

The Unknown world of Analytical Chemistry

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Why unknown?

Analytical Chemistry is often considered the technique able to measure the pH or the concentration of an analyte.

but

Analytical Chemsitry doesn't mean only to use spectrophotometers, electronic microprobe and so on: it means experimentation, observation, revealing the facts and drawing deductions. *P.W. West, Anal. Chem.* **1974** 46(9), 784A

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Research topics of the group

- Reduction of environmental impact of waste waters: geopolimers
- «Forest bathing» the role of volatile compounds
- Hexacyanometallates: powerfull compounds
- Analytical answers through statistical elaborations of data

• Reduction of environmental impact of waste waters: geopolimers

Inorganic polymers based on silicate and aluminosilicate materials.



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Reduction of environmental impact of waste waters: geopolimers

Inorganic polymers based on silicate and aluminosilicate materials.



Chemistry Wednesdays March 24, 2021

Chemistry Division

Synthesis of geopolymer

Reagents	Metakad
iteu Seines	(g)

Γ

Metakaolin	Sodium Silicate	NaOH	Waste water
(g)	(g)	(g)	(mL)
51	52,7	7	20





Leaching test

4weeks



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THE QUALITY OF THE AIR the added value of the AMP Tremiti Islands By Martina Fattobene graduating student

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Determination of BVOCs with therapeutic effect on human health

1.Study of the area of interest2.Sampling

3.Analysis



1. Botanical reliefs to determine the most important tree species

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2. Sampling to capture BVOC emitted from plants (terpenes)





3. Analysis to determine which and how many BVOCs



Extraction and qualitative/quantitative analysis (GC/MS)



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Tremiti Island: perfect match between sea and forest Hexacyanometallates: powerfull compounds

Prussian Blue and its analogues have the general formula

 $A_xFe^{+2}[Fe^{+3}(CN)_6]*mH_2O$ $A_xM_y[B(CN)_6]*mH_2O$

M & B = transition metals A = alkali metal cation

x and y = stoichiometric coefficients

m = water molecules intercalated in the structure (< 14)

M and Fe are octahedrally coordinated by $-N\equiv C$ and $-C\equiv N$ ligands

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Introduction to Hexacyanometallates



Introduction to Hexacyanometallates



Applications of Prussian Blue analogs by our group

- <u>Electrochromism and Thermochromism</u>
- Batteries
- <u>Cation Exchange</u>
- Ionic sensors
- Electrocatalysis

Electrochromism

Electrochromism is the property of an electroactive species to exhibit optical absorption bands due to an electron-transfer or "redox" reaction in which it either gains or loses an electron (it undergoes reduction or oxidation)





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Thermochromism

Journal of Solid State Electrochemistry Volume 1, Issue 1, 1997, Pages 88-93

Spectroelectrochemical identity of Prussian blue films in various electrolytes: Comparison of timederivative voltabsorptometric responses with conventional cyclic voltammetry (Article) Kulesza, PJ,⁸, Zamponi, S.^b, Malik, M.A.^{s,c}, Miecznikowski, K.^s, Berrettoni, M.^b, Marassi, R.^b, Q

*Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland *Dipartimento di Scienze Chimiche, Università di Camerino, via S. Agostino 1, I-62032 Camerino, Italy *Division of General Chemistry, Department of Metallurgy, Technical University of Sciescholowa, Armii Krajowej 19, PL-42-200 Czestochowa, Poland

Journal of the Electrochemical Society Volume 143, Issue 1, January 1996, Pages L10-L12

Countercation-sensitive electrochromism of cobalt hexacyanoferrate films (Article)

Kulesza, P.J.ª, Malik, M.A.ª,c, Miecznikowski, A.K.ª, Wolkiewicz, A.ª, Zamponi, S.^b, Berrettoni, M.^b, Marassi, R.^b 🙎

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Electrochimica Acta

Volume 43, Issue 8, 22 December 1997, Pages 919-923

Spectroelectrochemical characterization of cobalt hexacyanoferrate films in potassium salt electrolyte $_{\rm (Article)}$

Kulesza, P.J.^a, Zamponi, S.^b, Malik, M.A.^{a,c}, Berrettoni, M.^b, Wolkiewicz, A.^a, Marassi, R.^b <u>A</u>

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Materials Chemistry and Physics Volume 120, Issue 1, 15 March 2010, Pages 118-122

Cobalt hexacyanoferrate-poly(methyl methacrylate) composite: Synthesis and characterization

Zanotto, A.ª 🖂, Matassa, R.^b, Saladino, M.L.^a, Berrettoni, M.^c, Giorgetti, M.^c, Zamponi, S.^d, Caponetti, E.^{a,b} 🙎

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Electrochimica Acta

Volume 51, Issue 1, 5 October 2005, Pages 118-124

Cobalt hexacyanoferrate in PAMAM-doped silica matrix: 1. Solid state electrochemistry and thermochromism $_{\rm (Article)}$

Zamponi, S.ª, Giorgetti, M.^b, Berrettoni, M.^b 🖾, Kulesza, P.J.^c, Cox, J.A.^d, Kijak, A.M.^d 🔍

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Thermochromism is the ability of substance to change color due to a change in temperature



CoHCF absorbed in gel has a purple-brown color and shows thermochromic reversible behavior when heated between 25°C to 85°C.

The color turns from purple-brown to emerald-green.



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Cation exchange



Journal of the Electrochemical Society Volume 143, Issue 1, January 1996, Pages L10-L12

Countercation-sensitive electrochromism of cobalt hexacyanoferrate films (Article)

Kulesza, P.J.ª, Malik, M.A.ª,c, Miecznikowski, A.K.ª, Wolkiewicz, A.ª, Zamponi, S.^b, Berrettoni, M.^b, Marassi, R.^b Q

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Analyst

Volume 126, Issue 12, 2001, Pages 2168-2171

Nickel hexacyanoferrate membrane as a coated wire cation-selective electrode

Giorgetti, M., Scavetta, E., Berrettoni, M., Tonelli, D. 🙎

Department of Physical Chemistry, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

International Journal of Electrochemical Science Open Access

Volume 13, Issue 6, 1 June 2018, Pages 5535-5551

An overview on the facile and reversible cations intercalation in nickel-hexacyanoferrate open framework (Article) (Open Access)

Ciabocco, M.ª, Berrettoni, M.ª 🖾, Zamponi, S.^b, Spinosi, R.^b, Conti, P.^b 🙎

^aDipartimento di Chimica Industriale Toso Montanari, UOS, Campus di Rimini, Università di Bologna, Rimini, Italy ^bScuola di Scienze e Tecnologie, Università di Camerino, Camerino, Italy

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Chemometrics comes to the rescue

CHEMOMETRICS, WHAT IS IT FOR?

Chemometrics is a scientific discipline born in 1974 since the scientist Svante Wold (Umeå University - Sweden) and Bruce Kowalski (University of Seattle - USA). Chemometrics is the science of extracting information from chemical systems by data-driven means. Chemometrics is inherently interdisciplinary, using methods frequently employed in core data-analytic disciplines such as multivariate statistics, applied mathematics, and computer science, in order to address problems in chemistry, biochemistry, medicine, biology and chemical engineering.

Chemometrics uses mathematics, statistics and formal logic:

- to design or select optimal experimental procedures;
- to provide maximum relevant chemical information by analyzing chemical data;
- to obtain knowledge about chemical systems.

The ingots of the Gela Museum

A unique archaeological treasure of 40 **brass** ingots was recovered from the sea near Gela, that was major harbour of Sicily in the ancient Greek period. The ingots, found near the remains of a ship, were dated around the end of the VI century BC, and coming from the eastern Mediterranean and the Aegean sea. The ingots mostly consist of copper and zinc although many have a significant amount of lead; therefore these ingots are made of brass, or more appropriately, of orichalcum, the rarest and most precious alloy of ancient times.

Further 47 ingots were found in February 2016 in the seabed of Contrada Bulala (Gela)



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Measurements on the 40 ingots of the first discovery

Eugenio Caponetti, Armetta Francesco, Delia Chillura Martino, Maria Luisa Saladino, Stefano Ridolfi, Gabriella Chirco, Mario Berrettoni, Paolo Conti, Nicolò Bruno, Sebastiano Tusa; Mediterranean Archaeology and Archaeometry, 17(2), 2017, 11-18 Eugenio Caponetti, Francesco Armetta, Lorenzo Brusca, Delia Chillura Martino, Maria Luisa Saladino, Stefano Ridolfi, Gabriella Chirco, Mario Berrettoni, Paolo Conti, Nicolò Bruno, Sebastiano Tusa; Microchemical Journal 135 (2017) 163–170

Dimension of the ingots

Elements quantified by ICP-OES for the majority, and ICP-MS for trace elements





Apparently no information

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Chemometric analysis: Clustering

The dendrogram, obtained by Ward method, shows 4 groups The grouping is confirmed even with PCA



The final clusters are considered natural groups only after validation





But is all this meaningfull?

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Lentil authentication by XRF spectroscopy

Paolo Conti, Silvia Zamponi, David Ranganathan, Mario Berrettoni, Marco Giorgetti, Fabio Bruzzechesse, Mirko Marangoni; La Chimica & l'Industria, 2011, 84-87

Map of sampling sites





Chemometrics: PLS-DA latent space



Fig. 4 - Rappresentazione dei campioni sulle prime tre variabili latenti della PLS-DA (40% della varianza degli spettri ritenuta); dati pretrattati con SNV e autoscalati per colonna

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Evolutionary analysis of operando-EXAFS spectra

Paolo Conti, Silvia Zamponi, Marco Giorgetti, Mario Berrettoni, William H. Smyrl; Analytical Chemistry, 82(9), 2010, 3629–3635. Angelo Mullaliu, Paolo Conti, Giuliana Aquilanti, Jasper Rikkert Plaisier, Lorenzo Stievano, Marco Giorgetti; Lorenzo Stievano, Marco Giorgetti; Condens. Matter, 3(4), 2018, 36 Angelo Mullaliu, Giuliana Aquilanti, Paolo Conti, Jasper R. Plaisier, Marcus Fehse, Lorenzo Stievano, Marco Giorgetti; J. Phys. Chem. C, 122, 2018, 15868–15877. Marcus Fehse, Antonella ladecola, Moulay Tahar Sougrati, Paolo Conti, Marco Giorgetti, Lorenzo Stievano; Energy Storage Materials, 18, 2019, 328–337

Evolution of the cathodic material K_{0.44}Fe_{1.56}Co(CN)₆

MCR-ALS permit, without any preexisting model or a priori information on the system, to decompose the operando data matrix XS,W in a product of two matrices $X_{S,W} = C_{S,F} \cdot A_{W,F}$, where $C_{S,F}$ contains the pure concentration profiles and $A_{W,F}$ the pure spectral components.





release/insertion reaction induce a deep modification at the Fe K-edge, while the Co Kedge remained mostly unchanged. This highlights the electroactivity of the iron site with consequent electronic and structural adjustments. For instance, the Fe main edge shifted towards higher energies while charging, evidencing an oxidation of the metal, while the opposite trend was observed in the insertion process.



Figure 3. MCR-ALS analysis results: (**a**) concentration profile; (**b**) pure spectral components. In panel (**c**), the electrochemical potential profile is reported, while the linear combination fit on the pristine sample is illustrated in panel (**d**). The MCR-ALS results have been adapted from reference [36].

Moreover, to confirm that the pristine species is in fact a combination of more contributions, we carried out an independent linear combination fitting: panel d illustrates the additive contributions at the Fe K-edge of the fully charged (33%) and discharged states (67%)

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Thanks for the attention

see you soon in our facilities

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