

## Spectrophotometric determination of Pt(IV) with N-decylpyridine-4-amine from succinate media

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N-decylpyridine-4-amine in xylene is used for the extractive separation of platinum(IV) from succinate media. Platinum(IV) has been extracted quantitatively with 10 mL of  $1 \times 10^{-4}$  M reagent in xylene from 0.025 M succinic acid. It is stripped from organic phase with water and estimated spectrophotometrically with stannous chloride. The effect of metal ions, acid, reagent concentrations and various foreign ions has been investigated. The method affords quantitative binary separation of platinum from base metals, and is applicable to the analysis of synthetic mixtures and alloys. The method is fast, accurate and precise. The molar absorptivity and Sandell's sensitivity of Platinum(IV)-N-decylpyridine-4-amine complex is found to be ( $4.9 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and ( $0.0078 \mu\text{g cm}^{-2}$ ), respectively which indicates the applicability of the method.

**Keywords:** Platinum(IV), N-decylpyridine-4-amine, Solvent extraction

The platinum is one of the important precious metals. It is widely used as catalyst in petroleum industry, chemical engineering. Solvent extraction of precious metals has been widely employed in chemistry and industry for many years<sup>1</sup>. Barkat and Mohmoud<sup>2</sup> proposed a method for platinum recovery from the losses of catalytic gauze in nitric acid manufacturing plant by solvent extraction using trioctylamine in kerosene. Platinum was then removed as diammonium hexachloroplatinate (precipitation using ammonium chloride). High purity of platinum over 97% was obtained after the decomposition of the precipitate. For the recovery of rhodium from spent catalyst, Kayanuma *et al.*<sup>3</sup> applied another technique that involves metal vapor deposition to form intermetallic compounds prior to dissolution in aqua regia. The rhodium recovery rate was over 99% as compared to 8% without the metal vapor processing. Mhaske and Dhadke<sup>4</sup> used a combination of Cynex-921 in toluene and the presence of stannous chloride

to separate PGMs. Levitin and Schmuckeler<sup>5</sup> employed gel permeation chromatography for separation of rhodium from palladium and platinum in acid solutions. Sephadex G-10 gel was able to bond with the three metals and then released them separately upon elution with an aqueous electrolyte solution. Platinum and palladium in chloride solution were reported to form complexes with thiocyanate ions, and the complexes then separated by polyTHF-impregnated filter<sup>6</sup>. Ion exchange technique was employed to recover platinum from spent industrial dehydrogenation catalyst, after leaching the catalyst with cyanide<sup>7</sup>. Lee and Kumar<sup>8</sup> found that Alamine 308 diluted in kerosene was able to separate Pt(IV) and Rh(III) from chloride solutions with the separation factor of 184.7. From thermodynamic analysis using the data of equilibrium constant and temperature, they concluded that the extraction phenomena follow the exothermic type processes. The recycling capacity of Alamine 308 was demonstrated at ~100% for 12 consecutive cycles of extraction/stripping. Kumar *et al.*<sup>9</sup> studied the LLE on Pt(IV) extraction from acidic solution using bis(2,4,4-trimethylpentyl) monothiophenic acid and found that sulphate solutions provided better extraction, loading with good kinetics compared to that of chloride and nitrate solutions. Superior extraction performance was achieved using Cynex 302 even without a salting-out agent. Recycling and reuse of extractant was demonstrated up to ten cycles with nearly 100% efficiency. A number of amine derivatives have been employed as extractant for recovering a range of heavy metals including Ni(II), Co(II), Pt(IV), Rh(III) via LLE<sup>10-12</sup>. Most of the research and development on PGMs separation/purification employed low concentration of PGMs in stock solution<sup>13</sup>. This is a part of process intensification for liquid-liquid extraction that can help to reduce the size of the equipments, the amounts of various chemicals involved, waste treatment duty, and environmental impact.

### Experimental Section

A JascoV-530 UV-Vis spectrophotometer with 1cm quartz cell and Systronics digital pH meter Model No. 802 was used for absorbance measurements respectively.

### Reagents and chemicals

#### Standard platinum (IV) solution

A stock solution of platinum(IV) was prepared by dissolving 1 g of platinum chloride hydrate in dilute analytical reagent grade hydrochloric acid (1M) diluted to 100 mL with distilled water as stock solution and standardized gravimetrically (Furman1963). A working solution  $100 \mu\text{g mL}^{-1}$  of platinum(IV) was prepared from it by diluting the stock solution with distilled water. Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in distilled water or dilute hydrochloric acid.

### Synthesis of extractant

#### Synthesis of mesoporous MCM-41

Magnetic material present in fly ash was removed and remaining portion of fly ash was used as precursor for synthesis of MCM-41. An alkali fusion method reported by Kumar *et al.*<sup>14</sup> was adopted to obtain the alkali fused coal fly ash (CFA) powder. The fusion process was carried out by mixing as received CFA powder and sodium hydroxide at a ratio of 1:1.2 and then mixture was heated in oven at 850 K for 4 h. The resultant product was cooled and milled overnight after that, the obtained alkali fused CFA powder was mixed with deionised water and aged for at least one day under stirring condition in an air atmosphere. The mixture was subsequently filtered to obtain sodium silicate solution. The cetyltrimethyl ammonium bromide (CTAB) was dissolved in 140 mL of warm deionised water and to that sodium

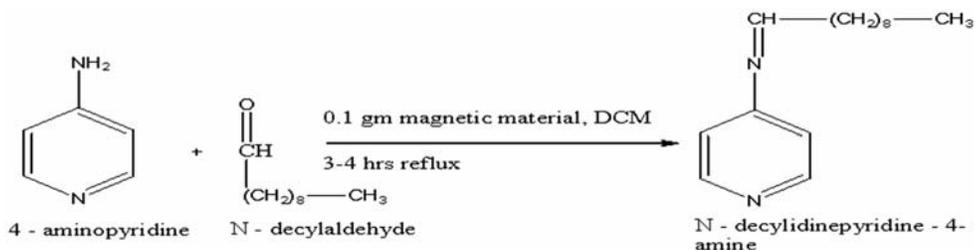
silicate was added with constant stirring up to 4 h, pH of the resulting solution was adjusted to 8-9 by using 1 M HCL, resulting gel was poured in to Teflon packed glass bottle and heated at 373 K for 48 h. White solid so obtained was filtered, washed with deionized water and dried at 60°C overnight. The template was removed by calcinations at 550°C for 4 h to obtain surfactant free mesoporous material MCM-41<sup>15,16</sup> which is used as metal catalyst for synthesis of extractant.

#### Step 1

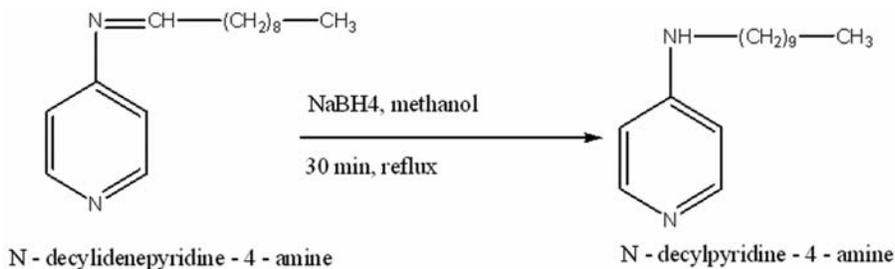
N-decylpyridine-4-amine was synthesized using equimolar proportion of N-decylaldehyde and 4-Aminopyridine (1 millimole each) in 20 mL DCM (4-aminopyridine is soluble in DCM) and 0.1 mg of metal catalyst (MCM-41) and was refluxed for 3-4 h. Then reaction mixture was cooled, the white solid product was separated by filtration and recrystallized from hot ethanol as white shiny needles (m.p. 68-70).

#### Step 2

Product of step 1 (Schiff base) was reduced by  $\text{NaBH}_4$  by taking equimolar amounts of Schiff base (N-decylidene-pyridine-4-amine) and  $\text{NaBH}_4$  in absolute methanol. Schiff base was dissolved in sufficient amount of absolute methanol and keep reaction mixture for 30 min at room temperature then reaction mixture keep in ice bath and  $\text{NaBH}_4$  added portion wise, when reaction completed then refluxed for 30 min, reaction mixture was cooled product was separated by filtration and recrystallized from hot ethanol (m.p. 245°C).



Step 1



Step 2

The purity of compounds was monitored using  $^1\text{H}$  NMR, FT-IR and mass spectra.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 0.87 (3H, t- $\text{CH}_3$ ), 1.87 (2H, d- $\text{CH}_2$ ), 1.26 (2H, d- $\text{CH}_2$ ), 3.4 (2H, s, - $\text{CH}_2$ ), 4.1 (1H, s, -NH), 6.5 (2H, d, d,  $J = 8$ , Hz, aromatic protons), 8.2 (2H, d,  $J = 8$  Hz, aromatic protons); IR: 2922 (=C-H), 1331(C-N), 1513-1640 (C=C), 3429  $\text{cm}^{-1}$  (N-H); Mass  $m/e$ : 236 (100.0%) (M+).

All chemicals used were of AR grade, doubly distilled water was used throughout the work.

#### General procedure

An aqueous solution containing 100  $\mu\text{g}$  platinum(IV) was mixed with sufficient quantity of sodium succinate to make its concentration 0.025 M in total volume of 25 mL of the metal solution, then  $p\text{H}$  was adjusted in the range 6-10 using dilute hydrochloric acid and sodium hydroxide in total volume of 25 mL, to effect quantitative extraction of pt(IV), The solution was transferred into a 125 mL separating funnel and shaken with 10 mL of  $1 \times 10^{-4}$  M N-decylpyridine-4-amine in xylene for just 15 s. After equilibration, the mixture was allowed to separate and the metal was stripped from the organic phase with two 10 ml portions of distilled water. The extract was evaporated to moist dryness. The residue was dissolved in minimum amount of 1 M hydrochloric acid and transferred in to 50 mL volumetric flask, 10 mL of 20% potassium iodide was added, the solution was mixed well and heated for 15 min in boiling water bath. To the cooled solution, 10 mL of 10% stannous chloride solution was added and diluted with distilled water containing 1 M hydrochloric acid in final concentration. The unstoppered flask was kept in boiling water bath for 2 min. The solution was then cooled and the absorbance of yellowish brown solution was measured at 403 nm against a reagent blank<sup>17</sup>.

#### Results and Discussion

Platinum(IV) reacts with extractant and forms 1:1 metal-ligand complex. The complex has maximum absorption at 403 nm. The molar absorptivity ( $4.9 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and Sandell's sensitivity ( $0.0078 \mu\text{g cm}^{-2}$ ), of the complex suggest that trace and ultra trace level quantities of palladium can be quantified with required accuracy and precision. The influence of various factors like  $p\text{H}$ , reagent concentration, choice of solvent and effect of foreign ions on the extraction efficiency of platinum(IV) have been studied for optimizing the conditions for the selective and rapid

extraction at trace level quantities.

#### Spectra

The absorption spectra of the Pt-N-decylpyridine-4-amine complexes were measured against a reagent blank, that of the reagent treated in a similar manner against a stannous chloride. The pt-N-decylpyridine-4-amine complex has yellowish colour and one strong absorbance peak at 403 nm. Therefore all the measurements have performed at 403 nm.

#### Extraction as a function of $p\text{H}$

Platinum(IV) was extracted in the  $p\text{H}$  range 6-10 in the presence of weak organic acids such as sodium salts of succinic acid (0.025M) out of different organic acids such as sodium salt of malonic acid, salicylic acid, tartaric acid, acetic acid. In tartaric acid, acetic acid media and mineral acid media very less extraction was found. There is 90% extraction in salicylate media at 6  $p\text{H}$ . There is quantitative extraction in succinic acid media, this shows that the equilibrium in the  $p\text{H}$  range 6-10 is favorable for the formation of ion pair complex from sodium succinate media. Hence, sodium salt of succinate is used for further studies.

#### Extraction as a function of N-decylpyridine-4-amine concentration

The extraction of platinum(IV) was carried out with varying concentration of N-decylpyridine-4-amine at constant sodium succinate concentration. The concentration was varied from  $1 \times 10^{-5}$ - $1 \times 10^{-1}$  extractant in xylene. The quantitative extraction of 100  $\mu\text{g}$  of platinum(IV) was observed at  $1 \times 10^{-5}$ , but in recommended procedure  $1 \times 10^{-4}$  concentration of N-decylpyridine-4-amine in xylene was used to ensure the complete extraction of metal ion. There was no adverse effect if one can use excess of extractant.

#### Extraction as a function of weak organic acid concentrations

The study of the chlorocomplexes of the platinum group metals clearly indicates that the strength of interaction with ion exchangers is highly dependent on the charge of the complex. Therefore, the platinum(IV) chlorocomplex is poorly extracted which is due to the charge of the complex as well as its labile character towards aquation. Hence, it is worthwhile to develop the solvent extraction procedure in weak organic acid media. One of the distinct advantage of the malonate media is the facility of controlling the concentration of complexing ligand, the ease of adjustment of  $p\text{H}$  and wide

differences in *pH* at which various metal ions form anionic complexes. It is observed that malonate media offers better phase separation possibly due to high stability of metal organic acid complex. The extraction of platinum(IV) was carried out at *pH* range 6-10 with  $1 \times 10^{-4}$  M N-decylpyridine-4-amine in xylene in the presence of varying concentration of sodium succinate, sodium salicylate, sodium malonate and sodium oxalate as weak acid media. The extraction of ion-pair complex of platinum(IV) was found to be quantitative in the range of 0.02-0.03 M sodium succinate concentration. With increased concentration of sodium succinate there is decrease in the extraction of platinum(IV). The decrease in the extraction at high acid concentration is presumably due to preferential formation of the succinate of the N-decylpyridine-4-amine. Therefore, a 0.025 M concentration of sodium succinate was used throughout this work. While extraction was found to be incomplete in mineral acid, sodium salicylate and no extraction from sodium malonate and sodium oxalate media.

#### Effect of diluents

It is well known that diluents have played an important role in the solvent extraction of metals. In the field of solvent extraction technology, the diluents constitutes a rather important part in the economy of the process. The diluents has to be cheap, shows practically negligible losses and impart good solubility to the extractant and its various compounds, it should be less toxic. The extraction of platinum(IV) was quantitative with hydrocarbon solvents such as benzene, toluene and xylene because the ion-pair complex has high value of distribution ratio in them, Where as chloroform (70%) and methyl isobutyl ketone (MIBK) (66%) were found to be very poor solvents, while there was no extraction of the complex, in carbontetrachloride, amyl alcohol, isoamylalcohol, *n*-butyl alcohol, 4-methyl-2-pentanol, amyl acetate. However, benzene and toluene are too toxic than xylene, it is recommended for further extraction procedure as it is a nonpolar solvent. In nonpolar solvent in absence of repulsive forces, the extraction is maximum while in polar solvent the association of cationic species with extraction is minimum, xylene doesn't form emulsion and offers better phase separation. Hence xylene was preferred as a diluent for further study.

#### Effect of stripping agents

Stripping is the reverse of extraction, so it should be promoted by those factors that affect extraction

negatively, such as acidic and salt media. Alkalis were unsuccessful because the anion complex adhered in the organic medium under these conditions. The stripping of platinum(IV) was quantitative with distilled water. The stripping was found to be incomplete with nitric acid (60%), sulphuric acid (40%) and with sodium chloride (20%), where as platinum(IV) was not stripped with ammonia, sodium hydroxide and water.

#### Extraction of platinum(IV) as a function of aqueous to organic volume ratio

The results of contacting different volume ratios of organic to aqueous phase have been studied that a preferred aqueous/organic (A/O) phase ratio and found to be 5:1 or less. This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of platinum(IV) when phase ratio (A/O) changed from 20:1 to 5:1, This may simply be due to the unavailability of reagent for metal extraction and so a crowding effect occurs at low phase ratio. However, in the recommended procedure the phase ratio is maintained as 2.5:1 so as to avoid the large consumption of sodium succinate.

#### Effect of time of equilibrium

The effect of time was observed for a period of 5 seconds to 30 min (handshaking). The extraction was found quantitative over the periods longer than 15 s. But to ensure the complete extraction of platinum(IV) 1 minute time was recommended. However, a prolonged equilibration period (10 min) was found to have an adverse effect on the extraction and should be avoided. Variation of the stripping period showed that a 30 s time was sufficient for quantitative recovery of platinum(IV) from organic phase.

#### Loading capacity of N-decylpyridine-4-amine

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of varying concentration. For a 10 mL, ( $1 \times 10^{-4}$ ) solution of N-decylpyridine-4-amine in xylene at 0.025 M sodium succinate concentration and a A/O of 2.5 : 1, the maximum loading capacity for platinum(IV) was found to be 7.5 mg.

#### Effect of various foreign ions on percentage extraction of platinum(IV)

Platinum(IV) was extracted in the presence of a large number of foreign cations and anions (Table 1).

Table 1 — Effect of foreign ions on the extraction of platinum(IV)

Foreign ion	Added as	Tolerance limit (mg)	Foreign ion	Added as	Tolerance limit (mg)
Pd (II)	PdCl <sub>2</sub> .H <sub>2</sub> O	2	Sr (II)	Sr (II)	30
Rh(III)	H <sub>2</sub> PtCl <sub>6</sub>	3	Pb (II)	Pb(NO <sub>3</sub> ) <sub>2</sub>	5
Au (III)	HAuCl <sub>4</sub>	3	Ti(IV)	K <sub>2</sub> TiF <sub>6</sub> .H <sub>2</sub> O	15
Ru (III)	RuCl <sub>3</sub> .H <sub>2</sub> O	2	U(VI)	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	10
Cr (III)	CrCl <sub>3</sub>	15	Bi(III)	Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O	10
Mn (II)	MnCl <sub>2</sub> .6H <sub>2</sub> O	20	Iodide	Iodide	30
Co (II)	CoCl <sub>2</sub> .6H <sub>2</sub> O	30	Fluoride	Fluoride	30
Ni (II)	NiCl <sub>2</sub> .6H <sub>2</sub> O	30	Bromide	Bromide	15
Cu (II)	CuSO <sub>4</sub> .5H <sub>2</sub> O	30	Oxalate	Oxalate	15
Fe (III)	NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	15	Nitrate	Nitrate	30
Fe (II)	FeSO <sub>4</sub> .7H <sub>2</sub> O	30	Thiourea	Thiourea	30
Zn(II)	ZnSO <sub>4</sub> .7H <sub>2</sub> O	30	Succinate	Succinate	30
Hg (II)	HgCl <sub>2</sub>	20	Chloride	Chloride	15
Mg (II)	MgCl <sub>2</sub> .6H <sub>2</sub> O	10	EDTA	EDTA	50
Sn (II)	SnCl <sub>2</sub> .2H <sub>2</sub> O	10	Tartarate	Tartarate	40

Table 2 — Separation and determination of platinum(IV) from binary mixtures

Composition of metal ions	Recovery Pt(IV)	Relative standard deviation (%)	Recovery added metal ions	Relative standard deviation (%)
Pt(IV)100; Pd(II)100	99.9	0.08	99.7	0.11
Pt(IV)100; Rh(III)100	99.9	0.08	99.6	0.18
Pt(IV)100; Au(III)100	99.9	0.08	99.6	0.18
Pt(IV)100; Ru(III)100	99.7	0.11	99.3	0.17
Pt(IV)100; Cu(II)1000	99.8	0.09	99.6	0.18
Pt(IV)100; Co(II)1000	99.9	0.08	99.8	0.06
Pt(IV)100; Ni(II)500	99.8	0.09	99.4	0.19
Pt(IV)100; Fe(III)500	99.9	0.08	99.9	0.16

The tolerance limit was set out as the amount of the foreign ion that could be present to give an error less than  $\pm 2\%$  recovery of platinum(IV). The reproducibility of extraction was investigated from six replicate measurements. After the phase separation, organic phase was stripped with two 10 mL portions of distilled water. The residue was dissolved in minimum amount of 1M HCL and transferred in to 50 mL volumetric flask and platinum(IV) was determined spectrophotometrically by stannous chloride method 14.

### Applications

#### Binary separation of Pt(IV) from Pd (II), Rh(III), Au (III), Ru (III), Cu (II), Co (II), Ni (II), Fe (III)

The method allowed separation and determination of platinum(IV) from a binary mixtures containing Pd(II), Rh(III), Au (III), Ru(IV), Cu(II), Co(II), Ni (II), Fe (III). In a typical experiment, solution containing 100  $\mu$ g of platinum(IV) was taken and known amounts of other metals were added. Platinum(IV) was estimated spectrophotometrically at 403 nm. The recovery of platinum(IV) and that of added ions was 99.5% and results are reported in (Table 2).

#### Analysis of synthetic mixtures

The separation of platinum(IV) from other Platinum group metals (rhodium, palladium and gold) was carried out by taking the advantage of differences in their optimum extraction and stripping conditions. The proposed method was successfully used in the determination of platinum(IV) from different synthetic mixtures. A solution containing 100  $\mu$ g of platinum(IV) was taken and known amounts of other metals were added. Under the optimum extraction conditions of platinum(IV) there is quantitative extraction of Pd (II), Rh(III), Ru (III) and Au (III) but the co-extracted metal ions cannot be back stripped by distilled water, thus, the reagent N-decylpyridine-4-amine is made selective towards platinum(IV) by taking the advantage of stripping used. The results of the analysis are reported in (Table 3).

#### Analysis of alloys

To ascertain the selectivity of the reagent, the proposed method was successfully used in the determination of platinum(IV) in alloys. The synthetic mixtures were prepared corresponding to the composition of alloy. The results of the analysis are reported in (Table 4). The average recovery of platinum(IV) was 99.5%

Table 3 — Analysis of synthetic mixture

Composition(ug)	Platinum(IV)	Average(%)	R.S.D <sup>b</sup>
	Found(ug)	Recovery	(%)
Pt,100: Ru, 500	99.8	99.5	0.07
Pt,100: Pd,500: Ru ,200	99.7	99.4	0.06
Pt,100: Pd ,500: Au, 200	99.9	99.6	0.05
Pt,100: Rh,500 : Au,200	99.7	99.4	0.06
Pt,100: Rh,500: Pd,200: Ru,200: Au,500	99.8	99.5	0.07
Pt,100: Pd,500: Ru,500: Au,200: Cu,500: Co,500: Ni,200: Fe,100	99.9	99.6	0.05

<sup>a</sup>Average of six determinations.

<sup>b</sup>RSD (%) = (standard amount-amount found/standard amount) × 100.

Table 4 — Analysis of synthetic mixtures corresponding to alloys

Alloys	Composition (%)	Amount of Platinum(IV)	R.S.D <sup>b</sup>
		found by proposed method <sup>a</sup> (%)	(%)
Platinum-Rhodium thermocouple alloy	90Pt,; 10Rh	88.8	0.77
Cooper's pen metal	50Pt, 38Ag, 12Cu	49.9	0.78

<sup>a</sup>Average of five determinations.

<sup>b</sup>RSD (%) = (standard amount-amount found/standard amount) × 100.

## Conclusion

The important features of the method proposed are as :

- 1 The present work points out that the synthesized extractant shows a good potential for the extraction of platinum(IV) from succinate media.
- 2 The extraction time is short and the extractant presents a good loading capacity and reusable.
- 3 The proposed method is used for rapid and selective separation of platinum(IV) from associated ions in their binary mixtures, synthetic mixtures and alloys [Rh(III), Pd(II), Au(III), Ru(III), Cu(II), Ni(II), Fe(III), Co(II)].
- 4 Low reagent concentration is required for quantitative recovery of platinum(IV).
- 5 It is free from interference of a large number of foreign ions which are associated with platinum(IV) in xylene in its natural occurrence.
- 6 It is applicable to the analysis of platinum(IV) in binary mixtures, synthetic mixtures and alloys.
- 7 The developed method is very simple, selective, reproducible and rapid; requires less time for separation and determination.

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