A New Colorimetric Test for FeNa-EDTA in Flour

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Outline

AkzoNobel

Recommended iron fortificants for wheat flour

Methods to determine Fe contents
- intrinsic Fe vs. fortification Fe

Phenanthroline (orange color) method (NEW)

FeNa-EDTA (Ferrazone®)
- quality assurance
- additional information

Akzo Nobel: Key Figures

Net sales	€ 14 bln / year
Number of employees	approx. 60,000

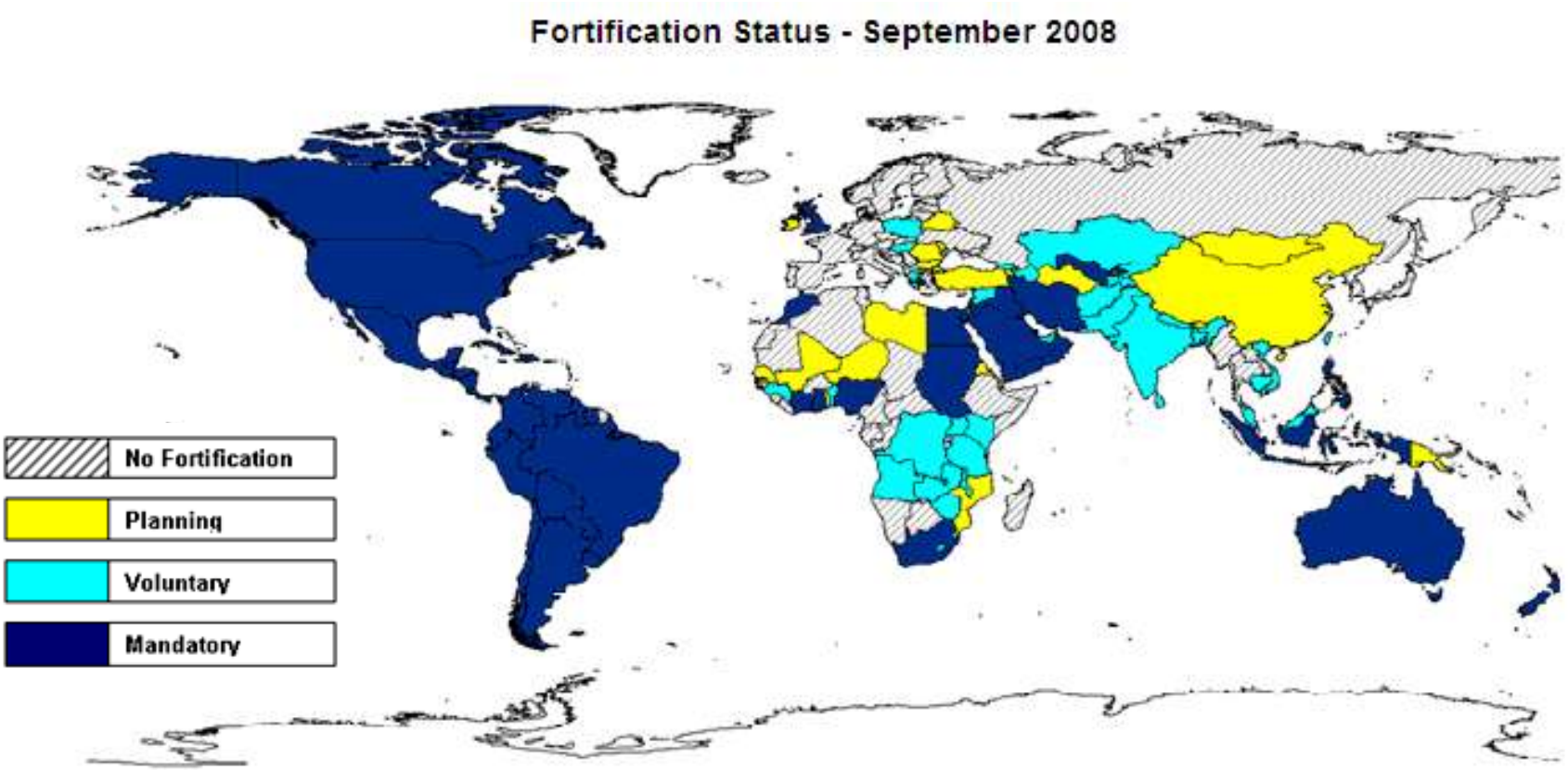
Decorative Paints
Specialty Chemicals
Performance Coatings

AkzoNobel
Tomorrow's Answers Today

Ferrazone ® ➔ Specialty Chemicals

Business Unit Functional Chemicals

National Wheat Flour Fortification Programs



…about 2/3 of the countries in the world run wheat flour fortification programs…

Source: Flour Fortification Initiative (FFI) at
http://www.sph.emory.edu/wheatflour/globalmap.php

Recommended Fe Fortification Levels

Second Technical Workshop on Flour Fortification
US CDC / FFI, Atlanta – USA, April 2008
http://www.sph.emory.edu/wheatflour/atlanta08/summary.html

Type of flour	Fortificant	Average daily consumption in g/d		
		> 300	150 – 300	< 150
LOW-extraction	**FeNa-EDTA**	**15**	**20**	**40**
	Ferrous sulfate or Ferrous fumarate	20	30	60
	Electrolytic iron	40	60	not recommended
HIGH-extraction	**FeNa-EDTA**	**15**	**20**	**40**

Intrinsic Fe Content in Flours

High-extraction wheat flour

- average: ~ 30 ppm
- range: 10 – 100 ppm (?)

Low-extraction wheat flour

- average: ~ 10 ppm
- range: 5 – 50 ppm (?)

Fe content may vary considerably from batch to batch

- and even within batches!

Total Fe Content

Determination

- dissolution of the flour in HNO_3/H_2O_2
- ultrahigh temperature in microwave
- all insoluble parts ➔ fully soluble ➔ clear solution
- injection into the flame of AAX / ICP

Total [Fe] can vary from 20 – 160 ppm

- [Fe] from fortification: 15 – 60 ppm
  - depending on iron compound and consumption level
- [Fe] of intrinsic origin: 5 – 100 ppm

Intrinsic vs. Fortification Fe?

How to differentiate intrinsic vs. fortification Fe?

- both types fully dissolve

Suppose: AAS/ICP ➔ 40 ppm Fe

- 10 ppm from fortification, 30 ppm intrinsic?
- or the other way round?
- or 20 ppm + 20 ppm?

Type of fortificant (bio-availability) is critically important

Total Fe content (AAS/ICP) is not suitable

Other Methods for Flour

Red Spot Test

- directly on the flour as such
- only for elemental iron types

Extraction of flour + colorimetric determination

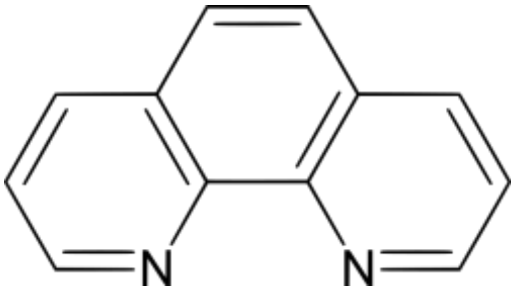
- flour is extracted with water/methanol ➔ suspension
- flour is separated from water layer
- coloring agents are added to filtrate solution

Phenanthroline (orange color) method (NEW)

Determination of [Fe] in Water

Phenanthroline (Phen)

also: ortho-phenanthroline



Gives a highly intense, orange color with ferrous ions

Fe^{2+} + 3 Phen ➔ $\{Fe(Phen)_3\}^{2+}$

Ferric ions should be reduced first (e.g. by ascorbic acid)

Fe^{3+} ➔ Fe^{2+}

Analytical method already known from 1930's

Widely-used for [Fe] determination in water

Semi-Quantitative Procedure (DEMO)

Mix 10 g of flour with 30 mL of water/methanol (80/20)

- shake vigorously during 1 minute

Separate water from flour over paper filter (~ 15 minutes)

Transfer 15 mL to 50-mL volumetric flask

Add the following reagents

- 5 mL vitamin C solution (1 g/L)
- 5 mL phenanthroline solution (1 g/L)

Fill up to 50-mL mark with water

Wait for 60 minutes

Assess color intensity by visual inspection with calibration samples

Mix with Water/Methanol

Transfer 10 g of fortified flour into a 50-mL test tube
Add 30 mL water/methanol (80/20) and mix thoroughly to suspend all flour
Shake resulting suspension vigorously for 1 minute

Filter Solution

1. Separate water from flour through a folded paper filter
2. Collect 15 mL filtrate in a 50-mL test tube

1.

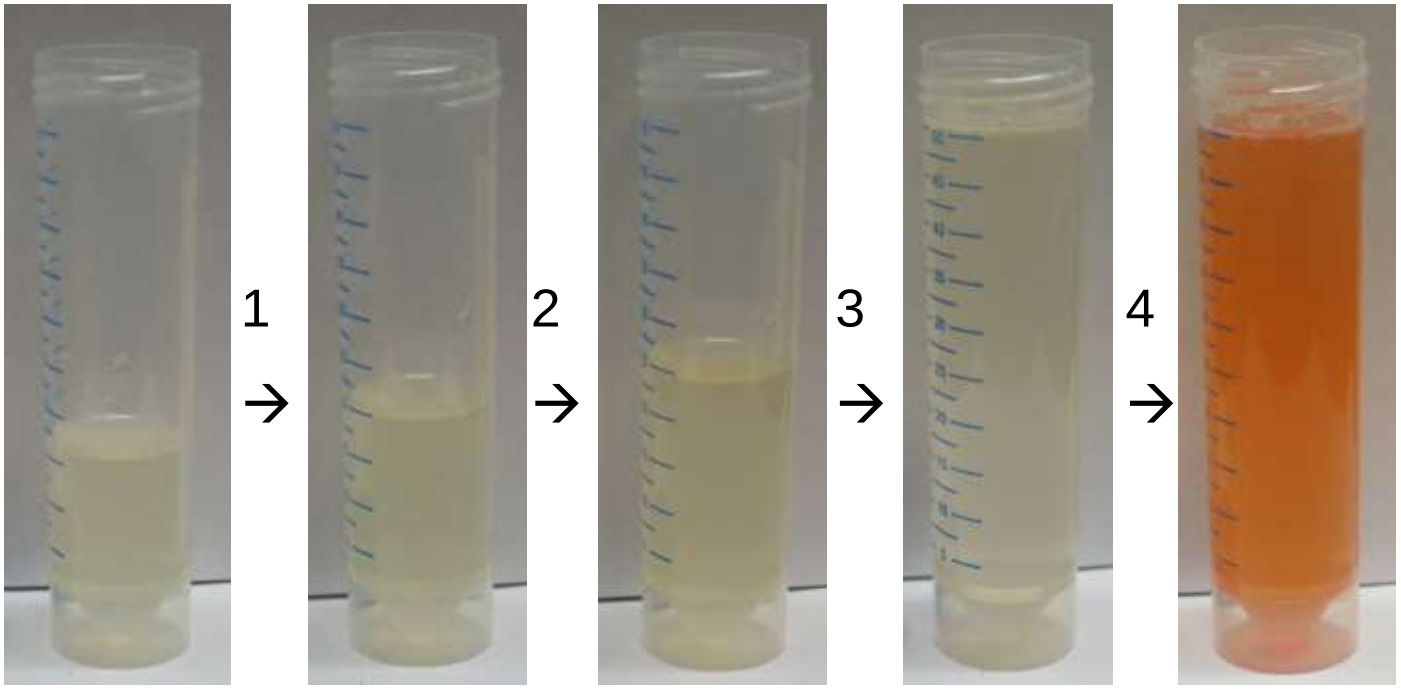
→

2.

→

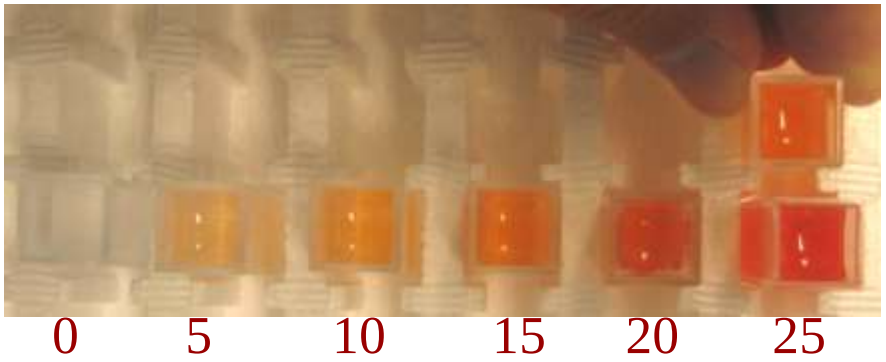
Add Reagents

1. 5.0 ml of vitamin C solution (1 g/L)
2. 5.0 ml of phenanthroline solution (1 g/L)
3. Fill up to 50 mL and mix
4. After 1 hour the color reaction has completed



Transfer to Cuvette

and Compare Visually



Other Iron Fortificants

In **HIGH**-extraction flour

- Fe as Ferrazone: can be determined reliably (2 – 30 ppm)
- Fe as *dried* $FeSO_4$: is NOT detected (bound to phytate?)
  - even heptahydrate $FeSO_4$ is hardly detected
- Fe as ferrous fumarate: is not detected either
- Fe as electrolytic iron: does not dissolve in water

Conclusion: phenanthroline method is suitable for discrimination Ferrazone vs. other (recommended) iron fortificants in high extraction wheat flour

Ongoing Research

Demo = *semi*-quantitative method

Also quantitative method available

- filtration ➔ centrifuge
- visual comparison ➔ spectrophotometer
- vitamin C ➔ hydroxylamine

HIGH-extraction flours: methods work OK

- other iron fortificants are not detected (phytate?)
- also true for LOW-extraction flours (low in phytate)?

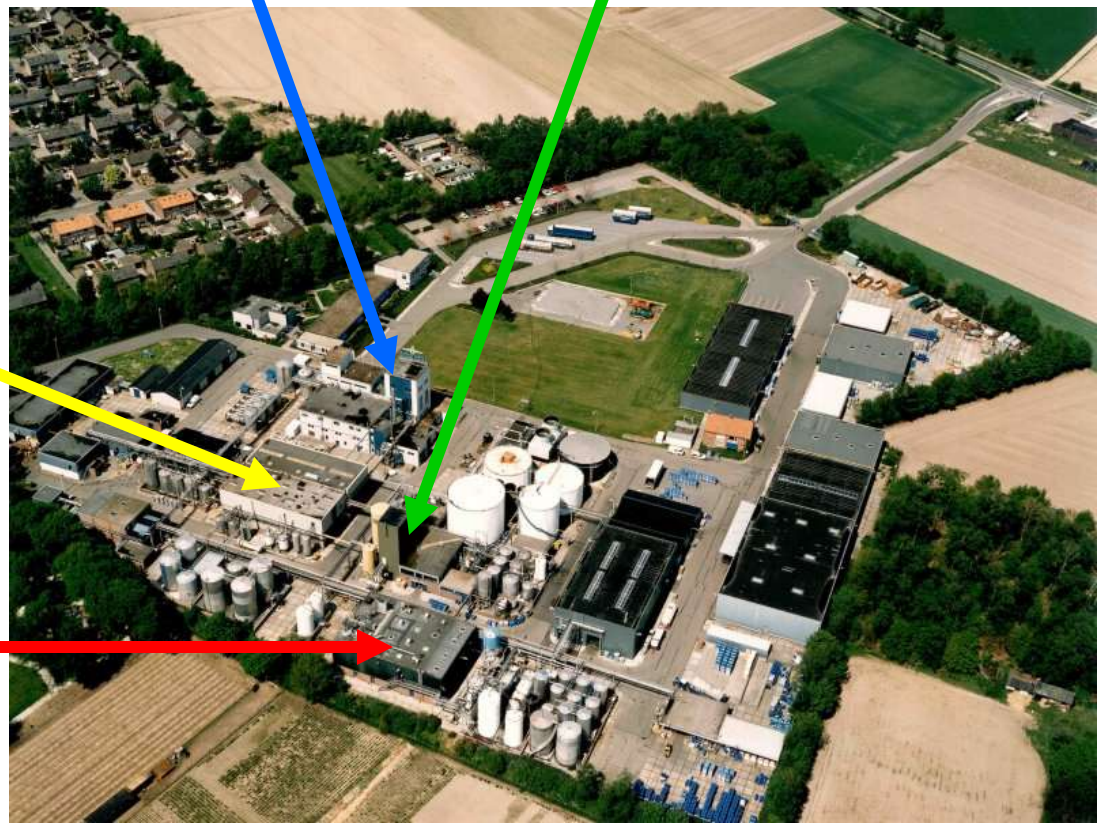
Manufacturing & Quality Assurance

Na_2H_2-EDTA

$CaNa_2$-EDTA

Na_4-EDTA

FeNa-EDTA



Production site in Herkenbosch, the Netherlands

Cross Contamination

- Major risk in food, pharma ingredients
  - inevitable with >1 product on same line
  - dedicated line >> multipurpose unit !
    - rigorous cleaning !
- Ferrazone: DTPA on same line
  - toxicology DTPA ≈ EDTA
    - low risk ➔ no “Critical Control Point” (CCP)

HACCP

Hazard Analysis Critical Control Points

- how to prevent illness and worse from food?
- Codex Alimentarius = WHO/FAO = worldwide

Food Safety System

- guidelines to check and recheck production
- audit by independent bureau => certificate

CCP: parts in the process with enhanced health risk

- e.g. micro-organisms in process water => extra controls

Certificates

HACCP since February 2004

Also for Dissolvine E-CA-10 and Dissolvine NA-2-P

Halal correct (below)

Halal Correct ® الأمانة الإسلامية

International Halal Correct Certification

Halal Certificate شهادة حلال

No: 070222-AN

AKZO NOBEL Functional Chemicals B.V.

6075 ZG Herkenbosch in The Netherlands

BUREAU VERITAS Certification

Certification

Awarded to

AKZO Nobel Functional Chemicals B.V.

Lispinweg 6, 6075 CE HERKENBOSCH, The Netherlands

The HACCP-system has been assessed by Bureau Veritas Certification Nederland B.V. and found to be in accordance with the standard defined by the "Dutch National Board of Experts HACCP"

STANDARD

Requirements for a HACCP based Food Safety System, September 2002

SCOPE OF SUPPLY

EDTA based food grade products.

Original Approval Date: 12 February 2004

Subject to the continued satisfactory operation of the organization's HACCP System, this certificate is valid until: 20 April 2010

Certificate Number: NL7001452 Date: 21 August 2007

MGMT. SYS. RvA C 248

Why Food Grade?

Cross contamination (see above)

FeNa-EDTA

- also used, and at a large scale, in agriculture!

Plants do not care about sand, dust, glass splinters, …

- humans do!

Starting materials

- should be 100% free of toxic contaminants
  - e.g. hydrochloric acid (HCl)
    - may contain traces of chlorinated phenols due to recycling
    - only “virgin” HCl should be used, made from H_2 and Cl_2.

Unsuitable FeNa-EDTA

FeNa-EDTA + water => clear brown solution

- no insoluble matter = sand, dust, glass splinters, …?

Filter test: paper should be entirely **white** after filtration

Brown precipitate and/or unidentifiable particles on filter

- FeNa-EDTA for agricultural use only

Regulatory Status FeNa-EDTA

JECFA (2007)

Sodium iron EDTA is suitable for use as a source of iron for food fortification to fulfill nutritional iron requirements …

US FDA

Gras Notices GRN 152 and 178

EU EFSA

Dossier submitted, final statement pending

India

Approved for atta flour and drinks by PFA

Approval also in Brazil, China, Mexico, Pakistan, Philippines, Vietnam, …

No formal approval yet in African countries

Current Applications

China: soy sauce, wheat flour

- voluntary program with strong government support
- locally sourced FeNa-EDTA

Vietnam: fish sauce (just launched)

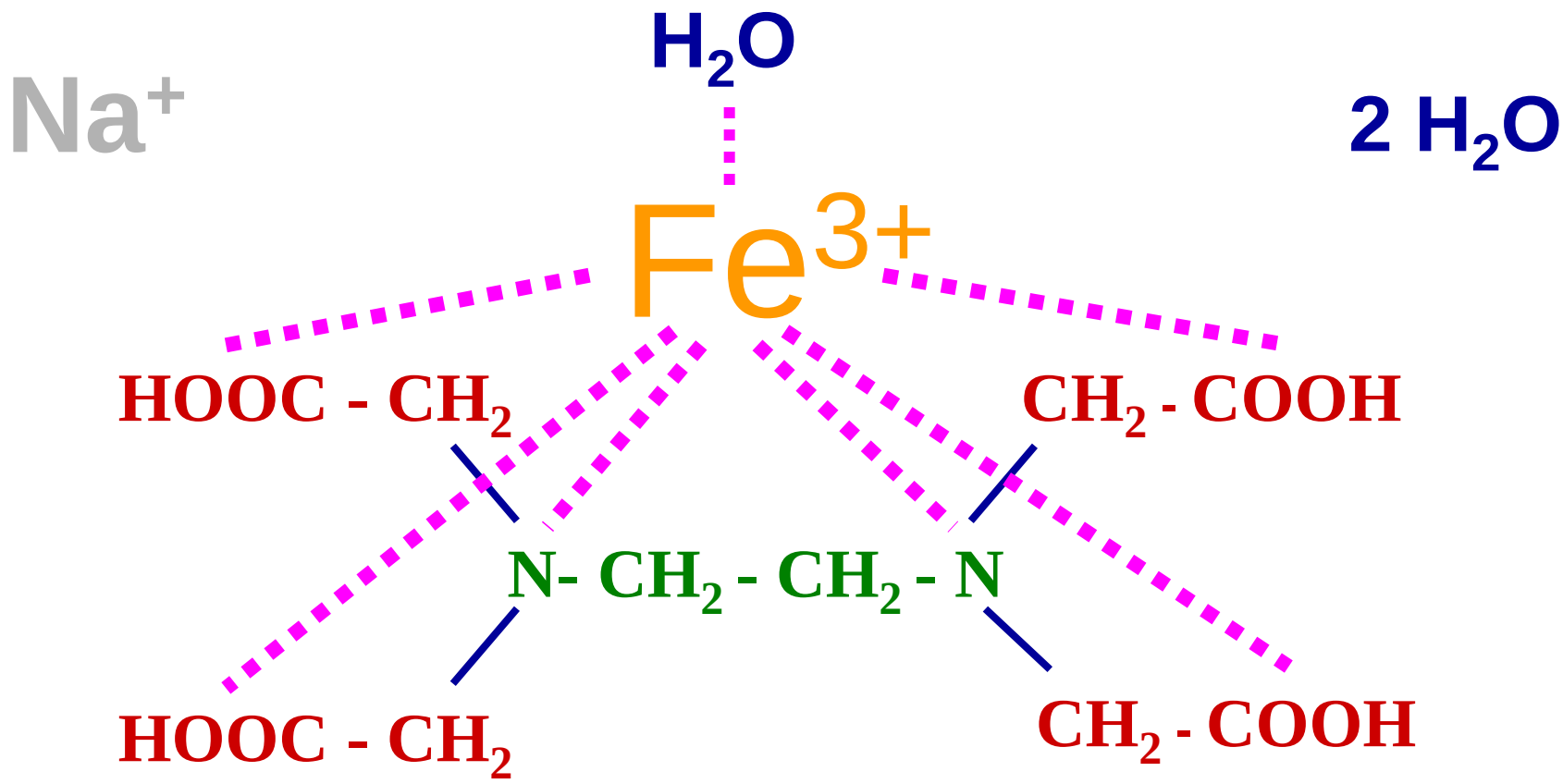
Pakistan: atta flour (started in 2007)

Brazil, Mexico, Philippines, …:

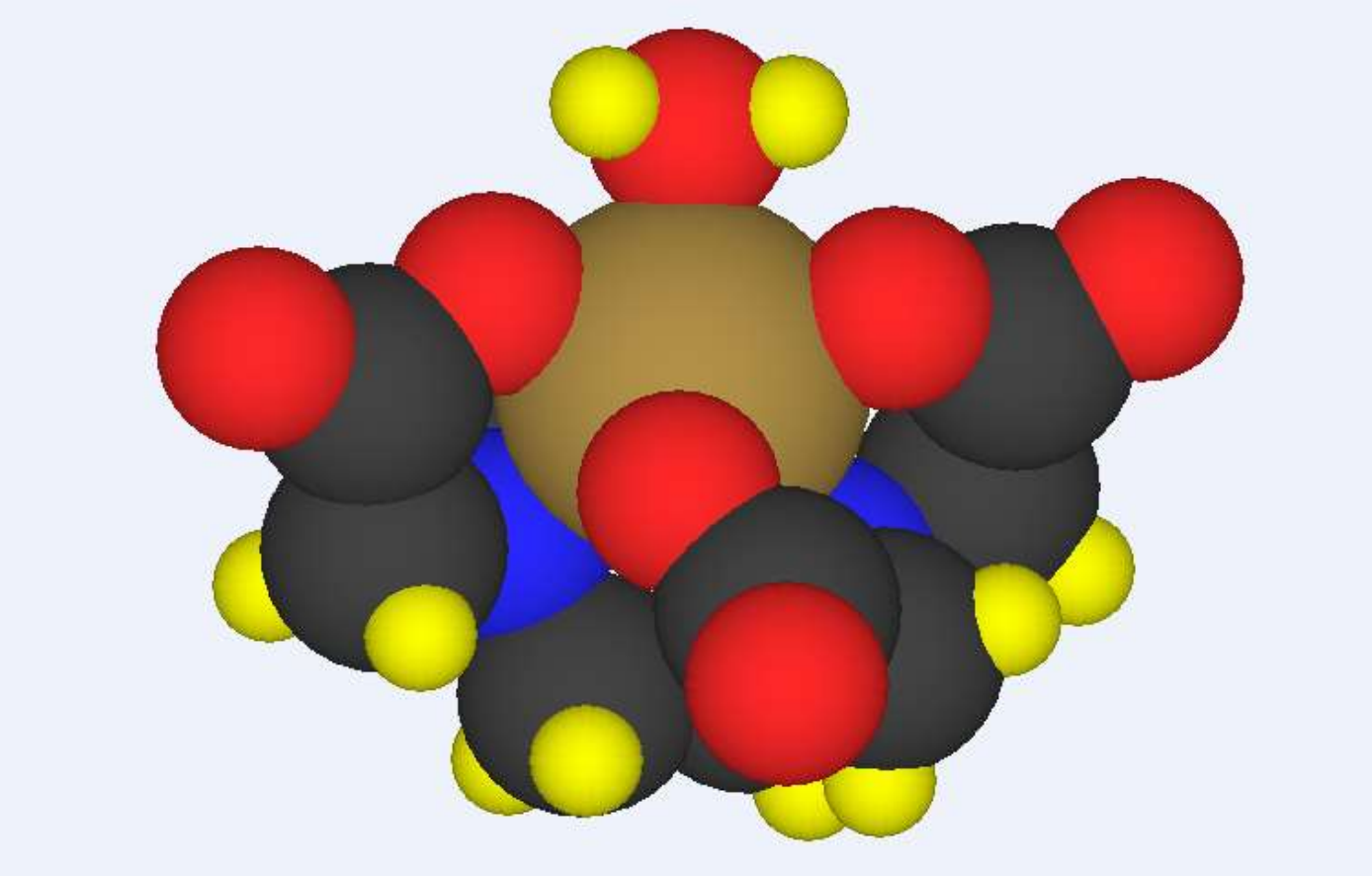
- powdered beverage (Tang) of Kraft

Ferric Sodium EDTA

$FeNa\text{-}EDTA.3H_2O$



3-Dimensional Model



Ferric-EDTA monohydrate complex-ion
Wageningen University 2007

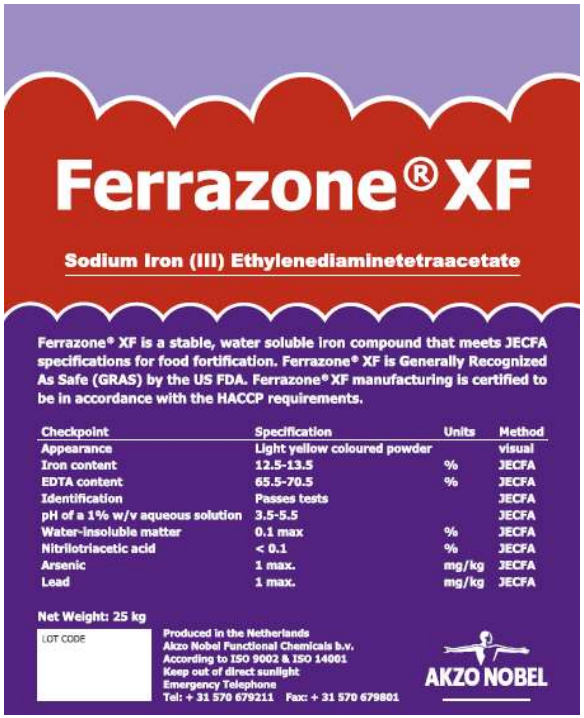
Ferrazone® XF

Food-grade ferric sodium EDTA ex AkzoNobel

➔**Ferrazone ®**

Wheat flour: particle size < 150 micron special “extra fine” grade

➔ **Ferrazone® XF**



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Thank You for Your Attention

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