A CONTRIBUTION TO THE DETERMINATION OF SOME ANIONS *via* TITRATION WITH A LEAD(II) NITRATE SOLUTION USING HETEROCYCLIC AZO DYES AS INDICATORS

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The determination of molybdate, phosphate, tungstate, and sulphate *via* titration with lead(II) nitrate, using 4-(2-pyridylazo)resorcinol, 4-(2-thiazolylazo)resorcinol, 2-(2-thiazolylazo)-4-methoxyphenol and 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid as indicators, was studied and the precision, accuracy and applicability of the individual methods were evaluated.

Püschel and Lassner with their coworkers[1–7] give procedures for the rapid titration determination of molybdate, tungstate, sulphate, and phosphate with a lead(II) nitrate solution at pH ~ 6 and at an elevated temperature, using 4-(2-pyridylazo)resorcinol (PAR) as an indicator, which indicates the equivalence point more sharply and more precisely than the indication systems of Cu^{2+}-EDTA-1-(2-pyridylazo)naphthol, xylenol orange or alizarin 3-sulphonate.

It follows from our experiments that the titrations of molybdate and phosphate with lead(II) nitrate yield, under defined conditions and using heterocyclic azo-dyes, PAR, 4-(2-thiazolylazo)resorcinol (TAR), 2-(2-thiazolylazo)-4-methoxyphenyl (TAMP) and 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid (1-PAN-4S) as indicators, very satisfactory results. The titration of tungstate and sulphate *via* precipitation is performable with greater difficulty in practice. Reproducible results are attainable only when the conditions are exactly maintained, they require considerable experience, and have no advantage over other methods of determination.

EXPERIMENTAL AND RESULTS

Chemicals and Instruments

0·05M and 0·1M lead(II) nitrate solutions with several drops of 2M-HNO_3 (standardized by chelatometric titration with xylenol orange as an indicator), a 0·1M aqueous solution of sodium molybdate (dihydrate) in water or after addition of 0·5 ml 1M-NaOH per 1000 ml (standardized gravimetrically with 8-hydroxyquinoline), and a 0·05M aqueous solution of sodium tungstate, containing 1 ml NaOH per 1000 ml (standardized gravimetrically with 8-hydroxyquinoline) were used. 0·1M potassium sulphate and 0·1M potassium dihydrophosphate were prepared by dissolving the dried substances.

The following buffer solutions were used: 0·5M hexamethylenetetramine buffers with pH 6·0 and 7·0; 0·5M pyridine buffers with pH 6·0, 6·3 and 7·0; 0·5M tris (hydroxymethyl)aminomethane buffers with pH 6·1, 6·4 and 7·0 (further denoted as Tris-buffer). The pH of the buffers was adjusted by adding the required amount of nitric acid under control with a pH meter and the solution was diluted with water to 500 ml.

Indicators used: 0·1% PAR in water, 0·1% TAR in 95% (v/v) ethanol, 0·1% TAMP in 95% (v/v) ethanol and 0·1% 1-PAN-4S in a water–ethanol mixture (1 : 1). All the chemicals were analytically pure or were recrystallized. The OP-205 pH meter (Hungary) with the Radiometer GK 2302B combined electrode were used for the pH measurement.

Statistical evaluation of the results was performed according to Dean and Dixon[8] on the basis of three titrations for each concentration. The titrations were performed under optimum conditions at a temperature of 80°C, under vigorous stirring by a magnetic stirrer, with 0·05M or 0·005M lead(II) nitrate using a 10 ml Schellbach burette divided to 0·02 ml; the pH was controlled with the pH meter after each titration.

The titration precision is characterized by the standard deviation of a single determination, s_i, the variation coefficient (%), $s_i \cdot 100/\bar{x}$, the confidence interval and its relative width for a statistical significance of $\alpha = 0{\cdot}05$. The titration accuracy is expressed by the relative error $(\mu - \bar{x}) \cdot 100/\mu$, where μ is the accurate value.

The Determination of Molybdate Using PAR as Indicator

At pH 5·5 – 6·5, a sharp colour transition from yellow to red occurs at the equivalence point in unbuffered solutions; the $PbMoO_4$ precipitate coagulates well in hot solution and does not interfere with the indication. The urotropine buffer, in an amount of 3 – 20 ml of 0·5M solution in 50 ml of the solution titated, causes an insufficiently sharp colour transition of the indicator, Pb^{2+} ions are partially coprecipitated, *i.e.* the precipitate is coloured by the indicator chelate before the equivalence point and the consumption is higher. A sharp colour transition at the equivalence point occurs in the presence of 5 – 15 ml of 0·5M Tris-buffer or 5 – 15 ml of 0·5M pyridine buffer (pH 6·1 or 6·0, respectively) in 50 ml of the solution titrated at 80°C, on addition of one drop of lead(II) nitrate (0·05M) at a titration rate of 1 – 2 drops of 0·05M lead(II) nitrate per s. The optimum indicator concentration is 0·15 ml of 0·1% PAR in 50 ml of the solution. At higher indicator concentrations, Pb^{2+} ions are prematurelly bound to the indicator, leading to premature equivalence point indication.

Ethanol, methanol, acetone and dimethylformamide up to 50% (v/v) show no substantial influence; dioxane makes the colour transition in the equivalence point worse at concentrations above 10% (v/v). The $PbMoO_4$ precipitate is coarser in the presence of detergents, gelatine, poly(vinyl alcohol) and cetylpyridinium bromide, and has a smaller active surface area. In the presence of Tris- or pyridine buffers, the detergent is, however, not necessary. The suitable concentration range in the titration with 0·05M lead(II) nitrate in a medium of 0·05M pyridine or Tris-buffer is 0·935 – 46·74 mg Mo; however, the end-point is less pronounced for concentrations below 9·35 Mo using Tris-buffer.

Procedure: 45 ml of a solution containing 9·3—46·8 mg or 0·9—4·7 mg of Mo is heated to the boiling point, 5 ml of 0·5M pyridine buffer and 0·15 ml of 0·1% PAR are added, and the titration is performed at 80°C with 0·05M or 0·005M lead(II) nitrate, to a colour change from light yellow to red. The titration rate should not exceed 1 drop per *s*, or, in titration with 0·005M lead(II) nitrate, 1 drop per 2 s. The resulting pH of the solution must be 5·6 to 5·9. Instead of pyridine buffer, 5 ml of Tris-buffer (0·5M) per 45 ml of the solution can be added, observing the same procedure as above, after heating the solution to the boiling point (the resulting pH of the solution is 6·1). The results of the statistical treatment of the titration are given in Table I.

The determination of molybdenum (83·4 mg Mo) is not affected by Na^+, K^+, NO_3^- (500 : 1), NH_4^+, Cl^-, ammonium acetate (100 : 1), sodium acetate (50 : 1), Mg^{2+}, Br^- (10 : 1), but Ca^{2+}, Se^{2+}, Ba^{2+}, F^- (0·02 : 1), HCO_3^-, SO_4^{2-}, tartrate, citrate (0·01 : 1), ClO_4^- (0·1 : 1) interfere. The numbers in parenthesis give the ratios of the molar concentrations of the interfering ions to molybdate.

The Determination of Molybdate Using the TAR Indicator

In titration of 0·9 to 47 mg Mo with 0·05 and 0·005 lead(II) nitrate solutions, after adding 0·2—0·3 ml of 0·1% TAR to 50 ml of the solution, a sharp colour transition is obtained in a medium of 0·05M pyridine buffer (pH 5·5—6·5). The colour transition gets worse in a medium of 0·03—0·2M Tris-buffer (pH 6·1), and no pronounced colour transition occurs in a medium of 0·03—0·25M hexamethylenetetramine buffer (pH 6·0).

Procedure: 45 ml of a solution containing molybdate is heated to the boiling point, 5 ml of 0·5M pyridine buffer (pH 6·0), and 0·3 ml of 0·1% TAR are added, and the titration is performed under vigorous stirring at 80°C, with 0·05 or 0·005M lead(II) nitrate to a colour change from yellow to red. The resulting pH should be 5·7—5·9.

TABLE I

The Titration of Molybdate with Lead(II) Nitrate Using PAR Indicator

Taken Mo, mg[a]	Standard deviation of the determination s_i, mg[b]	Variation coefficient	Relative width of the confidence interval % ($\alpha = 0{\cdot}05$)[b]	Relative error %
46·77—9·35	0·083—0·029	0·18—0·31	0·78—1·39	+0·13—0·32
4·68—0·93	0·11—0·006	0·24—0·62	1·05—2·72	+0·41—2·35
46·77—9·35[c]	0·024—0·083	0·10—0·70	0·22—3·09	−0·60—(+0·96)
46·77—9·35[d]	0·083—0·14	0·24—1·51	1·06—6·62	−0·30—(+0·85)

[a] The concentration limits (in the interval there are altogether 5—6 concentration values); [b] the data correspond to the lowest and highest value in the series for the given concentration interval; [c] 5 ml of Tris-buffer in 45 ml of the solution; [d] the procedure of Püschell and coworkers[1,3,7].

The Determination of Molybdenum Using the TAMP Indicator

The optimum condition for the precipitation reaction of molybdate with 0·05M lead(II) nitrate is pH 5·7–6·7, with the colour transition at the equivalence point from yellow – orange to blue – green. In media of pyridine (pH 6·0), Tris- (pH 6·1) and hexamethylenetetramine (pH 6·0) buffers, the colour transitions get sluggish, going through green, green–blue, and blue–green to a green–gray colour. The PbL^+ chelate of the TAMP indicator is adsorbed on the $PbMoO_4$ precipitate and it appears a blue colouration during the titration.

Procedure: 50 ml of a solution containing 9·4–47 mg Mo was neutralized, using phenolphthalein (pH ~ 7), with a dilute solution of sodium hydroxide (the first red colouration is removed with one drop of dilute nitric acid). The solution is heated to boiling and, after addition of 0·5 ml of 0·1% TAMP, is titrated with 0·05M lead(II) nitrate from yellow–pink to blue – green, at 80°C under vigorous stirring. The resulting pH at the equivalence point is 6·3–6·8.

The Determination of Molybdate Using 1-PAN-4S *as Indicator*

In the medium of 0·05–0·20M pyridine buffer (pH 6·0), there is a pronounced colour transition from yellow – orange to purple, at the optimum indicator concentration, 0·1–0·2 ml of a 0·1% solution per 50 ml of the solution titrated.

Procedure: 45 ml of a solution containing 0·9–47·0 mg Mo were heated to boiling, 5 ml of 0·5M pyridine buffer (pH 6·0) and 0·2 ml of a 0·1% indicator solution were added, and the hot solution (80°C) was titrated, stirring constantly, with 0·05 or 0·005M lead(II) nitrate to a colour change from yellow – orange to purple. The resulting pH at the equivalence point is 5·6–5·8. The results of the titrations using TAR, TAMP and 1-PAN-4S are summarized in Table II.

The Determination of Phosphate Using Heterocyclic Azo-Dyes as Indicators

At pH 7, a white precipitate is formed from a hot HPO_4^{2-} solution on addition of lead(II) nitrate, in which Püschell and coworkers[5,6] assumed a Pb–to–PO_4 ratio equal to 5 : 3, corresponding to a apatite-type phosphate[9], $Pb_5(PO_4)_3OH$. This molar ratio was confirmed by statistical evaluation of a set of titrations using various indicators, at pH 6·6–7·3 and under the conditions given below (Table III).

For PAR, a medium of 0·05M urotropine buffer (pH 7·0) or addition of solid urotropine after previous neutralization of the solution with sodium hydroxide using phenolphthalein proved to be suitable. At higher concentrations, the pyridine buffer (pH 7·0) causes a drawn-out colour transition of the indicator at the equivalence point. A medium of 0·25M Tris-buffer (pH 7·0) is also applicable, after previous neutralization of the solution with sodium hydroxide using phenolphthalein. In all the procedures, the resulting pH must be 6·6–7·2, the indicator concentration being 0·03–0·06 ml of a 0·1% solution in 40 ml of the solution, for the concentration range, 0·5–19 mg PO_4^{3-}.

Procedure: To 40 ml of a solution containing 0·48—1·90 mg PO_4^{3-}, neutralized using methyl red and heated to the boiling point, 4 ml of 0·5M urotropine buffer (pH 7·0) and an additional 2 g of solid urotropine are added in the case of contents of 4·9—19·0 mg PO_4^{3-}, then 0·02 ml of a 0·1% indicator solution is added and the boiling solution is titrated with 0·005M or 0·05M lead(II) nitrate, under constant stirring and at a rate of one drop every 2 s, to a colour change from

TABLE II

The Titration of Molybdate with 0·05M Lead(II) Nitrate Using Heterocyclic Azo-Dyes

Indicator	Taken Mo mg[a]	Standard deviation of the determination s_i, mg[b]	Variation coefficient	Relative width of the confidence interval % ($\alpha = 0{\cdot}05$)	Relative error %
TAR[c]	46·99—9·40	0·024—0·059	0·09—0·45	0·39—1·98	−0·19—(+0·85)
	4·70—0·94[f]	0·005—0·088	0·17—0·86	0·77—3·78	+0·47—2·34
TAMP[d]	46·99—9·40	0·053—0·142	0·23—0·70	0·99—3·06	−0·17—(+1·49)
1-PAN-4S	46·99—9·40	0·029—0·059	0·06—0·63	0·28—2·76	−0·36—(+0·21)
	4·70—0·94[e]	0·003—0·069	0·06—0·53	0·28—2·47	+0·02—(+0·96)

[a,b] See notes to Table I; [c] 0·05M pyridine buffer (pH 5·7—5·9); [d] unbuffered, pH 5·7—5·9; [e] 0·05M pyridine buffer, pH 5·6—5·8; [f] titration with 0·005M lead(II) nitrate.

TABLE III

The Pb : PO_4 Molar Ratio in the Lead(II) Phosphate Precipitate at pH 6·6—7·3

Evaluated statistically by titrations with the individual indicators (the theoretical value is Pb : PO_4 = 1·667).

Indicator	Confidence interval ($\alpha = 0{\cdot}05$) of the Pb : PO_4 molar ratio	1 ml of 0·05M-$Pb(NO_3)_2$ corresponds to mg PO_4[a]
PAR[b]	1·669 ± 0·010	2·844 ± 0·018
PAR[b]	1·687 ± 0·010	2·810 ± 0·014
PAR[c]	1·647 ± 0·006	2·883 ± 0·011
TAR[b]	1·641 ± 0·010	2·893 ± 0·018
TAMP[b]	1·659 ± 0·010	2·862 ± 0·019
1-PAN-4S[b]	1·643 ± 0·015	2·889 ± 0·026

[a] Theoretical value is 2·849 mg PO_4^{3-}; [b] urotropine buffer; [c] Tris-buffer.

yellow to red. It is also possible to neutralize 20 ml of a solution containing 0·48—19·0 mg of PO_4^{3-} to pH 7—8 (phenolphthalein indicator), to add 20 ml of 0·5M Tris-buffer (pH 7·0), heat the solution to the boiling point, add 0·06 ml of a 0·1% indicator solution and titrate.

A hexamethylenetetramine medium with pH 6·7—7·3 at the equivalence point was also found suitable, using TAR, TAMP and 1-PAN-4S indicators.

The optimum concentration of TAR is 0·05—0·1 ml of a 0·1% solution in 40 ml of the titrated solution. The solution turns temporarily red before the equivalence point, and the titration is performed slowly, at a rate of 1 drop per s, to the first permanent red colouration.

When using TAMP, the addition of 0·2—0·3 ml of a 0·1% solution to 40 ml of the solution to be titrated is suitable. During the titration, the colouration changes from dark purple to yellow — pink, at the equivalence point it is blue—green and quickly turns to green—blue and green — gray, while the lead phosphate precipitate is blue coloured. The rate of the titration is 1—2 drops of 0·05M lead(II) solution per s.

When using 1-PAN-4S, its optimum concentration is 0·05—0·1 ml of a 0·1% solution in 40 ml of the solution titrated, yielding a sharp colour transition at the equivalence point from yellow — pink to purple. At higher indicator concentrations, the colour transition occurs before the equivalence point. The results of the titrations with the individual indicators are summarized in Table IV.

The determination of phosphate (11·87 mg PO_4^{3-}) is not affected by K^+, NO_3^- (100 : 1), Na^+ (50 : 1), NH_4^+, Tl^+ (10 : 1) and small concentrations of Cl^-, Br^-, ClO_4^-, SO_4^{2-} (0·1 : 1), Mg^{2+}, F^-, ammonium acetate, sodium acetate (0·02 : 1), tartrate, citrate, Sr^{2+}, Ba^{2+}, Ca^{2+}, and HCO_3^- (0·01 : 1). The foreign ion—to—phosphate molar concentration ratios are given in parenthesis.

The Titration of Tungstate with Lead(II) Nitrate

$PbWO_4$ precipitates at pH 6 much more slowly than $PbMoO_4$ under the same conditions. Using PAR indicator (0·2—0·3 ml of a 0·1% solution in 100 ml of the solution titrated), Pb^{2+} ions are prematurelly bound to the indicator at <60°C (red solution); the precipitate appears only after heating and the solution turns yellow again. The displacement according to the equation

$$PbL + WO_4^{2-} \rightleftarrows PbWO_4 + HL^-$$

takes place only slowly, especially in the beginning of the titration, in dependence on the temperature and pH of the solution. More pronounced indicator colour transitions were observed only in media of 0·025—0·125M pyridine (pH 6·3) or Tris (pH 6·4) buffers. If the titration is carried out slowly, the equivalence point colour change from yellow to red can be determined with a precision of 2—3 drops of the 0·05M lead(II) nitrate standard solution. Ethanol, methanol, acetone and dimethylformamide have no effect on the indicator colour transition at the equivalence point, when present in contents of 5—50% (wt). A more pronounced colour change was not observed even in the presence of a detergent (gelatine, poly(vinyl alcohol), cetylpyridinium bromide).

Procedure: 85 ml of a solution containing 8·97—89·70 mg W or 1·3—9·0 mg W is heated to the boiling point, 15 ml of 0·5M pyridine buffer (pH 6·3) and 0·2 ml of a 0·1% PAR solution are added to the boiling solution and the titration is performed at a rate of 1 drop of the standard solution per 2 or 3—4 seconds with 0·05M or 0·005M lead(II) nitrate to a permanent red colour of the solution, stirring constantly. The resulting pH after the titration should be 5·9—6·2. The results of the titration were compared in Table V with the procedure employing 15 ml of 0·5M Tris-buffer (pH 6·4) in 100 ml of the solution and with the results of the procedure of Püschell and coworkers[2,3].

The Titration Determination of Sulphate with Lead(II) Nitrate

PAR and the other indicators react with free Pb^{2+} ions before the equivalence point even during titration in hot solution; *e.g.* when using PAR (0·2—0·3 ml of a 0·1% solution in 50 ml of the solution titrated) at pH 5·5—6·2, a permanent colour change occurs already after the addition of 1 drop of 0·05M lead(II) nitrate. Better results are obtained in 50% (v/v) acetone and a sharp colour transition is achieved in 50% (v/v) 2-propanol (see also Püschell and coworkers[4]) or in a 1 : 1 mixture of 50% (v/v) 2-propanol and acetone; however, even here, the colour transition takes place before the equivalence point. The titration is impossible at $t < 50°C$. In media of urotropine (pH 6·1) and Tris- (pH 6·1) buffers, the colour change at the equivalence point is not sharp, even in the presence of detergents. Only in 0·1M pyridine buffer it is possible to determine the equivalence point within 2—3 drops of 0·1M

TABLE IV
Titration of Phosphate with 0·05M Lead(II) Nitrate

Indicator	Taken mg PO_4[a]	Standard deviation of the determination s_i, mg[b]	Variation coefficient[b]	Relative width of the confidence interval, ($\alpha = 0{\cdot}05$) %	Relative error %
PAR	18·99—4·75[e]	0·029—0·065	0·25—0·99	1·11—4·4	−2·0—(+1·68)
	1·90—0·48[c,f]	0·005—0·008	0·25—0·71	1·10—7·42	−0·50—(+2·10)
	10·99—4·75[d]	0·029—0·083	0·37—0·93	1·68—4·08	−3·26—(−1·70)
TAR	18·99—4·75[e]	0·018—0·031	0·10—0·91	0·42—4·02	−3·60—(−0·21)
TAMP	19·99—4·75[e]	0·017—0·071	0·13—0·74	0·56—3·27	−2·05—(+1·26)
1-PAN-4S	18·99—4·75[e]	0·018—0·053	0·19—0·41	0·85—2·94	−3·69—(+1·68)

[a,b] See notes to Table I; [c] urotropine buffer, pH 6·6—6·9; [d] Tris-buffer, pH 6·6—7·1; [e] urotropine buffer, pH 6·7—7·3, [f] titration with 0·005M-$Pb(NO_3)_2$.

lead(II) nitrate, at the optimum indicator concentration, 0·1–0·2 ml of 0·1% PAR in 50 ml of solution, 50% (wt) in 2-propanol–acetone mixture (1 : 1).

Procedure: To 15 ml of a solution containing 12·0–72·0 mg SO_4^{2-} are added 25 ml of the 2-propanol–acetone mixture (1 : 1), the solution is heated to 70°C, 10 ml of 0·5M pyridine buffer (pH 6·0) and 0·2 ml of 0·1% PAR are added. The solution is titrated, under vigorous stirring, with 0·1M lead(II) nitrate at a rate of 1–2 drops per s, to a permanent red colouration of the solution. The resulting pH of the solution at the equivalence point is 5·3–5·6. The results of the titrations were statistically treated and, for 12·0–72·0 mg SO_4^{2-}, the standard deviation of a single determination, $s_i = 0{\cdot}06-0{\cdot}37$ mg, the variation coefficient is 0·50–0·74%, the relative width of the confidence interval (at $\alpha = 0{\cdot}05$) is 2·18–3·27%, and the relative error of the determination is (−1·79)–(−0·56) %.

CONCLUSIONS

The determination of molybdate *via* titration with 0·05 or 0·005M lead(II) nitrate (4·7–9·3 mg Mo or 4·7–0·9 mg Mo, respectively), using PAR, TAR and 1-PAN-4S indicators in a pyridine buffer medium (pH 5·6–5·9), is rapid, reliable, and more precise than the original procedure[1]. In this medium, the smallest positive systematic error is also encountered. In a medium of Tris-buffer (pH 6·1), and according to re-

TABLE V
Titration of Tungstate with 0·05M lead Nitrate Using PAR Indicator

Taken W, mg[a]	Standard deviation of the determination s_i, mg[b]	Variation coefficient %[b]	Relative width of the confidence interval % ($\alpha = 0{\cdot}05$)	Relative error %	Notes
89·70–8·97	0·083–0·260	0·29–1·76	1·26–7·60	−0·56–(+2·67)	pyridine buffer pH 5·9–6·2
8·97–1·34[c]	0·016–0·021	0·18–1·45	0·77–6·50	+1·45–4·09	
89·70–8·97	0·106–0·266	0·12–2·87	1·30–12·50	+0·73–3·45	Tris-buffer pH 6·3–6·4
89·70–8·97	0·695–0·745	0·78–2·94	3·43–12·93	+6·6–20·73	urotropine buffer pH 6·4–6·8 procedure as[2]

[a,b] See notes to Table I; [c] titration with 0·005M lead(II) nitrate.

ference[1], this error is negative at high concentrations and positive at lower concentrations of molybdenum. The determination is suitable only in pure solutions or after separation of molybdenum, since only the alkali metal ions, NO_3^-, Cl^-, Br^- and NH_4^+ do not interfere.

The analogous determination of phosphate (47 – 0·5 mg) *via* titration yields the most reliable results in hexamethylenetetramine buffer medium, as has already been recommended[5], at pH 6·6 – 6·9. The Tris-buffer at pH 6·6 – 7·1 also proved to be suitable, but the results are subject to a negative systematic error (−3·3) – (−1·7)%). More precise results are obtained using TAMP or 1-PAN-4S rather than PAR; however, when 1-PAN-4S and TAR are used, there is a greater span of the systematic error from negative values at higher concentrations to positive values at lower phosphate concentrations. Also in this case, only the alkali metal ions, Tl^+, NH_4^+, and NO_3^- in a limited excess do not interfere.

In the determination of tungstate (89·7 – 1·3 mg) *via* titration usable results were obtained only with PAR in a medium of Tris(pH 6·3 – 6·9) and pyridine buffers, but even in this case the reproducibility of results is poor and they are generally subject to a positive systematic error in titration. The original procedure of Püschell and coworkers[2], in a urotropine medium, is charged by a great positive systematic error.

The titration determination of sulphate (72 – 12 mg) with a 0·1M lead(II) nitrate solution is, even in a medium of mixed aqueous – organic solvents and pyridine buffer (pH 5·3 – 5·6), poorly reproducible and always subject to a large negative systematic error.

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