# LIFE12 ENV/IT/000352 "BIONAD"
## Naturalised dyes replacing commercial colorants for environmentally friendly leather dyeing and water recycle

**Duration**
**01.01.2014 to 30.06.2016**

**Total Budget**
**€ 1,469,056.00**

**EU contribution**
**€ 725,713,00**

### Coordinating beneficiary

**Chemical Institute of organometallic compounds of CNR (IT)**

### Associated beneficiaries

**Chemical Department "Ugo Schiff" Florence University (IT)**

**Serichim Srl (IT)**

**Asociación de Investigación para la industria del calzado (ES)**

**Biokimica Group (IT)**


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## Action C1 of the project
## Quantitative analysis of metals in commercial and naturalised dyes

**Beneficiary responsible for implementation**
**ICCOM-CNR**


**The metal content of supposedly metal free dyes involved in the BioNaD project was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Optima-8000, Perkin Elmer) and in the case of Hg with a direct analyzer (DMA-80, Milestone, Italy). Relatively high amounts of Al and Fe were found in the commercial disperse dyes and surprisingly, an unexpected high amount of Hg was detected for commercial Blue Teratop GLF and Foron Brown Yellow. The purification of disperse dyes using the Soxhlet technique furnished almost metal free chromophores, highlighting the low quality of the additives, used to formulate the commercial disperse products. The metal content of chromophores supplied in the wet press-cake form was good and this level of metals did not increase, when lactose was employed to convert them into the corresponding glyconjugated dyes.**


## The Equipment

ICP-OES, Optima-8000


Direct analyzer, DMA-80

## The Naturalized Dyes

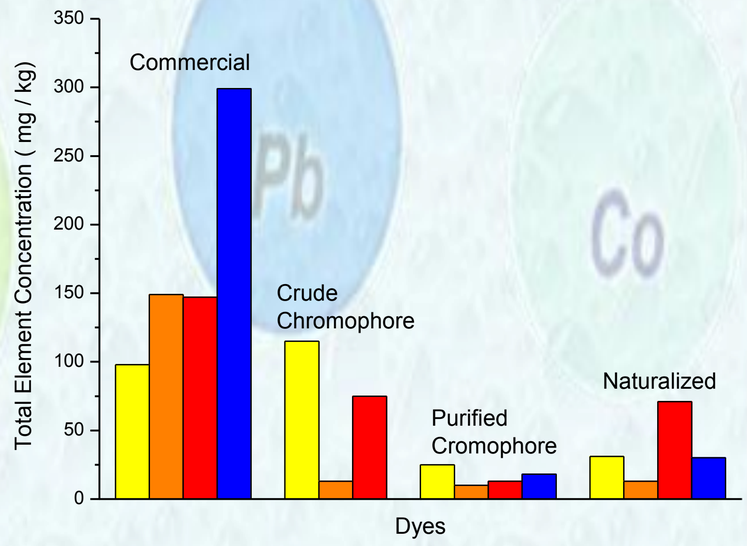

## Results

| | Commercial Dyes (mg/Kg) | | | | Crude Chromophores (mg/Kg) | | | $LOQ_m$ (mg/Kg) |
|---|---|---|---|---|---|---|---|---|
| **Metal** | Teratop Brown GWL | Foron Brown Yellow S-2RFL150 | Foron Brilliant Red S-RGL200 | Teratop Blue GLF | Disperse Yellow 42 | Disperse Orange 30 | Disperse Red 202 | |
| **Al** | 32.7 | **49.8** | **47.6** | 26.1 | **64.3** | - | - | 0.83 |
| **As** | 8.1 | -a | 7.5 | - | 0.94 | - | - | 0.83 |
| **B** | - | - | - | **64.1** | 3.6 | - | 29.0 | 0.83 |
| **Ba** | 0.84 | 0.63 | 4.8 | 3.0 | 1.7 | - | - | 0.02 |
| **Be** | - | - | - | - | - | 0.30 | - | 0.07 |
| **Cd** | 0.10 | 0.13 | - | - | 0.15 | - | - | 0.08 |
| **Co** | - | - | - | - | - | - | - | 0.17 |
| **Cr** | - | 3.8 | 3.3 | 2.8 | 0.59 | | 0.60 | 0.17 |
| **Cu** | - | - | - | 11.4 | 0.40 | | 1.4 | 0.33 |
| **Fe** | 21.5 | **49.9** | **44.5** | **112.4** | 29.2 | 1.8 | 33.7 | 0.08 |
| **Hg** | 0.0070 | **0.46** | 0.0017 | **0.66** | 0.060 | 0.010 | 0.090 | $8.5\times10^{-5}$ |
| **Mn** | 11.2 | 18.3 | 12.9 | 59.1 | 0.91 | 0.25 | 0.34 | 0.08 |
| **Ni** | - | 2.4 | 2.4 | 2.1 | 0.42 | - | | 0.42 |
| **Pb** | - | - | - | 3.5 | 2.0 | 1.5 | 1.3 | 0.83 |
| **Sb** | 2.1 | 1.9 | - | - | - | - | - | 1.70 |
| **Se** | 3.9 | 2.2 | 2.0 | - | 2.4 | | - | 1.70 |
| **Tl** | - | - | - | - | - | - | - | 1.70 |
| **V** | 9.8 | 14.3 | 22.1 | 1.8 | 0.73 | 1.1 | | 0.42 |
| **Zn** | 2.9 | - | - | 10.6 | 4.6 | 0.62 | 1.6 | 0.17 |
| **Total[b]** | **97.7** | **148.7** | **153.0** | **303.8** | **115.6** | 14.4 | 76.0 | [10.4][c] |

| | Purified Chromophores from Commercial Dyes (mg/Kg) | | | | Naturalised Dyes (mg/Kg) | | | | $LOQ_m$ (mg/Kg) |
|---|---|---|---|---|---|---|---|---|---|
| **Metal** | Disperse Yellow 42 | Disperse Orange 30 | Disperse Red 202 | Disperse Blue 27 | DY42-Nat | D030-Nat | DR202-Nat | DB27-Nat | |
| **Al** | - | - | - | - | - | 0.90 | 6.6 | - | 0.83 |
| **As** | 8.2 | - | 3.9 | - | - | - | - | - | 0.83 |
| **B** | - | - | - | - | - | - | - | - | 0.83 |
| **Ba** | 0.37 | - | - | - | - | 0.03 | 0.17 | 0.19 | 0.02 |
| **Be** | - | - | - | - | 0.31 | 0.29 | 0.27 | - | 0.07 |
| **Cd** | 0.13 | - | - | - | - | - | - | - | 0.08 |
| **Co** | - | - | - | - | - | - | - | - | 0.17 |
| **Cr** | - | - | - | 1.1 | 0.85 | 0.45 | 4.5 | 2.1 | 0.17 |
| **Cu** | - | - | - | 1.0 | - | - | - | - | 0.33 |
| **Fe** | - | - | - | 2.0 | 1.7 | 1.0 | 49.7 | 2.1 | 0.08 |
| **Hg** | 0.00015 | 0.0012 | 0.0001 | 0.0030 | 0.010 | 0.020 | 0.010 | 0.020 | $8.5\times10^{-5}$ |
| **Mn** | - | - | - | - | - | 0.19 | 0.57 | 0.25 | 0.08 |
| **Ni** | - | - | - | 0.50 | - | - | 2.1 | 1.2 | 0.42 |
| **Pb** | - | - | - | 3.7 | 2.2 | - | - | - | 0.83 |
| **Sb** | 3.7 | 1.7 | - | | - | - | - | | 1.70 |
| **Se** | 6.8 | - | - | - | - | - | - | - | 1.70 |
| **Tl** | - | - | - | - | - | - | - | - | 1.70 |
| **V** | - | - | - | - | 1.2 | 1.3 | 1.2 | 1.0 | 0.42 |
| **Zn** | - | - | - | 1.7 | 17.7 | 2.8 | 6.4 | 15.5 | 0.17 |
| **Total[b]** | 25.3 | 10.4 | 12.6 | 17.6 | 31.9 | 15.6 | 79.7 | 31.4 | [10.4][c] |

a - concentrations that are not reported are below LOQm.
b - sum of concentrations includes LODm whenever the determined values cannot be quantified.
c – sum of LOQm.

## Total metal content




## Conclusions

**The total metal content decreased in the order: commercial dyes > crude chromophores ≥ naturalized dyes > purified chromophores (from commercial products). The results demonstrate that: i) additives contribute to increase the content of toxic elements, which have an impact on both waste management and the quality of dyed leather and ii) the viability of lactose, as raw material, in the synthesis of water soluble naturalized dyes for dyeing applications, without the need to chase an additive based formulation.**