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Separation and Determination of Metals in Mixed Solvent System on Anion Exchanger Using Atomic Absorption Spectrophotometer

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Abstract

The use of 2-propanol in admixture with formic acid for the selective elution of cations on the ion-exchange resin Amberlite IRA-420 in Cl^- form is investigated. The elution technique was coupled with absorption spectrometry and atomic absorption spectrophotometry. The distribution coefficients of metal ions were measured in 2-propanol-water-formic acid mixture. By applying distribution coefficient data, conditions for column separation of mixtures have been effected by eluting with 2-propanol-water-formic acid solution of different compositions. The average recovery for all separations (n =18) was within 95.1 – 98.3 % and the standard deviation for all data was 10%. The developed analytical methodology was successfully applied for the separation and quantification of metal ions in the microgram range from the real samples collecting from natural water and industrial effluents using UV-Visible and AAS techniques.

Introduction

Ion-exchange is one of the most important chromatographic techniques for the separation of metal ions [1-8]. In recent years the use of anion exchange for the removal and separation of metal ions is of wide interest due to its simplicity, elegance and range of variable experimental conditions.

Several workers have reported ion-exchange for separation and determination of the metal ion at $mg.L^{-1}$ level. F. W. E. Strelow [9] separated the tetravalent rare earth metals and Scandium from Aluminium, Gallium, Indium, Thallium, Iron, Titanium, Uranium and other elements by cation exchange. A.G. Gaikwad and S.M. Khopker [10] reported the separation of Lead from mixed solvents by cation exchanger. Moreover, Alam et al. [11-16] separated various metal ions in ethanol, methnol, isopropanol, ethylene glycol, 1,4-Dioxan with cation exchange resin Zeocarb 225 and Dowex 50 x 8, 100-200 mesh.

F. W. E. Strelow and F. S. Von [17] reported metal ion separation by anion exchange in mixed solvents. Santoyo et al. [8] determined Lead, Copper, Cadmium, Cobalt, Zinc, Nickel ion in ground water using ionic separation column system including HPIC-CS2 of Dionex as cationic column, HPIC-AS4 of Dionex as anionic column and IonPac CS5 of Dionex as bifunctional ion-exchange column. Moreover, S. A. Nabi et al. [7] separated Copper(II) and Zn(II) with modified Amberlite IR-400 anion exchange (Cl^- form) with naphthol blue-black. Recently Alam et al. [18] started work with anion exchange resin and separated few metals using formic acid.

The information received from the thorough survey of literature show that some work have been done on cation exchanger in H^+ forms of Dowex, Dionex, Amberlite IRC 718 (Na^+ form) and anion exchanger with modified Amberlite IR-400 (Cl^- form) [7-16]. There has been no report in the literature of any successful and complete separation of metal ions using anion-exchange

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resin in Cl^- form, strongly basic anion, 100-200 dry mesh with 2-propanol (isopropanol) as organic solvent. Therefore, it is required to develop a separation technique with anion-exchange resin which can completely separate metal ions from a mixture. This work was undertaken in an attempt to develop a separation technique of metal ions using 2-propanol admixture with formic acid and water. However, strongly basic anion-exchange resin of the type Amberlite IRA-420 was chosen. The metals were chosen on the basis of their biological, environmental and industrial importance.

Experimental

Apparatus

The spectrometric measurements were carried out with a UV-visible recording spectrophotometer UV-160A (Shimadzu), Japan, with 1 cm quartz cells and some samples were analyzed by Atomic absorption Spectrophotometer AA-680 (Shimadzu), Japan.

Reagents and Materials

An air dried pretreated anion exchange resin (1.0 g) 'Amberlite' IRA-420, chloride form, strongly basic anion, 8% cross-linking, 0.30–1.2 mm particle size, 14-52 dry mesh, (BDH Laboratory Supplies, England) was used in the measurement of distribution co-efficient and column separations. The ion exchange capacity of 'Amberlite'IRA-420 was determined [5] and the exchange capacity for Ca(II), Fe(II), Ni(II) and Pb(II) were found 2.5, 2.8, 2.5 and 4.0 meq g^{-1} respectively. The EDTA, sodium thiosulphate and potassium dichromate solution (0.05M, 0.01M and 0.01M respectively) from analytical grade reagent (E Merck) was prepared for the complexometric, iodometric and oxidation-reduction methods respectively. Metal salts solution (0.05M) from analytical grade reagents were prepared. Each of the metal salt solution was standardized by appropriate complexometric, iodometric and oxidation-reduction method, using standard EDTA, sodium thiosulphate and potassium dichromate solutions. 1-2 mL of mineral acid was added to the metal solution to prevent hydrolysis. Preparations of reagents was made with distilled deionized water.

General procedure

An air dried pretreated anion exchange resin 'Amberlite' IRA-420 (1.0 g) was taken into a 100 mL glass stoppered bottle. To the bottle metal salt solution (4mL, 0.05M) and appropriate 2-Propanol (isopropyl alcohol) of analytical grade – water-formic acid mixture (50 mL) was added. The bottle was stoppered and shaken for 10 hours. An aliquot from the supernatant liquid was taken and after evaporation of the acid and organic solvent to near dryness the metal ion content was determined by an appropriate complexometric / iodometric / oxidation-reduction method [21]. The distribution coefficient on a dry weight basis was calculated [22].

Depending on the distribution coefficient of the metal ions, the separation of the mixture into components was effected by varying the composition of the eluting agent. The separated metals were analyzed at trace level by absorption spectrophotometry and atomic absorption spectrometry.

Results and Discussion

Distribution coefficients

The distribution coefficients of all metal ions were increased with increasing percentage of 2-propanol in 0.5M formic acid as shown in the Table-1 & Table-2. The distribution coefficients of Mg(II) and Co(II) were zero at 30% 2-propanol and were increased with increasing percentage of 2-propanol. The distribution co-efficient of Mn(II) had the same value zero at 30% and 50% 2-propanol and were increased with increasing percentage of 2-propanol. The distribution coefficients of Cu(II), Zn(II), and Ca(II) were very low at 30% 2-propanol and were increased with increasing percentage of 2-propanol. The distribution co-efficient of Ni(II), Pb(II) and Fe(III) were also low at 30% 2-propanol. Again, at 50% 2-propanol the distribution co-efficient of Cu(II), Mg(II), Ca(II) and Co(II) were very low. The distribution co-efficient of Cd(II) were high at all percentages of 2-propanol except 20%. So this eluting condition was chosen for the separation of Cd(II) ion. On the other hand, the distribution co-efficient of Ca(II) were very low compared to other metal ions at all percentage of 2-propanol.

The distribution coefficients of the metal ions Cu(II), Ca(II), Ni(II) and Fe(III) were gradually decreased with higher acid concentration at 50% 2-propanpl as presented in Table-2. For Cu(II) it becomes zero at 2, 2.5 and 3M formic acid and for Ca(II) it becomes zero from 1.5 to 3.0M formic acid in 50% 2-propanol. Whereas the distribution coefficients of Zn(II), Pb(II) and Cd(II) were gradually increased with the higher concentration of formic acid at 50% 2-propanol. On the other hand, the distribution co-efficient of Mn(II) were zero in 50% 2-propanol at all molar concentrations of formic acid. For Mg(II) and Co(II) the distribution co-efficient was very low at 0.5M formic acid and the values are zero from 1.0M to all the next higher molar concentrations of formic acid. The distribution co-efficient of Cu(II) were very low at 0.5M, 1.0M and 1.5M formic acid and zero at 2.0M, 2.5M and 3.0M formic acid. Similarly the values Ca(II) were very low at 0.5M and 1.0M formic acid and become zero from 1.5M to 3.0M formic acid in 50% 2-propanol.

Table 1. Distribution co-efficient of metal ions in various percent concentrations of 2-propanol at 0.5M formic acid.

Metal ions	**Distribution coefficient (mL g^{-1}) at % Concentration of 2-propanol**					
	30%	**50%**	**70%**	**80%**	**90%**	**95%**
Cu(II)	0.04	0.82	2.35	7.56	36.9	136.65
Zn(II)	0.08	9.51	128.04	612.34	1964.06	26662.61
Mn(II)	0.00	0.00	0.05	3.17	26.89	48.50
Mg(II)	0.00	0.11	0.79	2.32	11.61	29.31
Ca(II)	0.07	0.82	2.39	3.98	7.60	18.79
Ni(II)	2.35	4.00	5.69	7.55	32.96	127.65
Co(II)	0.00	0.09	1.55	3.15	5.72	32.98
Pb(II)	2.45	12.79	71.25	181.76	613.28	1280.57
Fe(III)	3.94	6.54	12.49	55.63	122.25	283.90
20%	**30%**	**50%**	**70%**	**80%**	**90%**	**95%**
Cd(II)	7.55	27.08	64.83	238.79	695.44	2342.25

Table 2. Distribution co-efficient of metal ions in various molar concentrations of formic acid at 50% 2-propanol.

Metal ions	**Distribution coefficient (mL g^{-1}) at Molarity of Formic Acid**					
	0.5M	**1.0M**	**1.5M**	**2.0M**	**2.5M**	**3.0M**
Cu(II)	1.25	0.82	0.04	0.00	0.00	0.00
Zn(II)	9.51	12.70	16.21	21.46	27.65	34.96
Mn(II)	0.00	0.00	0.00	0.00	0.00	0.00
Mg(II)	0.11	0.00	0.00	0.00	0.00	0.00
Ca(II)	0.82	0.07	0.00	0.00	0.00	0.00
Ni(II)	3.16	2.35	1.56	0.80	0.05	0.00
Co(II)	0.09	0.00	0.00	0.00	0.00	0.00
Pb(II)	12.79	15.09	16.31	18.86	21.62	26.16
Fe(III)	6.54	4.78	3.13	1.56	0.81	0.08
Cd(II)	64.83	69.72	73.66	77.87	80.85	83.96

Table 3. Distribution co-efficient of metal ions in various molar concentrations of formic acid at 30% 2-propanol.

Metal ions	**Distribution coefficient (mL g^{-1}) at Molarity of Formic Acid**					
	0.5M	**1.0M**	**1.5M**	**2.0M**	**2.5M**	**3.0M**
Cu(II)	0.04	0.04	0.00	0.00	0.00	0.00
Zn(II)	0.00	0.80	1.57	3.15	4.00	4.81
Ca(II)	0.07	0.00	0.00	0.00	0.00	0.00
Ni(II)	2.35	1.56	0.80	0.05	0.00	0.00
Pb(II)	2.45	4.08	5.82	7.66	10.65	13.92
Fe(III)	3.94	2.34	0.82	0.09	0.00	0.00
Cd(II)	27.08	28.76	30.51	32.33	33.60	34.90

The distribution coefficients of all the metal ions except Zn(II), Pb(II) and Cd(II) were gradually decreased and become zero with higher formic acid concentration at 30% 2-propanol as presented in the Table-3. The distribution co-efficient of Zn(II) was zero at 0.5M formic acid and the values were gradually increased with higher acid concentration but the change were not so significant. The distribution co-efficient of Ca(II) were zero over all concentrations of formic acid except 0.5M. For Ni(II) and Fe(III) the distribution coefficients were very low and the values were zero at 2.5M and 3.0M formic acid in 30% 2-propanol. Except 0.5M and 1.0M, the distribution co-efficient of Cu(II) were zero at other higher concentrations of formic acid. The values of distribution co-efficient of Cd(II) were high compared to other metal ions at 30% 2-propanol.

Separation of mixtures

In 2-propanol–water–formic acid system a four and five component synthetic mixtures have been successfully separated and analyzed quantitatively. Appropriate complexometric methods were applied for the quantitative estimation of each metal ion. Table-4 showed that the separations using eluting agents are affected by distribution co-efficient data. The average recovery for all separations was within 95.1 – 98.3 % and the standard deviation for all data (18 results) was 10%. The elution curve of five component mixtures was shown in (Fig.1)**.**

In the mixture of separations reported in Table-4, the following mixture of separations successfully separated and the individual metal ion determined quantitatively with complexomitric method.

1. Co(II)–Mn(II)–Zn(II)–Cd(II)
2. Ca(II)–Cu(II)–Pb(II)–Cd(II)
3. Mg(II)–Ni(II)–Fe(III)–Zn(II)–Cd(II)
4. Ca(II)–Mn(II)–Fe(III)–Pb(II)–Cd(II)

Theoretically the following mixtures also separated by the present work:

5. Co(II)–Ni(II)–Pb(II)–Cd(II)
6. Ca(II)–Ni(II)–Zn(II)–Cd(II)
7. Mg(II)–Mn(II)–Fe(III)–Pb(II)–Cd(II)

Slight tailing is observed in the elution curve (Fig.1). Tailing can be reduced by decreasing the flow rate [18]. However, a convenient balance between flow rate and the time required to elute a metal ion must be found. A normal flow rate of 0.2 mL to 0.3 mL per minute gives the most satisfactory result and this flow rate has been maintained in all measurements. Tailing can also be reduced by using finer mesh resin [18], but this alternative type of resin has not been tried. Transformation from a partially non-aqueous elution medium to an aqueous medium and from aqueous medium to partially non-aqueous medium does not hinder the performance of the column.

Table 4. Separation and recovery of synthetic metal ion mixtures on Amberlite IRA-420 in Cl^- form, 14 – 52 dry mash (metal appears in the order of elution with the amount of wash solution included with the first eluted metal) and analysis with suitable complexometric method.

Column dimension : 22.0 cm X 0.74 cm (Resin 6.0g)

No of series	Eluting agent	Taken mg	Found mg	Recovery %
1	**Co(II)–Mn(II)–Zn(II)–Cd(II)**			
	Co(II): 70 mL; 90% 2-propanol, 0.5M HCOOH	11.55	11.31	97.9
	Mn(II): 80 mL; 70% 2-propanol, 0.5M HCOOH	10.98	10.60	96.5
	Zn(II): 90 mL; 50% 2-propanol, 0.5M HCOOH	12.96	12.74	98.3
	Cd(II): 100 mL; 20% 2-propanol, 0.5M HCOOH	22.47	21.75	96.8
2	**Ca(II)–Cu(II)–Pb(II)–Cd(II)**			
	Ca(II): 100 mL; 90% 2-propanol, 0.5M HCOOH	8.03	7.88	98.1
	Cu(II): 70 mL; 70% 2-propanol, 0.5M HCOOH	12.66	12.30	97.2
	Pb(II): 140 mL; 30% 2-propanol, 1.5M HCOOH	41.50	39.58	95.4
	Cd(II): 100 mL; 20% 2-propanol, 0.5M HCOOH	22.62	21.92	96.9
3	**Mg(II)–Ni(II)–Fe(III)–Zn(II)–Cd(II)**			
	Mg(II): 100 mL; 90% 2-propanol, 0.5M HCOOH	4.87	4.71	96.7
	Ni(II): 90 mL; 80% 2-propanol, 0.5M HCOOH	11.82	11.59	98.1
	Fe(III): 100 mL; 70% 2-propanol, 0.5M HCOOH	11.31	10.97	97.0
	Zn(II): 90 mL; 50% 2-propanol, 0.5M HCOOH	12.93	12.46	96.4
	Cd(II): 100 mL; 20% 2-propanol, 0.5M HCOOH	22.56	21.58	95.7
4	**Ca(II)–Mn(II)–Fe(III)–Pb(II)–Cd(II)**			
	Ca(II): 90 mL; 90% 2-propanol, 0.5M HCOOH	7.98	7.76	97.2
	Mn(II): 90 mL; 80% 2-propanol, 0.5M HCOOH	12.06	11.76	97.5
	Fe(III): 100 mL; 70% 2-propanol, 0.5M HCOOH	11.24	10.69	95.1
	Pb(II): 110 mL; 30% 2-propanol, 1.5M HCOOH	41.44	39.89	96.3
	Cd(II): 110 mL; 20% 2-propanol, 0.5M HCOOH	23.00	22.59	98.2

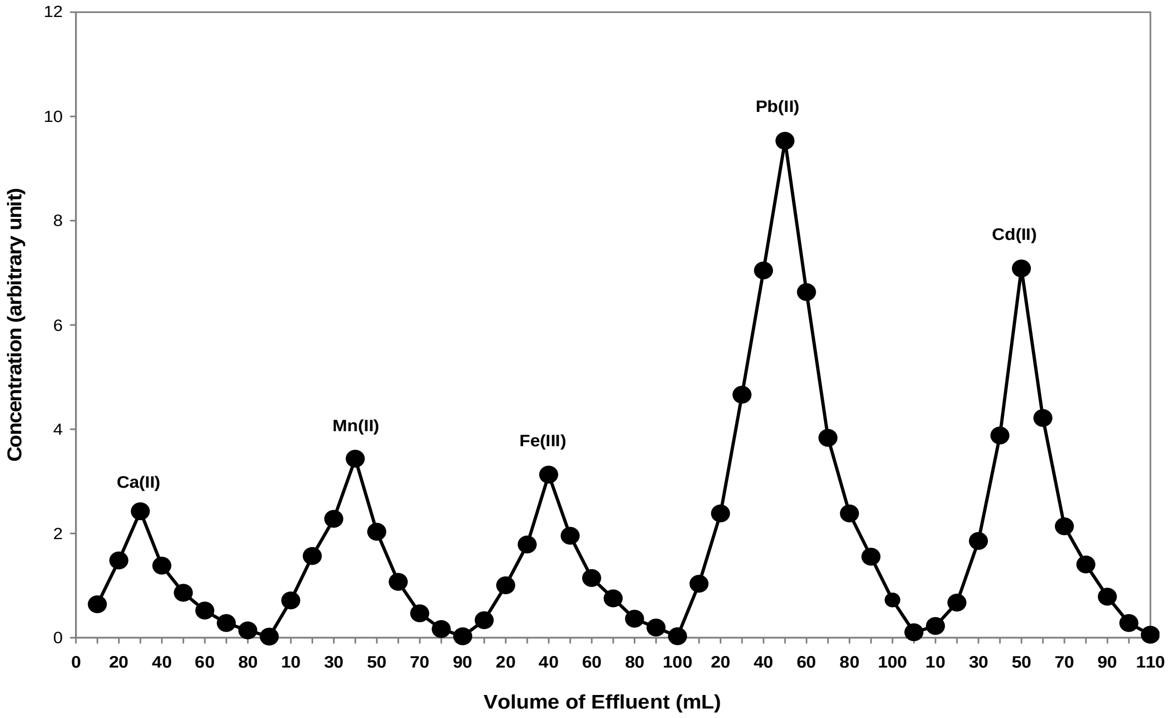

Fig. 1. Elution curve for Ca(II)–Mn(II)–Fe(III)–Pb(II)–Cd(II) in 2-propanol – water – formic acid system.

Preconcentration of metal ions and their determination

Sample water from the river Buriganga was collected at dry season and its pH and conductivity were measured (Table-5 & Table-6). In the preconcentration studies, one liter filtered sample water was passed through the resin column at maximum flow rate. The respective eluting agent for the two series Co(II)–Mn(II)–Pb(II)–Cd(II) and Mg(II)–Ni(II)–Fe(III)–Zn(II)–Cd(II) were passed through the column and the effluents were collected for each of the above metal. Organic solvent and acid were evaporated from the effluent. The fractions of effluent for the above metals were diluted and preserved in well-cleaned polythene container into a refrigerator for the determination of the quantity by Atomic Absorption Spectrophotometer (AAS).

The method of using Atomic Absorption Spectrophotometer (AAS) requires the construction of a calibration curve for the constituent being determined. So for every element a calibration curve was prepared using standard solution of the constituent within the proper linear range. In this work, all the metal ions at trace level were determined by AAS. The amount of Co(II), Mn(II), Pb(II), Mg(II), Ni(II), Fe(III), Zn(II) and Cd(II) found in the water of the river Buriganga at two location is represented in Table-9**.**

Table 5. Location, pH, specific conductivity and time taken for the preconcentration of one liter sample water of the river Buriganga.

River	Location	pH	Specific Conductance mS/cm	Time taken for preconcentration
Buriganga	Front site of the river at Mitford Hospital	7.45	9.3 x 0.1	15 hours and 30 minutes
	Front site of the river near Hazaribag Tannery	7.78	10.4 x 0.1	15 hours and 50 minutes

Table 6. Location, season, number and date of sample water collection have been shown in this table.

Location	Number of collection	Season of sample collection	Date and time of collection
Front site of the river at Mitford Hospital	2 sample	Dry	February 26, 2006 9.45 am.
Front site of the river near Hazaribag Tannery	2 sample	Dry	February 26, 2006 10.30 am.

For the determination of the metal ion Co(II), Mn(II), Pb(II), Mg(II), Ni(II), Fe(III), Zn(II) and Cd(II) by AAS, a calibration curve with the standard solutions for each of the respective metal was made before the sample solutions had analyzed.

Table 7. Separation and analysis of surface water of the river Buriganga for two series of metals on Amberlite IRA-420 in Cl$^-$ form, 14–52 dry mesh with atomic absorption spectrophotometric technique.

Column dimension : 7.5 cm × 0.74 cm (Resin 1.5g)

No of series	Eluting agent	Found (µg / liter)	
		Buriganga river at Mitford Hospital	*Buriganga river at Hazaribag*
1	**Co(II)–Mn(II)–Pb(II)–Cd(II)**		
	Co(II): 70 mL; 90% 2-propanol, 0.5M HCOOH	3.42	3.00
	Mn(II): 80 mL; 70% 2-propanol, 0.5M HCOOH	8.63	8.26
	Pb(II): 110 mL; 30% 2-propanol, 1.5M HCOOH	4.86	0.85
	Cd(II): 100 mL; 20% 2-propanol, 0.5M HCOOH	0.70	0.80
2	**Mg(II)–Ni(II)–Fe(III)–Zn(II)–Cd(II)**		
	Mg(II):100 mL; 90% 2-propanol, 0.5M HCOOH	124.08	67.24
	Ni(II): 90 mL; 80% 2-propanol, 0.5M HCOOH	2.89	2.93
	Fe(III):100 mL; 70% 2-propanol, 0.5M HCOOH	8.87	2.80
	Zn(II): 90 mL; 50% 2-propanol, 0.5M HCOOH	10.46	4.87
	Cd(II):100 mL; 20% 2-propanol, 0.5M HCOOH	0.65	0.76

Here, the metal ion Zn(II) has replaced by Pb(II) with proper eluting agent from the working series Co(II)–Mn(II)–Zn(II)–Cd(II) for the more significant result.

From the data presented in Table-7 it has been observed that the amounts of Mn(II), Mg(II), Fe(III) and Zn(II) are significantly higher in the surface water collected from the river Buriganga at Mitford Hospital than the same river at Hazaribag. Water of the river at Mitford Hospital is highly contaminated with hospital waste (both solid and liquid) and the waste of other industries located in this area. The composition of the hospital waste may consist of many toxic chemicals and drugs with different metal ions.

Conclusion

On the basis of distribution co-efficient data, a number of metal ion mixtures can be separated and analyzed successfully after selective elution from an anion exchange resin column in 2-propanol – water – formic acid system. Ni(II)–Mg(II), Mn(II)–Co(II), Mg(II)–Cd(II) and Mn(II)–Cd(II) mixtures could not be separated in absolute alcohol – water – formic acid system on anion exchanger. Again Ni(II)–Mg(II), Ni(II)–Co(II) and Cu(II)–Pb(II) mixtures could not be separated in acetonitrile – water – formic acid system on anion exchanger. Also the separation of Mg(II)–Pb(II) could not be worked out in ethylene glycol, 1,4-Dioxan and acetone – water – formic acid system on anion exchanger. Moreover, Ca(II)–Cu(II), Ca(II)–Mn(II), Ca(II)–Pb(II), Ca(II)–Fe(III) and Ca(II)–Cd(II) mixtures could not be worked out in absolute alcohol, ethylene glycol, 1,4-Dioxan and acetonitrile – water – formic acid system. But all these mixtures can be easily separated in 2-propanol – water – formic acid system on anion exchanger. So, 2-propanol has been proved to be useful solvent compared to absolute alcohol, acetone, ethylene glycol, 1,4-Dioxan and acetonitrile for the separation of above-mentioned mixtures of metal ions.

The most outstanding achievement of this piece of work is the success of separation and quantification of metal ions in a mixture with selective elution from an anion exchanger followed by atomic absorption spectrophotometric method at trace level.

Since ion-exchange is a continuous technique, this method (in combination with AAS) may be easily applied for the separation and determination of trace metals in natural water. This method can also be used in elemental trace analysis for biological system, clinical samples and in pharmaceutical analysis and monitoring of industrial effluents.

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