## **Phenolic compounds**



Polyphenols are ubiquitous secondary metabolites present in plant foods

Antioxidant is a natural or synthetic substance added to products to prevent or delay their oxidative deterioration

In food matrices, antioxidants have a broad action that include, for example, prevention of rancidity of fats, as well as decreasing the adverse effects of reactive species, such as reactive oxygen and nitrogen species (ROS and RNS)



MDPI

Revieu

Nanomaterial-Based Sensing and Biosensing of Phenolic Compounds and Related Antioxidant Capacity in Food



Beneficial effect on human health



Anti-microbial property



Additives in biomedicine practices



Food supplements (sensory and nutritional properties, shelf-life)



Quality and process indicators



Potentialtoolsforfunctionalization of materials

#### sensors



Review

An Overview of Optical and Electrochemical Sensors and Biosensors for Analysis of Antioxidants in Food during the Last 5 Years

Maryam Nejadmansouri<sup>1</sup>, Marjan Majdinasab<sup>1</sup>, Gilvanda S. Nunes<sup>2</sup> and Jean Louis Marty<sup>3,\*</sup>

## **Phenolic compounds**



Common food sources Food sources Chacko et al. Chinese Medicine 2010, 5:13 http://www.cmjournal.org/content/5/1/13 CHINESE MEDICINE REVIEW **Open Access** 

## Beneficial effects of green tea: A literature review

Sabu M Chacko<sup>1\*</sup>, Priya T Thambi<sup>1</sup>, Ramadasan Kuttan<sup>2</sup>, Ikuo Nishigaki<sup>1</sup>

## Selected Food sample for lab-practicals

Green tea contains polyphenols, which include flavanols, flavandiols, flavonoids, and phenolic acids; these compounds may account for up to 30% of the dry weight. Most of the green tea polyphenols (GTPs) are flavonols, commonly known as catechins. Products derived from green tea are mainly extracts of green tea in liquid or powder form that vary in the proportion of polyphenols (45-90%) and caffeine content (0.4-10%). The major flavonoids of green tea are various catechins, which are found in greater amounts in green

## Phenolic compounds and the biotechnologies

## General effects



Reduce degranulation Inhibit phosphorylation of myosin light chain Control histamine release and interleukin secretion

#### Anticancer activities

Induce apoptosis and autophagy Inhibit metastasis and angiogenesis Antiproliferation and antiinflammation effects Initiating pro-apoptotic protein expression

#### Antimicrobial activities

Binding with microbial cell membrane Inhibiting toxic metabolites production Preventing biofilm formation

#### Antiinflammatory activities

Regulate interleukins Modulate chemokins production Act on neutrophils Control expressing of adhesion molecules

#### CVD protective effects

Anti LDL oxidation, Antithrombosis Anti SMC proliferation migration Regulate endothelial function

#### Antidiabetic activities Reduce serum glucose

Regulate glucose absorption Attenuate damage of beta cells

#### Antioxidant activities

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Prevent ROS production Direct trapping of ROS Chelation of metal prooxidants

#### Antiobesity activities

Decreasing appetite Stimulating hepatic lipid metabolism Inhibiting adipose tissue expansion

#### Neuroprotective effects

Suppress cognitive deficit Regulation stress hormone secretion Reduction of oxidative stress Protection against Alzheimer's disease

# Green Tea

**Catechins** 

Effects on GIT bacteria

Enhancing HFD-induced dysbiosis

Interfere with metabolism of gut bacteria

Decreasing Firmicutes/Bocteroidetes ratio

Increase biodiversity

## **Phenolic compounds**

# In vitro effects

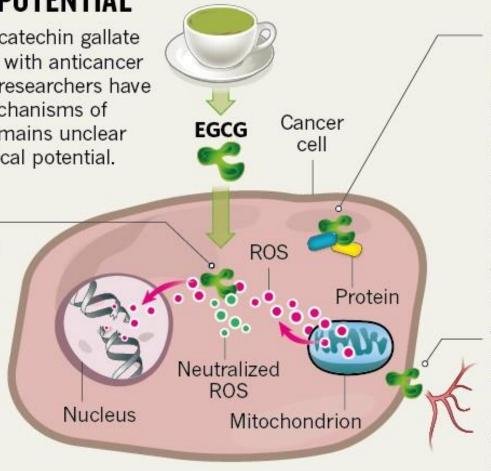
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# **STEEPED WITH POTENTIAL**

Tea is rich in epigallocatechin gallate (EGCG), a compound with anticancer properties. Although researchers have proposed several mechanisms of action for EGCG, it remains unclear whether any has clinical potential.

DNA damage

Heightened metabolic activity in cancer cells leads to the production of molecules known as reactive oxygen species (ROS), which damage DNA and promote tumour formation. EGCG might limit such damage by helping to neutralize ROS.



Cell proliferation EGCG might bind to various proteins, either inside cancer cells or on their surface, to halt cell proliferation or trigger signalling pathways that promote cell death.

- Tumour growth EGCG might help to starve cancer cells of oxygen and nutrients by inhibiting the growth of blood vessels.

## **Phenolic compounds**



## In vivo effects

Biotechnology Reports 24 (2019) e00370



Contents lists available at ScienceDirect Biotechnology Reports

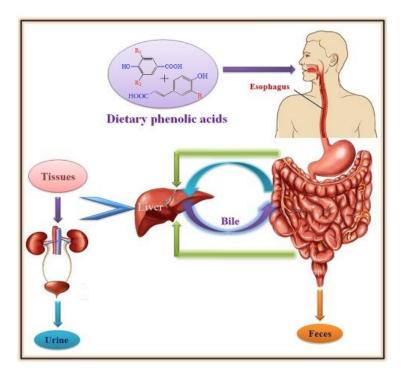
journal homepage: www.elsevier.com/locate/btre



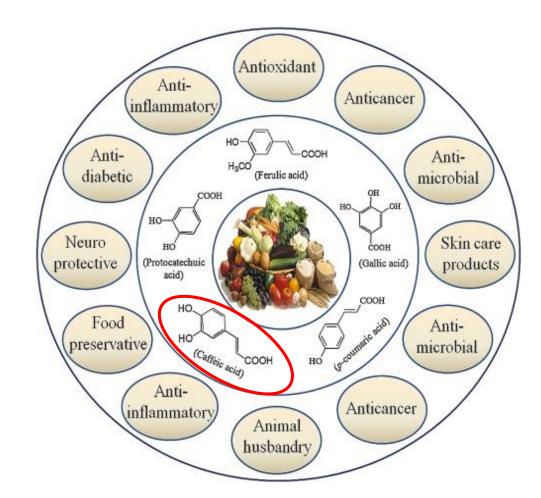
## Phenolic acids: Natural versatile molecules with promising therapeutic applications

Naresh Kumar<sup>a</sup>, Nidhi Goel<sup>b,\*</sup>

<sup>a</sup> Discipline of Biosciences and Biomedical Engineering, Indian Institute of Technology Indore, Simrol Campus, Indore, Madhya Pradesh-453552, India <sup>b</sup> Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, Uttar Pradesh-221005, India



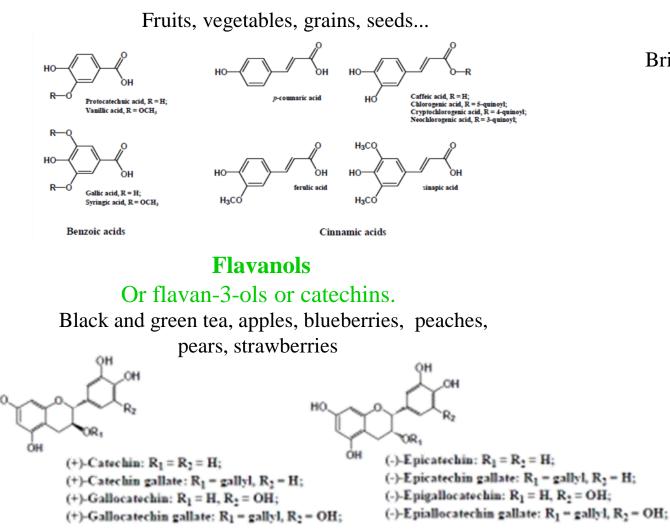
Polyphenolic compounds are bioactive substances widely distributed in the vegetable kingdom. They act as natural antioxidants and their presence contributes to the color, flavor and aroma of food. Therefore, they are considered dietary antioxidants with interesting benefits to health.



## **Phenolic compounds, how many structures?**

Phenolic compounds in food

#### **Phenolic acids in food**



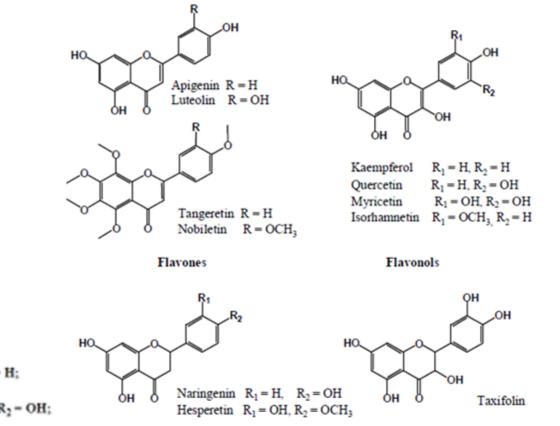
#### Flavonoids

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Flavones, Flavonols, Flavanones and Flavanonols

Brightly coloured fruits and vegetables: blueberries, plums, apples, cherries, oranges, strawberries, spinach...



Flavanonols

Flavanones

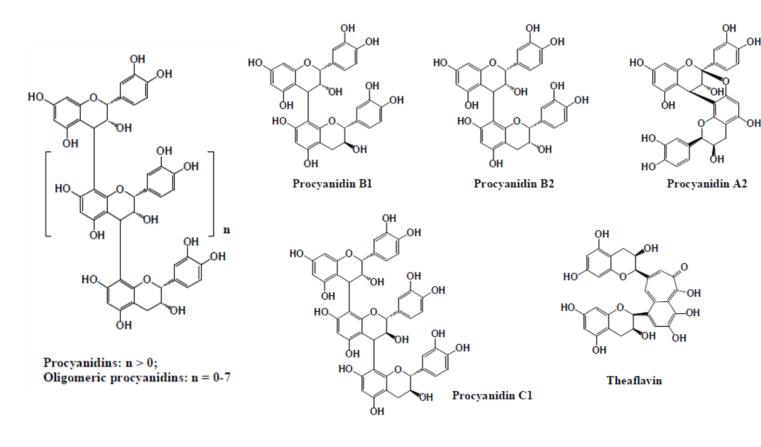
Tsao, R. (2010). Nutrients, 2(12), 1231-1246.

## **Phenolic compounds, how many structures?**

## Phenolic compounds in food

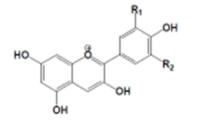
#### **Procyanidins**

Grapes (seeds and skins), apples, chocolate and cocoa, red wines, blueberries, cranberries, pecans, pistachios



#### Anthocyanidins

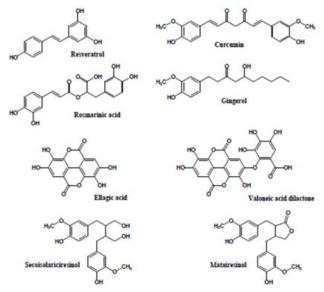
Blue and purple pigments food



Anthocyanidin	R <sub>1</sub>	R:	
Cyanidin	-OH	-H	
Delphinidin	-OH	-OH	
Pelargonidin	-H	-H	
Malvidin	-OCH3	-OCH;	
Peomidin	-OCH <sub>3</sub>	-H	
emnidin	-OH	-OCH3	

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#### **Other important polyphenols...**



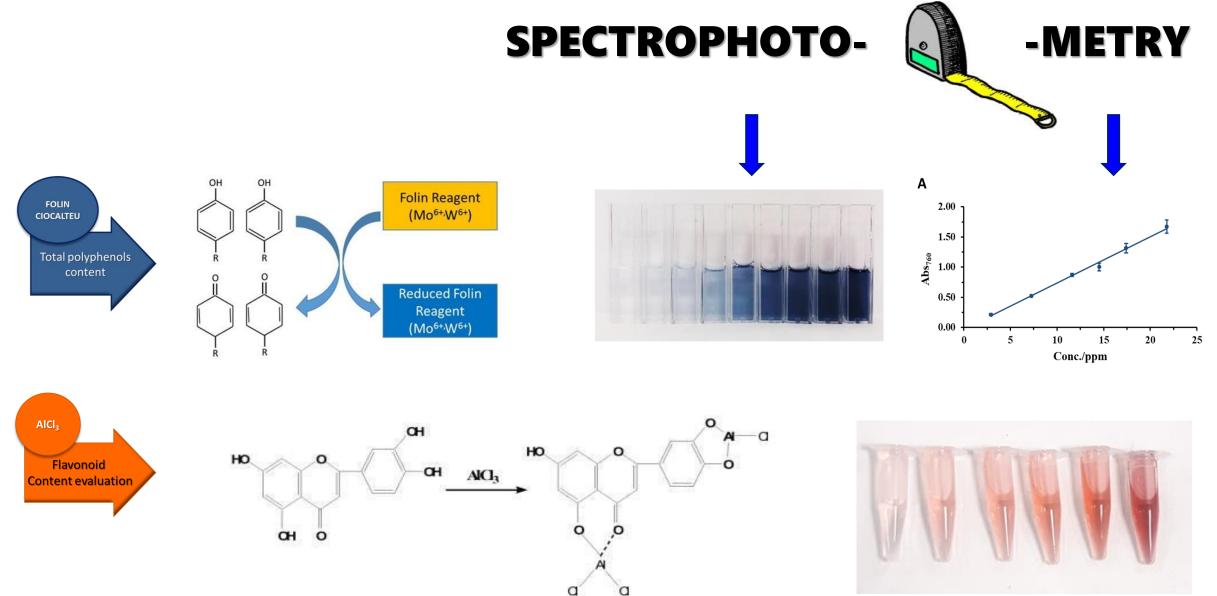
Tsao, R. (2010). Nutrients, 2(12), 1231-1246.

Neveu, V., Perez-Jiménez, J., Vos, F., Crespy, V., Du Chaffaut, L., Mennen, L., ... & Scalbert, A. (2010). Database, 2010.

## **Optical-based method**



#### Phenols content evaluation

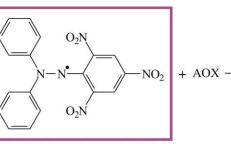


## **Optical-based method**

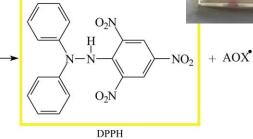


## Antioxidant capacity evaluation

Antioxidant capacity assay	Principle of the method	End-product determination	
	Spectrometry		
DPPH	Antioxidant reaction with an organic radical Colorimetry		
ABTS	Antioxidant reaction with an organic cation radical	Colorimetry	
FRAP	Antioxidant reaction with a Fe(III) complex	Colorimetry	
PFRAP	Potassium ferricyanide reduction by antioxidants and subsequent reaction of potassium ferrocyanide with Fe3+	Colorimetry	
CUPRAC	Cu (II) reduction to Cu (I) by antioxidants	Colorimetry	
ORAC	Antioxidant reaction with peroxyl radicals, induced by AAPH (2,2'-azobis-2-amidino-propane)	Loss of fluorescence of fluorescein	
HORAC	Antioxidant capacity to quench OH radicals generated by a Co(II) based Fenton-like system	Loss of fluorescence of fluorescein	
TRAP	Antioxidant capacity to scavenge luminol-derived radicals, generated from AAPH decomposition	Chemiluminescence quenching	
Fluorimetry	Emission of light by a substance that has absorbed light or other electromagnetic radiation of a different wavelength	Recording of fluorescence excitation/ emission spectra	

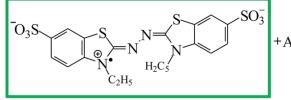


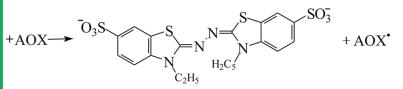
DPPH radical (2,2-diphenyl-1-picrylhydrazyl) intense purple color









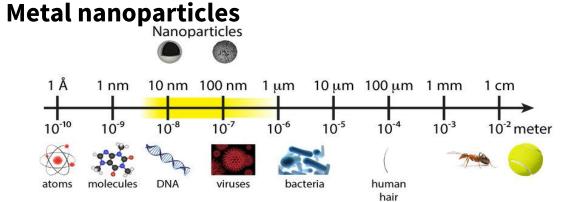


ABTS radical (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) blue green color

ABTS

## Nanomaterials





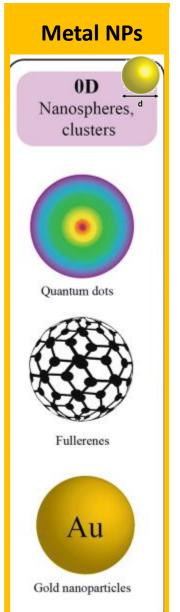
Materials with one external dimension in the range of 1-100 nm

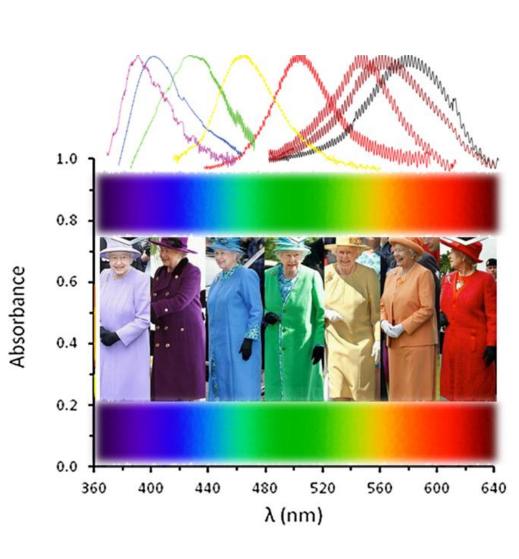
They exhibit a wide range of properties, including optical, electrical, catalytic, magnetic, and biological activity.



Considerations on the EU definition of a nanomaterial: Science to support policy making

Eric A.J. Bleeker<sup>\*</sup>, Wim H. de Jong, Robert E. Geertsma, Monique Groenewold, Evelyn H.W. Heugens, Marjorie Koers-Jacquemijns, Dik van de Meent, Jan R. Popma, Anton G. Rietveld, Susan W.P. Wijnhoven, Flemming R. Cassee, Agnes G. Oomen





## Nanomaterials



#### **Metal nanoparticles**

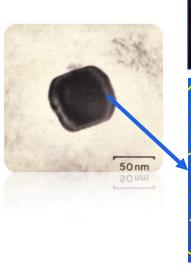
## From Romans...

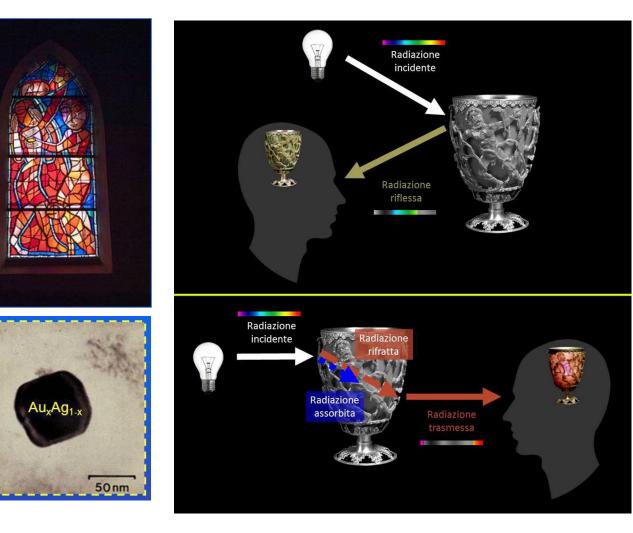


# Nanotecnologia romana

I colori cangianti della Coppa di Licurgo, datata IV secolo a.C., sono dovuti a nanoparticelle di oro e argento disperse nella matrice vetrosa.







Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D. A., Zhang, Y., Dubonos, S. V., ... & Firsov, A. A. (2004). science, 306(5696), 666-669.

## Nanomaterials



#### Metal nanoparticles: their camaleontic features

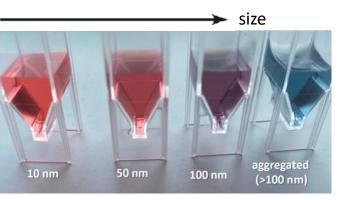


MNPs can interact in different ways with VIS-electromagnetic radiation depending on their shapes, sizes, and composition.

## Gold nanoparticles

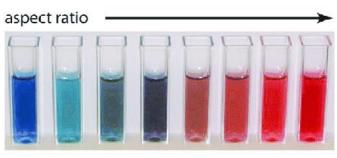
Diameter

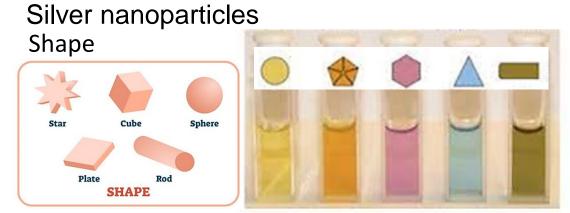
10 nm



#### Gold nanorods







## Silica-gold core-shell nanoparticles

Nanoshells

140 nm

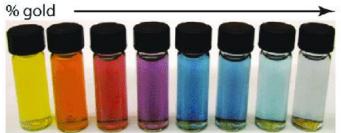


140 1111

Gold nanocages

Nanocages <sup>9</sup>





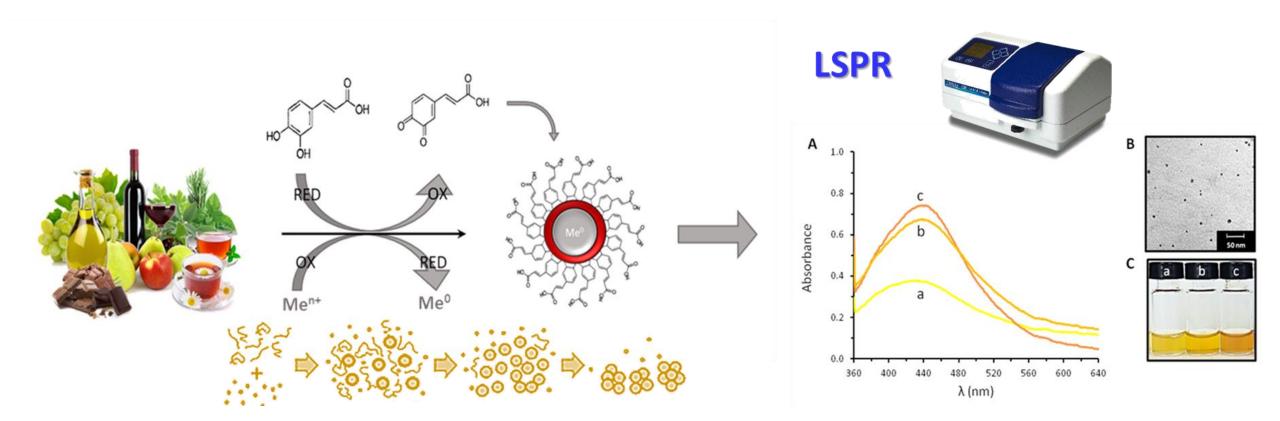
50 nm

## **Optical-based method**

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#### Metal nanoparticles-based spectrophotometric method. Main strategy

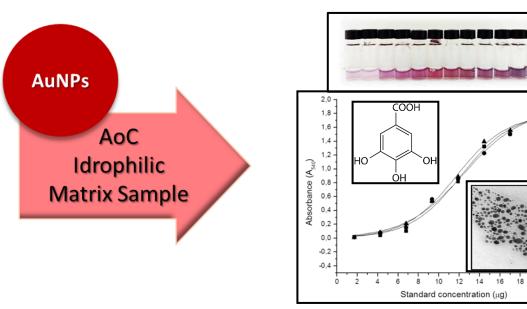


Della Pelle, F., & Compagnone, D. (2018). https://doi.org/10.3390/s18020462 Della Pelle, F., Scroccarello, A., Sergi, M., Mascini, M., Del Carlo, M., & Compagnone, D. (2018). https://doi.org/10.1016/j.foodchem.2018.02.141 Della Pelle, F., Sergi, M., Del Carlo, M., Compagnone, D., & Escarpa, A. (2015). https://doi.org/10.1021/acs.analchem.5b01489 Della Pelle, F., Vilela, D., Gonzàlez, M. C., Lo Sterzo, C., Compagnone, D., Del Carlo, M., & Escarpa, A. (2015). https://doi.org/10.1016/j.foodchem.2015.01.045

## Plasmonic-active nanostructured materials for sensing and biosensing



#### AuNPs from polyphenolic extract to fat matrix



#### MNPs formation is proportional to polyphenols content

	Food Chemistry 178 (2015) 70-75		
	Contents lists available at ScienceDirect	FOOD	
	Food Chemistry	CHEMISTRY	
ELSEVIER	journal homepage: www.elsevier.com/locate/foodchem	-	

#### Analytical Methods

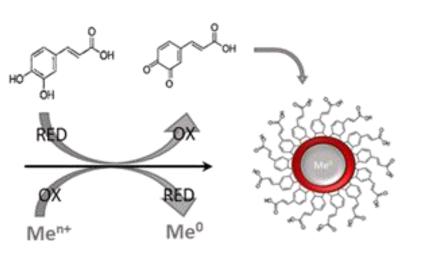
Antioxidant capacity index based on gold nanoparticles formation. Application to extra virgin olive oil samples

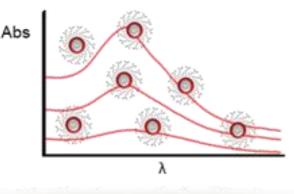


Flavio Della Pelle <sup>a,b</sup>, Diana Vilela <sup>a</sup>, María Cristina González <sup>a</sup>, Claudio Lo Sterzo <sup>b</sup>, Darío Compagnone <sup>b</sup>, Michele Del Carlo <sup>b,\*</sup>, Alberto Escarpa <sup>a,\*</sup>

<sup>a</sup> Departamento de Química Analítica, Química-Física e Ingeniería Química, Facultad de Química, Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, Spain <sup>b</sup> Facoltà di Bioscienze e Tecnologie Agro-Alimentari e Ambientali, Università degli Studi di Teramo, 64023 Mosciano Sant'Angelo, Italy



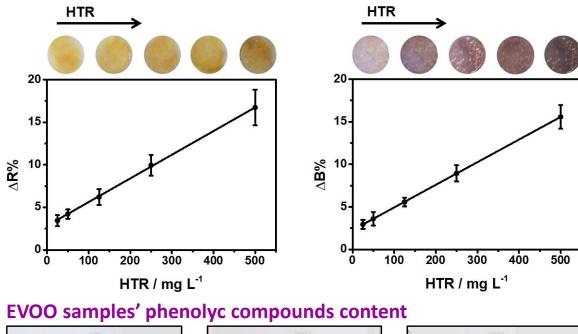






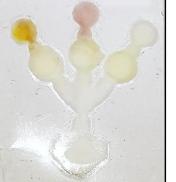
## **Paper-based colorimetric sensor**

#### Extraction-free olive oil phenolic compounds evaluation trough a seed growth strategy



#### **Dose-response curve**





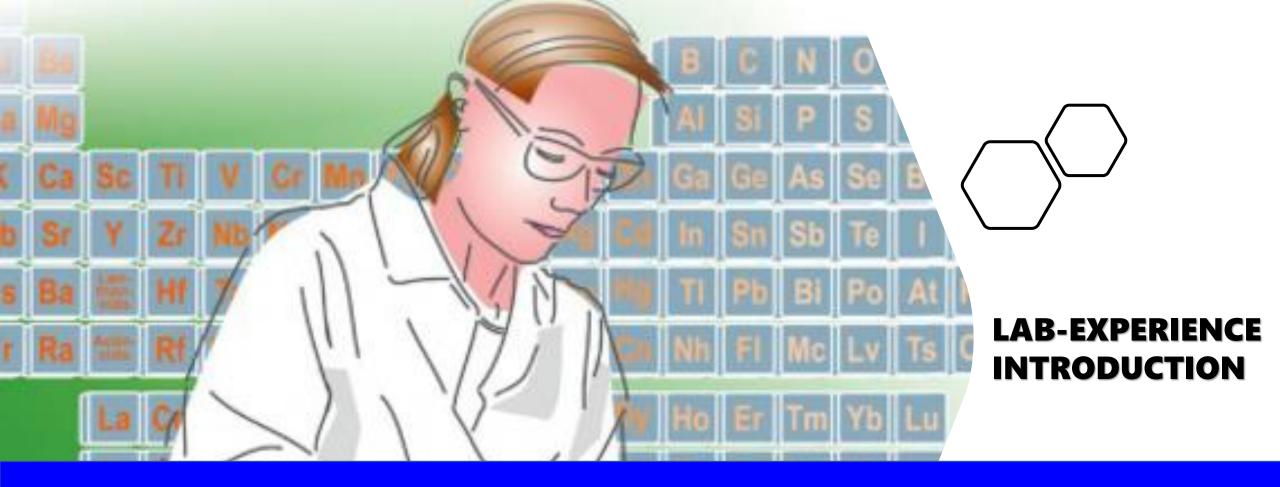


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Low



High

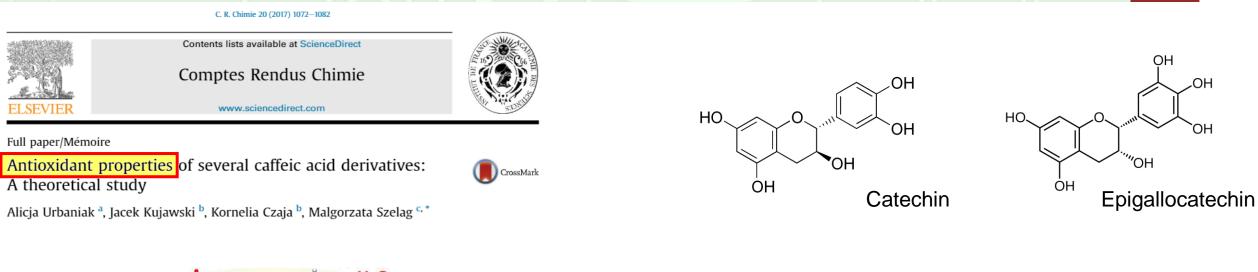


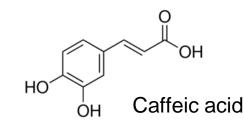
Simple and rapid gold nanoparticles (AuNPs) based antioxidant capacity assay



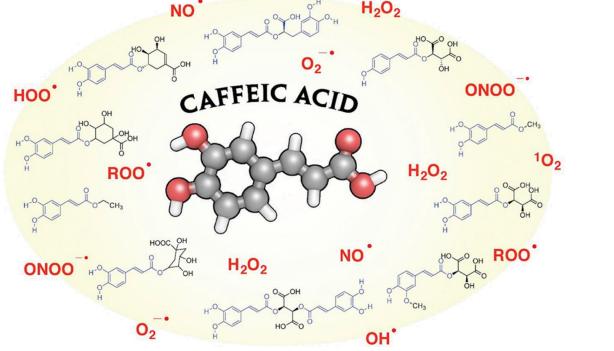
## **Analyte selection**







# Why we use the caffeic acid as standard to perform the calibration curve?



## 1) Stock solution preparation



## CAFFEIC ACID SOLUTION PREPARATION





Perform the calculation

## **Sample extraction**

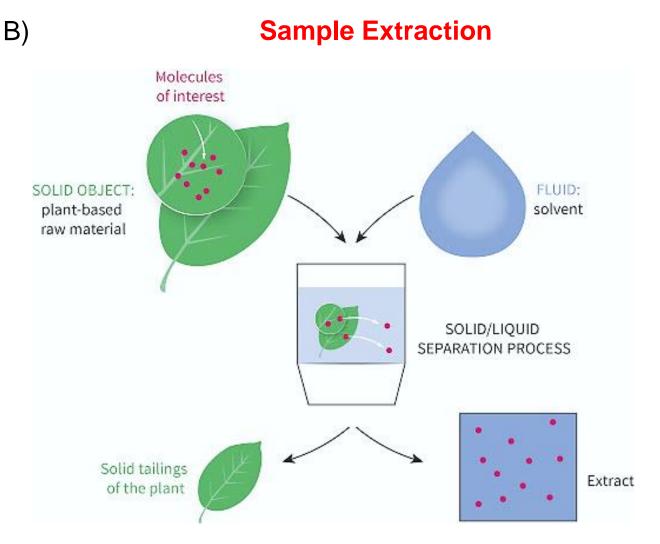
## Lab-experience Step n.2

Solid-liquid extraction. Phenolic compounds extraction form solid sample.

A) Sample Weight





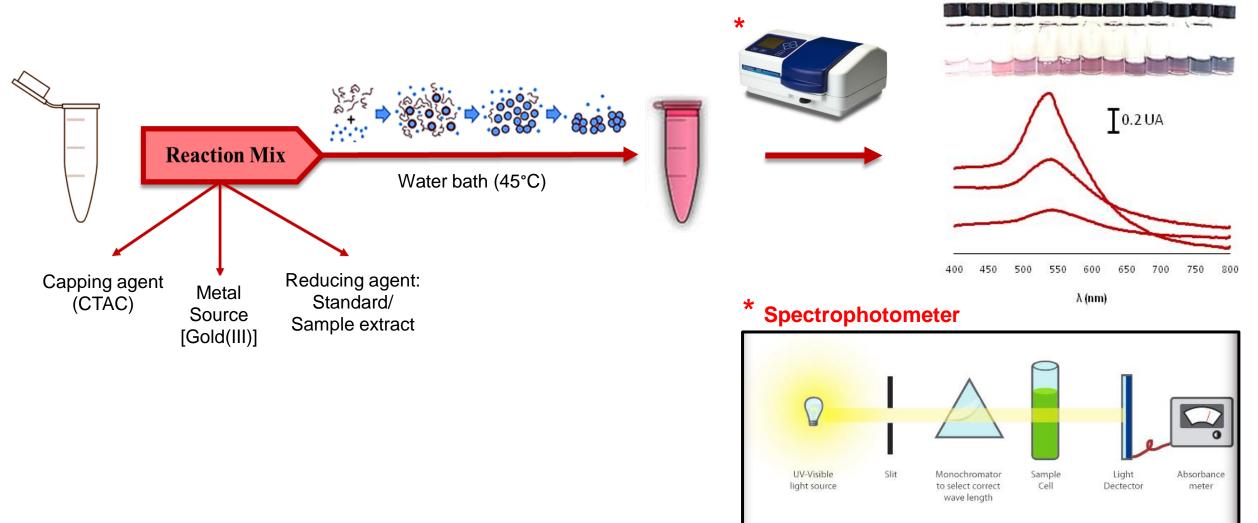


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## **Antioxidant capacity assay**

## Lab-experience Step n.3

Simple and rapid gold nanoparticles (AuNPs) based antioxidant capacity assay



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UNIT

**AuNPs** 

## 4.1) Caffeic acid evaluation in food sample



Experimental dose-response curve construction



## 4.6) Caffeic acid evaluation in food sample

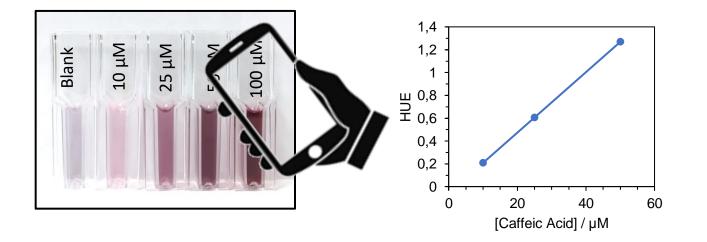
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## Colorimetric approach



## Dose-response curve

HUE vs. [Standard]



- 1) Take a picture of the reacted calibration curve using the white sheet as background
- 2) Take a picture of the reacted sample using the white sheet as background
- 3) With the downloaded app, take the analytical signal in the RGB colorimetric space
- 4) Try to build up the calibration curve using the RGB and the single hue (R, G, and B) as signal

#### SAMPLE and sample analysis

