

Short Communications

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VOLUMETRIC DETERMINATION OF PLATINUM WITH COBALT (III) ACETATE

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The high redox potential of cobalt (III) acetate has been successfully utilized by the authors for the determination of a variety of compounds.¹⁻⁸ These studies encouraged the authors to explore further possibilities of the volumetric oxidimetric use of this promising titrant for the standardization of analytical methods for various other compounds.

Volumetric procedures for the determination of platinum metals remain a fertile field for analytical chemists. In view of this state of affairs we have in a previous communication reported the results of ruthenium determination via its oxidation with the titrant.⁸ In order to extend its scope as a volumetric reagent for the determination of platinum metals we have tried to evolve a method for platinum (IV) estimation and the results of this study are reported here.

Experimental

Reagents. Cobalt (III) acetate solution was prepared and its factor was checked according to the method already described.¹

An appropriate solution of platinum (IV) was prepared by dissolving 245.0 mg of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$ Peking Chemical Works, China) in 500 ml of 5.0 N hydrochloric acid. Quadrivalent platinum was reduced to platinum (II) with copper (I) chloride, the excess of which was oxidized with air and the factor of the solution obtained was checked with permanganate according to the method after Grinberg *et al.*⁹

All other chemicals used were either of analytical grade or equivalent purity.

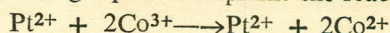
Apparatus. An electronic pH meter (WG Pye-Model 290) with platinum as indicating and saturated calomel as reference electrodes were used for potential measurements.

Procedure. A definite aliquot (0.5-15.0 ml) of platinum (II) solution, obtained and standardized after the reduction of platinum (IV), as referred above, was transferred to a 100 ml Pyrex glass beaker to which 50 ml of 10N H_2SO_4 were added. Titration was done by adding a definite volumes of cobalt (III) acetate

solution from a 10 ml microburette graduated at 0.2 ml intervals. The addition of the titrant was made in 0.2 ml portions before and after the equivalence point. The contents of the reaction vessel were stirred gently with electronic stirring arrangement throughout the course of the titration.

Results and Discussion

The method of determination of platinum, explained in this communication, is based upon the oxidation of platinum (II) to platinum (IV) in 10N H_2SO_4 and the following equation explains the reaction:



Hydrochloric acid (1-4 N), perchloric acid (1-10%), acetic acid (50% to glacial) and sulphuric acid (1-15 N) were tried to find out suitable media for quantitative oxidation of platinum (II) to platinum (IV) but 10N H_2SO_4 turned out to be the best.

TABLE. DETERMINATION OF MICROGRAMME AMOUNTS OF PLATINUM WITH COBALT (III) ACETATE IN 10N H_2SO_4

No.	Amount taken (μg)	Amount found (μg)	Standard deviation (%)
1	25.34	25.45	0.08%
2	50.67	50.70	0.04%
3	151.20	151.49	0.13%
4	253.36	252.50	0.08%
5	354.70	347.44	0.06%
6	506.72	525.19	0.04%
7	760.01	715.07	0.03%

The oxidation of platinum (II) to platinum (IV) was quantitative in this medium and the potential jump at equivalence point was quite reasonable. With the increasing amounts of platinum being taken, the potential leap showed an increasing trend but after a certain limit it started decreasing to the extent that with further increase in the platinum taken the oxidation did not proceed quantitatively, *i.e.* there did not appear any potential jump at the equivalence point. But for the amount as reported in the Table the oxidation was quantitative. The time taken to complete one titration went on increasing with the increasing amounts of platinum but within the limits exhibited in the Table the reaction proceeded at a reasonable rate and results of analytical importance were available.

According to the method reported platinum can be determined within the limits from 25.34 μg to 760.01 μg with a maximum standard deviation of 0.13%.

References

1. M. Hanif, N. A. Ginai and M. A. Chaudhry, Pakistan J. Sci. Ind. Res., **14**, 333 (1971).

2. M. Hanif, J. Dolezal and J. Zyka, *Microchem. J.*, **16**, 291 (1971).
3. M. Hanif, J. Dolezal and J. Zyka, *Ibid.* (in press).
4. M. Hanif, M. A. Chughtai and M. A. Chaudhry, *Pakistan J. Sci. Ind. Res.*, **15**, 37 (1972).
5. M. Hanif, I. Parveen and J. Zyka, *Chemia Analityczna (Warsaw)*, **17**, (4), 119 (1972).
6. M. Hanif, I. Ijaz, S. Haque and Z. Sheikh, *Pakistan J. Sci. Ind. Res.*, **16**, 176 (1973).
7. M. Hanif, M. Ahmad, Z. Sheikh and J. Zyka, *Mikrochim. Acta (Wien)*, (in press.)
8. M. Hanif, I. Ijaz and Z. Sheikh, *Mikrochim. Acta (Wien)* (submitted for publication).
9. A. A. Grinberg and J. Gold Braikh, *Gen. Chem. (USSR)*, **15**, 808 (1944).

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HEXAMINECOBALT (III) TRICARBONATOCOBALTATE (III) AS REDOX TITRANT FOR THE DETERMINATION OF TITANIUM

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Most of the volumetric methods reported in the literature for the determination of titanium either require stringent conditions or are time consuming or yield less accurate results.¹⁻⁴ In our previous communications, we have reported that hexaminecobalt (III) tricarbonatocobaltate (III) exhibits a high redox potential in acidic media (1.189V in 0.92 N-HCl) and the same has been successfully utilized for the determination of a variety of compounds, like nitrite, platinum iodide, sulphide, sulphite and thio-sulphate.^{5,10} With these considerations in view, a trial has been made to standardize a simple, quick, accurate and sensitive method for the determination of titanium and the effects of foreign ions have also been studied. These findings have been reported here.

Experimental

Reagents: Hexaminecobalt (III) tricarbonatocobaltate (III) [$\text{Co}(\text{NH}_3)_6\text{Co}(\text{CO}_3)_3$]. The solution of the titrant is prepared and standardized according to a previously described method.⁵

Titanium (III) Solution. An appropriate solution is prepared² by taking 0.7 g. titanium dioxide, 25 ml

concentrated sulphuric acid and 8 g. ammonium sulphate in a beaker and heating at low temperature till a clear solution is obtained. This solution is diluted with 4N sulphuric acid so that a one litre final solution is obtained.

The titanium (IV) in this solution is reduced to the trivalent form with zinc/mercury amalgam in a flask under pure nitrogen atmosphere. The final solution is standardized against potassium permanganate.² Ferroin 0.025 M (E. Merck) was used as such as indicator.

All other solutions required in this work were prepared from analytical grade chemicals, using conventional methods.

Apparatus. A 10 ml microburette graduated at 0.02 ml intervals was used. All other officially calibrated volumetric glass-ware was used for these experiments.

Procedure. A definite aliquot (1ml) of titanium (III) solution, from the stock solution kept under nitrogen atmosphere was transferred with a graduated pipette to a titration flask to which 24 ml of 4N sulphuric acid and 2 drops of ferroin as indicator were added and the titrant hexaminecobalt (III) tricarbonatocobaltate (III) was run from the burette shaking the contents of the flask with a swirling motion. The end-point, was reached when the colour of the indicator change from red to a persistent blue. A blank titration was run side by side to get exact volume of the titrant consumed by titanium (III).

The effect of foreign ions was investigated by adding known volumes of their solutions to titanium solutions and proceeding as above.

Calculations. The calculations were made using the formula:

$$\text{Amount of titanium in mg} = N \times V \times E$$

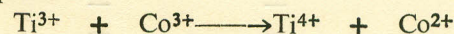
where N = Normality of $\text{Co}(\text{NH}_3)_6\text{Co}(\text{CO}_3)_3$.

V = Volume of $\text{Co}(\text{NH}_3)_6\text{Co}(\text{CO}_3)_3$ used for titre.

E = Equivalent weight of titanium.

Results and Discussion

The reaction proceeds according to the following equation:



Equivalent weights of these substances were calculated on the basis of these electronic changes. The reaction is very fast and one titration is completed within one min. We also used a special assembly¹¹ for observing the interfering effect of atmospheric oxygen upon the oxidation of titanium (III) to titanium (IV) but it was proved that with the above procedure this special assembly was not needed.

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Hydrochloric acid was also tried in different concentrations as a medium but 10N sulphuric acid proved to yield the best results. According to some of the results reported in Table 1, titanium (III) can be determined within the limits from 0.947 to 14.205 mg with a maximum error of 3.73%. With

further increase in the amount of titanium (III) taken, the error increases to the extent to yield results of no analytical importance.

Aluminium, magnesium, calcium and copper do not interfere with the determination of titanium up to the levels as reported in Table 2. These ions also neither affect the rate of reaction between Co^{3+} and Ti^{3+} , nor the colour of the indicator at the end point. When the amount of calcium (II) increases to about 15 folds more to that of titanium (III) in the test solution the error of determination increases to +1.91% and with about 6 fold excess of copper (II) to titanium (III) amount in solution the error shoots up to +4.03%. On the other hand Fe^{3+} and Fe^{2+} both seriously interfere with this determination, the reason being that Fe^{3+} oxidises Ti^{3+} and Fe^{2+} is oxidized by Co^{3+} .

On the basis of these findings it is clear that the method reported here for the determination of titanium is quite convenient, simple, precise, sensitive and accurate. It can be used for the determination of titanium in the presence of calcium, magnesium, and copper.

TABLE 1. DETERMINATION OF TITANIUM

Titanium taken (mg)	Titanium found (mg)	Error (%)
0.947	0.945	-0.21
1.894	1.890	-0.21
2.841	2.846	-0.18
3.788	3.791	+0.08
4.735	4.736	+0.02
9.470	9.473	+0.07
11.364	11.384	+0.18
14.205	14.735	+3.73

*All the results are the averages of seven titrations.

TABLE 2. DETERMINATION OF TITANIUM IN THE PRESENCE OF INTERFERING IONS

Titanium taken (mg)	Aluminium (III) added (mg)	Magnesium (II) added (mg)	Calcium (II) added (mg)	Copper (II) added (mg)	Titanium found (mg)	Error (%)
4.74	2.24	—	—	—	4.74	±0.00
	4.47	—	—	—	4.74	±0.00
	8.39	—	—	—	4.74	±0.00
	16.77	—	—	—	4.74	±0.00
	83.85	—	—	—	4.75	±0.21
4.74	—	3.94	—	—	4.74	±0.00
	—	11.83	—	—	4.74	±0.00
	—	19.72	—	—	4.74	±0.00
	—	39.44	—	—	4.74	±0.00
	—	78.88	—	—	4.74	±0.00
5.21	—	—	3.32	—	5.21	±0.00
	—	—	7.22	—	5.21	±0.00
	—	—	14.44	—	5.21	±0.00
	—	—	36.11	—	5.21	±0.00
	—	—	72.22	—	5.31	±1.91
5.21	—	—	—	2.04	5.21	±0.00
	—	—	—	6.12	5.21	±0.00
	—	—	—	16.32	5.21	±0.00
	—	—	—	30.60	5.42	±4.03

*All results are average of seven titrations.

References

1. R. A. Chalmer, *Quantitative Chemical Analysis*, 11th ed., Oliver and Boyd, London, (1951) p. 178.
2. B. A. Shippy, *Analy. Chem.*, **21**, 698 (1949).
3. J. A. Rahm, *Ibid.*, **24**, 1832 (1952).
4. Gilbert H. Ayres, *Quantitative Chemical Analysis*, Harper & Brothers, N. Y. (1958) p. 450.
5. M. Hanif, M. Saleem, Z. Sheikh and J. Zyka, *Mikrochim. Acta (Wien)*, 1976, II, 625-33.

6. M. Hanif, M. Saeed, M. Z. Iqbal and J. Zyka, Pakistan J. Sci. Ind. Res. (In press).
7. M. Hanif and M. Saleem, Pakistan J. Sci. Ind. Res. (In press).
8. M. Hanif and M. Javaid, Pakistan J. Sci. Res., 25, 265 (1973).
9. M. Hanif, M. A. Shaida and Z. Sheikh, *Ibid.* (In press).
10. M. Hanif, M. Ahmad and M. S. Chaudhry, Pakistan J. Sci. Ind. Res. (In press).
11. M. Hanif, I. Parveen and J. Zyka, *Chemia Anal.* 17, 1119 (1972).

Abstract. A new trematode, *Pagioporus heterotaxus* sp. n., is described from the fish *Pomadasys olivaceum* (Day) of Karachi coast. This species is characterized by possessing a very small fore body; indistinct esophagus; cirrus sac extending slightly posterior to acetabulum; genital pore at the base of pharynx; testis showing great morphological variation; vas deferens extending laterally, except posterior to testis from the base of pharynx to posterior end of the body; eggs 0.041-0.076 mm by 0.03-0.04 mm and excretory vesicle extending to the base of posterior testis.

A large number of species of the genus *Pagioporus* Stafford, 1904 have been reported both from fresh-water and marine fishes of distant countries (Yamaguti, 1971) but none was known from Pakistan fishes. A new species *P. heterotaxus* is reported here from a marine fish *Pomadasys olivaceum*. The species name refers to the morphological variations of the testis.

Material and Methods

In March 1975, viscera of a large fish *Pomadasys olivaceum* were brought to this laboratory from the West Wharf, Karachi, for collection of parasites. Only 4 trematodes were recovered from the intestine. For a detailed study permanent preparations were made by previous methods (Bilgic, 1974). Measurements are given length by width. Diagrams are made by a camera lucida. The holotype is in the School of Parasitology, Department of Zoology, University of Karachi.

Description

Pagioporus heterotaxus. Host: *Pomadasys olivaceum*. Location: Intestine. Locality: West Wharf, Karachi coast. Number: 4 specimens from a single host holotype: SPUK 295.
 Body length 1.35-2.34 mm; maximum 0.4-0.8 mm. Body tapering towards posterior end except in one specimen. Oral sucker 0.13-0.14 mm wide. Acetabulum 0.192-0.260 mm wide. Sucker ratio 1:1.5-1.9. Forebody 0.26-0.29. No prepharynx, pharynx 0.091-0.093 mm by 0.078-0.093 mm. Intestine indistinct bifurcating immediately anterior to acetabulum, caeca extending to near about posterior end of the body.

Testes tandem tandem in shape, smooth, notched or lobed close together, anterior testis just posterior to

