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## **The speciation of titanium(IV) in concentrated phosphoric acid : A spectroscopical and TD-DFT study.**

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### **Abstract:**

Phosphoric acid and phosphate salts are used worldwide as fertilizers, food additives, but also as etching agents for the manufacture of electronic devices and pharmaceutical excipients. The grade of each of these applications is defined by specifications<sup>1-4</sup> concerning trace metal impurities as well as concentrations of inorganic anions such as nitrate, sulfate, fluoride, chloride, etc. The conventional wet-process of phosphoric acid production consists in leaching phosphate ores by sulfuric acid with the drawback that certain impurities are co-leached. Selective liquid-liquid extraction was found to be very efficient to reduce the concentration of most impurities present in commercialized phosphoric acid<sup>5,6</sup>. The speciation of metal cations in concentrated phosphoric acid (8-14.5 mol.L<sup>-1</sup>) is a key information to design a selective extraction solvent for H<sub>3</sub>PO<sub>4</sub> towards metal impurities. For instance, classical extraction solvents used in the production of phosphoric acid are not sufficiently selective towards titanium(IV). In order to better understand the phenomena responsible for titanium(IV) co-extraction during solvent extraction of H<sub>3</sub>PO<sub>4</sub>, it is mandatory to know the speciation of titanium(IV) in a large range of phosphoric acid concentrations. Therefore, this presentation is focused on the study of the speciation of 2-20 mmol L<sup>-1</sup> titanium(IV) in 7-14 mol L<sup>-1</sup> phosphoric acid. Even though this speciation has been extensively investigated in acidic media<sup>7-9</sup>, the literature concerning phosphoric acid remains quite limited<sup>10,11</sup>.

In this work, synthetic phosphoric acid solutions containing titanium(IV) were studied by means of spectroscopic methods (NMR and UV-Visible spectroscopy). The calculation of apparent complexation constant was possible by the chemometric interpretation<sup>12,13</sup> of the spectral data. For the first time, a speciation diagram of titanium(IV) in concentrated phosphoric acid was plotted. Additional information of the structures of the complexes present in concentrated phosphoric acid were determined by performing time-dependent density functional theory (TD-DFT) calculations.

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