

Spectrophotometric Determination of Zirconium using Morin and Fluoride and its Application in Glass and Sediments

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Summary: The complexation reactions of zirconium (IV) with morin and fluoride ion were investigated in the absence and presence of polyvinylpyrrolidone as a protective colloid. In 0.05 M sulphuric acid medium and 15% ethanol by volume, a 1:2:1 and 1:3:1 ternary complexes (zirconium : morin : fluoride) were formed in both aqueous and sensitized complexes. The molar absorptivities of aqueous and sensitized complexes were 2.1×10^4 and 5.7×10^4 $\text{l.mol}^{-1}.\text{cm}^{-1}$ at 422 nm and Beer's law was followed in the ranges 0.18-5.47 and 0.09-2.18 mg/l of zirconium (IV), respectively. Optimal conditions for both two complexes for determining zirconium were given. A number of foreign ions were tested for their interference and some masking agents were used to improve the selectivity of the method. Results of analysis of zirconium (IV) in glass and sediments samples using the proposed method were in good agreement with those obtained by atomic emission inductively coupling plasma.

Introduction

Many spectrophotometric reagents have been described for the determination of zirconium (IV), such as arsenazo III⁽¹⁾, dibromocarboxy arsenazo⁽²⁾, chlorophos-phonazo-mA⁽³⁾, xylenol orange⁽⁴⁾, pyrocatechol violet⁽⁵⁾, 1-nitroso-2-naphthol⁽⁶⁾, chloranilic acid⁽⁷⁾, 1-amino-4-hydroxyanthraquinone⁽⁸⁾, 2'-quinolyflurone⁽⁹⁾, quercetin⁽¹⁰⁾, alizarine red S⁽¹¹⁾ and 5,7,2',4'-tetrahydroxyflavonal⁽¹²⁾.

Several sensitive methods for the determination of zirconium in the presence of surfactants include phenylflurone and its derivatives⁽¹³⁻¹⁵⁾, azo derivatives⁽¹⁶⁻¹⁸⁾, methyl thymol blue⁽¹⁹⁾, chrome azurol S⁽²⁰⁾, chromazol KS⁽²¹⁾, eriochrome cyanin R⁽²²⁾, alizarine red S⁽²³⁾. On the other hand, mixed micellar medium containing cationic and nonionic surfactants have been used to

determine zirconium with xylenol orange⁽²⁴⁾ and phenylfluorone⁽²⁵⁾, respectively.

Experimental

Apparatus

UV/VIS absorption spectra were obtained with a SHIMADZU UV-VIS-NIR double beam spectrophotometer model 3101 PC using 1-cm matched quartz cuvettes. A CRISON digit model 501 ion analyzer equipped with a combination glass-calomel electrode was used for pH measurements and pH adjustment, respectively.

Reagents

All chemicals used were of analytical grade. Surfactants and protective colloids were used as received without further purification. Zirconium (IV) stock solution (1×10^{-2} M), was prepared by dissolving 1.6113 g of zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$)[Merk] in water containing 1.0 ml of concentrated hydrochloric acid, and the solution was diluted to 250 ml with water in a volumetric flask. Working solutions were obtained by dilution. Morin (3,5,7,2',4'-pentahydroxyflavone)[BDH chemicals] solution (1×10^{-2} M) was prepared by dissolving 1.511 g of morin in ethanol and diluting to 500 ml in a volumetric flask with the same solvent. Sodium fluoride (0.1 M) was prepared by dissolving 4.199 g of sodium fluoride in water and diluting to 1.0 liter with water in a volumetric flask. Polyvinylpyrrolidone (PVP) of 10,000 average molecular weight (2% w/v) was prepared by dissolving 5.0 g of PVP in water and diluting to 250 ml with water in a volumetric flask. Sulphuric acid (0.05 M) for adjusting acidity was prepared by adding 2.6 ml of concentrated sulphuric acid of 97-98% to water and diluting to 1.0 liter in a volumetric flask.

Procedures

Determination of zirconium (IV) with morin and fluoride

To a solution containing up to 136.7 μg of Zr(IV) in 25-ml volumetric flask, 1.5 ml of 1×10^{-2} M morin, 4.0 ml of ethanol and 1.0 ml of 0.1 M NaF are added and the volume is completed to the mark with H_2SO_4 of 0.05 M. The mixture is allowed to stand for 20 minutes and the absorbance is measured at 422 nm against a blank.

Determination of zirconium (IV) with morin, fluoride and PVP

A suitable aliquot of sample containing not more than 67.5 µg of Zr(IV), 1.0 ml of 1×10^{-2} M morin, 4.0 ml of ethanol, 1.0 ml of 0.1 M of NaF and 0.5 ml of 2% w/v PVP are introduced into 25-ml volumetric flask. The volume is completed to the mark with H₂SO₄ of 0.05 M. After 25 minutes, the absorbance is measured at 422 nm against a blank.

Determination of zirconium (IV) in sediments

The open acid digestion was used⁽²⁶⁾. Weigh accurately 0.25 g of sediment sample, 10 ml of HF, 10 ml of HNO₃-HCl (3:1) and 2.0 ml of HClO₄ are added in Teflon beaker and the mixture is left overnight. The mixture is heated on hot plate to evaporate slowly to near dryness. This step is repeated using half of the above volumes of acids. After evaporation, 2.0 ml of the HNO₃/HCl mixture is added and heating is continued until the volume is reduced to about 2.0 ml and then transferred sample solution to a volumetric flask 50-ml. The above procedure utilizing morin, fluoride ion and PVP in the presence of selected masking agents is followed to determine Zr(IV) in sediment samples.

Determination of zirconium (IV) in glass

Weigh accurately 0.5 g of fine glass sample (completely grinding), 15 ml of HF, 3.0 ml of HNO₃ and 5.0 ml of HClO₄ are added in Teflon beaker. The mixture is heated on hot plate to evaporate slowly to near dryness. Bidistilled water is then added and the solution is transferred into 50-ml calibrated flask and completed to the mark. The above procedure utilizing morin, fluoride ion and PVP in the presence of selected masking agents is followed to determine the zirconium content in glass samples.

Results and Discussion

Effect of surfactants and protective colloids

The effect of some surfactants and protective colloids on the color reactions of zirconium (IV) with morin and fluoride has been investigated. The

utilized surfactants were cetyltrimethylammonium bromide (CTAB), benzyldimethyl tetradecyl ammonium chloride (Zephiramine), cetylpyridinium bromide (CPB), cetylpyridinium chloride (CPC) [cationic], polyoxyethylene p-octylphenol (Triton X-100), ethoxylated fatty alcohol (Emulsifier S), polyoxyethylene sorbitan monolaurate (Tween 20), polyoxyethylene sorbitan monopalmitate (Tween 40), polyoxyethylene sorbitan monostearate (Tween 60), polyoxyethylene sorbitan monooleate (Tween 80) [nonionic], sodium alkylbenzene sulphonate (SAS), sodium lauryl sulphate (SLS) and sodium dodecyl benzene sulphonate (SDBS) [anionic], whereas the examined protective colloids were gum Arabic, Gelatin, polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP).

A slight increase in the complex absorbance was obtained in the presence of cationic surfactants CTAB, Zephiramine, CPB and CPC and the protective colloid PVA. Maximum enhancement of the complex absorbance was obtained in the presence of the protective colloid PVP. Consequently, PVP has been selected to improve the sensitivity of the complex. The results are summarized in Table 1.

Table (1): Effect of surfactants and protective colloids on the spectral characteristics of zirconium (IV)-morin-fluoride ternary complex, [Zr(IV)], 1.2×10^{-5} M; [morin], 4×10^{-4} M; [sodium fluoride], 4×10^{-3} M; [surfactants], 2×10^{-3} M (1.0% for non ionic surfactant), protective colloid, 0.1% w/v; sulphuric acid, 0.05 M.

Surfactant or prot. Coll.	Type	λ_{\max} (nm)	Absorbance	$\epsilon \times 10^4$ $\text{l.mol}^{-1}.\text{cm}^{-1}$
Without	–	422.0	0.21	2.1
CTAB	Cationic	419.0	0.48	4.8
Zephiramine	Cationic	420.0	0.46	4.6
CPB	Cationic	417.5	0.45	4.5
CPC	Cationic	418.0	0.44	4.4
Tritox X-100	Nonionic	421.0	0.38	3.8
Emulsifier S	Nonionic	422.5	0.40	4.0
Tween 20	Nonionic	423.0	0.37	3.7
Tween 40	Nonionic	424.5	0.36	3.6
Tween 60	Nonionic	424.8	0.39	3.9
Tween 80	Nonionic	425.0	0.35	3.5
SAS	Anionic	430.0	0.32	3.2
SLS	Anionic	429.0	0.33	3.3
SDBS	Anionic	431.0	0.35	3.5
Gum Arabic	Prot. Coll.	415.0	0.28	2.8
Gelatin	Prot. Coll.	418.0	0.30	3.0
PVA	Prot. Coll.	418.5	0.52	5.2
PVP	Prot. Coll.	422.0	0.57	5.7

Absorption spectra

The absorption spectra of the system zirconium (IV)-morin-fluoride ternary complex in the absence and presence of protective colloid PVP at the optimum acidity are shown in Fig.1. The absorption spectra of Zr(IV)-morin-flouride ternary complex and the reagent morin-flouride are at 252 and 422 nm, respectively (Curves 1 and 2). Addition of PVP to the reagent and ternary complex at optimum acidity, the enhanced complex and the reagent shows a marked increase of absorbance at the same wavelengths (curves 3 and 4), respectively.

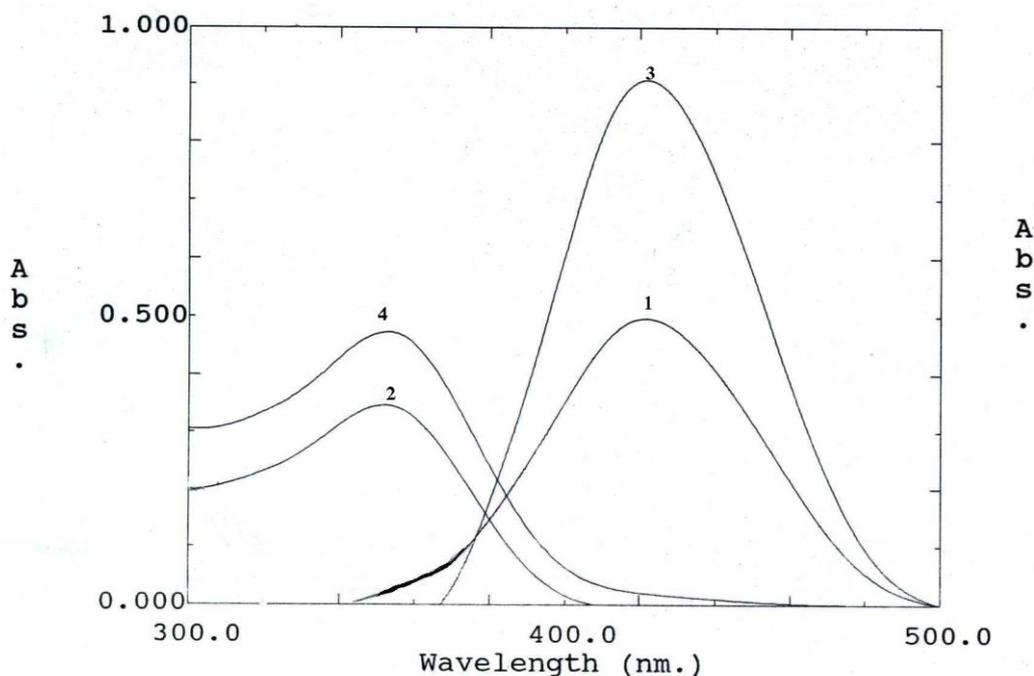


Fig.(1): Absorption spectra of Zr(IV)-morin-fluoride complex in absence and presence of PVP (curves 1 and 3) and its reagent blank (curves 2 and 4), respectively.

Effect of acidity

The influence of final acidity on the absorbance of the Zr(IV)-morin-fluoride ternary complexes in the absence and presence of PVP is shown in Fig. 2. A wide range of maximum absorbance was obtained 0.02-0.2 M, 0.02-0.15 M, 0.1-0.2 M and 0.05-0.2 M when use the acids; sulphuric, nitric, hydrochloric and perchloric, respectively. Moreover, sulphuric acid was used to adjust the final acidity exhibited a maximum absorbance of the formed complexes in the range 0.02-0.2 M. In the proposed procedure, the final acidity of zirconium (IV) complexes was adjusted at 0.05 M with sulphuric acid.

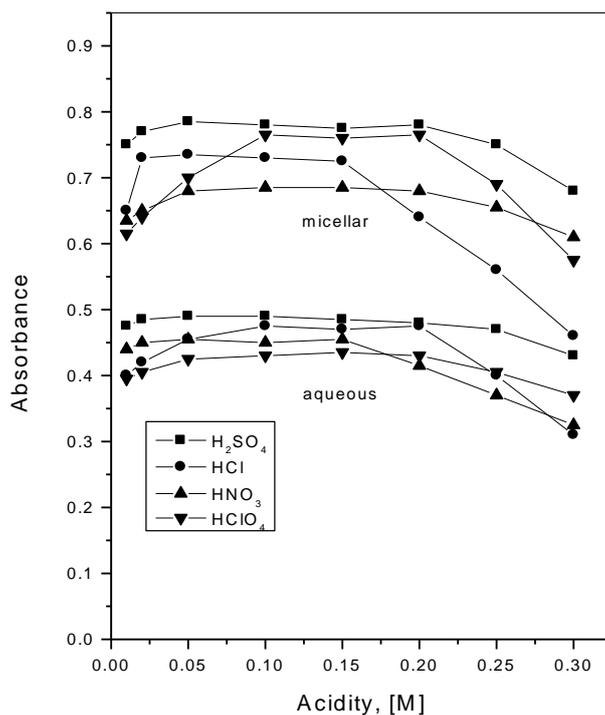


Fig. (2): Effect of final acidity on the absorbance of Zr-morin-fluoride ternary complexes.

Effect of some anions as secondary ligand

The influence of different anions as second ligand on the absorbance of the Zr(IV)-morin complex in the absence and presence of PVP has been investigated. The tested anions were salts of sodium, potassium and/or ammonium of fluoride, chloride, bromide, iodide, thiocyanate, oxalate, citrate, tartrate, EDTA and malonate, besides thiourea. Table 2, shows the spectral characteristics of the formed ternary complexes with the tested anions.

On the other hand, iodide, citrate, EDTA and thiourea were interfered and decreased the absorbance of the binary complexes. Both aqueous and enhanced complexes were exhibited maximum absorbance in the presence of sodium fluoride. Consequently, fluoride ion was used as second ligand for further studies.

Table (2): Effect of secondary ligand on the spectral characteristics of the aqueous and enhanced zirconium (IV)-morin complexes at the optimum acidity.

Secondary ligand	λ_{\max} (nm)	Aqueous complex		Enhanced complex	
		A	$\epsilon \times 10^4$ l.mol ⁻¹ .cm ⁻¹	A	$\epsilon \times 10^4$ l.mol ⁻¹ .cm ⁻¹
Without	422.0	0.08	0.8	0.24	2.4
Sodium fluoride	422.0	0.21	2.1	0.57	5.7
Sodium chloride	422.5	0.13	1.3	0.40	4.0
Potassium bromide	422.5	0.12	1.2	0.35	3.5
Potassium iodide	423.8	0.10	1.0	0.31	3.1
Ammonium thiocyanate	424.3	0.08	0.8	0.24	2.4
EDTA	428.8	0.04	0.4	0.09	0.9
Ammonium oxalate	421.0	0.14	1.4	0.42	4.2
Sodium citrate	423.7	0.07	0.7	0.23	2.3
Sodium tartrate	421.9	0.12	1.2	0.35	3.5
Thiourea	425.2	0.09	0.9	0.26	2.6
Malonic acid	424.0	0.11	1.1	0.30	3.0

Effect of morin concentration

The effect of morin concentration on the formation of the aqueous and enhanced zirconium (IV) complexes was studied using variable concentrations of morin ranging between 2×10^{-5} M and 7.8×10^{-4} M maintaining ethanol content constant in aqueous and enhanced complexes, respectively. Maximum color was developed using morin concentration $\geq 4 \times 10^{-4}$ M and $\geq 3 \times 10^{-4}$ M for both aqueous and enhanced complexes, respectively. In the procedure, 1.5 ml and 1.0 ml of 1×10^{-2} M of morin were used for the two complexes, respectively.

Effect of fluoride concentration

The influence of sodium fluoride concentration on the absorbance of the aqueous and sensitized zirconium (IV) complexes were investigated using fluoride ion concentration ranging between 8×10^{-5} M and 1.2×10^{-2} M throughout the study. The study revealed maximum and constant absorbance of the aqueous complex in the range 8×10^{-5} M and 8×10^{-4} M. Higher fluoride concentrations caused decrease in absorbance to minimum. On the other hand, the enhanced complex absorbance was maximum and constant in the presence of $\geq 2.8 \times 10^{-3}$ M of fluoride ion concentration. In the procedure, 1.0 ml of 0.1 M of sodium fluoride was used.

Effect of PVP concentration

The effect of PVP concentration on the formation of the Zr(IV)-morin-fluoride complex was studied using PVP concentration ranging between 0.002 and 0.16% w/v. The study revealed maximum and constant absorbance of the complex in the presence of $\geq 0.02\%$ w/v of PVP.

Effect of time

The formation and stability of the Zr(IV)-morin-fluoride complexes in the absence and presence of PVP with respect to time were examined using the optimal experiment conditions given in the procedure. The absorbance of these complexes increases during the first 15 and 20 minutes for both aqueous and enhanced complexes from mixing, respectively. The absorbance of both complexes remained maximum and constant for more than 24 hours. A standing time of 20 and 25 minutes were selected for both aqueous and enhanced complexes, respectively.

Calibration graphs and statistical analysis of results

The calibration graphs are rectilinear up to 5.47 and 2.18 mg/l of zirconium (IV), with a correlation coefficient for 0.9999 in the Zr(IV)-morin-fluoride and Zr(IV)-morin-fluoride-PVP complexes as shown in Fig. 3 (curves 1 & 2), respectively. The corresponding molar absorptivities, as determined by

least-squares fit for nineteen and sixteen results were 2.1×10^4 and 5.7×10^4 $\text{l. mol}^{-1} \cdot \text{cm}^{-1}$, at 422 nm. The values of Sandell's sensitivity index were 4.41 and $1.60 \mu\text{g. cm}^{-2}$ of zirconium (IV) and the detection limits were 0.06 and 0.02 mg Zr l^{-1} for both aqueous and enhanced complexes, respectively.

The precision of the methods has been determined by twelve replicate of a solution containing 2.2 and 0.73 mg l^{-1} of Zr(IV), the absorbances were 0.5 and 0.46 with standard deviations of 0.009 and 0.007, respectively.

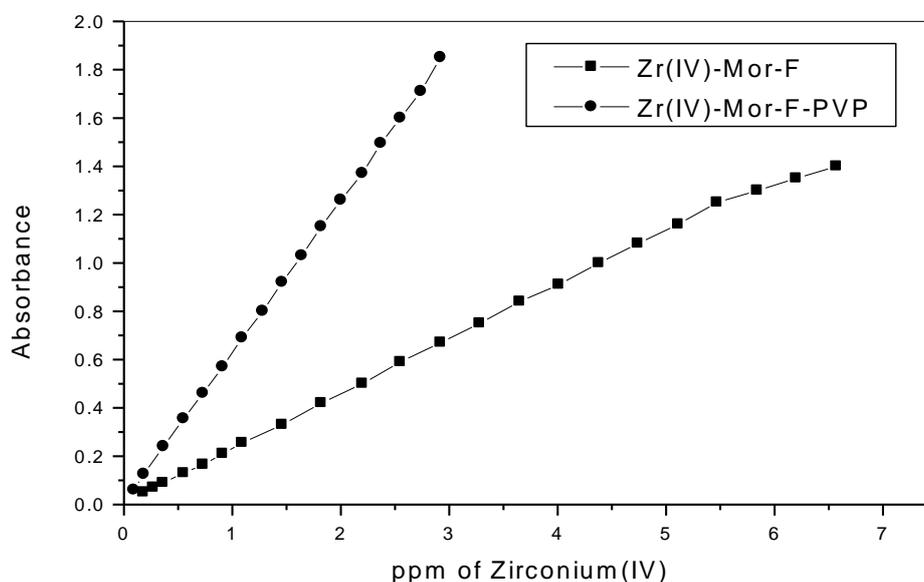


Fig.(3): Calibration graph of the determination of zirconium (IV) with morin and fluoride in the absence and presence of PVP.

Stoichiometry and stability of the complexes

The composition of Zr(IV)-morin-fluoride complex in the absence and presence of PVP at the optimum experimental conditions has been determined using molar ratio and continuous variation methods. These methods confirm a metal-reagent-second ligand of 1:2:1 and 1:3:1 for aqueous and enhanced complexes, respectively as shown in Figs. 4 and 5.

Measurements of stability constants have been carried out at a constant ionic strength using continuous variation method. The determined value of the

stability constant for aqueous complex is 4.7×10^{11} , whereas for enhanced complex is 6.1×10^{14} .

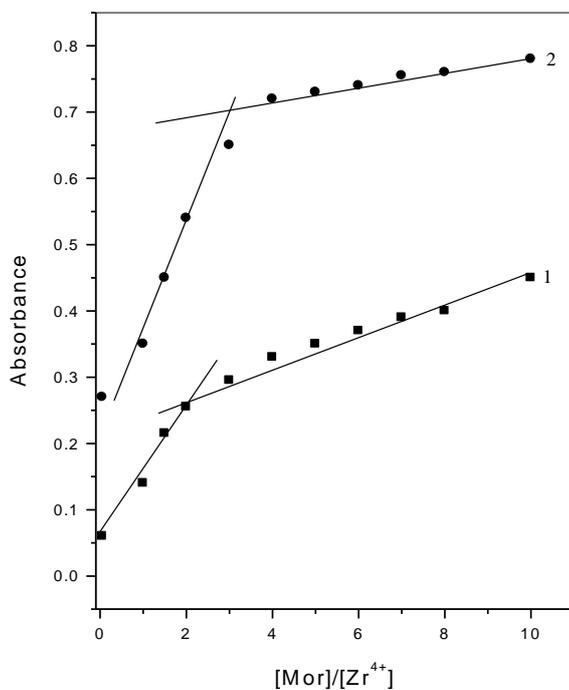
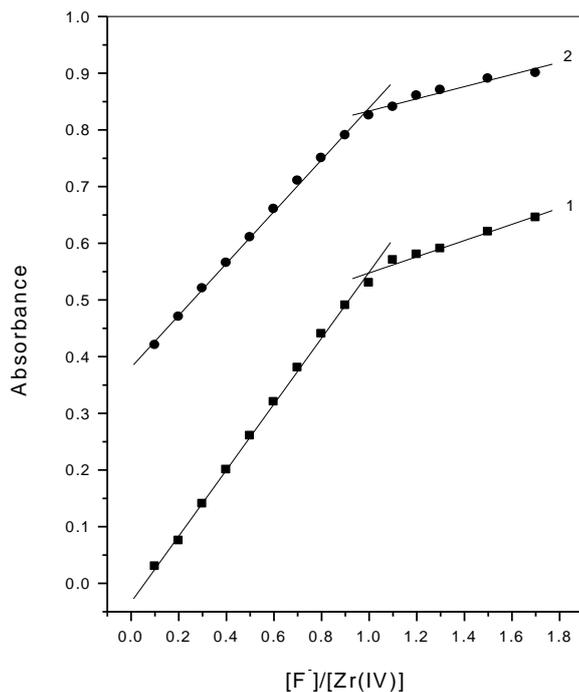


Fig.(4): Determination of Zr(IV) : morin ratio in the ternary complex using the molar ratio method. Curve 1, aqueous complex; curve 2, enhanced complex.

Fig.(5): Determination of Zr(IV) : F⁻ in the ternary complex using the molar ratio method. Curve 1, aqueous complex; curve 2, enhanced complex.



Effect of interfering ions

A systematic study of interfering ions on the determination of 0.55 μg zirconium (IV) has been made by applying the recommended procedure to solutions containing a 3000 fold (mol/mol) ratio of interfering ion to zirconium (IV); if interference occurred, this ratio was reduced until the interference ceased. Metal ions are added as nitrate, chloride or sulfate, while the anions are added as ammonium, potassium or sodium salts. The tolerance limit was taken as the amount that causes $\pm 2\%$ error in the absorbance value. Common masking agents such as ascorbic acid and ammonium citrate were used to improve the selectivity of the method. The tolerance limits of iron (II) and (III), chromium (VI), molybdenum (VI), titanium (IV) and tungsten (VI) increased by addition of 2.0 ml of 0.1 M ascorbic acid whereas, 1.0 ml of 0.1 M ammonium citrate in 25-ml measuring flask was used to improve the tolerance limits of aluminium, beryllium, vanadium (V) and uranium (VI). The results obtained are given in Table 3.

Table(3):Effect of diverse ions on the determination of Zr(IV)-morin-fluoride-PVP ternary complex [Zr(IV)], 1.2×10^{-5} M; [morin], 4×10^{-4} M; [sodium fluoride], 4×10^{-3} M; [PVP], 0.02% w/v; [sulphuric acid], 0.05 M.

Ions added	Tolerance limit {[Ion]/[Zr(IV)]}
K^+ , Li^+ , Na^+ , Cl^- , ClO_4^- , $S_2O_3^{2-}$, SO_4^{2-} , formate, acetyl acetone, ethanol amine.	> 10000
Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Zn^{2+} , Cd^{2+} , NO_2^- , NO_3^- , thiourea, malonic acid, sulfosalicylic acid, phthalate, succinate, ethylenediamine, diethanol amine, phosphate.	> 3000
Hg^{2+} , Co^{2+} , Ni^{2+} , B^{3+} , As^{3+} , Br^- , I^- , Fe^{2+a} , Fe^{3+a} , Cr^{3+a} , $Cr(VI)$, SCN^- .	> 1000
Cu^{2+} , Mn^{2+} , Sn^{2+} , $Sn(IV)$, Fe^{3+} , $Ti(IV)^a$, $Mo(VI)^a$, $W(VI)$, Citrate, tartrate, ascorbic acid, EDTA.	> 500
Be^{2+b} , Al^{3+b} , $V(V)^b$, $U(VI)^b$.	>100

Masking agents:

- a. 8×10^{-3} M ascorbic acid, b. 4×10^{-3} M ammonium citrate

Application of the method

The proposed method utilizing Zr(IV)-morin-F-PVP system has been used to determine zirconium (IV) in sediment and glass samples. The open acid digestion was used for the dissolution of samples utilizing concentrated hydrofluoric, nitric, hydrochloric and perchloric acids ⁽²⁶⁾. A suitable aliquot was transferred into a 50-ml measuring flask. Add 1.0 ml each of ascorbic acid and ammonium citrate to the sample solution to ensure that the other metals do not interfere. Then, the recommended procedure for zirconium (IV) determination in micellar medium is followed. The results presented in Tables 4 and 5 are consistent with the standard values of inductively coupled plasma atomic emission spectrometry. The accuracy and precision of the method are satisfactory. The calculated t- and F- test values are less than tabulated values at different confidence levels. We conclude that, there is no difference in the precision between the proposed and standard methods.

Table (4): Determination of zirconium (IV) in sediment and soil samples of River Nile using morin, fluoride and PVP.

Sample No.	Location	Zirconium (IV), mg/l			F-test	t-test
		AES-ICP	*Found	Standard Deviation		
1	Murshid 378 km southern HD	0.2408	0.2416	0.002	1.8	2.35
2	Armant 210 km Northern HD	0.3524	0.3534	0.002	1.53	
3	Luxor 230 km Northern HD	0.313	0.3142	0.001	0.55	
4	Nag Hammady 350 km Northern HD	0.218	0.2186	0.001	1.35	
5	Assuit 544 km Northern HD	0.072	0.0728	0.001	1.19	
6	El-Roda	0.266	0.2666	0.0005	0.67	
7	Tokh Tanbensha	0.232	0.2666	0.0005	2.1	
8	Ganzour	0.230	0.2288	0.0004	1.47	

Note: HD = High Dam

W.l. of Zr(IV) is 343.823 in case of AES-ICP

* Average of five determinations.

Table (5): Determination of zirconium (IV) in glass using morin, fluoride and PVP.

Sample No.	Source of samples	Zirconium (IV), mg/l			F-test	t-test
		AES-ICP	*Found	Standard Deviation		
1	National Research Center (Glass lab.)	1.29	1.288	0.09	2.25	1.36
2	National Research Center (Glass lab.)	1.35	1.568	0.03	1.07	
3	Egyptian Company for flat glass (10 th Ramadan)	0.46	0.4674	0.04	1.67	
4	Egyptian Company for flat glass (10 th Ramadan)	0.48	0.5234	0.03	1.3	

Note: W.I. of Zr(IV) is 343.823 in case of AES-ICP

* Average of five determinations.

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