Selective extraction of titanium as titanium thiocyanate complex on polyurethane foam and its spectrophotometric determination in glass and ceramic materials

Nibedita Chakrabarti & S K Roy
(Analytical Chemistry Division
Central Glass & Ceramic Research Institute, Calcutta 700 032)
Received 23 January 1989; revised and accepted 10 April 1989

A method for selective extraction of titanium as titanium thiocyanate complex on polyurethane foam and its spectrophotometric determination in glass and ceramic materials have been described. Parameters affecting the extraction of the complex [Ti(SCN)₆]²⁻, such as acid concentration, reagent concentration and equilibration time have been studied. Beer’s law is obeyed from 0.1 µg to 2 µg/ml of Ti. The method yields satisfactory results for glass and ceramic materials.

Small amounts of titanium are found to be present in glass, quartz and in pure zirconia and alumina. Determination of titanium in such materials is essential for characterisation, evaluation and quality control. Of the various spectrophotometric methods available, chromotropic acid method is followed widely in aqueous medium and in presence of matrix elements. But this method also has various limitations and is unsuitable for general application. For obvious reasons, extraction technique has been introduced in various procedures for determination of traces of titanium practically in a matrix-free system. However, these extraction procedures are lengthy and complicated.

After Bowen’s pioneering work, open cell polyurethane foam has received considerable attention for its ability to extract ionic species of various elements from aqueous solution. Unloaded foams have been used successfully for extracting various materials as their thiocyanate complexes. But the sorption behaviour of titanium(IV) thiocyanate complex in acidic medium on polyurethane foam is yet to be studied.

The present study aims to critically examine the parameters for effective and quantitative extraction of titanium thiocyanate complex on polyurethane foam from aqueous solution in order to develop a simple spectrophotometric method for determination of titanium in glass and ceramic materials.

Experimental

Spectrophotometric measurements were made with a Spectromom 360 instrument.

All the chemicals used were of AR grade. Doubly distilled water was used for all the experiments.

Titanium stock solution (50.0 µg ml⁻¹) was prepared by heating 0.093 g of potassium titanyl oxalate with 13 ml cone. H₂SO₄ for 3 hr, cooling and diluting the solution with water to 250 ml.

A working solution (5.0 µg Ti ml⁻¹) was prepared by diluting the stock solution.

Preparation of foam

Pieces of commercial U-foam were cut in the form of a small cylinder (2-3 mm diameter; 2.5 cm long; and 0.05 g average weight). The foam chips were soaked in 3M HCl for 4 hr with occasional squeezing and releasing with a glass plunger at 15 min intervals. The foam chips were transferred to a 50 ml syringe and washed 5-6 times with doubly distilled water and finally twice with acetone. The foam chips were air-dried and stored in a coloured bottle.

Procedure

To an aliquot of titanium solution containing 5-50 µg/ml of titanium, required amounts of dilute sulphuric acid, water and potassium thiocyanate solution were added to maintain the acid and potassium thiocyanate concentrations at 0.5 -1N and 4M respectively in a volume of 20 ml. The solution was allowed to stand for one hour when the pink colour of iron thiocyanate complex (produced from the impurity present in thiocyanate) disappeared. Then 4-5 pieces of foam were put into the solution. The foam pieces were squeezed with the help of a flat-ended plunger to facilitate the aqueous solution to flow freely through the foam cell. The foam was allowed to equilibrate for 2 hr, squeezing 10 strokes at a time at intervals of 15 min. The foam chips were transferred into a syringe (5 ml) and washed thoroughly with distilled water several times. Then, the titanium-thiocyanate complex was eluted with acidified acetone (1 ml 0.1 N HCl in 99 ml acetone) into a 25 ml calibrated flask.

The optical density of the above solution was measured at 410 nm against a reference blank prepared in the same way.
A calibration curve was drawn by taking titanium solution containing 0, 0.2 to 2 µg/ml of titanium after developing the colour in the same way as described in the procedure.

Preparation of the sample solution

For the determination of titanium in real samples, 0.2 g of dried (110°C) sample was weighed in a teflon basin and moistened with water. 3 ml of H\textsubscript{2}SO\textsubscript{4} (1:1 v/v) and 10 ml of HF (40%) were added and the contents digested on a sand bath till copious fumes of SO\textsubscript{3} evolved. The sample was cooled and a few drops of conc. HNO\textsubscript{3} were added; it was heated again to fumes for destroying any organic matter present in the sample. The digested liquid was cooled and transferred to a 25 ml volumetric flask. The volume was made up with water.

Five ml of this sample solution were transferred to a 50 ml beaker to which were added 13 ml of 6 M thiocyanate, 1 ml of 9 N H\textsubscript{2}SO\textsubscript{4} and 1 ml of water and the volume made up to 20 ml. Four or five pieces of foam chips were added to the solution and the estimation was carried out as described under procedure.

Titanium was estimated using the formula,

\[
\% \text{TiO}_2 = \frac{a \times b \times 5 \times 100 \times 79.9}{C \times W \times 10^6 \times 47.9}
\]

where \(a\) = concentration of Ti µg/ml (std.), \(b\) = optical density obtained in the case of test sample, \(c\) = optical density obtained in the case of standard titanium solution, and \(w\) = weight of the sample taken in g.

Results and discussion

Titanium forms\textsuperscript{18} yellow coloured complex with thiocyanate in acid solution. However, for low concentrations of titanium, yellow colouration is not perceptible to the naked eye. But it has been observed that the polyurethane foam gradually becomes coloured due to sorption of the thiocyanate. This is probably due to the displacement of the hydroxyl group of titanium-thiocyanate complex in aqueous medium by ketonic oxygen group of the polyurethane foam. The exact composition of titanium-thiocyanate complex has not been studied here; but literature survey\textsuperscript{19,20} showed that the formation of [Ti(SCN)\textsubscript{6}]\textsuperscript{2-} in acid medium is more likely. Therefore, this anionic complex is possibly extracted by polyurethane foam following the anion exchange mechanism\textsuperscript{21}.

Quantitative elution of the complex from foam is also an important parameter. It has been observed that elution with acetone only is not quantitative as the bonding between titanium thiocyanate and foam is strong. However, acidified acetone (1 ml of 0.1 N HCl in 99 ml acetone) has been found to be ideal for quantitative elution of the complex; probably the ketonic oxygen of acetone gets protonated and it facilitates the process of elution. Further, it has been observed that protonated acetone not only helps in quantitative elution but also stabilises the complex in acetone medium\textsuperscript{22}.

The maximum absorption of the [Ti(SCN)\textsubscript{6}]\textsuperscript{2-} complex was observed at 410 nm. During preliminary studies, it was observed that extraction of titanium as titanium thiocyanate by polyurethane foam depends on acid concentration, thiocyanate concentration and equilibration time with foam.

The effect of acid concentration on the extraction of titanium-thiocyanate complex by polyurethane foam was studied. It was found that the extraction of titanium-thiocyanate complex was optimum in the presence of 0.5-1.0 N H\textsubscript{2}SO\textsubscript{4}.

Concentration of thiocyanate has been found to be an important parameter for extraction of titanium-thiocyanate complex by polyurethane foam from 0.5 to 1.0 N H\textsubscript{2}SO\textsubscript{4} medium. It was found that the extraction of titanium increased with increase in thiocyanate concentration up to 4 M and then it became constant up to 6 M.

Another important parameter is the equilibration time with foam chips. It was found that the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean % TiO\textsubscript{2} obtained by chromotropic acid method*</th>
<th>Mean % TiO\textsubscript{2} obtained by the present method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia</td>
<td>0.280</td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>0.274</td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>0.280</td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>0.022</td>
<td>0.022</td>
</tr>
<tr>
<td>Opal glass</td>
<td>0.021</td>
<td>0.021</td>
</tr>
<tr>
<td>NBS 91</td>
<td>0.021</td>
<td>0.019†</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.015</td>
<td>0.017</td>
</tr>
<tr>
<td>(standard)</td>
<td>0.019</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>(sample)</td>
<td>0.012</td>
<td>0.011</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.010</td>
<td>0.012</td>
</tr>
<tr>
<td>(sample)</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>0.014</td>
<td>0.013</td>
</tr>
<tr>
<td>(sample)</td>
<td>0.015</td>
<td>0.012</td>
</tr>
</tbody>
</table>

*Ref. No. 7.<br>†N.B.S. certified values
optimum equilibration time between titanium thiocyanate complex and polyurethane foam is 3 hr.

Based on the above preliminary experiments, effect of titanium concentration on extraction was studied by taking 0.1 to 2 ug/ml of titanium solution. Beer's law was obeyed for Ti concentration in the range 0.1 to 2 ug/ml. Stability of titanium-thiocyanate complex is also an important parameter which was also studied after elution with acidified acetone (1 ml 0.1 N HCl in 99 ml acetone). The titanium-thiocyanate complex was found to be stable up to 30 minutes. The optical density of the eluted solution decreased after 30 minutes probably due to the dissociation of titanium thiocyanate complex in acidified acetone medium. Interference of other ions like Fe, Co, Ni, Cu, V, Mo, Cr, etc., was also studied. Except iron and cobalt, other ions do not interfere up to concentration of 250 ug/ml. Iron and cobalt interfered seriously as the thiocyanate complexes formed by these two metals are also extractable by polyurethane foam from aqueous medium. However, cobalt up to 1 ug/ml (for 1 ug/ml of titanium) has no significant effect. Interference due to iron up to 2 ug/ml could be eliminated by aging the solution for one hour before extraction. Iron, if present in higher concentrations, could be separated previously by using MIBK.

The new method developed on the basis of the above studies was applied to the estimation of titanium present in glass, quartz and zirconia samples. The results obtained are given in Table 1.

Preconcentration of titanium thiocyanate complex (0.1 ug/ml-2 ug/ml) on polyurethane foam has been found to have advantages over other methods due to the following factors. (i) This method eliminates matrix effects because polyurethane foam extracts selectively titanium thiocyanate complex from aqueous solution. (ii) Operational techniques are very easy and simple compared to those used in solvent extraction methods. (iii) The material is cheap and the amount of sample required for operation is less (0.2 g) compared to that required in other method (1.0 g) used in aqueous system. (iv) The method works well in strong acid medium.

Acknowledgement

The authors are thankful to Dr. B.K. Sarkar, Director, Central Glass & Ceramic Research Institute, Calcutta 700 032 for his kind permission to publish the paper and to Dr. S.K. Guha, Deputy Director for his keen interest in the work.

References