

# U(VI) complexation with selected flavonoids investigated by absorption and emission spectroscopy at light acidic conditions

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Flavonoids are secondary plant compounds and have important properties. Beside their antioxidant activity and effects as enzyme inhibitors, they can bind metals ions.<sup>[1]</sup> The possible release of flavonoids from the root into the soil can affect the migration of radionuclides in the biological and geological environment. In this work, the complexation behavior of selected flavonols and a flavonol glycoside towards U(VI) were spectroscopically investigated and the corresponding complex stability constants were determined.

**EXPERIMENTAL.** Methanolic solutions containing a constant concentration of flavonol (Fig. 1,  $2 \times 10^{-5}$  or  $5 \times 10^{-5}$  M) and variable uranyl perchlorate concentrations ( $5 \times 10^{-6}$ – $2.5 \times 10^{-4}$  M) at ionic strength of 0.1 M were prepared. The redox voltage of 230 mV (~ pH 3) was adjusted with methanolic HClO<sub>4</sub> or NaOH.

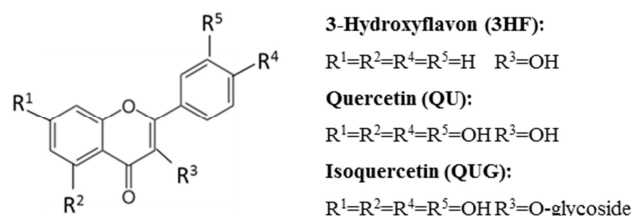


Fig. 1: Chemical structure of selected flavonols (neutral form at 230 mV).

The UV-vis spectra were recorded with a Varian Cary 50 Bio spectrophotometer. Time-resolved laser-induced fluorescence (TRLF) measurements were carried out by using a Spectra-Physics fs-laser system (800 nm, 1 kHz) with a pulse width of 130 fs and variable excitation wavelengths in the range of 270 and 410 nm. All spectroscopic measurements were performed at room temperature.

**RESULTS.** Figure 2 illustrates the evolution of the UV-vis spectra of QUG-U(VI) system with increasing metal/ligand concentration ratios.

Beside the decrease/increase of the absorption intensity of the bands for the free ligand, a new band appears at 420 nm (3HF/U(VI) – 390 nm, QU/U(VI) – about 450 nm).

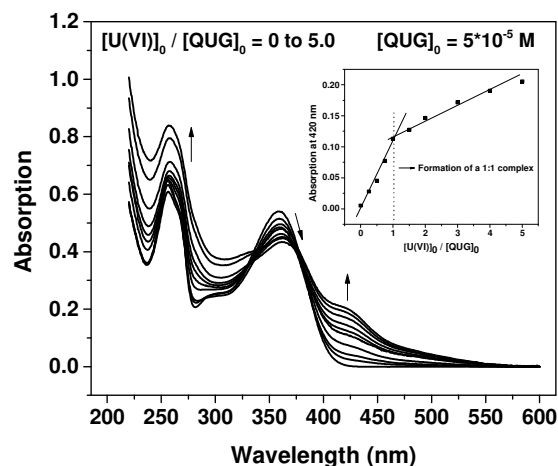


Fig. 2: UV-vis absorption spectra of QUG as a function of the U(VI) concentration and analysis of the data at 420 nm.

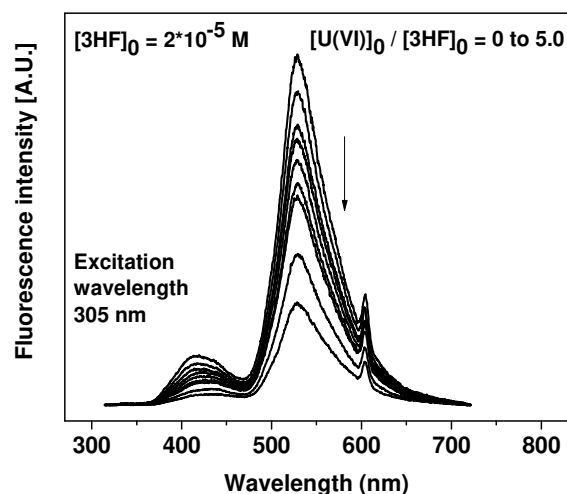


Fig. 3: Fluorescence spectra of 3-Hydroxyflavon as a function of the U(VI) concentration.

The plot of the absorption values at  $\lambda = 420$  nm of the molecule complex spectra versus the metal to ligand ratio (Fig 2, inset) suggests the formation of a complex showing a 1 : 1 stoichiometry under light acidic conditions. Comparable results were obtained for the complex behavior of 3-Hydroxyflavon and quercetin under the given experimental conditions.

The formation of U(VI)-flavonol complexes was also demonstrated by the decrease of the fluorescence intensities of the free ligands with increasing U(VI) concentration (static quenching; example in Fig. 3), as the organic U(VI) complexes showed not fluorescence.

The stability constants of the complexes were assessed based on the following reaction equations at constant proton concentration (230 mV, equations 1 and 2):



$$K = \frac{[U(VI)\text{flavonol}]}{[\text{Flavonol}] \cdot [U(VI)]} \quad (2)$$

Using factor analysis program HypSpec<sup>[2]</sup> or slope analysis, comparable complex stability constants (log *K*) were obtained for both spectroscopic methods and summarized in Tab. 1.

Tab. 1: Stability constants log *K* of the 1:1 U(VI) flavonol complexes.

Flavonol	UV-vis (HypSpec)	Femto-TRLFS (Slope)
3HF	4.90 ± 0.02	4.55 ± 0.35
QU	4.45 ± 0.01	4.67 ± 0.49
QUG	4.39 ± 0.03	4.01 ± 0.27

[1] Kasprzak, M. M. *et al.* (2015) *RSC Adv.* 5, 45853–45877.

[2] Gans, P. *et al.* (2008) Protonic Software, Leeds.