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Titanium Determination under High-Sensitivity Conditions with 2-(5-Chloro-2-pyridylazo)-5-dimethylaminophenol. II. Ternary Compounds of Ti(IV)-H_2O_2-5-ClDMPAP

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Ti(IV) together with pyridylazo-type reagents and other molecular compounds form ternary complexes that may stand as the basis for analytical methods designed for the quantitative determination of the metal. This paper reports the results obtained by the use of the system Ti(IV)–H_2O_2–5-ClDMPAP in aqueous ethanolic solutions, and application to routine analyses of Ti(IV) in various types of samples. The spectral characteristics of the complexes formed, the pH ranges appropriate for their formation, ethanol influence, composition and stability have been studied. The complex selected for this analytical work is formed between pH 2.5 and 6.5 with a 1:2:2 Ti(IV)–H_2O_2–5-ClDMPAP molar ratio. The system fulfils Beer's law up to a Ti(IV) concentration of 0.7 ppm, working at λ_{max} 534 nm. The molar absorptivity and Sandell index are 4.59×10^4 dm^3 mol^{-1} cm^{-1} and 0.0010 μg cm^{-2} respectively.

Reactions involving ternary compounds are important in determination and separation methods, specially in absorptiometric analysis, liquid–liquid extraction and masking. Babko[1] describes four basic types of ternary compounds which form the following systems: a) Lewis' metallic ion–electronegative ligand–base; b) metallic ion–two different electronegative ligands; c) ternary heteropolyacids; d) two different metallic ions–one ligand. According to the general qualities of each of these types, our Ti(IV)–H_2O_2–2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol, system, belongs to type b). Ternary compounds belonging to this type have been extensively studied and applied to absorptiometric determinations, as well as to complexometric titrations.[1] In the latter case, one of the complexing reagents helps in the process's kinetics for it destroys the existing hydroxopolynuclear complexes, and it usually activates the forming reaction of the ternary complex.

In the spectrometric determination of titanium, Ozawa[2] adds H_2O_2 together with 4-(2-pyridylazo)resorcinol, thus forming a ternary complex Ti(IV)–H_2O_2–PAR of 1:3:3 stoichiometry, and a molar absorptivity of 5.10×10^4 dm^3 mol^{-1} cm^{-1} at pH 7.9. When no H_2O_2 is addes, the complex formed at pH 3.2—3.8, Ti(IV)–PAR (1:2) has an absorptivity rate of 2.1×10^4 dm^3 mol^{-1} cm^{-1}. Nevertheless, no method to solve severe interferences caused by Cu(II), Fe(III), Co(II), Ni(II), Sn(II), Bi(III), V(V), and Zr(IV) is suggested.

Tsurumi and Furuya[3] have determined Ti(IV) by spectrometry, using 2-(2-thiazolylazo)-5-dimethylaminophenol (TAM) as a reagent of the azo group. This reagent together with Ti(IV) at a 1:2 (Ti(IV)–TAM) molar ratio, formed a complex capable of being quantitatively removed as an ionic association compound by means of 1,3-diphenylguanidine (DPG) in benzyl alcohol at pH 4.2—5.2. This proposed method becomes interesting due its relatively high molar absorptivity, but the interferences caused, in this case, by Fe(III), Co(II), Ta(V), and Zr(IV) are not solved. Cd(II), Co(II), Ni(II), Cr(VI), UO_2(II), Fe(III), Zr(IV), and Hf(IV) are severe interferers in most Ti(IV) spectrometric determination. These interferers could be drawn by means of an extraction technique with 8-quinolinol[4] and cupferron[5] when Ti(IV), under high sensitivity conditions, was determined by spectrometric with 5-ClDMPAP.[6] Although this method yields a relatively high molar absorptivity, its drawback is the complex's limited stability in solution. In order to solve this limitation, a method involving hydrogen peroxide was developed so as to greater stability to the system. The results attained by the use of ternary system Ti(IV)–H_2O_2–5-ClDMPAP in aqueous ethanolic solutions are shown in the present paper, as well as the studies on the spectral characteristics of the three species developed, proper pH ranges for forming them, the influence of the organic solvent used, stability and composition. An increase in both sensitivity and stability has been observed to occur when pyridylazo reagents are used and hydrogen peroxide is added to the reaction medium.

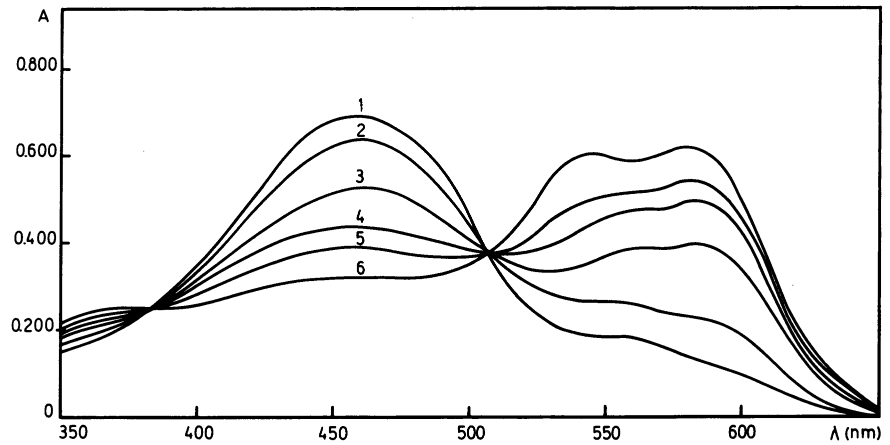
Experimental

Reagents. A 5-ClDMPAP solution was prepared by coupling *m*-dimethylaminophenol with sodium 5-chloro-2-pyridinediazotate, according to the method described by Shibata et al.[7] Purification was carried out by means of repeated cycles of dissolution-reprecipitation starting from ethanol–water mixtures. A 0.25% (w/v) solution of the pure material was prepared. Lower concentration solutions of the above one, were prepared by dilution with ethanol. All solutions were kept away from light. A 5×10^{-4} mol dm^{-3} solution can be kept unaltered for at least 25 d. The Ti(IV) solution was prepared according to that described by Roseman and Thornton.[8] Its titer was determined by complexometric titration.[9] To obtain reproducible results, the solution must be prepared daily. The hydrogen peroxide solution was prepared by dilution from H_2O_2 of 200 vol. All the other chemicals were also of an analytical-reagent grade.

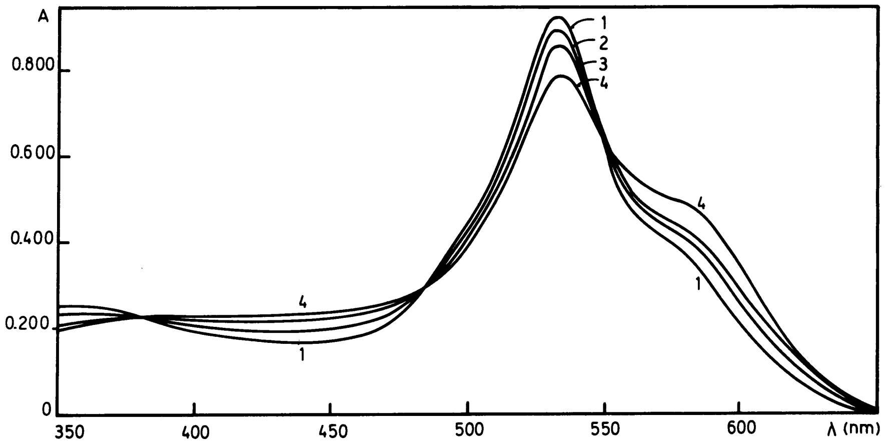
Apparatus. A Varian 634 UV-Vis. spectrophotometer with 10 mm optical path cell to obtain the absorption spectra an absorbance measures was used. An Orion 701-A pH meter for pH measurements was used. Volumes in Ti(IV) complexometric titrations were obtained by means of an automatic Metrohn Dosimat E412P buret.

Results and Discussion

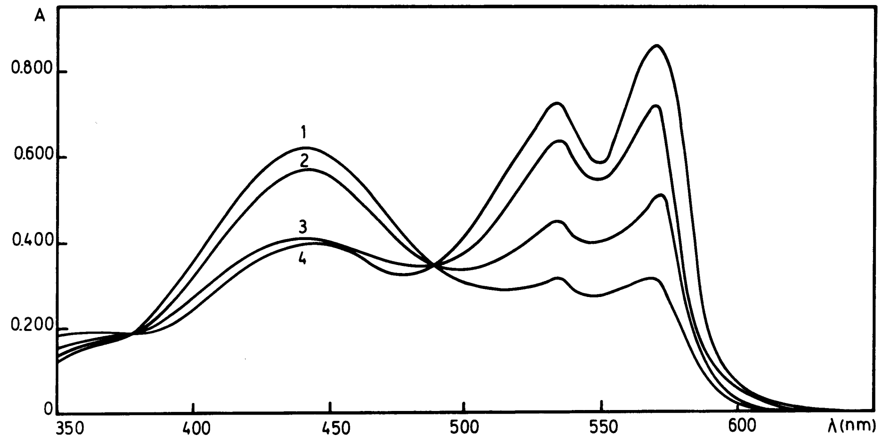
Study on Ti(IV)-H_2O_2-5-ClDMPAP. Influence of pH. In the presence of 5-ClDMPAP and H_2O_2, Ti(IV) forms three ternary complex species with compositions varying according to the pH value of the



1: pH=1, 2: pH=1.13, 3: pH=1.27, 4: pH=1.5, 5: pH=1.8, 6: pH=2



1: pH=4—5—6, 2: pH=3.5, 3: pH=3, 4: pH=2.5



1: pH=10, 2: pH=9, 3: pH=8.5, 4: pH=8

Fig. 1. Ternary complex's isosbestic point formed to different values of pH in presence of metal excess. $C_{Ti}=7.7\times10^{-5}$ M; $C_R=2.2\times10^{-4}$ M.

medium. For values ranging from 2.5 to 6.5 the prevailing species has λ_{max} at 534 nm; while the two other species are formed at pH values ranging from 1—2 to 7—9 with λ_{max} at 580 and 570 nm respectively.

The ternary species spectra formed show isosbestic points at different wavelengths, depending on the range (Figs. 1a, 1b, and 1c). For the analytical work, a ternary complex quantitatively formed between pH 2.5 and 6.5 was singled out bacause of its higher absorptivity values, stability and pH range of formation.

Stoichiometry of the Selected Ternary Species. Stoichiometry of the ternary complex was studied at pH 5.4. In order to determine Ti(IV)-5-ClDMPAP molar ratio, the method of continuous variations (Job)[10] was used, keeping H_2O_2 concentration constant at a rate of 0.3%. This methods proved to be uncapable of determining Ti(IV)-H_2O_2 molar ratio, so that the equilibrium shift methods[11] had to be employed (Fig. 2). Ti(IV)-H_2O_2-5-ClDMPAP molar ratio happened to be 1:2:2.

The order in which the reagents are added is very important. First, the reaction between Ti(IV) and H_2O_2 is caused at low pH values (<2), second a reaction between the Ti(IV)-H_2O_2 complex and 5-ClDMPAP is caused; and then a 5.4 pH buffer is added in order to select the wanted complex.

If it is accepted that the predominant Ti(IV) species at low pH values (2—3), is $[Ti(OH)_2]^{2+}$,[12,13] and that the reaction with H_2O_2 leads to the formulation of $[Ti(OH_2)_2]^{2+}$[15,16] the following equilibria can be written:

$$[Ti(HO)_2]^{2+} + 2H_2O_2 \rightleftharpoons [Ti(HO_2)_2]^{2+} + 2H_2O$$
$$[Ti(HO_2)_2]^{2+} + RH \rightleftharpoons [Ti(HO_2)_2R]^{+} + H^{+}$$
$$[Ti(HO_2)_2R]^{+} + RH \rightleftharpoons [Ti(HO_2)_2R_2] + H^{+}$$

The validity of the above formulation is guaranteed by the results obtained applying the equilibrium shift method[11] (Fig. 3). The equilibrium constant of the ternary compounds formation was studied by means of absorptiometric measurements,[14] the value obtained was 2.77×10^{13} at 25 °C.

Influence of the Solvent and the Hydrogen Peroxide Concentration. The influence of methanol, ethanol, dioxane, and acetone on the absorbance value was studied; whichever the solvent may be, the λ_{max} is the same. As the maximum absorptivity is attained when using methanol or ethanol, the latter was singled out for the present experiment. The best ethanol concentration is between 5 and 25% (v/v) (Fig. 4). The

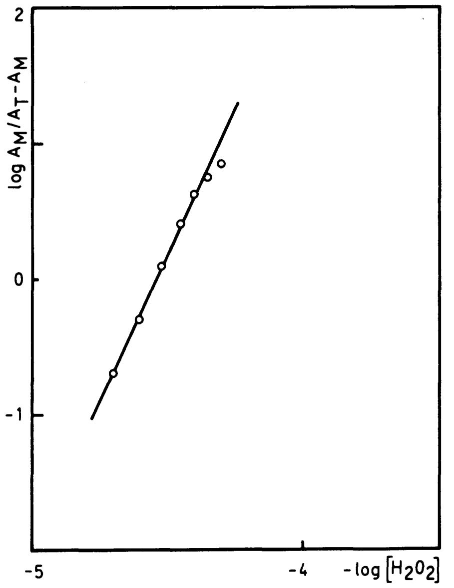


Fig. 2. Equilibrium shift method for the determination of the Ti(IV)-H_2O_2 molar ratio.
$C_{Ti}=1.3\times10^{-5}$ M; $C_R=2.2\times10^{-4}$ M; $C_{H_2O_2}$=Variable $\lambda=534$ nm. A_M=Absorbance read at unfavorable hydrogen peroxide concentration for the ternary complex formation. A_T=Absorbance corresponding to a $C_{H_2O_2}=5.5\times10^{-5}$ M and to a 1.3×10^{-5} M of the ternary complex formation.

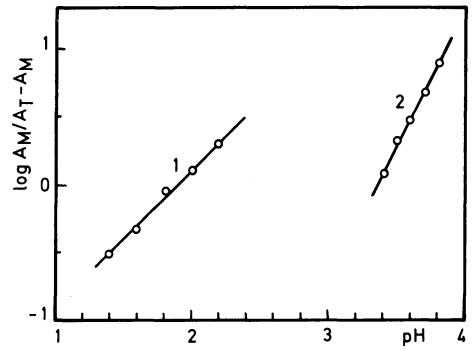


Fig. 3. Equilibrium shift method for determining hydrogen ions released during ternary complex formation.
$C_{Ti}=1.6\times10^{-5}$ M; $C_R=2.2\times10^{-4}$ M. A_M=Absorbance read at unfavorable pH values for the ternary complex formation. A_T=Absorbance corresponding to a 1) pH 2.4; 2) pH 3.9 solution and to 1.6×10^{-5} M of the ternary complex.

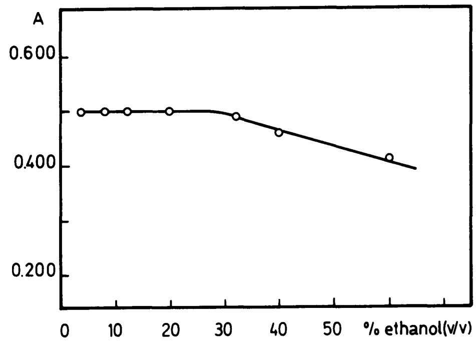


Fig. 4. Influence of the concentration of ethanol on the absorbance of ternary complex.
pH 5.4; $\lambda=534$ nm; $C_{Ti}=1.1\times10^{-5}$ M; $C_{H_2O_2}$= 0.3% (v/v); $C_R=2.2\times10^{-4}$ M.

minimum H_2O_2 concentration needed to get a maximum absorbance is 0.25%, and no transformations take place for concentration up to 1.2% (Fig. 5).

Reagent Concentration and Calibration Curve. The reagent concentration appropriate for the quantitative work was evaluated by plotting the saturation curve (Fig. 6) at pH 5.4. Ti(IV) concentration was kept constant (1.1×10^{-5} mol dm^{-3}), that one corresponding to 5-ClDMPAP was changed between 1×10^{-6} and 5.5×10^{-4} mol dm^{-3}, while H_2O_2 concentration remained constant (0.3% v/v). Absorbance was read at λ_{max} 534 nm and the ethanol concentration remained constant at 16% (v/v).

For a 1:10 Ti(IV):5-ClDMPAP molar ratio, the complete development of a complex is achieved, and this is kept unaltered for proportions up to 1:50. The ternary complex solutions at pH 5.4, keeping a 1:20:10000 metal-ligand-H_2O_2 ratio, change neither their absorption spectrum nor their absorptivity at λ_{max} 534 nm, during 1 h. Aqueous ethanolic solutions of the studied ternary species obey Beer's law up to a concentration of 0.7 ppm when they are made up in a medium with a pH 5.4 and are controlled by means of acetic acid-sodium acetate. The outstanding aspects referring to Ti(IV) absorptiometric determination are stated in Table 1.

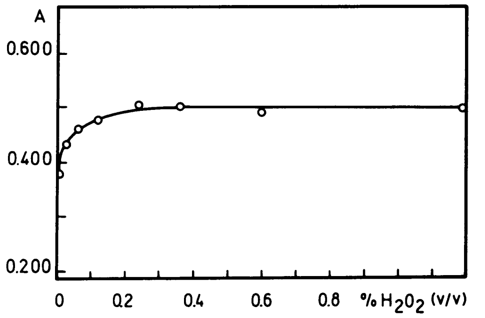


Fig. 5. Influence of the concentration of hydrogen peroxide on the absorbance of ternary complex. pH 5.4; λ=534 nm; ethanol-water 16% (v/v); C_{Ti}=1.1×10^{-5} M; C_R=2.2×10^{-4} M.

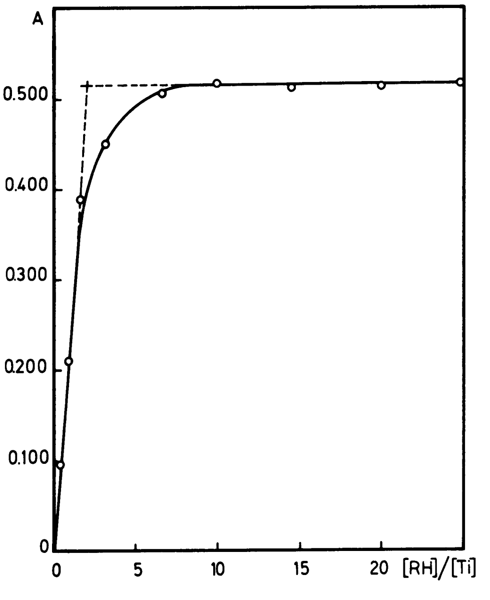


Fig. 6. Saturation curve. C_{Ti}=1.1×10^{-5} M; $C_{H_2O_2}$=0.3%(v/v); pH 5.4; λ=534 nm; ethanol-water 16%(v/v).

Effect of Foreign Ions. The reagent used reacts with ions different from Ti(IV) and produces various colors, depending upon the experimental complexation conditions. The interferences brought about by Fe(III), Cu(II), Ni(II), Co(II), W(VI), Nb(V), Ta(V),

Table 1. Experimental Variables of Ti(IV) Absorptiometric Determination

pH range	2.5—6.5
Solvent	Ethanol-Water 16% v/v
Stoichiometry	1 : 2 : 2 (Ti(IV)-H_2O_2-R)
Maximum absorption of ternary complex:	534 nm
Maximum absorption of reagent	: 440 nm
$\Delta\lambda$:	94 nm
Stability of ternary complex: 1 h	
Beer's law-sensitivity	
Acidity (pH):	5.4
Molar absorptivity: 4.59×10^4 dm^3 mol^{-1} cm^{-1}	
$\left(s=2400;\ \text{Cl}\ \begin{matrix}43381-48418\\ \alpha=0.05\end{matrix}\right)$	
Optimum concentration range (Ringbom)	0.05—0.7 ppm
Sensitivity of sandell: 0.0010 μg/cm^2	
Beer's law fulfilment: Up to 0.7 ppm	

Table 2. Tolerances for Some Common Anions

Ion	Ion/Ti(IV) tolerated molar ratio	Ion/Ti(IV) tolerated mass ratio
Acetate	10000	12.3×10^3
Hydrogen phthalate	5000	17.1×10^3
Bromide	5000	8.3×10^3
Chloride	5000	3.7×10^3
Thiourea	5000	7.9×10^3
Nitrate	4000	5.1×10^3
Thiosulfate	3000	7.0×10^3
Perchlorate	3000	6.2×10^3
Sulfate	2000	4.0×10^3
Sulfamic acid	2000	6.6×10^3
CDTA	500	3.6×10^3
EDTA	500	3.8×10^3
Fluoride	100	40
Tetraborate	30	77
Citrate	10	40
Phosphate	Int	—
Oxalate	Int	—
Iodide	Int	—
Tartrate	Int	—
Ascorbic acid	Int	—

and V(V) have severe effects on the systems and they cannot always be controlled by masking. Zn(II), Mn(II), Mo(VI), and Cr(VI) ions are tolerated in a 10:1 ratio (foreign ion:Ti(IV)). The tolerated ratio for Al(III) and Mg(II) is a 50:1 and for Na(I) and K(I) is 1000:1. Table 2 shows the tolerances for anions, coming from strong acids, used to dissolve samples, as well as for other anions or compound added as possible masking agents. In order to finish with the negative effects of the differents interferers the liquid–liquid extractions method was applied, using 8-quinolinol[4,6] as a removing reagent and chloroform as a solvent, and adjusting pH value in the presence of adequate complexing agents.

Methods and Applications. The method proposed by Cheng,[5] makes use of EDTA and cupferron. Adequately varying the concentration of both species, the selective and quantitative extraction of Ti(IV) present in complex samples as *cast iron* and *nickel bases Alloy* can be obtained. It is important to take into account that EDTA and cupferron concentration will be in agreement with the Ti(IV) concentration and to the other metal interferents concentration in the sample (Fe, Cu, Ni, Cr, and Mo).

Determination of Titanium in Standard Samples. The methodology developed was applied to two kinds of samples.

1. Nodular Cast Iron (NBS 342): A sample of 1 g was digested with 20 cm^3 of hydrochloric acid on a hot plate until action ceased. The insoluble matter was filtered while still hot and washed with 1% hydrochloric acid (F1). After drying, the paper and residue were ignited in an uncovered platinum crucible. 1 cm^3 of 48% hydrofluoric acid and 1 cm^3 of to sulfuric acid were added and the solution was evaporated to dryness. The residue was fused with 1 to 2 g of sodium carbonate. The melt was dissolved in 50 cm^3 of water and digested for 15 min at 90 to 95 °C. The remaining residue was filtered and washed with water. The residue was ignited with 1 g of potassium disulfate for 10 min. The melt was cooled and dissolved with a minimum amount of 2 mol dm^{-3} sulfuric acid. This solution was added to the original (F1) filtrate and diluted to approximately 250 cm^3. To a 25 cm^3 aliquot a slight excess of the disodium salt of EDTA (1 g) was added, followed by sufficient 6 M aqueous ammonia to adjust the solution to pH 5.4. The solution was boiled for 2 min and cooled. Then it was transferred to 125 cm^3 separatory funnel, and diluted to approximately 50 cm^3. 5 cm^3 of 0.4% freshly prepared cupferron were added dropwise with swirling. After standing for 5 min, the solution was extracted with 10 cm^3 of methylisobutylketone. Separate the organic phase, put it dry into a porcelain

Table 3. Results in the Determination of Ti(IV) in Samples

Sample	Composition/% (w/w)		Found/% (w/w)	Error/%
Nodular cast	C	2.450		
iron	Mn	0.369		
	P	0.020		
(NBS 342)	S	0.014		
	Si	2.850		
	Cu	0.140		
	Ni	0.023		
	Cr	0.032		
	V	0.005		
	Mo	0.009		
	Ti	0.019	$0.0187\left(s=7.53\times 10^{-5};\ \mathrm{Cl}\ \begin{matrix}0.0186—0.0188\\ \alpha=0.05\end{matrix}\right)$	1.6
	Mg	0.053		
	Fe	Rem.		
Nickel based	C	0.015		
alloys	Mg	0.007		
	Si	0.150		
Monel-alloy-400	Cu	31.700		
	Fe	0.130		
(BNF B. 7002)	Mn	2.650		
	Cr	0.100		
	Ti	0.015	$0.0152\left(s=6.44\times 10^{-4};\ \mathrm{Cl}\ \begin{matrix}0.0144—0.0159\\ \alpha=0.05\end{matrix}\right)$	1.3
	Al	0.060		
	Co	0.100		
	Ni	Rem.		

crucible on sand bath and melt it with 0.4 g of potassium hydrogensulfate. Cool it take it with 3 cm^3 of 3% (v/v) hydrogen peroxide and pour it into a 25 cm^3 flask; then add 2 cm^3 of reagent, 2 cm^3 of ethanol, buffer acetic–acetate up to pH 5.4 and bring it to gauging. Read the solution absorbance at λ_{max} 534 nm against a reference prepared as usual. Results are shown in Table 3.

2. Synthetic Nickel Based Alloys Sample Corresponding to Metals Technology Center (BNF B. 7002 MONEL-ALLOY 400): To an aliquot of 25 cm^3 of synthetic sample, 0.5 g of the disodium salt of EDTA was added for masking purposes. The solution was made slightly acid and heated for a few minutes to hasten the reaction of EDTA and chromium. The solution was cooled and adjusted to pH 5.4. 5 cm^3 of 1.5% freshly-prepared cupferron were added and the solution was extracted with 25 cm^3 of the solvent. After the extraction, the method used for the *cast iron sample* is applied. Results and shown in Table 3.

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