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Lecture Iron(III)

HEALTH AND ENVIRONMENT SECTION

AN EXTRACTION-CHROMOGENIC SYSTEM FOR IRON(III) BASED ON 4-NIROCATECHOL

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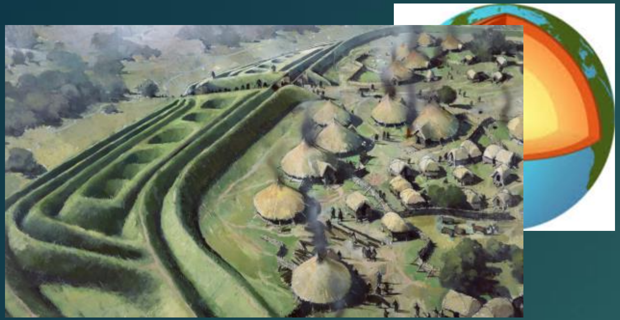
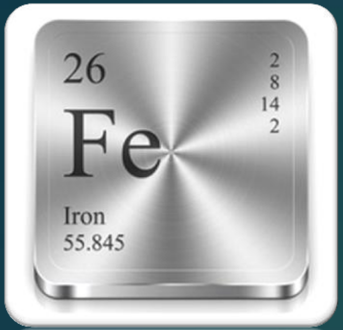


Iron in ancient civilizations

- Iron has been known as an instrumental material since ancient times.
- The most ancient iron products found during archaeological excavations date back to the 4th millennium BCE. – ancient Sumerian and ancient Egyptian civilizations.
- These products are made of meteorite iron – an alloy of iron and nickel (5 to 30%) – decorations from Egyptian tombs (about 3800 BCE) and a dagger from the Sumerian (about 3100 BCE).
- The Hittites were the first to master the method of smelting iron.
- According to the descriptions of ancient historians, in the most ancient times, iron was valued more than gold.



Iron characterization

- Iron (Fe) is a silvery-gray, malleable metal with a shiny surface that oxidizes easily.
- The pure iron crystals are soft (softer than Al). The addition of relatively small impurities enhances its hardness and strength;
- Good conductor of electricity and heat, pronounced magnetic properties;
- High chemical reactivity, in pure oxygen iron burns, and in a finely dispersed state, it ignites spontaneously in air;
- Forms compounds mostly in two oxidation states – Fe^{3+} and Fe^{2+} ;
- Specific properties of iron and its alloys make it "metal No 1" in importance for humans;
- In practice, iron-carbon alloys are often used: steel (up to 2.14% C) and cast iron (more than 2.14% C), as well as stainless (alloyed) steel with alloying metals (Cr, Mn, Ni and etc.).

Iron occurrence

- Iron – one of the most common elements in the solar system, especially on the planets like the Earth.
- Much of the iron on Earth is found in the core of the planet.
- The Earth's core is believed to largely be composed of iron (80%), along with nickel (20%) and one or more light elements.

Iron occurrence

- In the Earth's crust – Fe is 5%; of the metals, Fe is second only to Al in its bark;
- In the mantle – Fe is about 12%;
- In the human body – on average 4 - 5 g (~38 mg iron/kg body weight for women and ~50 mg iron/kg body for men);
- In river water – on average - 2 mg/L
- In marine water – very small quantities 0,002—0,02 mg/L

Biological importance

- Iron plays an important role in the lives of virtually all organisms except some bacteria.
- In animals, iron is part of many enzymes and proteins involved in redox reactions, such as respiration, as it is part of hemoglobin. The main intracellular depot of iron is a globular protein complex - ferritin.
- Hemoglobin contains about 68% of the total iron in the body, ferritin - 27%, myoglobin - 4%, transferrin - 0.1%.

The body of an adult contains about 3 - 4 g of iron (about 0.005%), of which only about 3.5 mg is in the blood plasma.

Iron& Nutrition

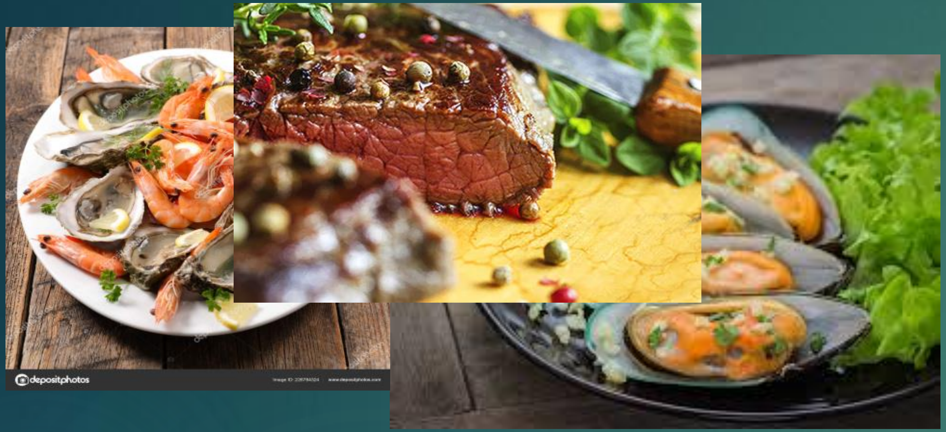
- **Iron** – mineral that is naturally present in many foods, added to some food products, and available as a dietary supplement.
- **Iron** – essential component of hemoglobin, an erythrocyte (red blood cell) protein that transfers oxygen from the lungs to the tissues. As a component of myoglobin, another protein that provides oxygen, iron supports muscle metabolism and healthy connective tissue.
- **Iron** is also necessary for physical growth, neurological development, cellular functioning, and synthesis of some hormones.
- **Dietary iron** has two main forms:
  - ✓ heme
  - ✓ nonheme.
- **Plants** and iron-fortified foods contain *nonheme iron only*, whereas **meat**, **seafood** and **poultry** contain *both heme* and *nonheme iron*. Heme iron, which is formed when iron combines with protoporphyrin IX, contributes about 10% to 15% of total iron intakes in western populations.

Iron& Nutrition

- The WHO and European Commission's Directorate-General for Health and Food Safety introduces terms concerning <u>iron intake</u>:
- . Recommended Dietary Allowances (RDAs)
- for adults – 20-50 year – 8 mg/day for males;
- for adults – 20-50 year – 18 mg/day for females.
- . Tolerable upper intake level (UL)
- for adults – 14-70 year – 45 mg/day.

The body of an adult contains about 3 - 4 g of iron (about 0.005%), of which only about 3.5 mg is in the blood plasma.

Top 6 foods rich in iron



Beef, Poultry, Shrimp and Oysters

Nuts and Dried Fruit

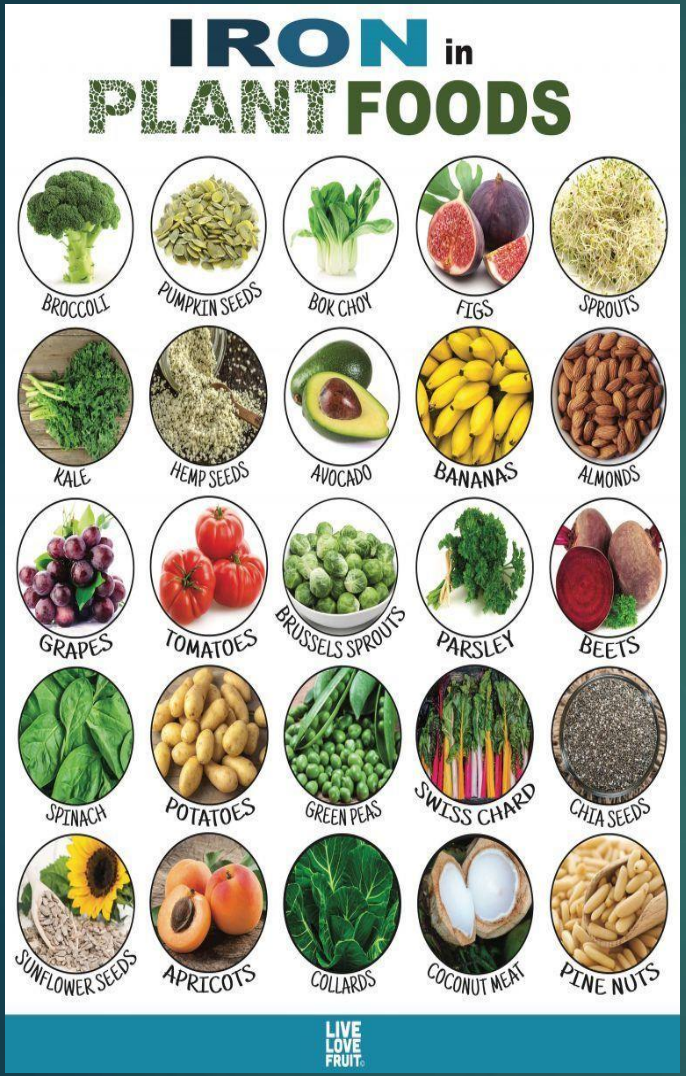
Tofu

Dark green Leafy

Fish

Cereals

Iron deficiency



- The **need of a person** for **iron** per 1kg of body weight is:
- children - 0.6 mg of iron per day
- adults - 0.1 mg of iron per day
- pregnant women - 0.3 mg of iron per day.
- **Iron deficiency** manifests itself as a disease of the body: chlorosis in plants and anemia in animals and humans.
- As a rule, the iron we take with food is enough for the nutrition of a healthy person.

Iron toxicity

- **Excess iron** can enter the body along with rusty tap water (through cast iron pipes). Also, the use of iron and cast iron utensils in cooking increases the iron content in it.
- The iron content in water more than 1-2 mg/L significantly impairs its organoleptic properties, giving it an unpleasant astringent taste, and makes the water unsuitable for use. Such water causes allergic reactions in humans, can cause blood and liver disease - hemochromatosis.
- The maximum concentration limit for iron in water is 0.3 mg/L.
- **Iron overdose** stimulates the production of free radicals, inhibits the body's antioxidant system, and probably contributes to the development of atherosclerosis; therefore, it is not recommended to use iron supplements in healthy people.

Excessive accumulation of iron in the body is toxic.

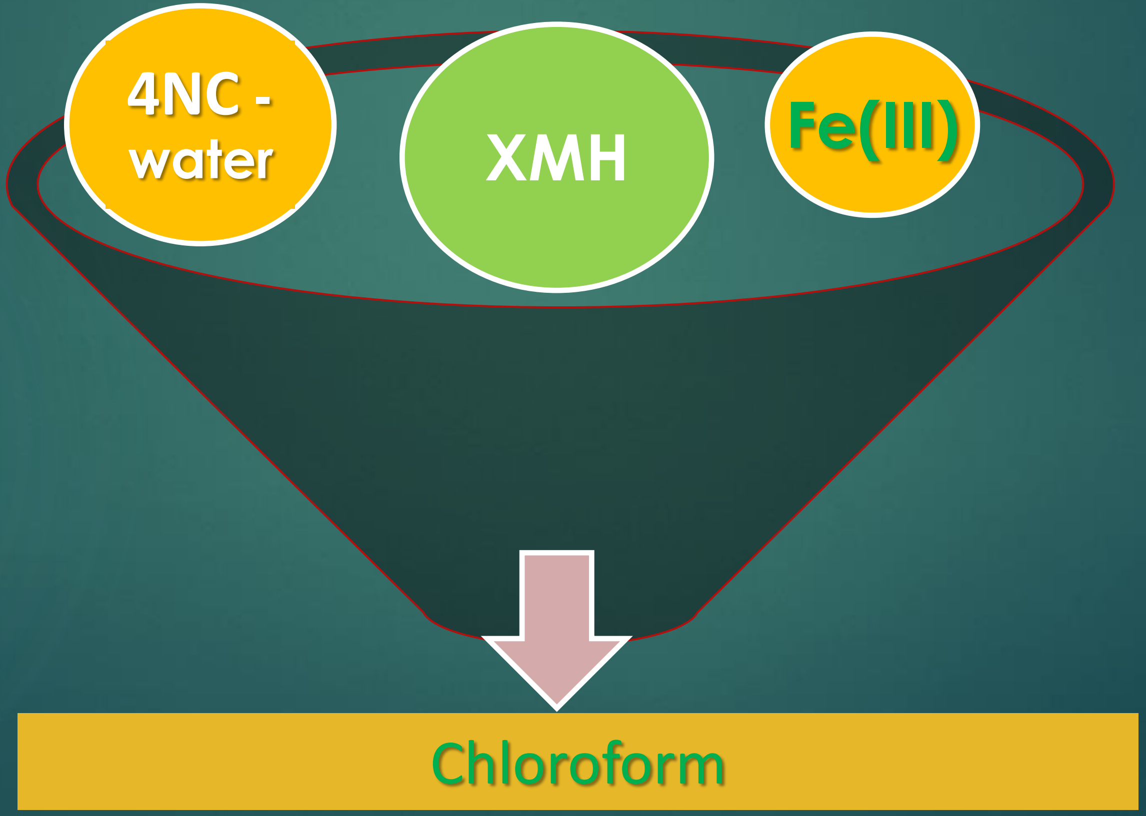
Iron in analytical techniques

Methods involving spectrophotometry

- simple and low-cost;
- can be easily combined with procedures for preliminary separation and concentration;
- can be easily combined with cloud point extraction;
- can be easily combined with liquid-liquid extraction.

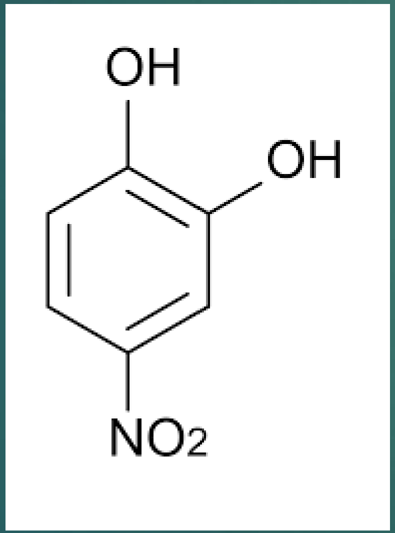
The present work aims at to study:

- water-chloroform extraction-chromogenic system for iron(III);
- Fe(III) – 4-nitrocatechol (4NC) – xylometazoline hydrochloride (XMH)

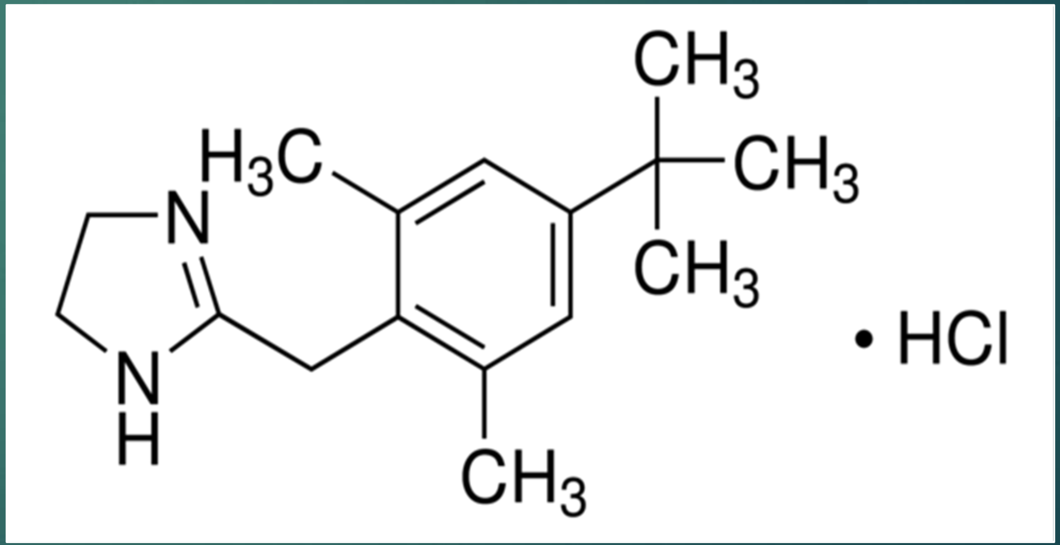


Reagents and apparatus

- .4-nitrocatechol (4NC) – a well-known analytical reagent;
- xylometazoline hydrochloride (XMH) – has been used in medicine and analytical chemistry.



4NC



XMH

Reagents and apparatus

- Stock solution of Fe^{III} (1.7×10^{-2} mol dm^{-3}; pH ~2) was prepared by dissolving $(NH_4)_2SO_4\cdot Fe_2(SO_4)_3\cdot 12H_2O$ (Sigma-Aldrich, 99.999%) in distilled water containing H_2SO_4. Working solutions with a concentration of 8.95×10^{-4} mol dm^{-1} were obtained by a suitable dilution of the standardized stock solutions with distilled water.
- 4-nitrobenzene-1,2-diol (Fluka GmbH) – aqueous solutions with concentrations of 2×10^{-3} mol dm^{-3} were used.
- Xylometazoline hydrochloride (XMH) (Sigma-Aldrich) – aqueous solutions with concentrations of 5×10^{-3} mol dm^{-3} were used.
- The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2.0 mol dm^{-3} aqueous solutions of CH_3COOH and ammonia.
- Absorbance measurements were performed by using a Camspec M508 and a Ultrospec3300 pro UV-Vis spectrophotometers (UK).

Results and Discussion

1. Liquid–liquid extraction–spectrophotometric optimization
1.1. Absorption spectra of complexes in chloroform

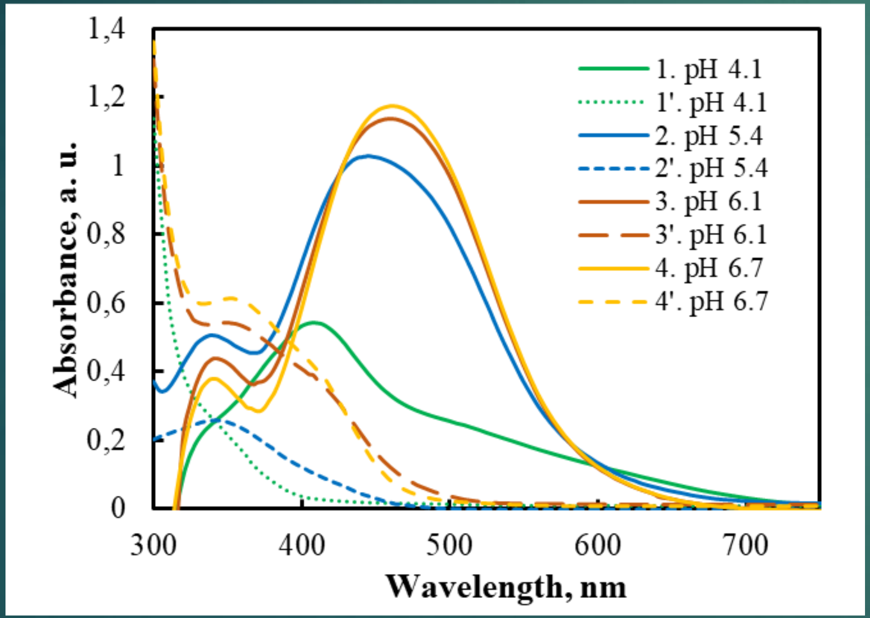


Figure 1. Absorption spectra in chloroform of complexes against blanks (1 – 4; c_{Fe} = 2.4×10^{-5} mol dm^{-3}, c_{4NC} = 4×10^{-5} mol dm^{-3}, c_{XMH} = 1×10^{-5} mol dm^{-3}, $V_{aq.\ phase}$ = 10 cm^{3}, extraction time t = 60 sec) and corresponding blanks against chloroform (1' – 4').
– pH 4.1; – pH 5.4; – pH 6.1; – pH 6.7.

The absorption spectra show that several complexes are formed in the system.

Iron(III) –4NC – XMH

1.2. Effect of pH on the extraction

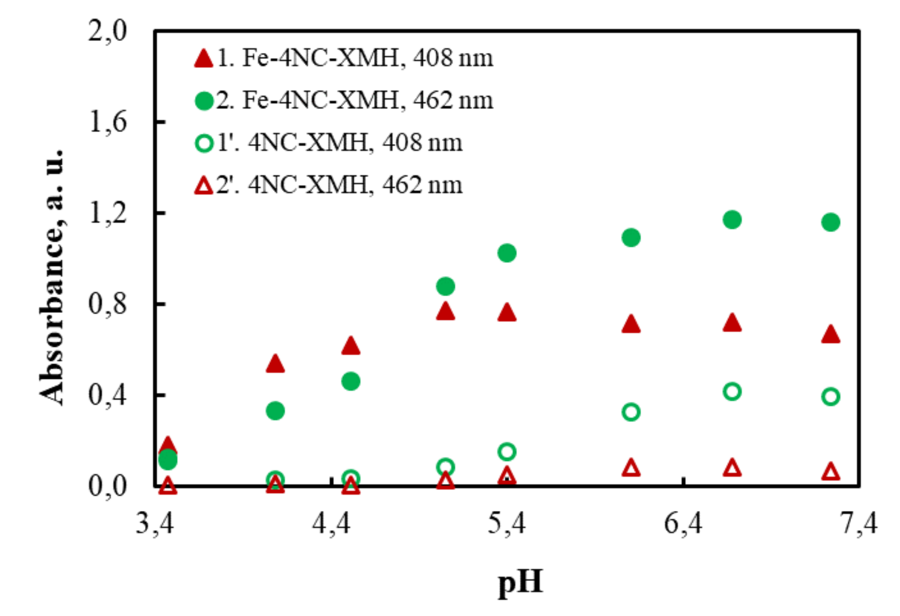


Figure 2. Absorbance of the complexes at λ=408 nm and λ=462 nm vs. pH of the aqueous phase. c_{Fe} = 2.4×10^{-5} mol dm^{-3}, c_{4NC} = 4×10^{-4} mol dm^{-3}, c_{XMH} = 1×10^{-3} mol dm^{-3}, $V_{aq.\ phase}$=10 cm^3, extraction time t = 120 sec.

Absorbance is maximal in the range of pH 6.6-7.2.

Iron(III) – 4NC – XMH

1.3. Effect of shaking time on the extraction

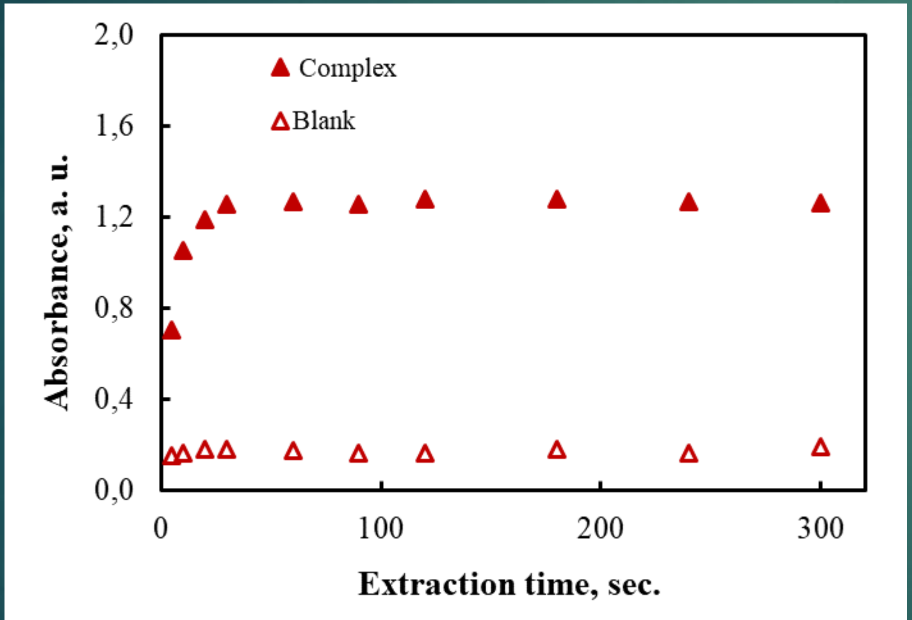
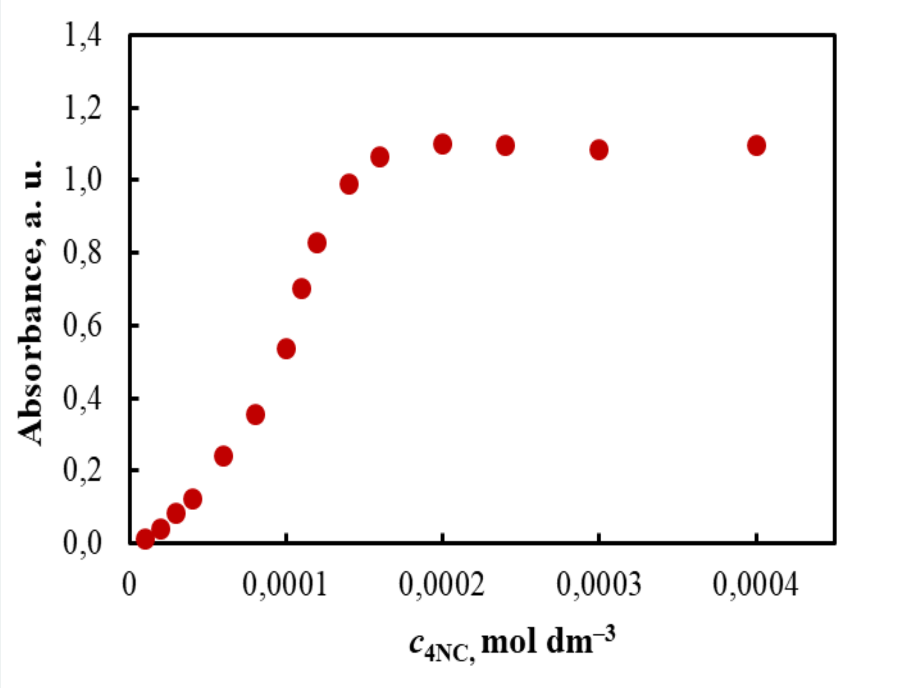


Figure 3. Absorbance of the complex $c_{Fe} = 2.4\times10^{-5}$ mol dm^{-3}, $c_{4NC} = 4\times10^{-4}$ mol dm^{-3}, $c_{XMH} = 1\times10^{-3}$ mol dm^{-3}, $V_{aq.\ phase}$=10 cm^3

Iron(III) –4NC – XMH

1.4. Effect of the 4NC concentration



- **Figure 4.** Absorbance vs. concentration of 4NC.
- c_{Fe} = 2.4×10^{-5} mol dm^{-3}, c_{4NC} = 2×10^{-3} mol dm^{-3}, c_{XMH}= 7.5×10^{-4} mol dm^{-3}, pH 6.7, $V_{aq.\ hase}$ = 10 cm^{3}, extraction time t = 120 sec.

Iron(III) – 4NC – XMH

1.5. Effect of the XMH concentration

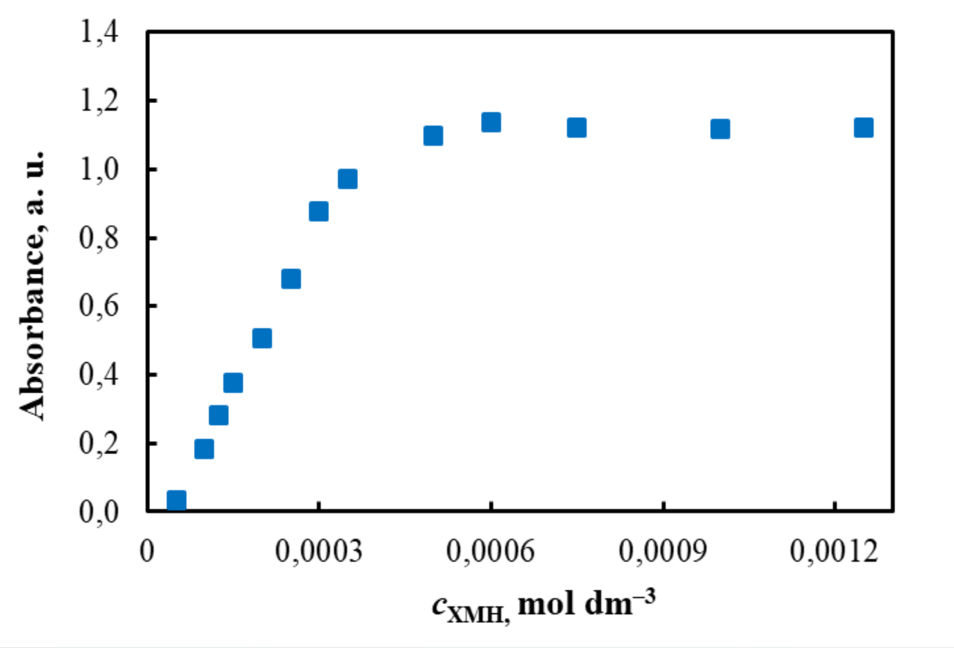


Figure 5. Absorbance vs. concentration of XMH. c_{Fe} = 2.4×10^{-5} mol dm^{-3}, c_{4NC} = 2×10^{-4} mol dm^{-3}, c_{XMH}= 5×10^{-3} mol dm^{-3}, pH 6.7, $V_{aq.\ hase}$ = 10 cm^3, extraction time t = 120 sec.

Iron(III) –4NC – XMH

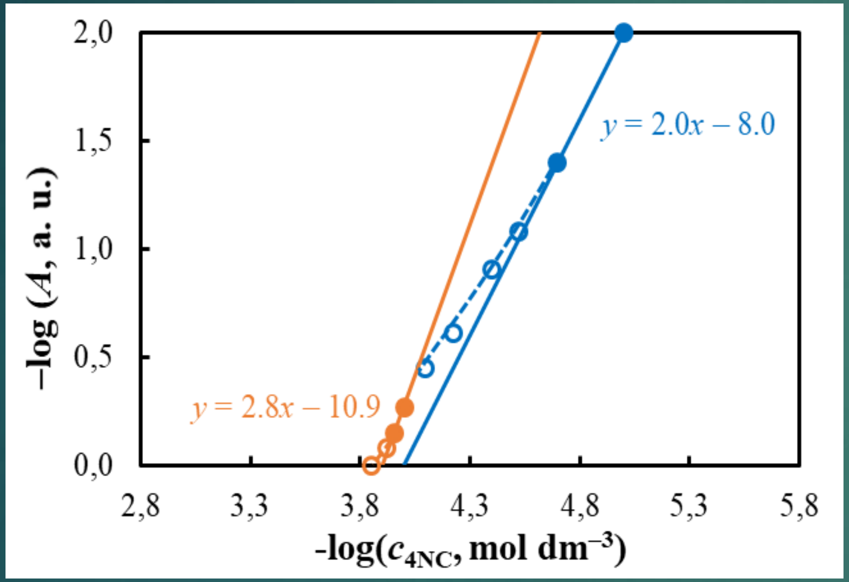
Parameter	Optimization range	Optimal value
Wavelength, nm	Visible range	462
pH	3.4 – 7.2	6.7
Volume of the aqueous phase, cm^{-3}	5 and 10	10
Concentration of 4NC, mol dm^{-3}	$(0 - 4.0)\times10^{-4}$	2.4×10^{-4}
Concentration of XMH, mol dm^{-3}	$(0 - 1.25)\times10^{-3}$	7.5×10^{-4}
Extraction time, seconds	5 – 300	120

Table 1. LLE-spectrophotometric optimization of the Fe^{III}–4NC–XMH–water–chloroform system. The volume of the organic phase was 10 cm^3.

Iron(III) –4NC – XMH

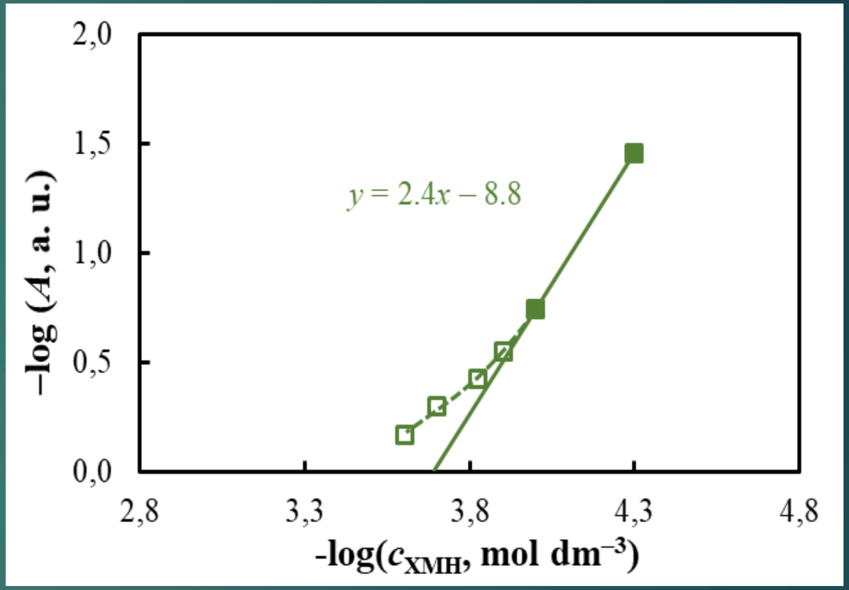
2. Molar Ratios

2.1. Determination of the Fe^{III}/4NC and Fe^{III}/XMH molar ratios – limited logarithm method of Bent-French



Fe^{III}/4NC molar ratio

(a)



Fe^{III}/XMH molar ratio

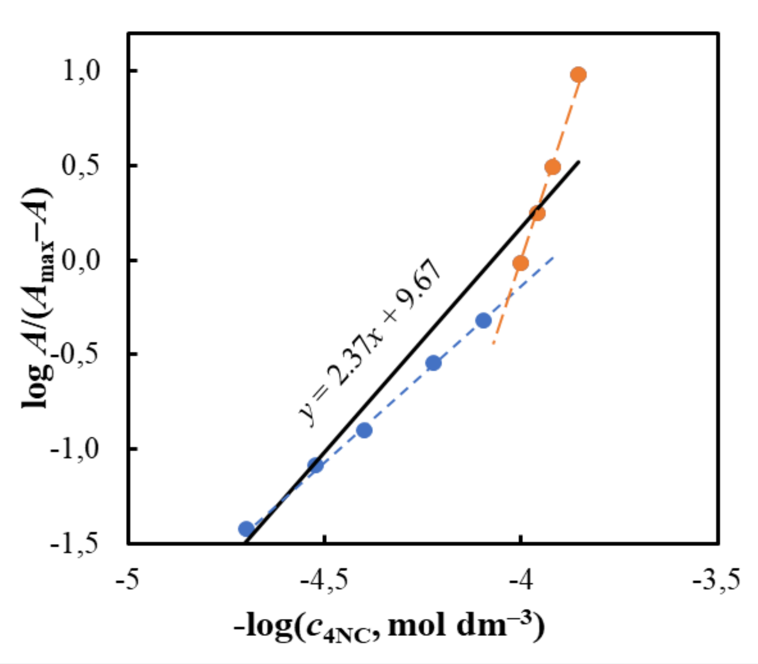
(b)

Figure 6. Determination of the **Fe^{III}/4NC** (**a**) and **Fe^{III}/XMH**(**b**) molar ratios by the method of **Bent-French**. The experimental conditions are given in Fig. 3 and Fig. 4, respectively.

Iron(III) –4NC – XMH

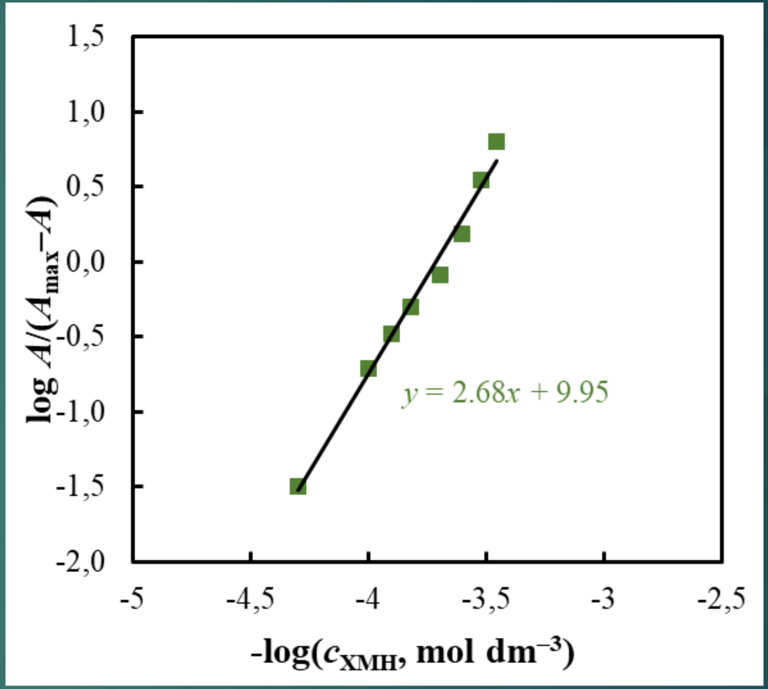
2. Molar Ratios

2.1. Determination of the Fe^{III}/4NC and Fe^{III}/XMH molar ratios- **equilibrium shift method**



Fe^{III}/4NC molar ratio

(a)



(b)

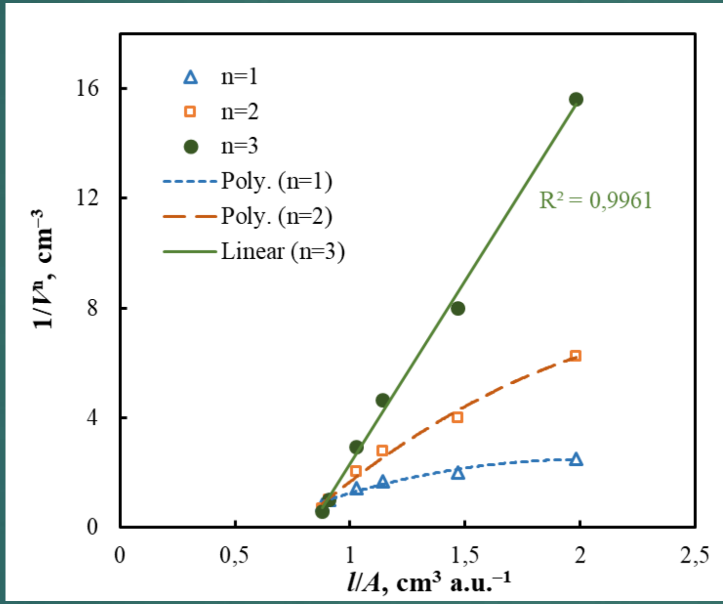
Fe^{III}/XMH molar ratio

Figure 7. Determination of the Fe^{III}/4NC (**a**) and Fe^{III}/XMH(**b**) molar ratios by the **equilibrium shift method**. The experimental conditions are given in Fig. 4 and Fig. 5, respectively.

Iron(III) –4NC – XMH

2. Molar Ratios, Structure and Equations of Complex Formation and Extraction

2.2. Determination of the Fe^{III}/XMH molar ratios – state line **method of Asmus**



Fe^{III}/XMH molar ratio

Figure 8. Determination of the **Fe^{III}/XMH** molar ratios by the method of **Asmus**. The experimental conditions are given in Fig. 4.

Iron(III) – 4NC – XMH

3. Beer's law

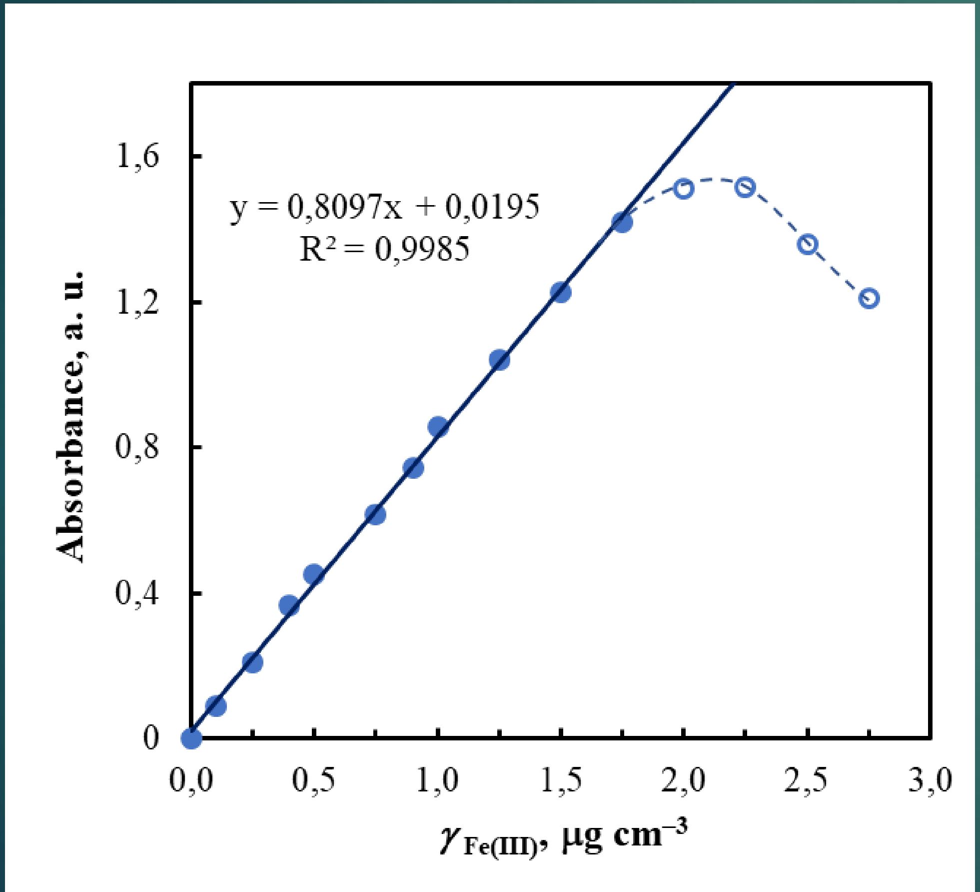


Figure 9. Beer's law

c_{4NC} = 2×10^{-4} mol dm^{-3}, c_{XMH}= 7.5×10^{-4} mol dm^{-3}, pH 6.7, λ=462 nm, extraction time t = 120 sec.

Iron(III) –4NC – XMH

4. Beer's Law and Analytical Characteristics

- The dependence between the concentration of Fe^{III} in the aqueous phase and the absorbance of the extract was studied under the optimal conditions (Table 1).
- A good linearity was obtained in the range of 0.1 – 1.75 µg cm^{-3} (R^2 = 0.99853, N = 10).
- The linear equation was $A = 0.8097\gamma - 0.0195$, where A is the absorbance and γ is the concentration (µg cm^{-3}) of Fe^{III}.
- The limits of detection (LOD) and quantitation (LOQ), calculated as 3- and 10-times standard deviation of the intercept divided by the slope, were LOD = 36 ng cm^{-3} and LOQ = 120 ng cm^{-3}.
- The molar absorptivity were $\varepsilon = 4.5\times10^4$ dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity were S = 1.2×10^{-3} µg cm^{-2} at λ_{max} = 462 nm .

Iron(III) –4NC – XMH

5. Conclusions

- The described investigations shed light on the complex formation between Fe(III) and 4NC in the presence or absence of XMH.
- Under the optimum conditions complex composition is 1:3:3 (Fe^{III}:4NC:XMH)

Thank you for your attention