

Reversed Phase Extractive Chromatographic Separation of Titanium(IV) on Malonato Complex Using High Molecular Weight Amines

PRAKASH NARAYANAN & S M KHOPKAR*

Department of Chemistry, Indian Institute of Technology, Bombay
400 076

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Titanium is quantitatively extracted in pH range 2.5 to 6.0 from 0.01 *M* malonic acid on silica gel column coated with Amberlite LA-1 and is separated by stripping with (1-4 *M*) hydrochloric and nitric acid and (0.05 to 1.0 *M*) sulphuric acid and is determined spectrophotometrically at 360 nm. Separation of titanium from binary mixtures containing alkali, alkaline earths, chromium (III), manganese, iron(II), cobalt, nickel, lead, aluminium and yttrium is made possible since these elements do not form malonato complexes. It is possible to separate it from zirconium, uranium, vanadium, niobium, thorium, molybdenum and iron(III) by exploiting the differences in the stabilities of malonato complexes in the presence of complexing acids. Titanium has been separated from ternary and quaternary mixtures containing chromium, molybdenum, iron, manganese and nickel, the elements which are normally present in alloys.

Tributylphosphate^{1,2} and tri-*n*-octylphosphine oxide^{3,4} have earlier been used for the extractive chromatographic separation of titanium from niobium, molybdenum and vanadium. Titanium could be separated from iron on haloport-F column by 2-octanone⁵. Separations with tri-*n*-octylamine^{6,7} have been reported to be rapid and applicable at microgram concentrations. But systematic investigations on extraction chromatography of titanium from organic acids do not appear to have been carried out so far. Titanium forms anionic malonato complex⁸, extractable with Amberlite LA-1. This fact has been presently utilised for the development of a method for the extractive chromatographic separation of titanium on silica gel column.

Apparatus and reagents used were the same as described earlier^{9,10}.

A stock solution containing 2.34 mg/ml of titanium was prepared by dissolving titanium dioxide (2g) in sulphuric acid (10 ml), diluting the solution to 500 ml and standardising gravimetrically with cupferron⁹.

An aliquot of solution containing 117 µg of titanium solution was mixed with 5 ml of 0.01 *M* malonic acid and the pH of the solution adjusted to 2.5 to 6.0. It was

passed through a column of silica gel (100-200 mesh) coated with Amberlite LA-1 as described earlier¹⁰. Titanium was stripped with various mineral acids. Ten fractions (5 ml each) were collected and titanium in each fraction was determined spectrophotometrically¹¹.

In the batch extraction with 0.1 *M* Amberlite LA-1 in xylene titanium was quantitatively extracted in pH range of 3.5 to 6.0 from 0.01 *M* malonic acid and was stripped with 1 *M* hydrochloric acid. Although the extraction was insignificant till pH 2.0 (46.6%), it was quantitative between pH 2.5 and 6.0 and decreased beyond pH 6.5 (86.7%). The optimum concentration of malonic acid for quantitative extraction of titanium at pH 3.5 was 0.01 *M*. It was observed that 1.0-4.0 *M* of hydrochloric, nitric acid or sulphuric acid completely stripped titanium from the column.

Several elements like alkali, alkaline earths, chromium(III) iron (II), cobalt, nickel, copper, zinc, cadmium, aluminium, thallium and lead do not form anionic malonato complexes at the specified pH and hence do not interfere in the separation of titanium even when present in 10-fold excess in binary combination with titanium. The acid used in stripping titanium in the presence of these elements was 0.1 *M* sulphuric acid. Some elements like uranium, zirconium, hafnium, molybdenum, thorium and niobium formed relatively stable complexes with malonic acid and were extracted alongwith titanium. Sulphuric acid (0.1 *M*) was found to be a good stripping agent for titanium but not for all these elements, which were re-extracted as their anionic sulphato complexes on the column and were eluted later with either 2 *M* hydrochloric acid or nitric acid.

It was possible to strip off titanium at any concentration of hydrochloric acid, sulphuric acid or nitric acid from a multicomponent mixture containing iron (III), uranium, zirconium, molybdenum and thorium. While uranium and iron(III) formed anionic chloro complexes, zirconium, molybdenum, thorium and uranium formed anionic sulphato complexes in dilute sulphuric acid. In a multicomponent mixture these elements were re-extracted while titanium was stripped off. This formed the basis for separation of titanium in multicomponent mixtures (Fig. 1).

The mixture of chromium(III) or iron(II), vanadium (V) and titanium (IV) was separated by passing it through the column when chromium or iron (II) was not extracted and passed through the column. Vanadium was stripped with 1 *M* malonic acid and titanium was eluted with 0.1 *M* sulphuric acid.

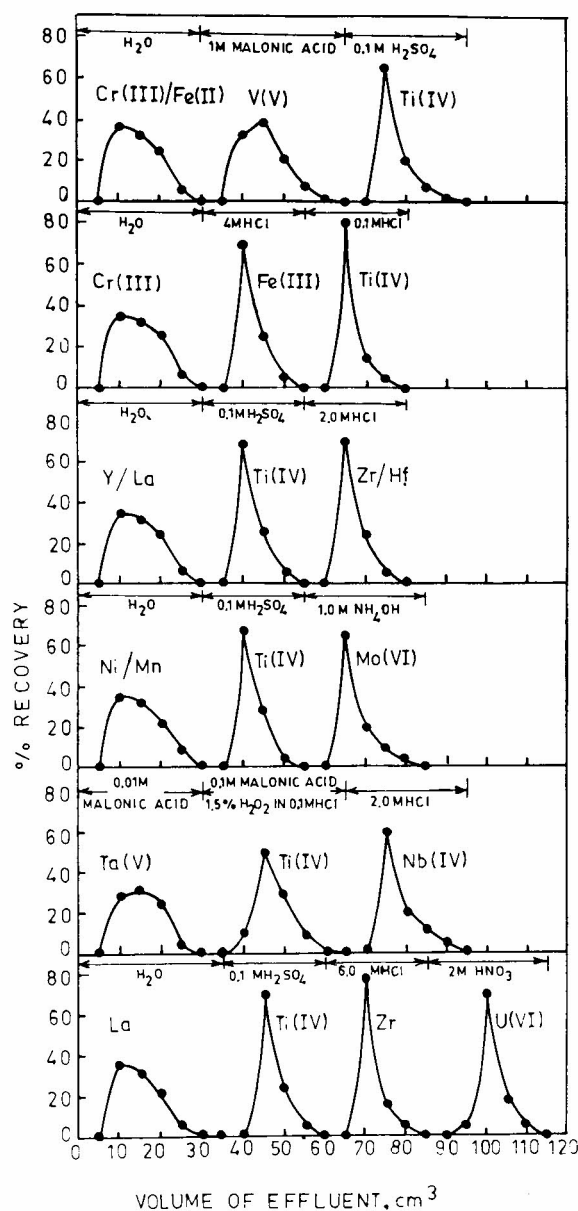


Fig. 1—Separation of titanium from multicomponent mixtures

A mixture containing chromium (III), titanium (IV) and iron (III) could be separated into individual components by passing it through the column, when chromium (III) was washed with water, titanium with 4 *M* hydrochloric acid and iron with 0.1 *M* hydrochloric acid.

Yttrium or lanthanum, titanium (IV) and zirconium or hafnium were separated by passing the mixture through the column when yttrium or lanthanum was not extracted. The extracted titanium was stripped with 0.1 *M* sulphuric acid and during the process zirconium or hafnium was re-extracted as sulphato complex on the column. Zirconium or hafnium was finally stripped with 2 *M* hydrochloric acid.

A ternary mixture containing nickel or manganese, titanium (IV) and molybdenum (VI) could be separated by passing it through the column, when nickel or manganese was not extracted and passed through the column. The extracted titanium was stripped with 0.1 *M* sulphuric acid and molybdenum with 1 *M* ammonium hydroxide.

The separation of tantalum, titanium (IV) and niobium was carried out by passing the mixture through the column. Tantalum was washed with 0.01 *M* malonic acid buffered at pH 3.5 and titanium was stripped with 0.1 *M* malonic acid and hydrochloric acid containing 1.5% hydrogen peroxide. Niobium was finally stripped with 2 *M* hydrochloric acid.

Lanthanum, titanium (VI), zirconium and uranium (VI) were separated by passing the mixture through the column. Lanthanum passed through the column with water, while titanium was stripped with 0.1 *M* sulphuric acid, zirconium with 6.0 *M* hydrochloric acid and uranium with 2.0 *M* nitric acid.

Titanium from steel sample AISI No. 321 was separated by first passing an aliquot of solution through the column when chromium, manganese, nickel were not extracted. The extracted titanium was stripped with 4 *M* hydrochloric acid and iron with 0.1 *M* hydrochloric acid. Titanium found was 0.42% against a certified value of 0.45%.

In all the separations from binary and multicomponent mixtures, the pH of the mixture was first adjusted to 2.5 to 6.0 in the presence of 0.01 *M* malonic acid and then passed through the column at a flow rate of 1 ml/min. The elements after stripping from the organic phase were determined spectrophotometrically with suitable chromogenic ligands¹².

The proposed method is useful as it permits separation of titanium from commonly associated elements like chromium, nickel, manganese and molybdenum. The separation of titanium from niobium, uranium, zirconium, thorium, lanthanum and yttrium is important as they are found together in fission products. The method is rapid, simple and reasonably selective. The method is applicable at microgram concentrations of the metals.

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