Analytica Chimica Acta, 262 (1992) 41–47
Elsevier Science Publishers B.V., Amsterdam

Spectrofluorimetric determination of titanium with 2-acetylpyridine picolinoylhydrazone and application to agricultural soil extracts

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(Received 13th August 1991; revised manuscript received 24th December 1991)

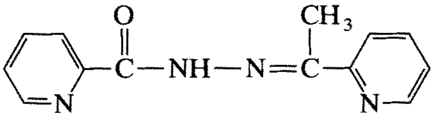
Abstract

The synthesis, solubility, electronic, fluorescence, infrared and mass spectra, ionization constants and analytical applications of 2-acetylpyridine picolinoylhydrazone are described. This compound forms a fluorescent system (blue) with titanium(IV) [λ(ex) 366 nm, λ(em) 445 nm] in an acidic medium. A procedure based on the direct or standard additions methods has been proposed for the determination of Ti(IV) concentrations down to 100 ng l^{-1}. The effect of 70 ions on the proposed method was evaluated and different masking reactions were tested. The method has been used satisfactorily for the determination of titanium at the $\mu g\ l^{-1}$ level in acetate extracts of agricultural soils.

Keywords: Fluorimetry; Soils; Titanium

Although titanium has not been proved to be an essential oligoelement for plants and animals, its biological importance has been stated [1]. Titanium in soils is not considered as a trace element as its concentration can range from several tenths to units or even tens percent. However, amounts of titanium extractable from mineral horizons do not exceed 30 $\mu g\ g^{-1}$ and are usually below 3 $\mu g\ g^{-1}$ as there is little exchangeable titanium [2,3]. It has been shown that titanium accumulates at decreasing level in roots, stems, and leaves, causing a decrease in plant growth [4]. It has also been pointed out that high titanium levels in plants can be attributed to polluted soils [5]. Grigoryan and Galstyan [6] reported a relationship between irrigation using industrial waste waters (containing heavy metals, such as Ti, Fe and Cu) and the decrease in enzymatic activity of the irrigated soils. This happens because the concentration of some heavy metals in soils becomes higher (1.6 times greater for titanium) in these instances. Hence the determination of titanium in soil extracts is interesting not only as a measure of pollution of the soil itself [7,8] but also to investigate the relationship between the element content in a given soil and plant growth in that soil [9].

2-Acetylpyridine picolinoylhydrazone (APPH) has been used for the fluorimetric determination of subtrace amounts of Ti(IV) by means of its catalytic aerial oxidation.



APPH

Only a few fluorimetric methods have been described for the determination of titanium and they are not reliable when applied to smaller than nanogram levels in samples. Most are based on fluorescent complex formation, using salicylaldehyde [10], azomethines [11,12], 5-hydrochromone [13], 5-hydroxyflavones [14], fluorones [15], Bromopyrogallol red [16] and biacetylmonoxime nicotinoylhydrazone [17,18]. Two methods are based on fluorescent species formed as products of picolinaldehyde nicotinoylhydrazone oxidation by titanium [19,20].

EXPERIMENTAL

Reagents

APPH was prepared by condensation of equimolar amounts of the ketone (0.3049 g) and picolinoyl hydrazide (0.3000 g) in 10 ml of absolute ethanol. One drop of concentrated hydrochloric acid was added and the mixture was heated in a water-bath with stirring. The white product was filtered off and recrystallized from ethanol; m.p. 194°C.

The reagent is soluble (> 30 g l^{-1}) in ethanol, *N,N*-dimethylformamide (DMF) and isobutanol, soluble (2–10 g l^{-1}) in acetone and isobutyl methyl ketone and poorly soluble (< 1 g l^{-1}) in water and chloroform.

Elemental analysis conformed to the empirical formula $C_{13}H_{12}N_4O$. A reagent solution in water or chloroform (4.16×10^{-6} and 6.66×10^{-5} M, respectively) showed a main absorption maximum at 302 nm ($\epsilon = 1.35 \times 10^4$ l mol^{-1} cm^{-1}) or 310 nm ($\epsilon = 1.89 \times 10^4$ l mol^{-1} cm^{-1}), respectively [21].

The main IR bands of APPH (KBr disc) are 3320 cm^{-1}, weak (ν_{N-H}); 3050–3010 cm^{-1}, weak ($\nu_{=CH}$); 2920 cm^{-1}, weak (ν_{CH3}); 1705 cm^{-1}, very strong (amide I); and 1515 cm^{-1}, strong (amide II) [22–26]. Selected mass fragmentation data of APPH are: $C_{13}H_{12}N_4O$, $m/z = 240$ (3.5%); $C_{13}H_{13}N_4O$, m/z 241 (1.2%); PyCO, $m/z = 106$ (79.9%); PyMeC=NNH, $m/z = 134$ (100%); PyCONH, $m/z = 121$ (8.2%); PyCNMe, $m/z = 119$ (8.3%); PyCONHMe, $m/z = 136$ (6.0%); and PyCN, $m/z = 104$ (16.3%) [22,27,28].

All reagents used were of analytical-reagent grade. A standard solution of Ti(IV) was prepared by drying titanium metal at 110°C, dissolving an appropriate amount in 100 ml of 6 M HCl and diluting to 1 l with distilled water. Further dilutions were made daily as required. Ethanol and acetone solutions of APPH (0.025%, w/v) were used. These solutions are stable for at least several days. Several acetate buffers (pH 3.5–6.5) of 1 M concentration were prepared. Other buffer solutions were prepared by conventional methods.

Apparatus

A Perkin-Elmer LS-5 spectrofluorimeter was used with 1-cm quartz cells and a xenon arc source, in addition to an ARL inductively coupled plasma (ICP) spectrometer, a Perkin-Elmer 1600 IR spectrometer and a VG 12250 (70 eV) mass spectrometer were also used.

Procedures

Direct Ti(IV) determination. To a 25-ml volumetric flask, containing appropriate volumes of Ti(IV) solutions (to give a final concentration of titanium up to 50 ng ml^{-1}), add 5 ml of the acetate buffer (pH 4.9) and 10 ml of 0.025% (w/v) APPH solution in ethanol or acetone and dilute to the mark with deionized distilled water. Measure the fluorescence intensity [λ(ex) 366 nm, λ(em) 445 nm] after 25 min against a reagent blank prepared in a similar way without titanium, using appropriate slit widths for both excitation and emission.

Standard additions method. Add two series (I and II) of increasing, known amounts of Ti(IV) [(I) 0, 25, 50, 100, 150 and 200 ng; (II) 0, 2.5, 5.0, 10.0, 15.0 and 20.0 ng of Ti(IV)] to aliquots of sample solutions (25 ml) containing 25 or 2.5 ng of Ti(IV), respectively, and follow the procedure described above.

Determination of titanium in soil extracts. Prepare a soil extract by weighing exactly ca. 10 g of a wet sample and adding 33 ml of 1 M ammonium acetate buffer (pH 7) with stirring for 5 min. After repeating the extraction twice more, transfer the extracts into a 100-ml volumetric flask and dilute to volume with the same ammonium acetate solution [29]. Then follow the standard additions method [second set of Ti(IV) standard concentrations] in ethanolic medium as described above, employing 1- or 2-ml aliquots of acetate sample solution. Plot the relative fluorescences against the concentration of the six titanium-containing solutions of each sample, and the intersection of the straight line obtained with the abscissa gives the concentration of the unknown sample. All parameters in the regression equation were calculated using the least-squares method.

RESULTS AND DISCUSSION

Analytical properties of the reagent

The method used by García-Villanova and García-Villanova [30] was used for the determination of the ionization constants. The average pK values were found to be 1.1, 4.1 and 11.1, which may be caused by protonation of the C=NH–N group and the pyridine nitrogen atoms and deprotonation of the CONH group, respectively [22,25,26,30–32].

The reagent shows greenish yellow fluorescence in the solid state, and very weak fluorescence in ethanol, acetone and chloroform. Reagent solutions exhibit maximum fluorescence intensity at pH 5.2 (Fig. 1), and are stable for 4 h between 10 and 30°C. APPH forms coloured systems with V(V), Ni(II), Co(II), Fe(II, III) at pH 4.5 and Fe(II, III) at pH 8.5. Only the reaction with titanium(IV) (pH 4.5–9.5) gives rise to a fluorimetric system.

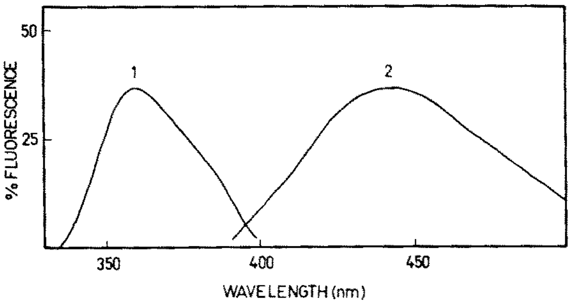


Fig. 1. (1) Excitation and (2) emission spectra of 1.0×10^{-3} M APPH solutions in water–ethanol (4 + 1, v/v) (pH 5.2). λ(ex) 366 nm and λ(em) 445 nm for (2) and (1), respectively. Slit widths, both 10 nm.

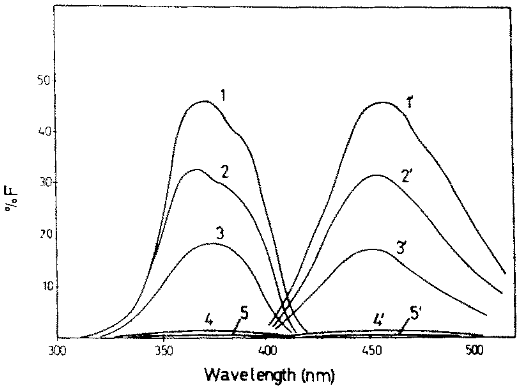


Fig. 2. (1–5) Excitation and (1'–5') emission spectra of Ti–APPH system in water–ethanol (3 + 2, v/v) solutions in acetate buffer (pH 5.2). 1,1', In the presence of air or oxygen; 2,2', bubbling N_2 for 5 min; 3,3', bubbling N_2 for 10 min; 4,4', in the absence of oxygen; 5,5', in the absence of titanium (reagent only). λ(ex) 366 nm, λ(em) 445 nm; slit widths, both 5 nm.

Spectrofluorimetric study of the reaction of APPH with titanium(IV)

Titanium(IV) system. Titanium(IV) forms a colourless system with APPH which has intense fluorescence. The excitation and emission spectra of the Ti(IV)–APPH system in different buffers show one band [λ(ex) 366 nm, λ(em) 445 nm] as shown in Fig. 2 (curves 1 and 1'). The pH range for maximum fluorescence is 4.5–5.7 (Fig. 3).

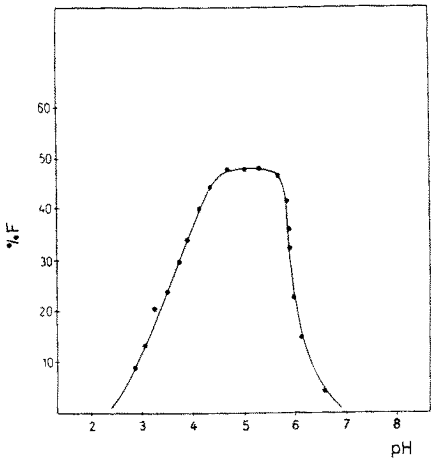


Fig. 3. Influence of pH on the fluorescence of Ti–APPH. [APPH] = 4.16×10^{-4} M; [Ti^{4+}] = 50 ng ml^{-1}; λ(ex) 366 nm, λ(em) = 445 nm; slit widths both 5 nm.

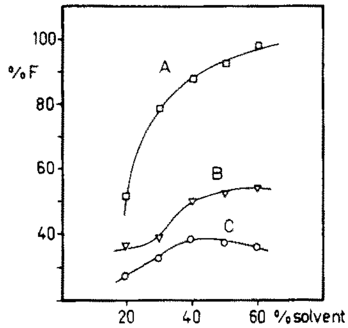


Fig. 4. Effect of the nature of the solvent on the fluorescence of Ti(IV)–APPH system: (A) acetone, (B) ethanol and (C) dimethylformamide, [APPH] = 4.16×10^{-4} M; [Ti^{4+}] = 50 ng ml^{-1}; λ(ex) 366 nm, λ(em) 445 nm; slit widths both 5 nm.

Acetate ion (0.016–0.28 M final concentration) is the most suitable medium to develop the reaction, as in its absence the time required to reach the fluorescence maximum is longer. The Ti(IV) fluorescent system in acetate medium (pH 5.2) remains stable from 20 min to 24 h.

The effect of the nature of the solvent (ethanol, acetone and DMF) on the Ti(IV)–APPH system was also studied (Fig. 4). A medium containing 40% ethanol or acetone was chosen for further experimental work.

The maximum constant relative fluorescence was obtained within the temperature range 10–30°C. An increase in temperature above 30°C decreases the intensity by 0.40% $°C^{-1}$. An APPH excess increases the fluorescence of the system, but APPH:Ti molar ratios between 80 and 800 did not produce any change in fluorescence. Molar ratios above 800 decreased the fluorescence, probably owing to inner filter effects. Variations in ionic strength in the range 0–0.2 by adding KCl, KNO_3 or $NaClO_4$ and the order of addition of reagents did affect the fluorescence.

Nature of the reaction. All attempts to find a stoichiometric relationship between Ti(IV) and APPH failed, probably because the fluorescence is not due to the formation of a chelate. Figure 2 shows the spectra obtained in presence and absence of titanium. Further experiments have shown, in agreement with Luque de Castro and Valcarcel [19] and Lázaro et al. [20], that aerial oxidation of the reagent occurs that is catalysed by traces of Ti(IV). Solutions of Ti(IV) samples made from oxygen-free reagents and measured in an inert atmosphere (nitrogen or helium) showed a dramatic decrease in fluorescence intensity (Fig. 2, curves 2–4 and 2′–4′). When these systems were exposed to air for 10 min or air was bubbled through, the relative fluorescence values were the same as those corresponding to the initial samples prior to oxygen removal. Although the oxidation mechanism of the reaction has not been completely elucidated, as the reaction is first order with respect to both Ti(IV) and APPH, according to Luque de Castro and Valcarcel [19] the different steps may be

$$\mathrm{APPH} + \mathrm{Ti(IV)} \rightarrow \mathrm{APPH_{(ox)}} + \mathrm{Ti(III)}$$

$$\mathrm{Ti(III)} + 1/2\mathrm{O_2} \rightarrow \mathrm{Ti(IV)}$$

where $\mathrm{APPH_{(ox)}}$ is the oxidized reagent.

Fluorimetric determination of Ti(IV)

Two methods of calibration (direct and standard additions) were tested. Using the first method, three calibration lines for two sets (ethanol, acetone) of aqueous–organic solutions, (3 + 2, v/v) were obtained by appropriate selec-

TABLE 1

Direct method for fluorimetric determination of Ti(IV)

Medium [a]	Regression equation: $y = ax + b$	Correlation coefficient	Concentration range ($\mu g\ l^{-1}$)	R.S.D. (%) [b]
Ethanol	$1.0140x + 0.56$	0.9999	5–50	0.80 [c]
Acetone	$1.5440x + 0.46$	0.9844	5–50	1.31 [c]
Ethanol	$4.5350x + 0.81$	0.9971	1–10	1.29 [d]
Acetone	$6.1650x + 1.89$	0.9970	1–10	1.34 [d]
Ethanol	$0.0194x + 0.05$	0.9933	100–2000 [e]	1.91 [f]
Acetone	$0.0292x + 0.66$	0.9970	100–2000 [e]	5.89 [f]

[a] 40% (v/v). [b] Relative standard deviation for eleven samples with a significance level of $\alpha = 0.05$. [c] Sample concentration = 30 $\mu g\ l^{-1}$. [d] Sample concentration = 5 $\mu g\ l^{-1}$. [e] ng l^{-1}. [f] Sample concentration = 500 ng l^{-1}.

TABLE 2

Standard addition method for determination of Ti(IV)

Ti(IV) added (μg l^{-1})	Regression equation ($a_1x + a_0$)	Medium (40%, v/v)	Ti(IV) found (μg l^{-1})	S_c [a]	Correlation coefficient
2	$5.8959x + 12.68$	Ethanol	2.15	0.20	0.9979
2	$10.1450x + 17.88$	Acetone	1.76	0.62	0.9980
100 [b]	$0.0188x + 1.98$	Ethanol	105.6 [b]	3.6	0.9983
100 [b]	$0.0290x + 2.71$	Acetone	93.6 [b]	34.9	0.9944

[a] Given by the square root of the variance: $S_c^2 = (-1/a_1)^2 S^2(a_0) + (a_0/a_1^2)^2 S^2(a_1) - 2(1/a_1)(a_0/a_1^2) S^2(a_0 a_1)$ where S = standard deviation, a_1 = correlation coefficient, and a_0 = constant. [b] Concentration in ng l^{-1}.

tion of the two slit widths (5/5, 10/10 and 2.5/20 nm, for excitation/emission) and integration time (8.4, 8.4 and 16.8 s) for regression lines up to 50, 10 and 2 μg l^{-1}, respectively. From the precision of the methods used, it can be concluded that the water–ethanol mixture is more suitable than the water–acetone mixture (Table 1).

In order to increase the accuracy and precision of the APPH fluorimetric method, the standard additions method was also applied in both water–ethanol and water–acetone (3 + 2, v/v) media. With the aim of studying the accuracy of the method, four titanium-containing solutions were made, containing 50 and 2.5 μg of Ti(IV) in 1000 ml of distilled water. The standard additions method was applied to 1-ml aliquots of samples as described under *Procedures* using the first and second set of additions. The results obtained are given in Table 2, and show that the method in water–ethanol medium is more accurate and precise than in water–acetone medium. Final Ti(IV) concentrations down to 100 ng l^{-1} can be determined with relatively good accuracy and precision.

Selectivity of the method

The effect of 70 ions on the proposed method was evaluated. The tolerance limit was the concentration of a species which gives a relative error lower than 4% in the concentration of Ti(IV) found (50 μg l^{-1}). Cations were added as chlorides, nitrates or acetates and anions as sodium or potassium salts; the maximum concentration of foreign ions investigated was 50 mg l^{-1}.

As can be seen from Table 3, most anionic species are tolerated at relatively high concentrations, as 77% of the anions have tolerance limits higher than 2000 μg l^{-1}. Citrate, oxalate, vanadate, chromate, dichromate and permanganate cause the highest interferences. Mostly the cations are tolerated at concentrations higher than titanium. The more problematic species, copper,

TABLE 3

Tolerance limits in the determination of 50 μg l^{-1} of Ti(IV)

Amount added (μg l^{-1})	Species tolerated [a]
50000	CH_3COO^-, AsO_4^{3-}, Bz^-, borax, BO_3^-, CO_3^{2-}, CN^-, ClO_4^-, Cl^-, $Fe(CN)_6^{3-}$, HPO_4^{2-}, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SCN^-, IO_3^-, IO_4^-, I^-, Be(II), Bi(III), Ca(II), K(I), Li(I), Na(I), Rb(I), Sn(II), Sb(III), Tl(I), DMG
40000	Nd, Mg
25000	$S_2O_8^{2-}$, SeO_4^{2-}
20000	Ba
13000	La(III)
7000	Br^-, MoO_4^{2-}
5000	Mn(II), AsO_3^{3-}, TEA
3000	Ce(IV)
2500	Ho(III), U(VI), NO_2^-
2000	Pb, $Fe(CN)_6^{4-}$, Er(III)
1000	AA
725	Zr, Yb
525	Co, TGA, phen
425	F^-
375	Cd
350	Au(III)
275	Al
175	WO_4^{2-}
100	Hg(II)

[a] DMG = dimethylglyoxime; TGA = thioglycolic acid; phen = *o*-phenanthroline; TEA = thriethanolamine; AA = ascorbic acid.

iron(II and III), nickel, zinc and palladium interfere at the same concentration as titanium.

In order to reduce and/or eliminate the interferences, different masking reactions were tested. The masking agents thioglycolic acid (TGA), ascorbic acid (AA) and *o*-phenanthroline (phen) at concentrations higher than those given in Table 3, produce in general a slight decrease in the relative fluorescence of the Ti–APPH system. However, when the standards and the samples are matched for the masking ion concentration, titanium can be determined without large errors (< 4%). The results obtained from masking are summarized in table 4. In this way, zinc, copper, iron(II and III), nickel, vanadium(V), oxalate, dichromate and citrate can be tolerated at concentrations several times that of titanium (3-, 4-, 4-, 10-, 1.5-, 10-, 100-, 10- and 10-fold, respectively). Other ions, such as gold, cadmium, mercury and tungstate, also increase their tolerance limits (5.7-, 2.7-, 5- and 2.9-fold, respectively).

TABLE 4

Tolerance limits of interferences in the fluorimetric determination of 50 μg l^{-1} of Ti(IV) by addition of masking agents

Interfering species [a]	Tolerance level (μg l^{-1})
$C_2O_4^{2-}$ (Ca, 50)	5000
Au(III) (CN^-, 50)	2000
Cd(II) (TGA, 5 or 50); Cd(S^{2-}, 5)	1000
$Cr_2O_7^{2-}$, V(V) (AA, 50); citrate (Ca, 5); WO_4^{2-} (Ca, 25) Fe(III) (SCN^-, 50); Hg(II) (S^{2-} or TGA, 5)	500
$C_2O_4^{2-}$ (Ca, 5); Fe(III) (phen, 5)	250
Cu(II) (I^-, 50); Fe(II) (S^{2-}, 50); Hg(II) (TEA, 5)	200
Au(III) (CN^-, 5); Cu(II) (TGA or SCN^-, 5); WO_4^{2-} (Ca, 5) Zn(II) (SCN^- 5)	150
V(V) (TEA, 1); Zn(II) (S^{2-}, 5)	100
Fe(III) (SCN^-, 5); Fe(II) (S^{2-}, 5); Ni(II) (DMG, 5)	75
Ni(II) (S^{2-} or SCN^-, 5)	50

[a] Masking agents, and their concentrations in mg l^{-1} are given in parentheses.

Application to soil extracts

The proposed method has been applied satisfactorily to the determination of Ti(IV) in acetate extracts of agricultural soils using the technique under *Procedures* (Table 5). For comparison, titanium was also determined in all samples by the ICP method (second order, 334.95 nm). As shown in Table 5, both methods gave similar results. Thus, at a significance level $\alpha = 0.05$, the comparison of the null hypothesis ($H_0 : \mu_1 = \mu_2$) that both means are equal against the alternative hypothesis ($H_A : \mu_1 \neq \mu_2$) shows that the experimental value of t is smaller than $T = 0.5394 \leqslant t_{22,0.025} = 2.074$. Therefore, the alternative hy-

TABLE 5

Comparison between ICP and molecular spectrofluorimetric methods for the Ti(IV) determination in soil extracts

Sample No.	Wet weight (g)	Dry weight (g)	APPH–Ti method		ICP method [a]	
			Extract (μg l^{-1})	Dry sample (μg g^{-1})	Extract (μg g^{-1})	Dry sample (μg g^{-1})
1	10.1713	9.1440	15.3	0.17	12.2	0.13
2	10.0329	9.4280	5.3	0.06	7.5	0.08
3	10.4073	9.9301	5.5	0.06	7.5	0.06
4	10.4883	9.5903	5.5	0.06	8.8	0.10
5	10.2661	9.3153	13.6	0.15	12.1	0.13
6	10.0350	8.4322	7.7	0.10	8.3	0.10
7	10.1402	9.2364	9.0	0.10	12.1	0.13
8	10.2080	9.5387	10.4	0.11	10.7	0.11
9	10.1460	9.2974	9.1	0.10	8.7	0.10
10	10.1468	9.0826	6.7	0.07	8.9	0.10
11	10.1107	8.7768	9.6	0.11	10.4	0.12
12	10.1484	9.1488	3.3	0.04	2.2	0.02

[a] Detection limit for titanium determination was 1.5 μg l^{-1}.

pothesis is rejected. The fluorimetric method is recommended for the determination of exchangeable titanium in soils when the concentrations titanium in the extract are below 5 μg l^{-1}.

This work was supported by the Comisión de Investigación de Ciencia y Tecnología del MEC (CICYT): PB86/0224, Spain.

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