**Total Phenols in Oilive Oil Sensor Based on Graphene Quantum Dots**

**S. Benítez-Martínez**, M. Valcárcel

Department of Analytical Chemistry, University of Córdoba, Córdoba, Spain.
Phone and fax. 957218616. E-mail: qa1meobj@uco.es

**Abstract**
Graphene Quantum Dots (GQDs), or Graphene Quantum Disks, is an emerging carbon-based nanomaterial with smaller sheets than 100 nm. GQDs exhibit special properties such as low toxicity, high fluorescent activity, robust chemical inertness and excellent photostability, due to quantum confinement and edge effect. Nowadays, phenolic compounds are receiving considerable attention due to their benefits on health, showing, antioxidant, anti-inflammatory and anti-microbial effects and for their role in prevention of cardiovascular diseases.

In this work, GQDs are synthesized by a bottom up method using citric acid as precursor agent [1]. This nanomaterial is used as sensitive sensor for phenols extracted from olive oil. In order to synthesize GQDs, citric acid was heated at 200 ºC for 30 minutes and then dissolved in 10 mg·mL$^{-1}$ NaOH aqueous solution until homogeneity. Nanoparticles have been characterized by High-Resolution Transmission Electron Microscopy (HR-TEM) and Mid Infrared Spectroscopy (MIR).

A liquid-liquid extraction (LLE) was carried out to extract the phenolic fraction from extra virgin olive oil (EVOO)[2]. Adequate volumes of GQDs and phenols (from the extraction) were mixed and measured in a spectrofluorometer. The reaction between GQDs and phenols occurs immediately and the quenching effect is related directly to the total concentration of phenols. The quenching effect can be attributed to the phenols interaction with the GQDs surface-pasivated through carboxylic group, at the edge of GQDs, besides π – π interactions owing to the aromatic structure of both species.

GQDs emit blue light (475nm) when they are excited from 365 to 420 nm, the maximum emission being at 379 nm excitation. Nanoparticles synthesized diameters had between 2.8–4.5 nm and flat circular shape, which have been characterized by HR-TEM. MIR spectra show the presence of carboxyl and hydroxyl groups. The influence of pH on the fluorescence emission and on the quenching process has been investigated, finding pH 10.00 more favorable for the phenols interaction in spite of the maximum emission level was found at pH 7.00. Volumes of GQDs and sample were also evaluated. The 1:1 ratio was the most effective value for our study. MeOH has been selected as solvent for the redisolution of the phenolic fraction after the extraction procedure because led to a better FL quenching and shows greater stability over time. Absolute recoveries of spiked Refined Olive Oil (ROO) were better than 73.4 % for gallic acid (simple phenol) and 80.5% for oleuropein (polyphenol), used as model analytes and commonly presents in Spanish olive oil. GQD as sensor has been evaluates in terms of sensitivity, limits of detection (LOD), quantification (LOQ) and precision for both phenols. LOD were 0.21 mg·L$^{-1}$ for gallic acid and 0.15 mg·L$^{-1}$for oleuropein and LOQ were 0.68 mg·L$^{-1}$ and 0.52 mg·L$^{-1}$ respectively. Reproducibility of the proposed method has been measured as relative standard deviation (RSD) for five independent measurements of each analyte. RSD was 0.96% for gallic acid and 0.26% for oleuropein. Phenols extraction of real olive oil samples have been carried out. Four different olive oils have been compared: refined, “lampante”, virgin and extra virgin olive oil. Extra virgin olive oil shows more fluorescence quenching than the others types of olive oil due to the higher phenols content.

From the best of our knowledge, this is the first time GQDs have been used as sensor of phenols extracted from olive oil, giving rise to a rapid, sensible and selective analytical method. Our studies allow us to state that GQDs are very sensitive to reducing agents such as phenols and polyphenols.

**References**

[1] Y. Dong, J. Shao, C. Chen, H. Li, R. Wang, Y. Chi, Xiaomei Lin, G. Chen. Carbon, **50** (2012), 4738-4743.

[2] F.M. Pirisi, P. Cabras, C.Falqui, M. Migliorini, M. Muggelli. Food Chemistry, **48** (2000),1191-1196.

## Figures

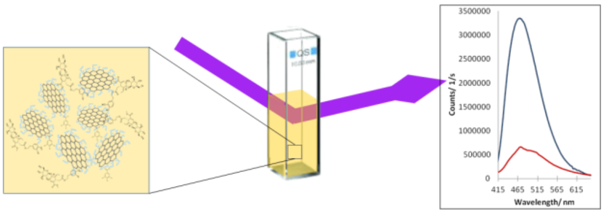


*Fig.1: Scheme of GQDs FL quenching by interaction of phenols.*