

## SHORT COMMUNICATION

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### A simple, rapid complexometric determination of titanium in the presence of other metals

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The determination of titanium in the presence of other metals, *e.g.* lead, by the usual gravimetric or titrimetric methods are very time-consuming<sup>1,2</sup>, hence a rapid, titrimetric method was developed in which lead does not interfere. In our particular case, the method had to be applicable to the determination of titanium in complex compounds such as lead titanyle oxalate tetrahydrate ( $\text{PbTiO}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$ ).

Various publications have presented methods based on the back-titration of an excess of EDTA with standard bismuth<sup>3</sup> or copper<sup>4</sup> solutions, in which the titanium-EDTA complex is stabilized with hydrogen peroxide.

Back-titration of the excess of EDTA with a standard lead solution and xylenol orange as indicator was examined here. Lead was used as titrant because, if this metal is present in the titanium solution to be analyzed, the titration remains straightforward and because the titration of lead with EDTA and xylenol orange as indicator is well known to be very accurate with a distinct colour change. If lead is present in the solution, it can be determined together with the titanium from the amount of EDTA solution consumed. The lead content may then be determined by a separate titration after masking of the titanium with lactic acid. The difference between the quantities of lead solution used in these titrations then gives the titanium content. Of course, it is necessary to ensure that no metal ions are present in the solution with the same complex-forming properties as titanium, *i.e.* reacting with both EDTA and lactic acid.

#### *Experimental*

**Reagents.** The 0.1 M EDTA solution was standardized against p.a. lead nitrate (Baker) and the 0.1 M lead nitrate solution against the EDTA solution. The titanium salt— $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ —was prepared as described previously<sup>5</sup>.

**Procedure.** To 40–300 mg of the titanium salt, dissolved in a small volume of 4 M sulphuric acid, add 3 drops of 30% (vol.) hydrogen peroxide and 10 ml of 0.1 M EDTA solution. Dilute the solution with water to about 100 ml. Add 3.5 g of hexamine as buffer, adjust the pH to 5.5 with ammonia liquor, and add 3 drops

of 0.5% (w/v) xylenol orange indicator solution. (After addition of the hydrogen peroxide, the solution turns orange-yellow and this changes to yellow after the pH adjustment.) Back-titrate the excess of EDTA with the standard 0.1 M lead(II) solution until a stable colour change to purple-red is reached.

If lead(II) is present, the method does not have to be changed. Because the lead sulphate formed originally is soluble in EDTA, the total metal content (Ti + Pb) is determined. The lead content is found by adding 5 ml of 90.4% (w/v) lactic acid solution instead of the hydrogen peroxide to the titration vessel. After this, the rest of the procedure described above is followed. The colour change is more pronounced in this case.

### Results and discussion

All determinations were performed in triplicate, except for the determination of titanium in a perchloric acid solution in the presence of lead, which was done six times; the errors given in Table I correspond to half the difference between the extreme results. The titanium content of the standard titanium salt used was determined by calcining at about 900°C and weighing as TiO<sub>2</sub>. The lead content in the lead nitrate added was simply calculated.

TABLE I

#### TITRATION OF TITANIUM UNDER DIFFERENT CONDITIONS

(In all cases, the theoretical result was 15.56% Ti)

Conditions	% Ti found
Ti salt in H <sub>2</sub> SO <sub>4</sub> , no Pb present	15.55 ± 0.03
Ti salt in H <sub>2</sub> SO <sub>4</sub> , Pb present	15.56 ± 0.02
Ti salt in HClO <sub>4</sub> , no Pb present	15.56 ± 0.05
Ti salt in HClO <sub>4</sub> , Pb present	15.00 ± 1.3
Ti salt in HCl, Pb present	15.58 ± 0.02

The results for titanium are very good, even when lead is present (Table I). This method was also tested in the presence of various acids; the results were reasonably good except for the determination of titanium in the presence of perchloric acid and lead. The use of the other acids has one drawback: the solutions are brown-yellow instead of clear yellow, making the colour change less easy to see.

The effectiveness of the masking agent and the accuracy of the method was proved by the determination of lead in lead nitrate in the presence of titanium. The results obtained were 62.54 ± 0.05% lead in sulphuric acid solution, and 62.56 ± 0.11% lead in nitric acid solution (calculated 62.56%).

The hydrogen peroxide and the lactic acid must be added to the relatively concentrated acid solutions before neutralization, otherwise the titanium may precipitate as hydroxide, which is only slightly soluble in EDTA. The results show that when these precautions are followed, the accuracy is good, except for the determination in perchloric acid in the presence of lead, the cause of which is not clear. The spread is small, when compared with that of gravimetric methods where it usually is of the order of at least ± 1% relative.

Moreover, the total time necessary for the determination of both titanium and lead is only 15 min, compared to at least one and a half days for the gravimetric method.

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