Sorption of the Peroxocomplex of Titanium on Silica Gel and its Analytical Use

Z. Čižek*
Central Research Institute, Škoda Works, Pilsen, Czechoslovakia

Z. Šulcsek
Geological Survey, Prague, Czechoslovakia

J. Doležal
Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia

Key Words
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Summary
Sorption of the titanium peroxocomplex on silica gel was studied in dependence on the pH and on the presence of various complexing substances, especially tartaric and citric acids. The distribution coefficients for the titanium peroxocomplex and for some other components were determined. Optimum conditions were established for the separation of small amounts of titanium from a number of accompanying cations and anions on a column and under static conditions.

A suitable combination of separation techniques and instrumental methods used for determination (hybrid methods [1, 2]) is a reliable procedure for the determination of trace concentrations of elements in inorganic materials with variable and complex composition. Sorption on inorganic ion-exchangers, especially silica gel, has recently found use in the analysis of complicated mixtures of solid inorganic substances and natural waters. In our previous study [3], the sorption of the peroxocomplex of titanium on silica gel and its separation from excess V, Mo and W were briefly mentioned. In the present work the behaviour of the titanium peroxocomplex is studied in detail and the conditions are given for the separation of titanium from a number of accompanying elements.

Experimental

Instruments
Spectrophotometric measurements were carried out on a Spekord UV VIS (Zeiss, Jena, GDR) and ACTA M7 (Beckman, USA) instruments. The AAS determination of elements were determined using a Model 403 atomic absorption spectrometer (Perkin Elmer, USA). The pH of the solution was measured with a MV87 pH-meter (Präzitronic, GDR).

Chemicals
For most measurements, silica gel prepared according to Šťrba and Pitra [4] or silica gel Biosil (Bio-Rad Laboratories, USA) with a particle size of 80 to 200 μm were used. A titanium stock solution was prepared from pure titanium (min 99,9 %; Ventron, USA) dissolving it in a mixture of HF and HNO₃ and repeated evaporation with concentrated H₂SO₄, or by dissolving TiCl₄ in HCl. Solutions of other metals were prepared from the pure metals or their salts. Diantipyrilmethane (DAM) was obtained from FLUKA, Switzerland. All other chemicals were of p.a. purity.

Analytical Methods
The titanium content was determined spectrophotometrically as the complex with hydrogen peroxide or with DAM [5, 6], suppressing the effect of Fe(III) by the addition of ascorbic acid. Tungsten and uranium were also determined spectrophotometrically as the peroxocomplexes [7, 8] while the other elements studied were determined by atomic absorption spectrophotometry [9].
Results and Discussion

Sorption of Peroxocomplexes under Static Conditions

The sorption of the peroxocomplexes of titanium and other elements was studied by the batch method. The effects of the pH of the medium, of complexing agents and of other components were studied in order to find optimum conditions for the separation of titanium from the accompanying elements. The following procedure was observed in all experiments: An amount of 2 g of silica gel, predried at 150°C for ca 24 hours, was weighed into a 100 ml stoppered polyethylene bottle and 50 ml of the solution containing the required components (an appropriate amount of the metal studied, hydrogen peroxide, complexing agents, buffer) were added. The solution was buffered with monochloroacetic and acetic acids, ammonia and NH₄Cl with a resultant concentration of 0.1 mol. l⁻¹; the pH of the solution was adjusted with diluted ammonia. Most experiments were carried out with 1.00 mg Ti and 1 ml 30% H₂O₂; under these conditions, less than 2% of the sorbent’s capacity was saturated. The solution was shaken for ca 4 hours to equilibration, the resultant pH measured and the components in the solution determined.

The titanium peroxocomplex is sorbed quantitatively from pH 5.5 to 7.5, with the values of the distribution coefficient (Dₑ) exceeding 10³ (Fig. 1). In strongly acidic media (1 to 10 mol. l⁻¹ HCl or H₂SO₄) the peroxocomplex is not sorbed at all. The ionic strength (I) of the medium exerts no effect on the sorption process (I = 0.1 to 1). In alkaline solutions a certain decrease in the sorption occurs, probably due to competition from sodium ions (NaCl) or to a change in composition of the complex. On changing the temperature from 25 to 50°C there is no substantial change in Dₑ, but the excess hydrogen peroxide is slowly decomposing and, thus, the stability of the titanium peroxocomplex decreases.

When studying the effect of the amount of hydrogen peroxide on the sorption of titanium it has been found that the molar excess of H₂O₂ over titanium must be at least two orders of magnitude in order to suppress hydrolytic effects. Hydrogen peroxide itself is not sorbed on silica gel and its excess does not interfere. As the peroxocomplex of titanium changes its composition and its stability decreases with decreasing hydrogen ion concentration, the excess of hydrogen peroxide should be greater than 1:400, especially in neutral and alkaline solutions. On increasing the excess of H₂O₂ from 1:100 to 1:1000, the distribution coefficient (Dₑ) increased from 2500 to more than 5000. On the other hand, in a weak acid solution (pH ~ 4) a 100-fold excess of hydrogen peroxide is quite sufficient and Dₑ does not change with further increase in the peroxide concentration.

Tartaric, citric and oxalic acids, used as masking agents for suppressing the hydrolytic reactions of various accompanying cations, significantly affect the sorption of the titanium peroxocomplex through formation of anionic complexes. With increasing concentration of these substances (from a molar ratio of 1:5 to that of 1:500) the value of the distribution coefficient decreases; this effect is strongest with citric acid (Fig. 2). The smallest effect is exhibited by tartaric acid; even at a 50-fold molar excess the sorption of the titanium peroxocomplex is virtually complete at a pH of 6.0 to 7.5 (Dₑ ~ 10³; Fig. 3). Acetic acid, used as an active component of the buffers, has no effect.

The sorption of the titanium peroxocomplex is also significantly affected by polyaminopolycarboxylic acids (Fig. 4). Iminodiacetic acid (IDA) decreases the sorption only to a small extent. In solutions containing nitrilotriacetic acid (NTA), anionic compounds are formed to a greater extent and the maximum of the distribution coefficient curves decreases to 10² at 5-fold molar excess of NTA. In the presence of EDTA and DTPA, in a 5-fold

![Fig. 1](image1.png)

Fig. 1
Sorption of the titanium peroxocomplex under static conditions as a function of the medium pH and ionic strength (I). Dₑ = distribution coefficient, %S = percent of the complex sorbed.
Curves 1, 3: I = 0.1; curves 2, 4: I = 1; Dₑ for curves 1, 2; %S for curves 2, 4; 1.00 mg Ti.

![Fig. 2](image2.png)

Fig. 2
Sorption of the titanium peroxocomplex from a citric acid solution under static conditions. Dₑ = distribution coefficient %S = percent of the complex sorbed.
Curves 1, 3: molar Ti: citric acid ratio = 1:50; curves 2, 4: molar Ti: citric acid ratio = 1:500; Dₑ for curves 1, 2; %S for curves 3, 4; 1.00 mg Ti.