# Extractive Spectrophotometric Determination of Niobium (V) Using 3-Hydroxy-2-(4'-Methoxyphenyl)-4-Oxo-4*H*-l-Benzopyran as a Complexing Agent

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Abstract: 3-Hydroxy-2-(4'-methoxyphenyl)-4-oxo-4*H*-l-benzopyran (HMPB) forms a yellow colored (1:3) complex with niobium (V), which is extracted into dichloromethane from 1.04–4.40 $molL^{-1}$ $HClO_4$ solution showing an absorption maximum at 398 – 412 nm (figure curve A: 1.0 µg Nb ml^{-1} versus blank; curve B: blank versus DCM) with Beer's law range of 0–1.3 µg Nb ml^{-1}, molar absorptivity of 3.764×10^4 L mol^{-1} cm^{-1} and the detection limit as 0.036 µg ml^{-1}. The results are highly reproducible with a standard deviation of ± 0.0037. The linear regression equation is Y=0.399X + 0.006 and the correlation coefficient, r = 1.0004
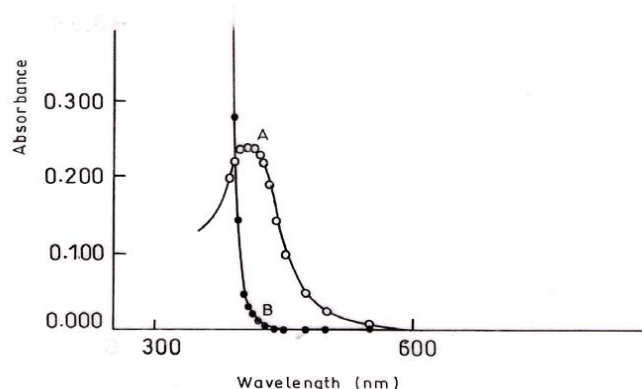
The method is free from the interference of a large number of analytically important elements. The proposed method handles satisfactorily the analysis of several samples of varying complexity.

Keywords: Niobium(V), 3-hydroxy-2-(4'-methoxyphenyl)-4-oxo-4H-1-benzopyran, extraction, spectrophotometric determination.

INTRODUCTION

An extractive spectrophotometric method is developed for the trace determination of niobium in acidic medium. A yellow (1:3) complex of niobium(V) is formed with 3-hydroxy-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran(HMPB) in perchloric acid medium. The colored species is quantitatively extractable into dichloromethane from 1.04 – 4.40 mol L^{-1} $HClO_4$ showing an absorption maximum in the region 398 – 412 nm. Beer's law holds over the niobium concentration range of 0-1.3 µg Nb ml^{-1}, with a molar absorptivity and Sandell's sensitivity of 3.764×10^4 L mol^{-1} cm^{-1} and 0.0025 µg Nb cm^{-2}, respectively at 405 nm. The linear regression equation of the method is Y=0.399X + 0.006 and the correlation coefficient, r = 1.0004. The method is highly reproducible with a standard deviation of ± 0.0037 and the detection limit 0.036 µg ml^{-1}. Out of a number of

cations, anions and complexing agents studied, only Sn(II) and fluoride interfere even in traces in the method. The method is simple, fast, sensitive, selective and handles satisfactorily the analysis of several samples of varying complexity.

Various existing methods [1-14] of spectrophotometric determination of niobium(V) suffer from interferences from a large number of foreign ions like Ti, V, Mo, W, Pt, Re, U and Ta. The methods are usually time consuming [1,3-5], though sensitivity is slightly improved in a few cases. The highly sensitive and reliable methods for quick determination of niobium such as atomic absorption and atomic emission are not found suitable in routine analysis because of their high cost and the requirement of a separate lamp source for each element to be determined. The literature survey on the methods of extraction and spectrophotometric determination of niobium reported in the past, employing benzopyrans as complexants [3-5,11,14], reveal that there is still a lot more to be done regarding rapidity, selectivity and sensitivity to find their usefulness concerning the analytical chemistry of niobium. With this

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end in view, 3-hydroxy-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran(HMPB) has been used for the first time in a spectrophotometric determination system involving niobium in microgram amounts.

EXPERIMENTAL

Apparatus and reagents: UV-visible (Shimadzu-140-02) spectrophotometer with 10 mm matched glass cells is used for absorbance measurements and spectral studies.

A stock solution of niobium (1 mg ml^{-1}) is prepared by fusing accurately weighed amount (0.1430 g) of niobium pentaoxide, Nb_2O_5, with potassium hydrogen sulphate (3g) in a silica crucible. The melt is then dissolved in hot 5% tartaric acid solution, cooled and made up to the mark with the acid solution in a (100 ml) volumetric flask. The solution thus obtained is standardised gravimetrically with cupferron [15]. Working solutions at μg ml^{-1} level are prepared fresh by suitable dilution of the stock solution with 2% tartaric acid solution. Similarly, a standard solution of tantalum (V) (1 mg ml^{-1}) is prepared by fusing 0.1221 g of Ta_2O_5 with $KHSO_4$. Lower concentrations of the metal ion are prepared exactly as for niobium above. The solutions of other metal ions are prepared by dissolving their commonly available chemically pure salts in water or dilute hydrochloric or sulfuric acid to give ≤ 10 mg ml^{-1} concentration of the ions.

3-Hydroxy-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (HMPB; mp 234°C) is prepared by the literature method [16] and dissolved in acetone to give 0.1 % (w/v) solution. Dichloromethane (RANKEM) is used as such.

Preparation of HMPB: Solutions of 2-hydroxyacetophenone(0.01 mol in 30 ml ethanol) and KOH(0.03 mol in 10 ml of ethanol) are mixed and stirred (2 h, below 60°C) after adding 4-methoxybenzaldehyde (1.21ml = 0.01mol) dropwise. The mass I thus obtained is neutralized with 0.2 mol L^{-1} HCl and crystallized from water and ethanol. Solutions of compound I(1 g in 20 ml ethanol), NaOH (8 ml of 20% in ethanol) and H_2O_2 (4 ml of 70 volume) are mixed, stirred(2 h, below 10°C) and neutralized with CH_3COOH. The yellow compound so obtained after crystallization from ethanol and water is HMPB (m.p. 234°C)
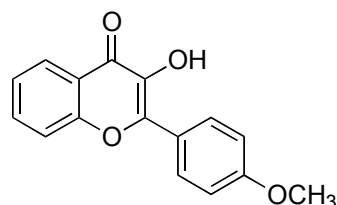
HMPB

Perchloric acid (Qualigens, "Excelar") 8 mol L^{-1} is prepared by diluting 70% (11.6 mol L^{-1}) acid with deionized water.

Samples: Synthetic samples are prepared by mixing niobium (V) solution with solutions of other metal ions in suitable proportions, as shown in Table **1**.

Reverberatory flue dust: Flue dust sample (0.1 g niobium free) from the copper manufacture unit is mixed with a solution of known niobium content (1 mg) in a silica crucible. It is dried in an oven at 1l0-120°C, fused with

sodium peroxide (0.8 g), dissolved in 25-30 ml of hot 2% tartaric acid solution and the final volume made to 250 ml in a volumetric flask with the same tartaric acid solution. Appropriate aliquots of the resulting solution are taken for the determination of niobium by the proposed method.

Water samples: Water samples (10 ml each) from tap and well are mixed separately with a known concentration of niobium, 6% H_2O_2 (1 ml) and aqueous ammonia (2 ml). The solution is boiled and evaporated to dryness. The residue is dissolved in 1-2 mol L^{-1} $HClO_4$ and niobium determined by the proposed method.

Procedure: To an aliquot of the sample solution containing up to 13 μg Nb (V) and other ions taken in a 100 ml separating funnel, 1.5 ml of 8 mol L^{-1} $HClO_4$ and 2.0 ml of 0.1 % HMPB solution are added. The whole mixture is diluted to 10 ml with deionised water to bring the final acidity of the aqueous phase to 1.20 mol L^{-1}. The contents are mixed gently and then equilibrated once with an equal volume(10 ml) of dichloromethane for 30 s taking care to release the pressure occasionally through the stop cock. After phase separation the organic extract is passed through Whatman No. 41 filter paper (pretreated with dichloromethane) to remove water droplets. The absorbance of the yellow extract is measured at 405 nm against the similarly treated reagent blank using 10 mm glass cells.

In case of samples containing Mo(VI), W(VI) and Ti(IV), the optimum amounts of masking agents required to be added to the aqueous solution prior to the addition of reagent (HMPB) are: 0.3 ml of H_2O_2 (6% w/v); for each of W(VI) up to 0.03 mg, Ti(IV) up to 0.1 mg and Mo(VI) up to 0.01 mg in a final 10 ml aqueous volume.

Finally, niobium content in various samples is computed from the calibration curve prepared under optimum conditions of the procedure.

RESULTS AND DISCUSSION

A yellow complex of niobium(V) is formed with HMPB in perchloric acid medium and the complex is quantitatively extractable into dichloromethane. The absorption spectrum of the complex indicates that the maximum lies in the range 398-412 nm where the reagent blank has minimal absorbance (Fig. **1**). The absorbance of the complex in the solvent is influenced by the nature and concentration of acids. The effect of different acids on the Nb(V) complex is studied at 0.2 mol L^{-1} acidity and it is found that the absorbance of the complex decreases in the order $HClO_4$ > HCl > CH_3COOH > H_2SO_4 > H_3PO_4. Therefore, $HClO_4$ medium has been preferred for further studies. It is found that maximum and constant absorbance is obtained when 1.04 – 4.40 mol L^{-1} of $HClO_4$ is used. Thus 1.20 mol L^{-1} of perchloric acid is selected for further work.

The optimum values of other parameters found for achieving maximum and constant absorbance are: 1.9-2.4 ml of HMPB (0.1% w/v in acetone) and 10-300 s equilibration time for ≤ 13 μg Nb per 10 ml aqueous solution (Table **2**).

A number of water immiscible organic solvents extract the niobium(V) complex in the decreasing order of absorbance as : dichloromethane > 1,2-dichloroethane > chloroform > amyl acetate > amyl alcohol > benzene >

Table 1.   Analysis of Samples by the Proposed Method

S. No.	Sample Composition		Nb Found[b]	
	Matrix[a]	Nb Added/μg	μg ± μg (SD)	PAR[l] Method
1.	Mn(2), Co(2), Cu(0.l), Zn(2)	10	10.07 ± 0.07	9.88
2.	Os(0.5), Ba(1), Au(0.1)	5	5.11 ± 0.14	5.19
3.	Th(1), Bi(1), V(0.05)	7	6.84 ± 0.19	6.91
4.	Cr^{VI}(0.l), Ce(1), U(1)	8	8.07 ± 0.14	8.27
5.	Pt(0.0l), Pd(0.0l), Al(l)	10	9.83 ± 0.08	10.12
6.	W(0.0l), Ti(0.0l), Se(0.5)[c]	5	5.19 ± 0.13	4.94
7.	Ta(0.1), Ir(0.0l), As(1)	12	12.27 ± 0.14	12.22
8.	Mo(0.0l), Mg(1), Cd(1)[c]	10	10.05 ± 0.14	9.88
9.	Cr^{III}(0.5), Ni(2), Sr(2)	5	4.99 ± 0.07	5.06
10.	Reverberatory flue dust(100)	10	9.93 ± 0.07	9.75
		5	5.06 ± 0.13	5.06
11.	Tap Water	10	10.00 ± 0.12	10.00
		8	7.95 ± 0.08	8.15
12.	Well Water	12	12.05 ± 0.06	12.10
		5	5.06 ± 0.13	4.94

[a]Figure in brackets indicates the amount of the metal ions in mg.
[b]Average of triplicate analyses.
[c]In presence of 0.3 ml H_2O_2 6% (w/v).

carbon tetrachloride > toluene. As dichloromethane gives maximum absorbance with a rapid and clear phase separation, it is chosen as the most suitable extractant. The coloured complex of Nb(V) with HMPB formed under optimum conditions is stable for more than 1h in dichloromethane at 405 nm.
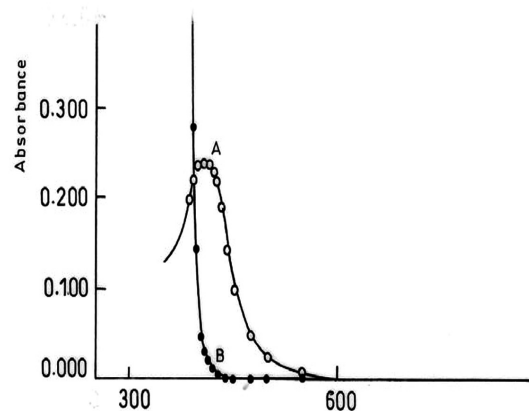

Fig. (1). Absorption Spectrum of Nb (V) - HMPB complex in dichloromethane. **A**: 1.0 μg Nb cm^{-3} measured against reagent blank, **B**: reagent blank against dichloromethane.

The method obeys Beer's law over the concentration range of 0.0 -1.3 μg ml^{-1} Nb(V). However, the optimum concentration range of niobium (V) that can be measured accurately, as evaluated from Ringbom plot [17] (Fig. **2**) is found to be 0.32 – 1.30 ppm. The molar absorptivity and Sandell's sensitivity of the complex at 405 nm are 3.764 × 10^4 L mol^{-1} cm^{-1} and 0.0025 μg Nb cm^{-2}, respectively. The detection limit of the method is 0.036 μg ml^{-1}. Ten replicate

determinations containing 1 μg Nb ml^{-1} give a standard deviation of ± 0.0037 absorbance unit. The linear regression equation is Y = 0.399X + 0.006 (Y = absorbance, X = μg Nb ml^{-1}) and the correlation coefficient, r = 1.0004

Stoichiometry of the Complex: Equimolar solutions of niobium and HMPB (2.152×10^{-3} mol L^{-1}) are utilized to determine the metal to ligand ratio by Job's method of continuous variations [18]. The absorbance values are measured at two different wavelengths, 405 and 425 nm. The obtained curves are indicative of 1:3 stoichiometry in the extracted species (Fig. **3**). This is further confirmed by the mole-ratio method [19] by taking the concentration of niobium as 2.152×10^{-3} mol L^{-1} and measuring the absorbance at two different wavelengths of 405 and 425 nm (Fig. **4**).

From the consideration of the data obtained from the above mentioned parameters, optimum conditions for the system are laid down as already described in the procedure.

Effect of Diverse Ions: Under the optimum conditions of the procedure in 10 ml aqueous volume (mg amounts in parentheses), chloride, phosphate, thiourea, EDTA 'disodium salt', sulfosalicylic acid, thiocyanate, bicarbonate, hydrazine sulfate and boric acid (100 each); bromide, ascorbic acid and dithionite (80 each); sulfate, nitrate, sulfite, acetate and iodide (50 each); tartrate and citrate (30 each); oxalate (3); glycerol (1 ml) and H_2O_2 6% (w/v) (0.3 ml) do not affect the absorbance of Nb (V)-HMPB complex. However, fluoride interferes even in small amounts.

Among the cations, Pb (II), Ca (II), Ba (II), Sr (II), Cd (II), Th (IV), Hg (II), Mn (II), Ag (I) and Mg (II) (10 mg each); Zn (II), Ni (II) and Co (II) (9 mg each); As (III), Bi

Table 2.   Effect of Various Parameters on the Absorbance of Nb-HMPB Complex

$HClO_4$(mol L^{-1})[a]	0.40	0.56	0.80	0.96	1.04–4.40	
Absorbance	0.190	0.215	0.240	0.260	0.280	
0.1% HMPB(ml)[b]	0.5	1.0	1.5	1.7	1.9–2.4	2.5
Absorbance	0.200	0.280	0.365	0.380	0.405	0.385
Equilibration time (s)[c]	0	5	10–300			
Absorbance	0.050	0.290	0.405			

Conditions: [a] Nb(V) : 10 µg, HClO$_4$= variable, 0.1% HMPB = 1 ml, equilibration time = 30 s, solvent = dichloromethane, aqueous volume = solvent volume = 10 ml, [b]HClO$_4$=1.20 mol L^{-1}; other conditions being the same as in (a) except for the variation in HMPB concentration, also b = 3-hydroxy-2-(4'-methoxyphenyl)-4-oxo-4*H*-1-benzopyran(HMPB). [c] 0.1% HMPB in acetone =2.0 ml, other conditions being the same as in (b) except for the variation in equilibration time.

(III), Ce (IV) and Al (III) (5 mg each); U (VI) (4 mg); Be (II), Cr (III), Os (VIII), Cu (II) and Se (IV) (1 mg each); Cr (VI) (0.5 mg); Ta (V) (0.3 mg); V (V), Zr (IV), Au (III), Pt (IV), Fe (III) and Ir (III) (0.1 mg each); Pd (II) and Ru (III) (0.05 mg each) cause < 1 % error. Mo (VI), W (VI) and Ti (IV) do not interfere in presence of the masking agents as described under the modified procedure. However, Sn (II) even in traces gives dark yellow color showing high absorbance values and hence interferes seriously.
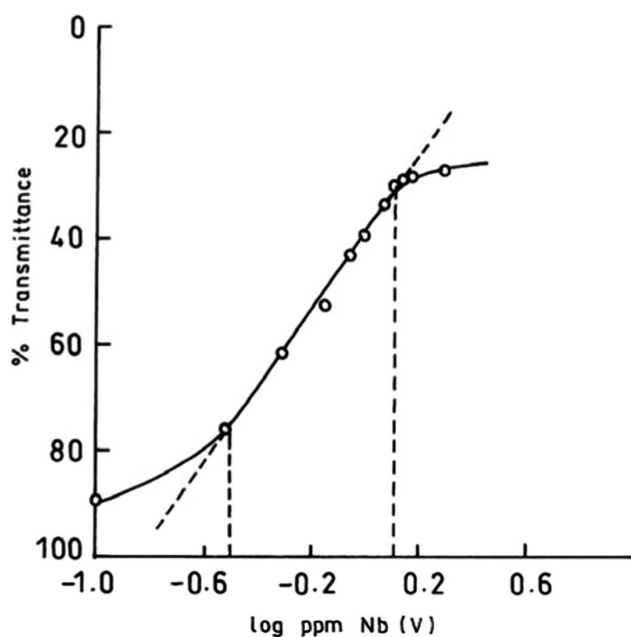
Fig. (2). Ringbom plot for Nb (V) – HMPB complex.

Applications: The wide applicability of the method is tested by the satisfactory analysis of a variety of synthetic and technical samples containing niobium up to 13 µg in the aliquot (Table **1**). The proposed method is quite selective for niobium determination in the presence of large number of elements especially Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Ta, Zr, Ce, Th, U, Bi, Cd, As, alkaline earth and platinum metals, which seriously interfere in most of the existing methods of niobium determination. The proposed method compares favourably with the existing ones (Table **3**) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.
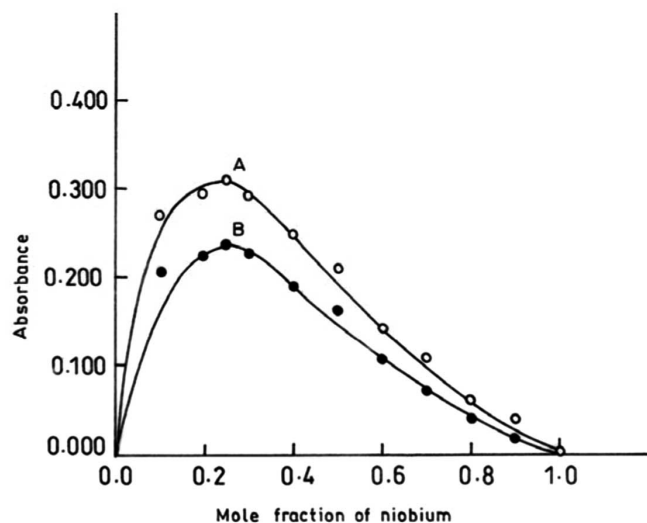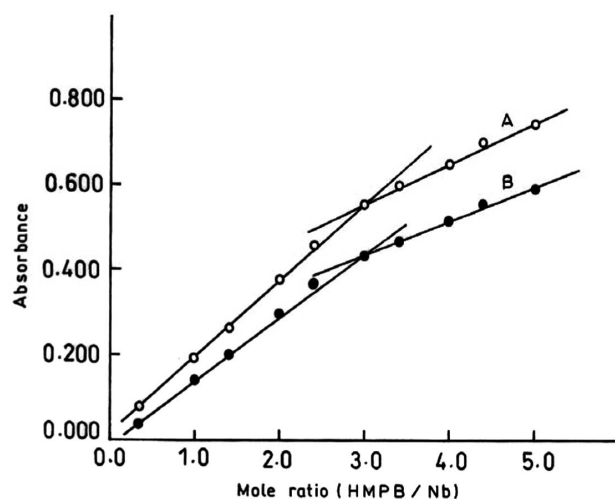

Fig. (3). Job's method of continuous variations. Total concentration [Nb]+[HMPB]= 2.15 x 10-3 mol dm^{-3}. Curve A: 405nm, Curve B: 425nm, HClO$_4$ = 1.2 mol dm$^-$.

Fig. (4). Mole ratio method. Total concentration of metal ion fixed, [Nb] = 2.15 x 10-3 mol dm^{-3}. Curve **A**: 405nm, Curve B: 425nm. HClO$_4$ = 1.2 mol dm^{-3}.

Table 3. **Comparison of the Proposed Method of Niobium Determination with Existing Ones**

Sr. No.	Aqueous Conditions	Solvent, λ_{max} (nm), B.L. Range ($\mu g\ ml^{-1}$)	Sandell's Sensitivity ($\mu g\ cm^{-2}$), Molar Absorptivity (L mol^{-1} cm^{-1}) Precision/Standard Deviation	Interfering Metal Ions	References
1.	Nb(V), 3 mol L^{-1} HCl, 5% $SnCl_2$, 12% KSCN, color development time 5 min	Diethylether, 385, –	0.0026, 3.5 x 10^4, -----------	Mo(VI), W(VI), V(V)	[1]
2.	Nb(V), 4 mol L^{-1} $HClO_4$, 3-hydroxyflavone, color development time 3 min.	Chloroform, 395, 0.0 – 3.2	0.002, 4.09 x 10^4, ± 0.0034	Mo(VI), W(VI), V(V), Ti(IV)	[3]
3.	Nb(V), 4 mol L^{-1} $HClO_4$, 3-hydroxy-2-(2-thienyl)-4*H*-chromen-4-one, color development time 2 min.	Dichloromethane, 420, 0.0 – 1.9	0.0018, 5.047 x 10^4, ± 0.0026	Mo(VI)>0.5 $\mu g\ ml^{-1}$, W(VI)>1.5 $\mu g\ ml^{-1}$	[4]
4.	Nb(V), 4 mol L^{-1} $HClO_4$, 3-hydroxy-2-(4-methoxyphenyl)-6-methyl-4*H*-chromen-4-one, color development time 2 min.	Chloroform, 412, 0.0 – 1.7	0.0019, 4.79 x 10^4, ± 0.004	Mo(VI)>0.4 $\mu g\ ml^{-1}$, W(VI)>2.0 $\mu g\ ml^{-1}$	[5]
5.	Nb(V), pH 1.0-4.0, tartaric acid, 2-(3, 5-dibromo-2-pyridylazo)-5-diethylaminophenol (PADAP)	–, 630, 0.0 – 1.6	0.0035, 2.6 x 10^4, –	–	[7]
6.	Nb(V), 4 mol L^{-1} $HClO_4$, 0.4% 6-chloro-2-(2'-furyl)-3-hydroxy-4-oxo-4*H*-1-benzopyran	Chloroform, 410, 0.0 – 1.2	0.0033, 2.79 x 10^4, ± 0.001	–	[11]
7.	Nb(V), pH 3-7, 7-(4-methylphenylazo)-8-hydroxyquinoline-5-sulfonic acid, H_2O_2	–, 395, –	–	Mo(VI), U(IV), Ti(IV), Ta(V)	[12]
8.	Nb(V), pH 3, 3-hydroxy-2-methyl-1-phenyl-4-pyridone, xylenol orange	Chloroform, Solution of Tetraphenyl-phosphonium chloride, 565, –	0.0025, 3.72 x 10^4, –	–	[13]
9.	Nb(V), 3.20 mol L^{-1} $HClO_4$, 0.1% 3-hydroxy-2-[1'-phenyl-3'-(p-chlorophenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran	Chloroform, 415, 0.0 – 1.2	0.0033, 2.79 x 10^4, ± 0.0015	–	[14]
10.	Nb(V), 1.2 mol L^{-1} $HClO_4$, 2.0 ml of 0.1% 3-hydroxy-2-[4-methoxyphenyl]-4-oxo-4*H*-1-benzopyran	Dichloromethane, 405, 0.0 – 1.3	0.0025, 3.764 x 10^4, ± 0.0037	Sn(11)	Proposed method

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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