



Spectrophotometric determination of vanadium (V) using an organic reagent [4-(6-nitro-2-benzothiazolylazo)pyrogallol]

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Abstract

A new chromogenic reagent [4-(6-Nitro-2-benzothiazolylazo)pyrogallol] (6-NO₂BTAPY), was synthesized by diazo coupling of (2-amino-6-nitro benzothiazol) (2-ANO₂BT) with pyrogallol, and used for the spectrophotometric determination of vanadium (V). This method was simple, sensitive, selective and rapid for reaction between V⁵⁺ and (6-NO₂BTAPY), to form a pink complex having a molar ratio of (1:2) (V-6-NO₂BTAPY) at pH 6.0. The molar absorptivity of the complex was $0.2279 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at λ_{max} 490 nm. Beer's law is obeyed in the range of (0.1–10) ppm of vanadium, and the stability constant was found to be $3.4 \times 10^8 \text{ L}^2 \cdot \text{mol}^{-2}$. The relative standard deviation for seventh replicate measurements, recovery, and relative error values of this method were found to be 2.5712%, 10.3%, and 3% respectively. The interference of foreign ions was also investigated. All the other ions studied did not interfere with vanadium determination except for Cr³⁺, Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, and Pb²⁺. The interferences were eliminated approximately using suitable masking agent.

Keywords: Vanadium (V), AzoPyrogallol, benzothiazol, Spectrometry.

Introduction

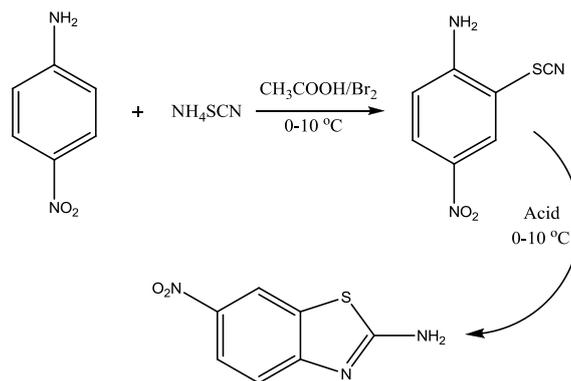
Vanadium is an element with an atomic weight of 50.94 g.mol^{-1} and the atomic number is 23. It has a density of 6.11 g.cm^3 , with a melting point of $1890 \text{ }^\circ\text{C}$ and boiling point of $3380 \text{ }^\circ\text{C}$. Metallic vanadium is a shiny, silvery metal with a metallic body-centered cubic structure and it has a few naturally occurring isotopes, i.e. ^{50}V (0.25%) and ^{51}V (99.75%), respectively. Pure vanadium is comparatively soft and ductile, but impurities have a hardening and embrittling effect [1]. different oxidation states, these being (+2 +3+4and+5). The most common commercial form of V(V) is vanadium pentoxide (V_2O_5), in which vanadium is in +5 oxidation state [2], Vanadium affects the numerous physiological processes and biochemical reactions, vanadium remains a relatively unknown trace element which still being targeted in various clinical application worldwide [3;4]. the toxicity of vanadium depends on its physiochemical state particularly on its valance state and solubility[5].vanadium can undergo changes in oxidation state (V) and (IV) forms and it can also bind with blood protein, V(IV) is less toxic than V(V) in environmental systems and can be produced by various industrial redox process, it was observed that V(IV) in aqueous solutions form complexes most easily with reagents containing oxygen or sulfur donor ligand [6]. crude petroleum and heavy oil occasionally contain a certain amount of vanadium by combustion of these materials, the vanadium is released into the environment the grater part of it is a toxic compound of vanadium pentoxide or a metal form of 5 valent vanadium V(V) but a small part is in the form of 4 valent vanadium V(IV) compound both V(IV) and V(V) are stable in environment and they have different biological activity in these five decades, the toxicity of V(V) has been interested and argued continuously whereas V(IV) is not harmful but has possibility to be used for medicines [7-9]. Environmental scientists have declared vanadium as a potentially dangerous chemical pollutant that can play havoc with the productivity of plants, crops and the entire agricultural system[10]. spectrophotometry is essentially a trace-analysis technique and its one of the most powerful tools in chemical analysis, there are a great number of spectrophotometric methods based on its ability to form complexes, mainly colored, with organic and inorganic compounds[11]. Many organic reagents have attracted much attention as they are sensitive, chromogenic reagents in addition to being interesting complexing agents, Azo colorants are the most important class of synthetic dyes representing (60-80%) of all organic colorants used widely in substrates such as textile fibers leather, plastic, papers, hair, mineral oils, waxes, food stuffs and cosmetics[12]. Benzothiazoles are heterocyclic compounds with multiple applications. Thiazolylazo compounds have been used as a reagents for spectrophotometric determination of metal ions. Many benzothiazolylazo compounds have been synthesized and proposed as a highly sensitive chromogenic reagents for the determination of several metal ions and give colored chelating complexes especially with some transition metal ions[13]. Several techniques such as X-ray fluorescence[14]. atomic fluorescence spectrometry[15]. polarography[16]. high performance liquid chromatography[17]. electro thermal[18] and derivative spectrophotometry[19] have been applied for simultaneous determination of these ions in different samples. The analytical methods are those based on UV-visible spectrophotometry techniques due to both experimental rapidity and simplification. The determination of trace amount of vanadium is important in metallurgy and environmental analytical chemistry and there is a growing need for procedures with high sensitivity and selectivity because they have important role in biological, industrial and medical science [20]. In this work, a new heterocyclic azo dye reagent (6- NO_2 BTAPY) has been synthesized, and used for the spectrophotometric determination of vanadium(V), this method is simple, sensitive, selective, and rapid.

Materials and Methods

(FTIR) Spectra ($4000\text{-}400\text{cm}^{-1}$) in KBr disk were recorded on a SHIMADZU FTIR – 8400 S Fourier Transform Infrared Spectrophotometer. (Japan), elemental analyses were carried out on a EURO EA3000 single elemental analyzer (Europe), absorption spectra were measured on a T80 UV-Vis spectrophotometer and absorbance were measured on Apel PD-303 UV-visible spectrophotometer using 1cm quartz cells, atomic content were measured on a SHIMADZU AA-6300 Atomic absorption spectrophotometer, A model WTW multi 740 pH-meter were used to adjusted and measure the pH of the solution, melting point were measured using SMP30 Stuart, UK. All chemicals were used of analytical grade – reagent unless otherwise stated. All solution were prepared using de-ionized water.

Synthesis of 2-Amino 6- Nitro Benzothiazol [2-ANO₂BT]

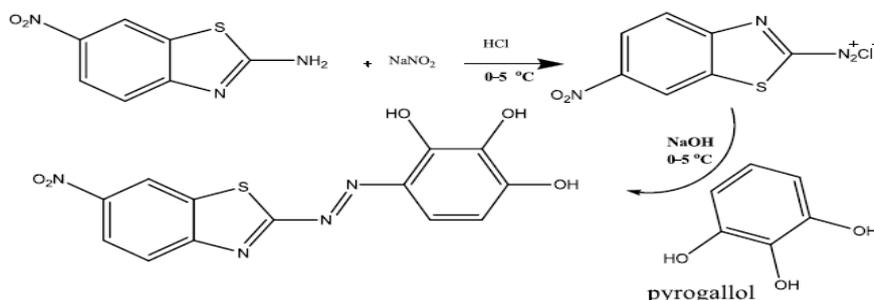
2-ANO₂BT is prepared by a typical procedure [21] direct thiocyanogenation ,it is described as follows: p-Nitro aniline(3.45 gm,0.025 mol) and ammonium thiocyanate (3.8 gm,0.05 mol) were dissolved in (70ml) glacial acetic acid, cooled in ice and stirred mechanically while a solution of bromine (4 gm) in (10ml) glacial acetic acid was slowly added drop by drop , external cooling was applied throughout the reaction to keep the temperature below 10°C and the stirring was continued for thirty minutes after all the bromine had been added ,the crude product was obtained by pouring in distilled water(D.W), an amount of cold NaOH solution was added to separate the precipitate and filtering. A purified gilt yellow solid was obtained by filtering, washing with D.W, and recrystallization with ethanol as shown in scheme 1.



Scheme1. Synthesis of 2-Amino 6- Nitro Benzothiazol [2-ANO₂BT]

Synthesis of the reagent4-(6- Nitro- 2- benzothiazolyazo) pyrogallol [6-NO₂BTAPY]

A (0.975 gm,0.005 mol) of (2-ANO₂BT) was dissolved in 5 ml of HCl (37%) and (20ml) glacial acetic acid and cooled to 0°C in ice-bath. A 5 ml of NaNO₂ solution (0.3450gm,0.005 mol) was added drop wise and stirred. A sprig orange diazo-salt solution was prepared after further stirring for 20 min at(0-5°C), separately A(0.6305 gm ,0.005 mol) of 1,2,3,- tri hydroxy benzene (pyrogallol) and (0.5 gm) of NaOH was dissolved in (50ml) of D.W and cooled to (0-5°C) , the above diazo-salt solution was added dropwise to this solution with vigorous stirring , after mechanically stirring for a further 2 hours ,the mixture was allowed to stand overnight , A red-purple solution was produced ,the crude product was obtained by pouring in D.W and filtering . A purified reddish orange solid was obtained by filtration and recrystallization with ethanol as shown in scheme 2.



Scheme 2. Synthesis of the reagent4-(6-Nitro-2-benzothiazolyazo) pyrogallol [6-NO₂BTAPY].

Standard solution of Vanadium

A solution of Vanadium(V) 100ppm was prepared by dissolving 0.1785 gm of V_2O_5 in (10ml) of distilled water containing(0.5M) of NaOH ,and acidifying by (0.5M) H_2SO_4 ,dilute the solution to volume 100 ml with water, working solutions were prepared freshly by appropriate dilution of the stock solution [22].

(6-NO₂BTAPY) solution

1.0×10^{-3} M. 6-NO₂BTAPY(0.0332gm) was dissolved with <5 ml of absolute ethanol, this was transferred into a100 ml calibrated flask and diluted up to the mark with absolute ethanol.

General procedure

Into a 10ml standard flask , transfer 1ml of sample solution containing 100ppm of Vanadium(V) and 2ml of 1.0×10^{-3} M (6-NO₂BTAPY) solution ,dilute to the mark with distilled water, adjust pH around 6 ,mix well and after 4 min measure the absorbance of solution at 490nm at (20-35)°C in a 1 cm quartz cells against a reagent blank prepared in the same condition.

Result and Discussion

Absorption Spectra

The absorption spectra of [6- NO₂BTAPY] and its vanadium complex under the optimum condition are shown in figure 1.

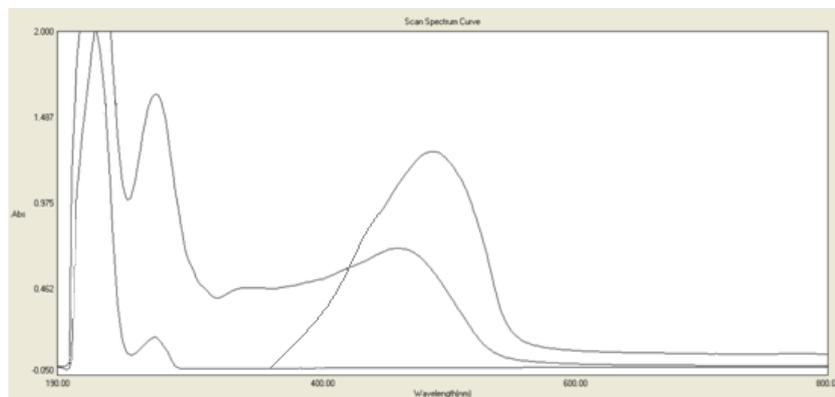


Fig.1 : Absorption spectra of A:Vanadium ion 100ppm , B: 6- NO₂BTAPY reagent 1.0×10^{-3} M , C: V-6-NO₂BTAPY complex at pH=6

The electronic spectrum of the reagent showed three characteristics bands, the two band at (230,270) nm is due to the ($\pi \rightarrow \pi^*$) transition of the phenolic ring , while the third band at (460)nm is due to the ($n \rightarrow \pi^*$) transition of the nonbonding electron pairs of the nitrogen atom . The complex of V(V) with this reagent appears the peak at 490nm, this indicate the reaction happen between V(V) and the reagent (6-NO₂BTAPY). The spectral data and physical properties of the synthesized compounds are shown in table 1, 2 respectively .

Table 1. Physical properties of the synthesized compounds.

Comp.	m.p.(°C)	Yield %	Elemental analysis C.H.N.S (calculated/ found)
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2-ANO ₂ BT	212-214	81	C,43.07/43.47 ;H,2.58/2.77; N,21.53/21.83; S,16.43/16.91
6-NO ₂ BTAPY	160-162	65	C,46.99/47.62 ;H,2.43/2.81; N,16.86/17.66; S,9.65/9.97

Table 2. The FTIR (KBr cm⁻¹) and H¹ NMR (δ= ppm)spectral data of the synthesized compounds.

Comp.	Ar-H	C=C	C=N	NO ₂	NH ₂	N=N	OH
2-ANO ₂ BT	3105	1591-1512	1637	1553-1335	3455-3282		
6-NO ₂ BTAPY	3022	1596-1505	1645	1551-1332		1422	3432
6-NO ₂ BTAPY	H ¹ .NMR	δ=4.8 (3H,-OH); δ=6.7(s,2H,ArH)Pyrogallol ring; δ=7.9(d,1H,ArH); δ=8.1(d,1H,ArH); δ=8.8(s,1H,ArH)aromatic ring.					

Effect of reagent concentration

Keeping a constant concentration (5μg.ml⁻¹) of V(V) solution ,the effect of reagent concentration (1.0 x 10⁻³ M) on absorbance of the complex was studied by varying the amount of the volume of reagent (0.5-4.0)ml ,it was obtained that the complex formation was complete and absorbance was maximum when the amount exceeds 2ml as shown in figure 2 .

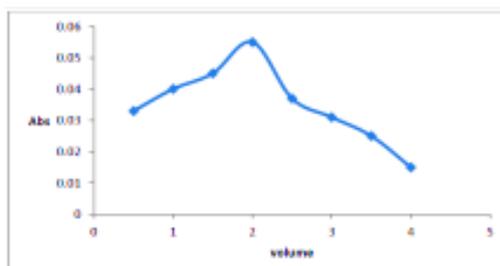


Fig.2: Effect of reagent concentration on the absorbance of vanadium complex[V⁵⁺]=5ppm

Effect of pH

The absorbance of the V-complex depends on the pH of the solution, the influence of pH was studied over the range (2-8) adjusted by means of dil. NH₄OH(0.01M) and dil. HCl(0.01M), the optimum pH was obtained at 6 of complex , figure3. shown the relationship between absorbance of complex and pH. At pH <6 a decrease in absorbance may be due to form a zoliumcation result from the reaction between hydrogen ion and the ion pair of electron on the nitrogen atom for thiazol ring ,and also when pH >6.5 a decrease in absorbance was observed due to formation of vanadium hydroxide.

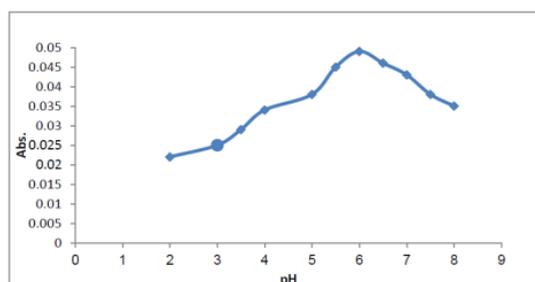


Fig.3 : Effect of pH on the absorbance of vanadium complex [V⁵⁺]=5ppm

The stability of chromogenic system for the complex at different time and different temperature

It was found that the absorbance of the complex chromogenic system reaches a maximum value within 4min and remain stable for 24 hrs. as shown in figure 4.

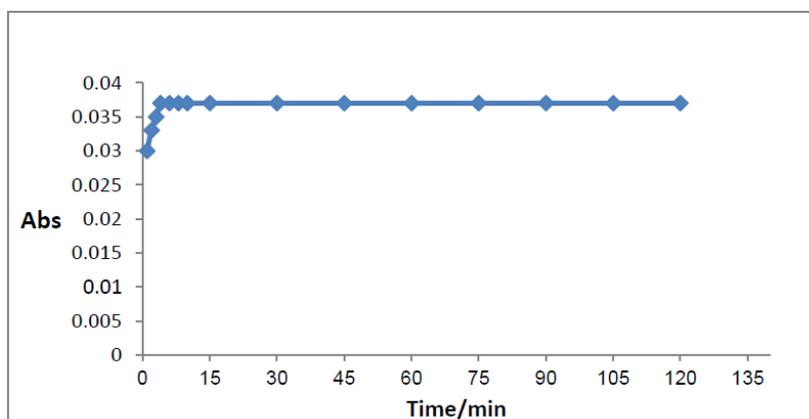


Fig.4: Effect of Time on the absorbance of vanadium complex $[V^{5+}] = 3\text{ppm}$

The effect of temperature on the absorbance of the complex was studied at the range between $(10-70)^{\circ}\text{C}$, the maximum and constant absorbance was obtained when the temperature in the range $(20-35)^{\circ}\text{C}$, and at a higher temperature of 35°C the absorbance was decrease which may be due to dissociation or vaporization of the complex as shown in figure 5.

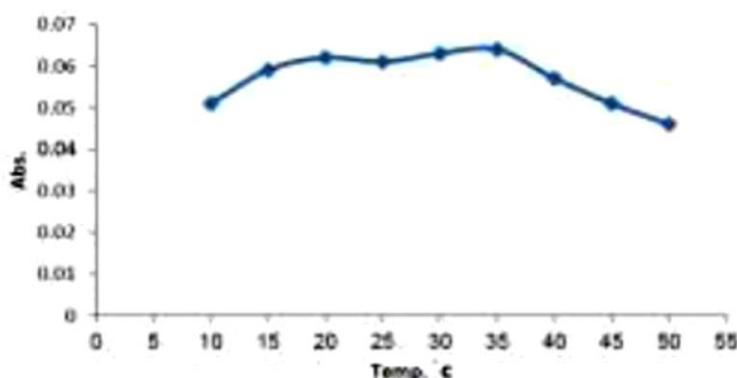


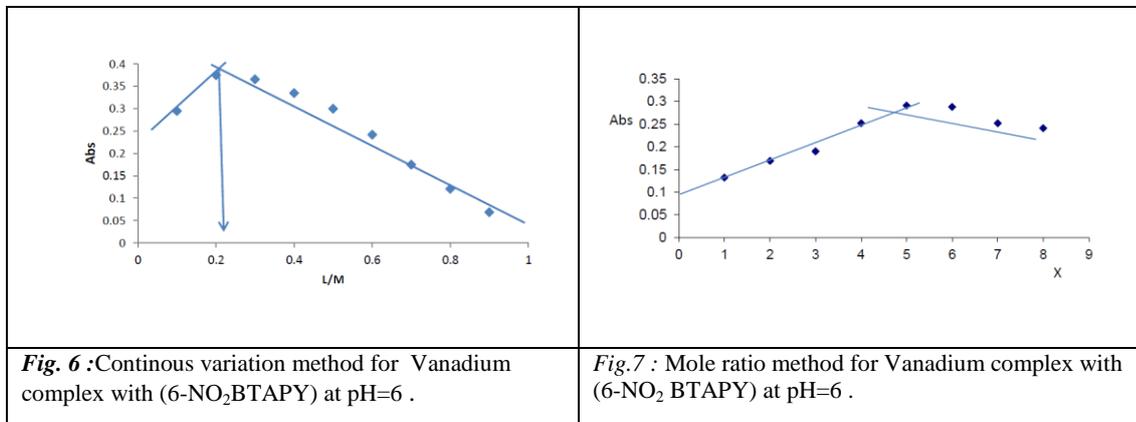
Fig 5 : Effect of Temperature on the absorbance of vanadium complex $[V^{5+}] = 6\text{ppm}$

Composition of complex and stability constant

The complex composition was determined by job's and mole-ratio methods in figure (6, 7), both methods indicated that the complex has a molar ratio of (1:2) (M:L) at pH 6 as shown in figure (8). The stability constant ($K_{\text{stab.}}$) and (α) of complex was found to be $(3.4 \times 10^8 \text{L}^2 \cdot \text{mol}^{-2})$ and (0.3608) respectively by using the following equations[23]. Where α =dissociation constant. c =total conc. of the complex which equal to 1.0×10^{-4} . n =mole ratio = 2. E_m = absorbance of a solution containing reagent two times excess than the amount of vanadium. E_s = absorbance of a solution containing a stoichiometric amounts $[\text{reagent}] = [\text{vanadium}] = 1.0 \times 10^{-4}$.

$$K_{stab.} = \frac{1}{K_{inst.}} K_{inst.} = \frac{(\alpha c).(n\alpha c)^n}{c(1-\alpha)}$$

$$\frac{E_m - E_s}{E_m} = \alpha$$



So that according to the above results we supposed structural formula of the complex as showed in figure 8.

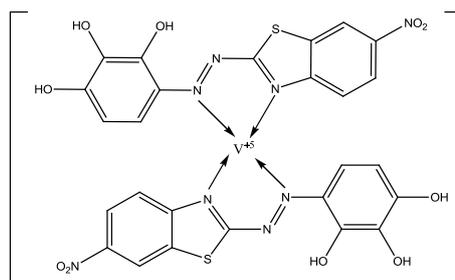


Fig.8 : the proposed composition of the complex

Analytical characteristics

The calibration curve as shown in figure(9) , it's described the experimental procedure and good correlation coefficient [24]. the some analytical parameters for this spectrophotometric determination of V(V) using this reagent are summarized in table 3 .

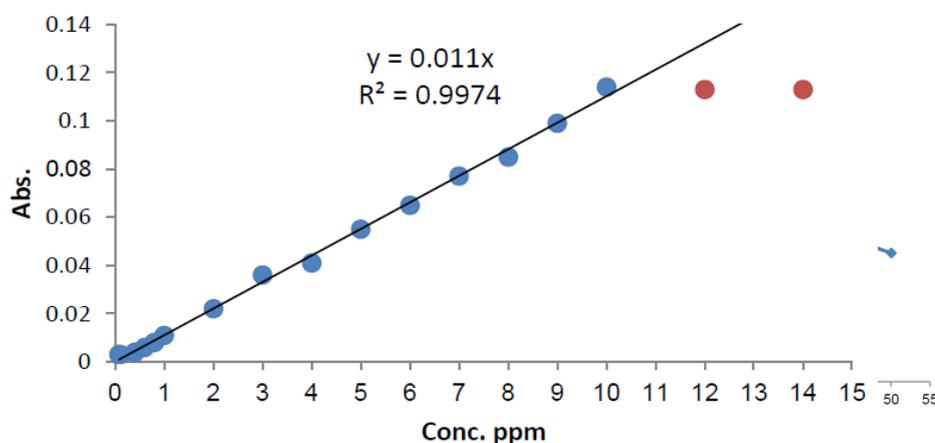


Fig.9: Calibration curve of V⁵⁺ Complex.

Table 3. Analytical characteristics of the proposed procedure (N =no . of determination)

Analytical parameter	Value
Molar absorptivity	$0.2279 \times 10^4 \text{L.mol}^{-1}.\text{cm}^{-1}$
Sandell Sensitivity	$0.0909 \mu\text{g}.\text{cm}^{-2}$
Correlation coefficient(r)	0.9974
Detection Limit(D.L)	0.3818
Linear dynamic range	(0.1 -10) ppm
Standerd deviation	0.0014
Relative .Standard .Deviation	%(N=7)2.5712
Percent Relative error	3%
Percent Recovery	103 %

These result indicating that this method is highly precise and suitable for the determination of V (V) spectrophotometrically.

Interferences

The effect of the ions (Cr^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and pb^{2+}) which form complex with the reagent during its reaction with vanadium(10ppm) were studied.on the other hand , suitable masking agent were examined for elimination the effect of the interferences of this ions[25], as shown in table (4).

Table 4. Effect of foreign ions on the determination of V (V) and suitable masking agents.

V^{5+} ppm	Foreign ion 100ppm	Error%	Masking agent ()ml,[]M	Error%
10	Cr^{3+}	-5.4	Oxalic acid (1.0)[0.02]	1.1
10	Cu^{2+}	14.5	5-Sulphosalicylic(0.75)[0. 1]	0.25
10	Co^{2+}	-12.3	Sodium acetate (1.5)[0.05]	0.1
10	Ni^{2+}	3.5	Oxalic acid (2.0) [0.2]	0.1
10	Zn^{2+}	1.7	NH_4OH at pH 5.5	0.3
10	pb^{2+}	2.5	Tartaric acid(1.0) [0.02]	0.5

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