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Automated High-Performance Liquid Chromatography Determination of Hydrocarbon Types in Crude Oil Residues Using a Flame Ionization Detector

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An automated high-performance liquid chromatographic (HPLC) analysis has been developed for the determination of saturates, aromatics, and resins in deasphaltened crude oil residues that boil above 343 °C (650 °F). By use of the Tracor LC flame detector, response factors were calculated for six crude residues that cover a wide range of compositions. These gave uniform response and normalization of corrected areas results in weight percent. A comparison with an open-column (gravimetric) method showed some differences in three of the residues. These differences were ascribed to overlapping of types that occurred in the open-column fractions and the use of different mobile and stationary phases for the two different methods. Analysis time for the HPLC method is 30 min, and approximately 20 samples can be analyzed per day. The method should also be applicable to any other fossil fuel samples, such as shale oil or coal liquids, that boil above 340 °C.

There has always been a need in the petroleum industry for group-type analysis of hydrocarbons. This includes the determination of saturates, aromatics, resins, and asphaltenes (SARA), which have traditionally been determined by open-column chromatography on silica or alumina columns after precipitation and removal of the asphaltenes (*1*, *2*).

The analytical method for SARA analysis currently used at Phillips Petroleum Co. (*3*) is labor intensive and requires approximately 8 h to complete one sample (although, one operator can run 10 samples at the same time and complete them in two days). HPLC methds for SARA have been reported (*4-10*) usually analyzing a deasphaltened sample. They use the refractive index detector for quantitation, and this can be tedious as column chromatography fractions must be prepared to calibrate the detector for different samples. A detector finish is the only route to a completely automated analysis, and for years attempts have been made to utilize the flame ionization detector (FID), which has been so successful as a universal detector in gas chromatography (*11*, *12*). For HPLC use an interface must be employed to remove the mobile phase. Moving belts, wires, and chains (*13-21*) have all been used to remove the solvent and transport the solute to the FID. These systems suffered problems with noise and reproducibility.

Rotating disk flame detectors have been reported by Szakits et al. (*22*) and by Dixon (*23*). The Tracor 945 LC/FID (*24*) is an improved version of the detector described by Dixon. It was first reported at the 1983 Pittsburgh Conference and appeared to have overcome many of the problems of earlier HPLC/FID detectors.

This report describes the development of an HPLC separation for saturates, aromatics, and resins in deasphaltened crude oil residues and the evaluation and use of the Tracor 945 LC/FID for quantitation.

EXPERIMENTAL SECTION

HPLC Method. *Apparatus.* The chromatographic system consisted of two Waters 6000A pumps, a Waters WISP 710B autosampler, a Waters 720 system controller, two Valco EC6W six-port valves with electric actuators, and a Hewlett-Packard 3390A recording integrator. An Isco Foxy 2200 fraction collector was used to prepare pure fractions. The following columns were used: two Whatman 10-μm PAC 25.0 cm × 4.6 mm i.d. (aminocyano) and one Supelco 5-μm LC.CN 25.0 cm × 4.6 mm i.d. (cyano)

Reagents. The mobile phases used were Burdick and Jackson UV grade *n*-hexane and methyl *tert*-butyl ether (MTBE).

Sample Preparation. Speight et al. (*25*) have made specific recommendations for removal of asphaltenes from crude oils and residues, and these recommendations were followed in deasphaltening our samples. A 2-g portion of sample was placed in a 130-mL wide-mouth bottle with 60 mL of *n*-hexane. The bottle was shaken until suspension of the sample was complete and was then allowed to stand overnight at room temperature (usually 16-18 h). The sample was filtered through a no. 1 Whatman filter paper, and the residue was washed with *n*-hexane until the filtrate was colorless. The filtrate was collected in a 100-mL volumetric flask and diluted to volume with *n*-hexane. This solution was used for the HPLC analysis, after dilution to a suitable concentration with *n*-hexane (usually 2-4 mg/mL), and for the open-column method described below. Thus both tests were carried out on the same stock solution.

Procedure. The configuration of the chromatographic system is shown in Figure 1. The 720 system controller regulated the switching of valves and controlling of pumps, and the schedule for this is given in Table I. The settings for the autosampler are

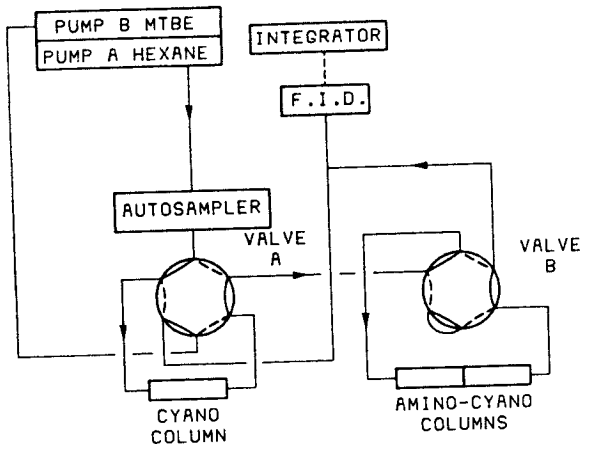

Figure 1. Block diagram of the chromatographic system used in the separation of hydrocarbon types: valve position 1 shown by solid line and valve position 2 shown by dotted line.

Table I. Gradient, Valve Switching, and Autosampler Conditions for Hydrocarbon Type Analysis

Gradient Schedule

time, min	flow rate, mL/min	% flow from pump A	% flow from pump B	curve used
initial	1.5	100	0	
15	1.0	0	100	11[a]
24	1.5	100	0	11[a]

Valve Switching Schedule

time, min	valve	action[b]
4.8	A	on
6.7	B	on
23.9	B	off
24.1	A	off

Wisp Auto Sampler Settings

run time	25 min
equilibration time	5 min
system message	76–01 (reduced sample draw rate)

[a] Curve 11 gives isocratic flow during the designated time period. [b] ON switches valves from initial position to second position. OFF returns the valves to the initial position.

also shown in this table. The Tracor fuel gases were set at the following rates: detector, hydrogen at 140 mL/min, air at 0.4 L/min; cleaning flame, hydrogen at 200 mL/min, oxygen at 200 mL/min. The block temperature controller was set to the following thermocouple readings: 1, 67 °C; 2, 69 °C; 3, 72 °C; 4, 68 °C (for location of thermocouples see ref 26).

Pump A pumps hexane at a flow rate of 1.5 mL/min with valves A and B in position 1. (See Figure 1). An injection of 25 μL of sample is made. The sample passes first through the cyano column where the most polar molecules (resins) are strongly retained. The neutral and slightly polar molecules pass on to the two aminocyano columns. Valve A is switched to position 2 (see Figure 1) in which the cyano column is isolated but the *n*-hexane eluent flow continues. As soon as the saturate peak has emerged from the aminocyano columns, valve B is switched to position 2. This allows the saturates to proceed to the flame detector while the retained compounds (aromatics) are backflushed out of the aminocyano columns. After the saturates and aromatics have eluted, pump A is switched off. Pump B then pumps MTBE at 1 mL/min through the cyano column and backflushes the polar compounds (resins) off the column to the flame detector. They form a sharp peak that emerges with the solvent front.

After the resins peak has eluted, the system is returned to the initial conditions and the cyano column is reequilibrated with hexane before the next injection.

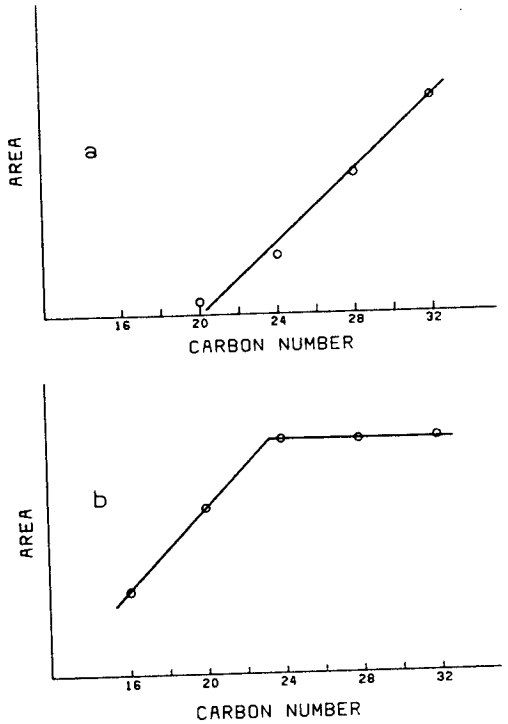

Figure 2. Plots of *n*-paraffin carbon number vs. area response: (a) block temperature is 150 °C and (b) block temperature is 68 °C.

Open-Column Method. A glass chromatography column (50 cm × 11.0 mm i.d.) is dry packed with 20 g of activated alumina (neutral, Brockman activity 1, 80–200 mesh). After the sample has been deasphaltened with *n*-hexane a 25-mL aliquot containing 0.5 g of sample is charged on the column, eluted with 45 mL of *n*-hexane, and the saturate fraction collected in a weighed flask. The aromatics fraction is eluted from the column by using 75 mL of toluene and collected in another weighed flask. The resins fraction is eluted from the column with 50 mL of methanol, followed by 50 mL of methylene chloride, and collected in a third weighed flask.

The solutions are evaporated to dryness, the weight of each fraction is determined, and the composition of the sample is calculated (Note: some alumina is present in the resins fraction and must be removed by filtration of a methylene chloride solution of the fraction).

RESULTS AND DISCUSSION

The automated analysis of crude oil residues described here uses the Tracor 945 LC/FID for quantitation and the columns and switching scheme described in the Experimental Section. The Tracor uses a heated interface to remove the mobile phase, and it was considered important to determine what effect the heated zone had on our specific analytical requirements.

Detector Evaluation. A metal disk with a peripheral quartz fiber belt around its perimeter rotates within a heated block (*24*). After the mobile phase reaches the belt, solvent is removed by heat and a gentle air flow to a vacuum pump. The eluate travels three-quarters of a rotation and passes between the jets of a dual-jet FID where it is detected. The belt immediately passes through a much larger flame that burns any remaining organic matter off the belt.

The reason for using an FID is its uniform response to hydrocarbons as demonstrated in gas chromatography (*11*, *12*). In our application it was important to determine if either the solvent removal interface or the particular geometry of the FID affected its response to different hydrocarbon types or different molecular weights.

As received, the detector had block settings of 150 and 180 °C. At the lower temperature a series of *n*-paraffin solutions were injected and area plotted vs. carbon number (see Figure

2a). Instead of obtaining equal areas for equal weights the response increased with carbon number up to carbon no. 32. Apparently the lower molecular weight paraffins are being lost from the belt in the heated zone. To reduce the block temperature, Tracor developed and installed an upgrade that provided complete control of block temperature from 60 to 160 °C. No provision for setting or measuring the block temperature was provided, so four thermocouples were installed in the block. The details of this modification have been reported previously (*26*). These give a temperature profile around the block showing that block temperatures stabilize quickly after changes are made and hold a given value within a degree. The cleaning flame also imparts some heat to the block, and to minimize this, the fuel gases were lowered to 200 cm^3/min. Below these settings considerable noise and flame instability occurred. A muffin fan was placed where it could blow across the detector to remove heat, and the detector was operated with the cover removed. With the block set to the lowest position the detector operates at 69 °C (no. 2 thermocouple) giving a good base line.

With the detector at these conditions the *n*-paraffin series was analyzed again, and Figure 2b shows the response plot obtained. It is apparent that for C_{24} and above the response does not change with molecular weight and that below C_{24} the areas are reduced. A large number of samples analyzed for SARA are crude oil residues with boiling points above 343+ °C (650+ °F). Because of the partial loss of C_{20} and lighter it was decided to restrict use of the HPLC method to these particular residues or samples with higher boiling points.

Columns and Valve Switching. A study of previously reported HPLC analyses for hydrocarbon types revealed that a variety of columns, valve-switching schemes, and solvent choices had been used (*4–10*). Silica and alumina columns were not considered in our work as they can adsorb water and polar compounds that cause retention time changes. An important criterion for an automated analysis is that the retention times be very consistent, so only bonded-phase columns were used.

None of the previously reported systems were satisfactory for our purposes, and a new chromatographic system was developed (Figure 1). This uses a cyano (alkylnitrile bonded to silica) column to separate the saturates and aromatics from the resins followed by two aminocyano (alkylnitrile plus alkylamine bonded to silica) columns to separate the saturates and aromatics. All flows are directed through the FID detector.

A cyano column was chosen for the first separation. Saturate and aromatic components elute rapidly (approximately 4.5-mL retention volume with *n*-hexane), and resins are strongly retained. With other bonded columns (amino and aminocyano) the aromatic components elute slowly. The cyano column is then isolated by switching valve A to position 1 until after the saturate and aromatic peaks have passed through the FID. The cyano column is then backflushed with a polar solvent to elute the resins.

Choice of Polar Solvent. Methylene chloride is frequently used to elute resins from open columns (*1, 2*). It is an excellent solvent for the resins and has a low boiling point (40 °C), which is desirable for the FID. In our use, however, two problems appeared. Severe corrosion of the chromium-plated brass block was attributed to the presence of traces of HCl in some batches of methylene chloride. While the resin was being eluted from the detector the peak suddenly went negative and recovered very slowly so that the peak could not be integrated. These problems make methylene chloride undesirable for use with this detector. The use of methyl *tert*-butyl ether (MTBE) for elution of resins has been reported (*7*), and its boiling point is suitably low (56 °C). This solvent was evaluated and performed well. It did not have the problems found with methylene chloride. When the changeover from hexane to MTBE occurs however, the chromatogram base line rises as the solvent point passes through the detector. Because this occurs as the resin peak elutes, it makes accurate integration difficult. A change in flow rate from 1.5 to 1.0 mL/min reduced the amount of solvent in the detector and eliminated this step in the base line.

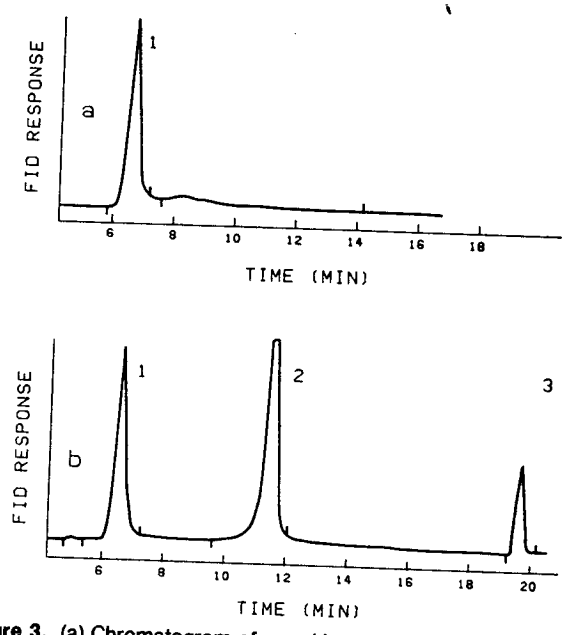

Figure 3. (a) Chromatogram of a residue sample with no backflush. Peak 1 is saturates. (b) Chromatogram of same residue sample with backflush. Peak 1 is saturates; peak 2 is aromatics; and peak 3 is resins. Conditions are as described in the Experimental Section.

Table II. Capacity Factors (k') for Hydrocarbons[a]

compd	k'
n-eicosane	0.08
n-dotriacontane	0.08
saturates, refinery residue 400+ °C (750+ °F)	0.08
nonylbenzene	0.51
cyclohexylbenzene	0.51
tetralin	0.62
1-methylnaphthalene	1.18

[a] Compounds eluted with *n*-hexane through one cyano column and two aminocyano columns.

Amino (alkylamine bonded to silica) and aminocyano columns were evaluated for the separation of saturates from aromatics and both performed equally well. However, the higher molecular weight aromatics are not as strongly retained by the aminocyano column (*7–9*) and should be easier to backflush off this column than off the amino column.

Figure 3a shows the saturates and aromatics as they elute from the two aminocyano columns (without backflush). It can be seen that the majority of the aromatics are strongly adsorbed and cannot be measured. When the flow is reversed by switching valve B to position 2 after the saturate peak has eluted, however, the aromatics are backflushed and form a sharp peak that can be integrated (Figure 3b).

The full analysis of a crude residue is shown in Figure 3b. After the saturates and aromatics have eluted, the hexane flow to the aminocyano columns is shut off, and the resins adsorbed on the cyano column are backflushed with MTBE.

Confirmation of Hydrocarbon Type. To verify that the first peak to elute from the system is only saturated compounds and not aromatics, the capacity factor (k') of several model compounds was determined. These are shown in Table

Table III. Relative Response Factors for Saturates and Resins[a]

substance	saturates	resins
Arab Light[b]	1.000	0.788
Arab Medium[b]	1.000	0.793
Arab Heavy[b]	1.000	0.811
North Slope[b]	1.000	0.799
Hondo[b]	1.000	0.789
refinery residue[c]	1.000	0.812

[a] These are weight response factors. [b] 343+ °C (650+ °F). [c] 400+ °C (750+ °F).

Table IV. Precision of Hydrocarbon Type Analysis by HPLC and Open-Column Methods[a]

hydrocarbon type	HPLC		Open Column	
	std dev	repeatability	std dev	repeatability
saturates	0.54	1.7	0.74	2.3
aromatics	0.47	1.5	0.55	1.7
resins	0.31	1.0	0.50	1.4

[a] All data are weight percent and represent pooled calculation of triplicate determinations on six crude residues.

II, and it is clear that only the saturated hydrocarbons have the same capacity factor as the saturate components. Additional evidence is found in Figure 4 in which a sample passes through a UV detector at 254 nm in series with the FID with no backflushing of the aromatics. The UV detector does not respond at all to peak 1 in chromatogram 4a (FID) confirming that these are saturated compounds. The k' values of the saturate peaks were the same for all the crude oil residues analyzed.

Capacity factors are also given for some aromatic compounds in Table II. These include a typical one-ring aromatic compound, nonylbenzene, which is peak 2 in Figure 4.

The capacity factors indicate a clear-cut separation between the saturates and the model aromatic compounds. The switching time for valve B to reverse and backflush the aromatics was set so that it occurred immediately after the saturate peak had eluted from valve B (see Table I) and well before any of the one-ring aromatic compounds had eluted. Figure 4b indicates that some UV absorbing material, of unknown nature, elutes before the one-ring aromatic model compounds. The switching of valve B is timed to separate this material from the saturate components and include it with the aromatics.

Relative Response Factors. The use of a flame detector is motivated by the expectation that the response will be sufficiently uniform to allow normalization to be used instead of individual calibration techniques. This is the case in gas chromatography (GC) where most saturates and aromatic hydrocarbons have equal responses, and normalization of areas gives weight percent (*11*). Heteroatom compounds in GC have widely differing relative response factors (RRF's), but when the percentage of carbon in the heteroatom molecule is high the RRF's lie between 0.7 and 0.9. (Heptane is assigned a value of 1.0 (*11*, *12*).) This suggests that the RRF's for the resin group of compounds in widely different crude oil residues might be sufficiently similar that a common RRF could be used for all samples.

The open-column fractions were not satisfactory for the saturate/aromatic response factor determination because HPLC analysis revealed that overlap between the hydrocarbon types had occurred. Because of this, pure fractions of saturates and aromatics were prepared by HPLC using the analytical column system and trapping out the saturate and aromatic peaks with an ISCO Foxy fraction collector. Approximately 100-mg portions of fractions from a 343+ °C (650+ °F) residue and a 400+ °C (750+ °F) residue were collected and used for the determination of RRF's.

Blends of the saturate and aromatic fractions were prepared at different concentrations so that each blend contained a known weight of the appropriate fractions. These were then analyzed and the area of each component determined. The saturate components were assigned an RRF of 1.0. The RRF of the aromatic components was calculated as follows:

$$\text{aromatic RRF} = \left(\frac{A_a}{A_s}\right)\left(\frac{C_s}{C_a}\right)1.0 \qquad (1)$$

where A_a is the area of the aromatic peak, C_s is the concentration of saturates in the blend, A_s is the area of the saturates peak, and C_a is the concentration of aromatics in the blend.

It was found that the aromatic fraction of the North Slope 343+ °C (650+ °F) had an RRF of 1.002, and that of the refinery residue 400+ °C (750+ °F) had an RRF of 0.994. These results confirmed that the saturates and aromatics had equal response in both sample types.

Response factors for the resin fractions of six crude residues were determined. Known weights of the saturate and resin fractions (1 mg/mL of each) were combined into one solution. The RRF of the resins was calculated by using eq 1 and substituting the resin values for the aromatics values as shown below

$$\text{resin RRF} = \left(\frac{A_r}{A_s}\right)\left(\frac{C_s}{C_r}\right)1.0 \qquad (2)$$

where A_r is the area of the resin peak, C_r is the concentration of resins in the blend, and C_s and A_s have the same meaning As defined in eq 1.

The resin RRF's are given in Table III. They fluctuate around a value of 0.80 despite the fact that the crude samples themselves are very different in composition and cover a wide range of crude types. This suggests that the HPLC method can be applied to a wide range of heavy petroleum feedstocks without the need for repeated calibration of the detector.

Linearity. The linearity of each hydrocarbon type was determined by using the solutions prepared for the determination of relative response factors. A correlation coefficient of 0.999 was obtained for saturates, aromatics, and resins over

Table V. Open-Column Data vs. HPLC Data[a]

crude residue[b]	HPLC-method			open-column method		
	saturates	aromatics	resins	saturates	aromatics	resins
Arab Light	36.6	48.4	10.7	36.1	47.4	11.3
Arab Medium	31.0	48.9	13.5	30.2	49.8	12.5
Arab Heavy	24.8	42.6	20.2	23.2	47.6	16.5
North Slope	33.9	36.4	25.7	35.0	40.2	20.5
Hondo	9.0	27.8	41.1	11.7	35.8	29.8
refinery residue	41.7	42.1	10.6	42.1	41.6	10.7

[a] Each data point is the mean of triplicate determinations in weight percent. [b] Conditions are given in Table III.

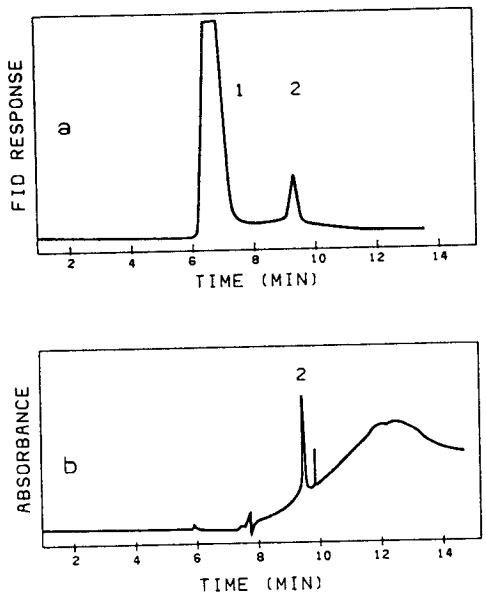

Figure 4. Chromatograms of a residue sample plus nonylbenzene and without backflush using two detectors: (a) flame detector and (b) UV detector at 254 nm. Peak 1 is saturates, and peak 2 is nonylbenzene.

a range of concentrations of 0–3 mg/mL.

Precision. The precision of both methods was determined. Pooled standard deviation and repeatability based on triplicate determinations for each hydrocarbon type were calculated for all six crude residues. These data are shown in Table IV. Both methods have good precision, and the HPLC method is better than the open-column method.

Comparison of Methods. Deasphaltened solutions of six crude residues with widely different hydrocarbon type compositions were analyzed by open-column chromatography using the method described in the Experimental Section and by the HPLC method reported here. The means of the triplicate determinations are given in Table V. The most significant differences occur between the aromatic and resin concentrations in Arab Heavy, North Slope, and Hondo. In each case the HPLC aromatics are lower than the open column, and the resins are the reverse.

Differences for the other three crudes are within 1%. An examination of the open-column fractions by the HPLC method revealed that overlap between hydrocarbon types had occurred. The saturate fractions contained aromatics, and the aromatics fraction contained both saturates and resins, but the resin fractions were free of overlap impurities. The overlap is the first factor contributing to the differences between the methods. The second factor is the use of different mobile and stationary phases for the two methods.

Despite the overlap between saturates and aromatics in the open-column fractions the agreement in saturate values between the two methods is good.

The HPLC method is superior because it is rapid and can be automated for unattended operation. The fractions it measures are composed solely of each specific hydrocarbon type. The use of the Tracor flame detector gives weight percent by normalization of corrected areas without frequent calibration, although it limits samples to those boiling at 343 °C (350 °F) or above.

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