobinemia

a disorder characterized by the presence of a higher than normal level of methemoglobin in the blood ⇨ tissue hypoxia can occur

• symptoms of methemoglobinemia (methemoglobin >1%) include shortness of breath and cyanosis
• infants under 6 months of age are particularly susceptible to methemoglobinemia caused by nitrates ingested in drinking water (called blue-baby syndrome

$$\mathbf{Hg\ (Fe^{2+}) + NO_2^- \rightarrow MHg\ (Fe^{3+}) + NO}$$

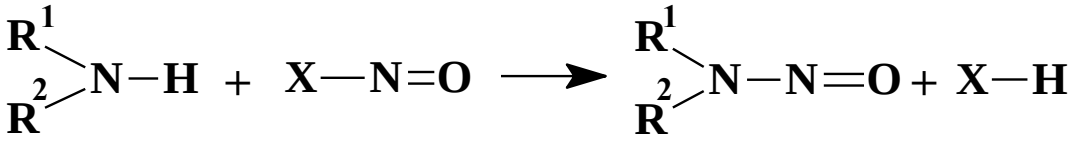
The current legislation standard of 15 ppm nitrate-nitrogen for drinking water is specifically designed to protect infants

nitrosamines

endogenous contaminants

products of reaction of sec. amines with nitrosation agents

toxicology - mutagenic, teratogenic and carcinogenic effects



secondary amine **nitrosation agent** ***N*-nitrosamine**

- under acidic conditions the nitrite forms nitrous acid (HNO_2), which is protonated and splits into the nitrosonium cation $N{\equiv}O^+$ and water: $H_2NO_2^+ = H_2O + NO^+$. The nitrosonium cation then reacts with an amine to produce nitrosamine
- high temperatures, as in frying, can also enhance the formation of nitrosamines

- these processes lead to significant levels of nitrosamines in many foodstuffs, especially beer, fish, and fish byproducts,

  also in meat and cheese products preserved with nitrite pickling salt

legislation established limits on the amount of nitrites used in meat products in order to decrease cancer risk in the population