Sudan Dyes in Foods

A Technical Presentation in
DIFSC2010

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Sudan Dyes in Foods

- **2003 May:** Sudan I detected in Chilli products (France)
- **2003 July:** The products contaminated with Sudan I in France were later found out to be produced in UK/produced in Italy and imported into UK.
- **2005 February:** A Worcester sauce was reported to be contaminated with Sudan I. This contamination led over 400 products being taken off the shelves.

*Cause of this contamination in many of these cases was linked to Chilli powder, chilli products or curry powder that had been illegally contaminated with Sudan dyes.*
Sudan Dyes in Foods

- **2005 May:** Sixty nine products were withdrawn from sale by companies in UK due to presence of Para Red.

- **2005 – 2007:** Sudan I traces were found in several spices (South Africa).
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Safety of Sudan dyes

- Sudan dyes are suspected carcinogens
- IARC considers Sudan I,II,III,IV as Group 3 carcinogens
- Sudan dyes have been reported as contact allergens and sensitisers.
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Regulations:

- Sudan dyes are not permitted colours in food regulations of many countries/agencies (e.g., UAE, EU, Australia, Canada, China, Hong Kong, …).
- Their presence, at any level is not permitted in foods.
Sudan Dyes in Foods

Introduction:

- Sudan dyes are Synthetic chemical dyes of similar chemical structure.
- They are oil-soluble, aromatic compounds containing azo group (-N=N-)
- Sudan I,II,III and IV are red dyes that are used for colouring hydrocarbon solvents, oils, waxes, petrol, plastics and shoe & floor polishes.

- Added to foods such as chilli powder to mimic/intensify their natural hues.
Sudan Dyes in Foods

<table>
<thead>
<tr>
<th>Sudan dye</th>
<th>CAS Number</th>
<th>CI No</th>
<th>Chem. Class</th>
<th>Molecular Formula</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sudan I</td>
<td>842-07-09</td>
<td>12055</td>
<td>Azo</td>
<td>C_{16}H_{12}N_2O</td>
<td>248.28</td>
</tr>
<tr>
<td>Sudan II</td>
<td>3118-97-6</td>
<td>12140</td>
<td>Azo</td>
<td>C_{18}H_{16}N_2O</td>
<td>276.33</td>
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<tr>
<td>Sudan III</td>
<td>85-86-9</td>
<td>26100</td>
<td>Azo</td>
<td>C_{22}H_{16}N_4O</td>
<td>352.39</td>
</tr>
<tr>
<td>Sudan IV</td>
<td>85-83-6</td>
<td>26105</td>
<td>Azo</td>
<td>C_{24}H_{20}N_4O</td>
<td>380.44</td>
</tr>
<tr>
<td>Sudan Red 7B</td>
<td>6368-72-5</td>
<td>26050</td>
<td>Azo</td>
<td>C_{24}H_{21}N_5</td>
<td>379.46</td>
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<td>Para red</td>
<td>6410-10-2</td>
<td>12070</td>
<td>Azo</td>
<td>C_{16}H_{11}N_3O_3</td>
<td>293.28</td>
</tr>
</tbody>
</table>
# Sudan Dyes in Foods

<table>
<thead>
<tr>
<th>Sudan dye</th>
<th>Melting Point (° C)</th>
<th>( \lambda_{\text{max}} ) (nm) (Toluene)</th>
<th>Chemical name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sudan I</td>
<td>131-133</td>
<td>476 (418)</td>
<td>1-phenylazo-2-naphthol</td>
</tr>
<tr>
<td>Sudan II</td>
<td>156-158</td>
<td>493 (420)</td>
<td>1-(2,4-Xylylazo)-2-naphthol</td>
</tr>
<tr>
<td>Sudan III</td>
<td>199 (dec.)</td>
<td>507 (354)</td>
<td>1-[4-(Phenylazo)phenylazo]-2-naphthol</td>
</tr>
<tr>
<td>Sudan IV</td>
<td>199 (dec.)</td>
<td>520 (357)</td>
<td>1-[2-methyl-4-(2-methylphenylazo)phenylazo]-2-naphthol</td>
</tr>
<tr>
<td>Sudan Red 7B</td>
<td>130 (dec.)</td>
<td>535 (372)</td>
<td>N-ethyl-1-[([p-(phenylazo)phenyl]azo]-2-naphthalamine</td>
</tr>
<tr>
<td>Para red</td>
<td>248-252</td>
<td>488 (328)</td>
<td>1-(4-Nitrophenylazo)-2-naphthol</td>
</tr>
</tbody>
</table>
Sudan Dyes in Foods

Chemical Structures of Sudan dyes

Sudan I

Sudan II
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Chemical Structures of Sudan dyes

Sudan III

Sudan IV
Sudan Dyes in Foods

Chemical Structures of Sudan dyes

Sudan Red 7B

Para Red
Sudan Dyes in Foods

Sudan dyes – Analytical Methodology

1) Sudan dyes are extracted from sample using mixed solvent (Acetonitrile & Acetone)

2) Sudan dyes in the clear extract are separated by HPLC
   a) Column: Lichrosorb 10 RP C-18 (4.6 mm i.d x 250 mm)
   b) Mobile phase: 10 mM NH$_4$OAc in water (pH: 3.6) + Acetonitrile at 1.5 mL/min

3) Sudan dyes are detected by PDAD at 480 nm & 550 nm.
STANDARD CHEMICAL SOLUTIONS

Standard Solution (2 mg/L)  Reagent Blank

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CHILLI POWDER SAMPLE

Spiked Sample (5 mg/kg)

Pure Sample
Sudan Dyes in Foods

CHILLI POWDER SAMPLE - ADULTERATED

Chilli powder Positive sample at 480 nm

Chilli powder Positive sample at 550 nm
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SAFFRON SAMPLE

Pure Sample

Spiked Sample (20 mg/kg)
Sudan Dyes in Foods

SAFFRON SAMPLE - ADULTERATED

Saffron Sudan positive sample at 480 nm

Saffron Sudan positive sample at 550 nm
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Sudan dyes – Method performance

1) Inter day precision: % RSD – 8
2) Limit of detection: 0.3 mg/kg of Sample
3) Linear range of Calibration graph: up to 20 mg/L with 20 µL injection volume
4) Recovery (for various matrices & in the spike level range of 1 to 20 mg/kg): 70 to 110 %
5) Chilli/Saffron matrix components did not give any peaks close to those of Sudan dyes.
# Sudan Dyes in Foods

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Name of Material</th>
<th>No. of Samples tested</th>
<th>Positive Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Number</td>
</tr>
<tr>
<td>1</td>
<td>Saffron</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Chilli powder</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Paprika powder</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Turmeric powder</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Mixed Spice powder</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Masala powder</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>Sumac</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>94</strong></td>
<td><strong>9</strong></td>
</tr>
</tbody>
</table>
Sudan Dyes in Foods

Surveillance of Sudan dyes in Spice products

![Graph showing the surveillance of Sudan dyes in various spice products.](image-url)
Sudan Dyes in Foods
Surveillance of Sudan dyes in Spice products
- Number of Samples
Sudan Dyes in Foods

Sudan dyes in Spice products – Number of Positive samples
Conclusions

1) Method standardised at F&ELS is found fit to detect Sudan I – IV, Para red & Sudan Red 7B at levels of current regulatory recommendation.

2) Chilli / Saffron matrix components did not interfere with analytes under consideration

3) Presence of Sudan dyes in some of the samples tested indicates the necessity of continuing this activity.
Sudan Dyes in Foods

Working Group:

Dr. A. G. Krishnamacharyulu & Mrs. Vaidehi Garimella
Sudan Dyes in Foods

THANK YOU

For your
Cooperation &
Patient listening

-Dr. Gopalakrishna