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ORIGINAL PAPER

Photometric determination of peracetic acid by reaction with potassium iodide solution

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Abstract

Peracetic acid (PAA) is a strong oxidizing agent and is considered an ideal disinfectant because of its excellent disinfecting effect at low concentration, low corrosiveness, and relatively low cost. Commercially available PAA solution is a mixture of PAA, acetic acid, and hydrogen peroxide. However, PAA naturally decomposes faster than hydrogen peroxide. Therefore, accurately quantifying the concentration of PAA in the PAA peroxide mixture via a simple method is important. In the present study, a new method was developed, in which the spectral change of I^- ion at 226 nm and the absorption value from the generated I_2 at 460 nm were used to determine the concentration of PAA, following a chemical reaction with 0.1 mM potassium iodide (KI) solution without the use of any other chemicals. In this work, the measurable concentration of PAA was as low as 0.0001 wt% (13.1 μM) and as high as 0.0015 wt% (197.2 μM), which matches well with high linearity (99.95% at 226 nm and 99.91% at 460 nm). This work could also be the high selectivity method toward PAA in the PAA peroxide mixture.

Keywords Photometric determination · Peracetic acid · Potassium iodide · Spectral change

Introduction

Peracetic acid (PAA, CH_3COOOH) is a strong oxidizing agent [1] used as a disinfectant in food [2] and wastewater treatment [3, 4], as a bleaching agent in the paper [5] and textile industries [1, 6], and as a common reagent in synthetic organic chemistry [7]. For example, bamboo knit fabrics with a high degree of whiteness, high water absorbency, and high tenacity were obtained with low energy consumption through PAA bleaching processes [1], and PAA was found to be a good material for washing fruit and improving postharvest life [2]. The ferrous iron-activated PAA system and its enhanced systems had been successfully used in degrading organic pollutants [8, 9], and PAA has also been used to effectively kill harmful microorganisms such as bacteria, viruses, and protozoan cysts in wastewater [4, 10, 11]. As such, PAA is considered an eco-friendly disinfectant because it exhibits an excellent sterilization effect even at low concentrations and because the final decomposition products—oxygen (O_2), water (H_2O), and acetic acid (CH_3COOH, AA)—only weakly affect the environment and the human body [12].

PAA is a fat-soluble, strong antibacterial agent with a redox potential higher than that of hydrogen peroxide (H_2O_2) [13, 14]. Commercial PAA solution is a mixture of PAA, AA, and H_2O_2 [15]. H_2O_2 tends to degrade slower than peroxycarboxylic acids [3]. Therefore, accurately measuring the concentration of PAA in a PAA peroxide solution is important for such solutions to be properly used in various applications.

Conventional methods for measuring the concentration of PAA include titration (with NaOH [16] or cerium(IV) sulfate [17]), potentiometric and amperometric methods (in conjunction with a glassy carbon (GC) indicator electrode [18], Pt and Au electrodes [19], porphyrin-functionalized Au nanoparticles [20], or an Au (111)-like Au electrode [21]), and spectrophotometry (titanium oxide oxalate

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(TiO-Ox):*N*,*N*-diethyl-*p*-phenylenediamine (DPD)/I^- and TiO-Ox:2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) [15], DPD [22], and ABTS and Fe^{2+}/KI [23]). The titrimetric method needs a long time process and shows low sensitivity. The chromatography methods require expensive operating instruments even though it has high sensitivity [24]. Among these methods, spectrophotometry is widely considered the most convenient, fastest, and most accurate analysis technique for quantitative analysis.

This study was conducted to develop a simple and reliable spectrophotometric method for the determination of PAA in PAA peroxide solution using potassium iodide (KI) solution without any other chemicals. In principle, the absorbance spectrum of I^- ion and I_2 (or I_3^-) shows a maximal peak at 226 nm and 460 nm (or 350 nm), and the intensity of these peaks are proportional to their concentration [25]. This method is based on the rapid oxidation reaction between KI and PAA. The chemical reaction between KI and PAA stoichiochemical forms a complex of CH_3COOK and free I^- ion which is converted to I_2 and I_3^- ion. This chemical reaction quickly results in a decrease in the concentration of total I^- ion and a formation of I_2 and I_3^- ion [24]. Therefore, the increase of the absorption peak of I_2 (or I_3) and the decrease in the absorption peak of total I^- ion can be in proportion to the concentration of the reacted PAA in the PAA solution. The reaction equation for KI and PAA is as follows:

$$CH_3COOOH + H_2O \leftrightarrow CH_3COOH + H_2O_2,$$

$$2KI + CH_3COOOH + CH_3COOH \rightarrow 2CH_3COOK + I_2 + H_2O,$$

$$I_2 + H_2O \leftrightarrow HOI + I^- + H^+,$$

$$I_2 + I^- \leftrightarrow I_3^-.$$

In the present study, we validated whether the change of the I^- ion spectral peak at 260 nm and the absorption value at 460 nm (or 350 nm) from the generated I_2 (or I_3^- ion) upon the reaction of KI with PAA could be used for the quantitative analysis of PAA without interference by coexistent H_2O_2 and AA in the PAA peroxide mixture.

Experimental

Chemicals

KI (DAEJUNG Chemical, Republic of Korea), PAA (Dong Myung ONC, Republic of Korea), standard H_2O_2 solution (Sigma-Aldrich contains inhibitor, 30 wt% in H_2O, ACS reagent), and AA (DAEJUNG Chemical, Republic of Korea, 99.7 wt%) were used as chemical reagents. All solutions were prepared in distilled water.

Apparatus

Absorption spectra from 200 to 500 nm and fixed-wavelength absorption measurements at 226 nm were acquired using a JASCO V-760 UV–Vis spectrophotometer with a 10 mm cell.

Determination of concentration of PAA

A 0.1 mM KI solution was prepared as a reagent agent for the determination of PAA in the PAA solution. PAA working solutions were prepared from the dilution of the commercial 20 wt% PAA solution. Concentrations of H_2O_2 and PAA coexistent in the commercial PAA solution were standardized colorimetrically using *N*,*N*-diethyl-*p*-phenylenediamine (DPD), and titanium oxide oxalate (TiO-Ox) (shown in the supplemental information file) [15, 22]. A 0.1 mL aliquot of each PAA solution was reacted with 0.9 mL of 0.1 mM KI solution in a 1.5 mL microcentrifuge tube for 2 min. The respective change in absorbance at 226 nm and 460 nm was subsequently measured for each product solution in a 10 mm glass cuvette.

Results and discussion

Absorption peak of the KI reagent solution

Spectrophotometric methods have been widely accepted as the most convenient analytical techniques for routine quantitative analysis. Diverse chromogenic agents such as N,N-diethyl-p-phenylenediamine (DPD) and ABTS were used for forming a colored complex. They are relatively expensive, and the sample preparation process is complicated [26]. It had been widely reported that PAA could react with excess KI to yield yellow-colored I_3^- [22]. Xiao et al. (2019) have reported a method for determining the concentration of PAA via measurement of the maximal absorption peak of I_3^- generated by the rapid oxidation of KI by PAA [24]. However, KI concentration and pH value are important factors to form the yellow-colored I_3^- in the study, Therefore, this method requires a high concentration of KI stock solution (1.2 M) and phosphate buffer solution, in which the analysis cost increases and more sample preparation step was required. We therefore developed a method that requires only a low-concentration KI solution (0.1 mM) to measure the concentration of PAA in a PAA solution within a single sample preparation step.

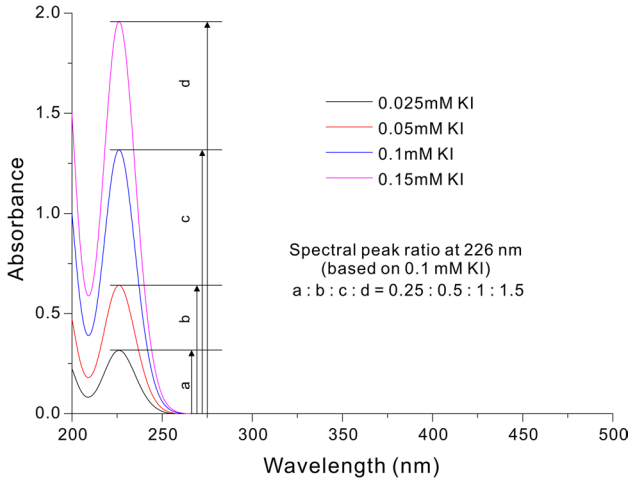

Fig. 1 Absorbance spectra of the KI reagent solution at concentrations ranging from 0.025 to 0.15 mM

First, to confirm a linear relationship between the absorbance and concentration of I^- ion from KI, we recorded and compared the absorption spectra of 0.025, 0.05, 0.1, and 0.15 mM KI solutions (Fig. 1). The spectrum of I^- in a pure KI solution shows a sigmoidal curve with a wavelength of maximum absorption of 226 nm and no peak at wavelengths longer than 280 nm. Three different iodine species showed distinct peaks: 226 nm (I^-), 350 nm (I_3^-), and 460 nm (I_2) [25]. KI solution is a metal-halide salt featuring a strong ionic bond between the K^+ cation and the I^- anion. Therefore, peaks of other iodide forms such as I_2 (460 nm) and I_3^- (290 and 350 nm), were not observed in the spectrum of pure KI solution (Fig. 1). The absorption values of the KI solutions at 226 nm were 0.32 (0.025 mM), 0.64 (0.05 mM), 1.32 (0.10 mM), and 1.96 (0.15 mM). These values are proportional to the KI concentration (0.025–0.15 mM) (Fig. 1). However, the spectrum of 0.2 mM KI was unstable near the peak area (shown in the supplemental information file). The rapid oxidation reaction of KI and PAA resulted in the fast conversion of I^- ion to I_2 and I_3^-, which resulted in a decrease in the intensity of the absorption peak of the I^- ion. In the present study, we selected 0.1 mM KI solution as a standard reagent solution to determine the PAA concentration because the intensities of the absorption peaks of 0.025 and 0.05 mM KI solutions at 226 nm are too weak to measure the decrease in the concentration of I^- ion by reaction with PAA.

Determination of PAA concentration by spectral delta value at 226 nm and absorption value at 460 nm from reaction with KI reagent solution

After the chemical reaction of each PAA sample solution, we calculated the spectral delta value at 226 nm by comparing the absorption peaks with that of a blank sample containing the 0.1 mM KI reagent solution, mixed with the same volume of distilled water. The reaction time (2 min) was determined by measuring the time until the increase in the spectral delta value of 226 nm no longer appeared. The spectral delta value of I^- at 226 nm increased initially and then reached a plateau after 2 min (Fig. 2). To validate the linear relationship between the spectral delta value at 226 nm and the PAA concentration, we recorded each spectrum and compared them (Fig. 3). It was noted that the wavelength of maximum absorption near 226 nm shifted to shorter wavelengths with increasing concentration of PAA (Fig. 3A). The spectral delta values at 226 nm were only proportional to the PAA concentration when the KI reagent solution was reacted with PAA samples of which concentrations were lower than 0.0015 wt%. For instance, the spectral delta value of the 0.0010 wt% PAA sample was twofold greater than that of the 0.0005 wt% PAA sample (Fig. 3A). However, the respective PAA sample solution of 0.0020 wt% and 0.0030 wt% showed delta value ratios of 3.68 and 4.67, which were lower than the expected value of 4 and 6, respectively. After the chemical reaction of each PAA sample solution mixed with 0.1 mM KI reagent solution, the formation of I_2 and I_3^- was observed (Fig. 3B). The intensity of the peak at 460 nm represents the generated I_2, which was proportional to the concentration of PAA. However, the spectral region including the peak of I_3^- between 260 and 380 nm, was unstable (Fig. 3B and supplemental information file). Therefore, it was concluded that the spectral delta value at 226 nm and absorption peak at 460 nm can be used to determine the concentration of the PAA solutions, based on the chemical reaction between KI and PAA.

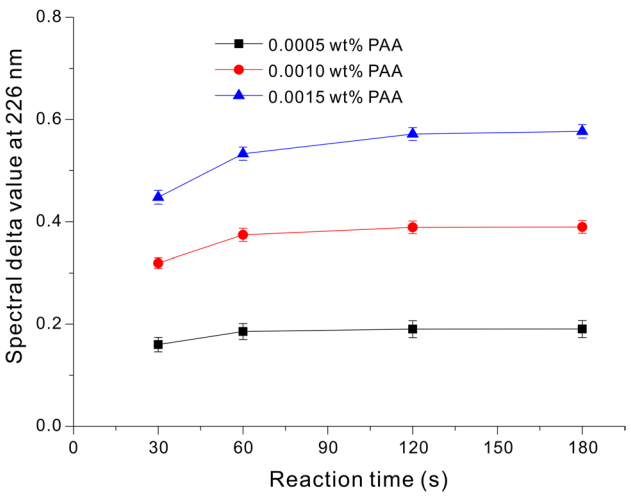

Fig. 2 Effect of reaction time on the spectral delta value (226 nm)

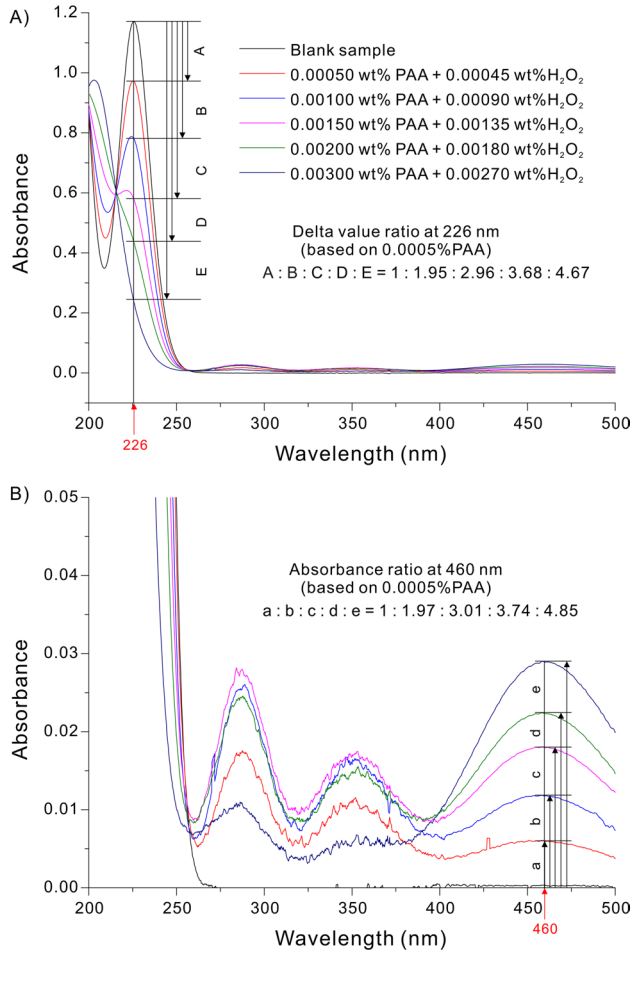

Fig. 3 **A** Spectral delta values at 226 nm and **B** absorption values at 460 nm of the solutions obtained after the oxidation of 0.1 M KI reagent solution with various concentration of PAA and H_2O_2, **B** shows the same spectra with an expanded absorbance axis

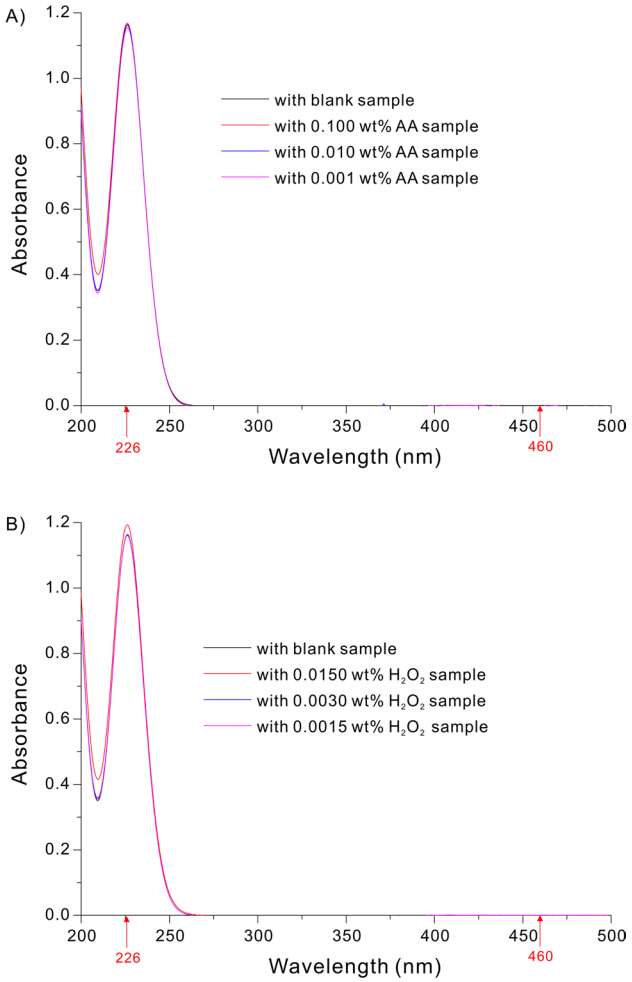

Fig. 4 Absorbance spectra showing the effect of various amounts of **A** AA and **B** H_2O_2 on the absorption peak of I^- ion (226 nm) and I_2 (460 nm)

Effect of AA and H_2O_2 on the absorption peak of I^- ion

When PAA dissolves in water, it decomposes into H_2O_2 and acetic acid (AA), which subsequently decompose into H_2O, O_2, and CO_2 [27]. To determine whether the coexistent AA and H_2O_2 in a PAA solution affect the absorption peak of I^- at 226 nm and of I_2 at 460 nm, 0.1 mM KI reagent solution was added to solutions with various concentrations of AA and H_2O_2 (Fig. 4). In the case of AA, a 0.1 wt% AA solution (66.6 times higher than the applicable maximum PAA concentration (0.0015 wt%)) did not affect the absorption peak of I^- ion and I_2 (Fig. 4A). In the case of H_2O_2, the absorption value at 226 nm slightly increased when a 0.015 wt% H_2O_2 solution was used; however, this concentration is also 10 times greater than the applicable maximum concentration of PAA (0.0015 wt%). When the standard KI reagent was added to a sample with 0.0030 and 0.0015 wt% H_2O_2 solutions, no substantial difference was observed between its absorption spectrum and that of a blank sample (Fig. 4B). It has been widely reported that both PAA and the coexistent H_2O_2 could react with excess KI to yield yellow-colored I_3^-. However, the rate of the reaction between KI and H_2O_2 (9.50×10^{-3} M^{-1} s^{-1}) was about five orders of magnitude slower than that of the reaction between KI and PAA (4.22×10^{2} M^{-1} s^{-1}) in pure water [24]. Moreover, the slow oxidation of excess KI by H_2O_2 to yield yellow-colored I_3^- could be further delayed at low concentration of KI. In the present study, a low concentration of KI solution (0.1 mM) was used for the determination of PAA.

The wt% concentration of coexistent AA and H_2O_2 could not be 2 times higher than the concentration of PAA in the solution prepared by diluting commercial PAA peroxide solution with water. In fact, 0.0010 wt% PAA solution showed 0.0010 wt% PAA and 0.0009 wt% H_2O_2 (shown in the supplemental information file). These results suggest that

the coexisting AA and H_2O_2 in PAA peroxide solutions with lower than 0.0015 wt% do not affect the measurement of the absorption peak of I^- ion and I_2. Therefore, the changes in the spectral delta value at 226 nm and absorption peak at 460 nm indicate only the concentration of a peracetic acid ion in the PAA peroxide solution (Fig. 4A, B).

Based on the aforementioned results, the calibration curve for the PAA concentration was plotted using the average spectral delta value at 226 nm and the absorption value at 460 nm, which corresponds to our experimental conditions (with high linearity of 99.95% at and 99.91%, respectively) (Fig. 5). The sensitivity was measured to be as high as 0.0015 wt% (197.2 µM), and the lower limit of detection was 0.0001 wt% (13.1 µM) PAA. Spectrophotometric methods are widely used for routine quantitative analysis due to their relatively low cost, easy operation, and high sensitivity. Compared to other photometric determination methods (Table 1), the limit of quantification (LOQ) value of the present study is much higher than other methods using DPD and ABTS. This helps to check the quality of commercial PAA stock solutions with a 2-min measurement process. Moreover, the proposed KI method is a simple process with only one single step using a low KI solution. Thus, this one-step measurement approach using the absorption values at 226 and 460 nm could validate and simultaneously obtain the concentrations of the PAA solutions.

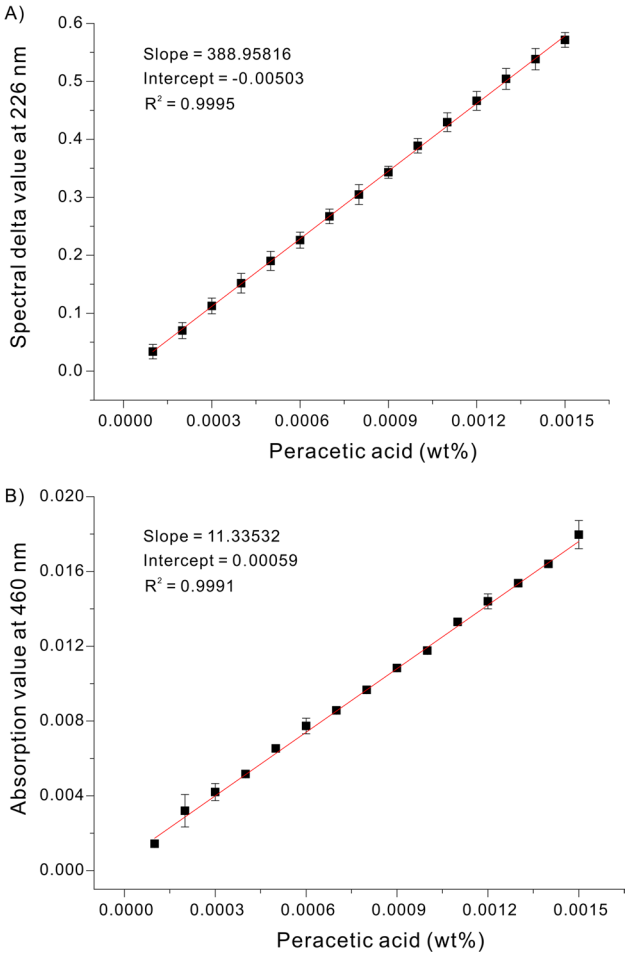

Fig. 5 Calibration curve for the spectrophotometric determination by **A** spectral delta values at 226 nm and **B** absorption values at 460 nm ($n=3$)

Conclusions

The chemical reaction between KI and PAA stoichiochemically forms a complex of $K^+CH_3COOOH^-$ and free I^- ion, which is rapidly converted to I_2 or I_3^- ion. The decrease in the concentration of the KI solution and the generated I_2 concentration are proportional to the concentration of PAA in the samples. This proportion was easily detected using a photometric method based on the spectral delta value at 226 nm and the absorption value at 460 nm. The measurement of the absorption peak of I^- and I_2 was not affected by the presence of AA and H_2O_2 in the PAA solutions. The spectral delta value at 226 nm and absorption value at 460 nm showed a highly linear relationship with the applied PAA concentration. With the proposed method, the lower limit of detection for PAA is 0.0001 wt%, and the applicable maximum concentration of PAA is 0.0015 wt%. Overall, the spectral delta value at 260 nm and absorption value at 460 nm could be used as an alternative method for the rapid and simple determination of PAA using only KI as a single reagent.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s44211-022-00265-6.

Table 1 Comparison with other photometric measurement for determination of PAA

Method	Limit and maximum of concentration of PAA (µM)	Reaction time	Literature
KI solution	13.1–197.2	2 min	In this study
TiO-Ox:DPD/I- and:ABTS	0.06–32.8	1 min	[15]
DPD	1.3–21.7	< 1 min	[22]
KI and Mo(VI)	0–70	30 s	[24]
ABTS	< 0.01	< 10 min	[26]

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Data availability All data generated or analyzed during this study are included in its supplementary information file.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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