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Chemical Fingerprinting of Materials Developed Due to Environmental Issues

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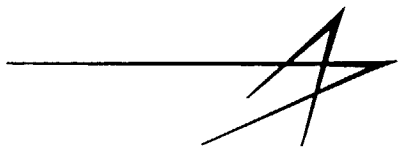
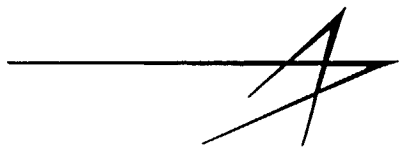
Chemical Fingerprinting



- *Aerospace Materials*
  - *Critical to performance*
  - *Replaced or modified due to environmental restrictions*
  - *Vary in composition from simple to complex; organic or inorganic; gas, liquid, or solid*
  - *Subject to variations in composition due to formulation changes, ingredient substitutions, degradation, contamination, and mislabeling*
  - *Must be adequately tested to detect variations*

Chemical Fingerprinting



- *Building Blocks of Capabilities*

Spectroscopy
- *Fourier Transform Infrared Spectroscopy (FTIR)*
- *Raman Spectroscopy*
- *X-ray Fluorescence (XRF)*
- *Inductively Coupled Plasma/Atomic Emission (ICP/AES)*
- *Mass Spectrometry (MS)*

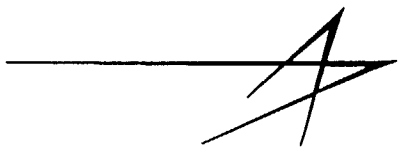
Micro-Analysis
- *Scanning Electron Microscopy (SEM)*
- *Energy Dispersive Spectrometry (EDS)*
- *Micro-FTIR*
- *Micro-Raman*
- *Chemical Microscopy*

Chromatography
- *Gas Chromatography (GC)*
- *Gas Chromatography/Mass Spectrometry (GC/MS)*
- *High Performance Liquid Chromatography (HPLC)*
- *Gel Permeation Chromatography (GPC)*
- *Ion Chromatography (IC)*

Surface Analysis
- *X-ray Photoelectron Spectroscopy (XPS)*
- *Secondary Ion Mass Spectrometry (SIMS)*

Thermal Analysis
- *Thermal Gravimetric Analysis (TGA)*
- *Differential Scanning Calorimetry (DSC)*

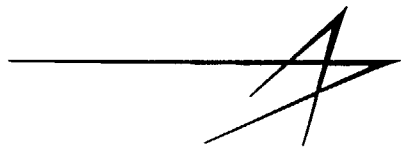
Chemical Fingerprinting



- *Spectroscopic Techniques: Atomic Spectroscopy*
  - *Used to identify and quantify elements present in samples*

X-Ray Fluorescence	*•Rapid detection of elements of atomic number ≥ 11* *•Solid & liquid samples, minimal sample preparation* *•Quantification requires matrix matched standards*
Atomic Absorption	*•Rapid single-elemental quantitative analysis* *•Sample must be in solution (accessory required for solids)* *•Sample preparation may be time consuming* *•Small linear response range, high matrix interference* *•Not applicable to most non-metals*
Inductively Coupled Plasma/ Atomic Emission	*•Multi-element qualitative and quantitative analysis* *•Sample must be in solution (accessory required for solids)* *•Sample preparation may be time consuming* *•Large linear response range*

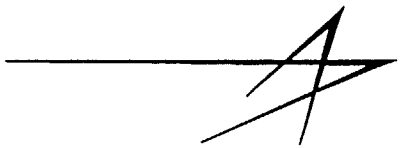
Chemical Fingerprinting



- *Spectroscopic Techniques: Molecular Spectroscopy*
  - *Used to identify and quantify molecular compounds present in samples*

Infrared Spectroscopy	*•Molecular functional group identification* *•Applicable to solids, liquids, gases* *•Not applicable to aqueous samples* *•Minor components masked by major*	*•Complements Raman spec.* *•Minimal sample preparation* *•Extensive reference libraries* *•Dipole moment change req.*
Raman Spectroscopy	*•Molecular functional group identification* *•Applicable to solids, liquids, aqueous* *•Polarizability change required* *•Not app. to colored or fluorescing samples*	*•Complements infrared spec.* *•Minimal sample preparation* *•Limited reference libraries*
Mass Spectrometry	*•Organic compound identification* *•Widely applicable to volatile samples* *•Accessory required for non-volatile samples*	*•Extensive reference libraries* *•Chromatographic detector*

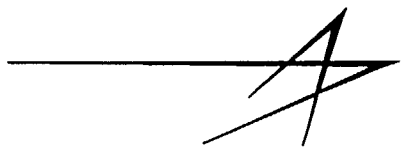
Chemical Fingerprinting



- *Chromatographic Techniques:*
  - *Used to separate and quantify components in samples*
  - *Used in tandem with other techniques to identify components*

Gas Chromatography (GC)	*•Separation of volatile components within mixtures* *•Quantitative or qualitative analysis* *•Not applicable to thermally unstable components* *•Not applicable to non-volatiles without derivatization*
High Performance Liquid Chromatography (HPLC)	*•Separation of soluble components within mixtures* *•Quantitative or qualitative analysis* *•Sample must be soluble in suitable solvent (many)* *•Method development time-consuming*
Gel Permeation Chromatography (GPC)	*•Separation of components based on molecular size* *•Determination of molecular weight distribution* *•Sample must be soluble in suitable solvent (few)*
Ion Chromatography (IC)	*•Separation and quantification of ionic species* *•Applicable to organic and inorganic* *•Method development time-consuming*

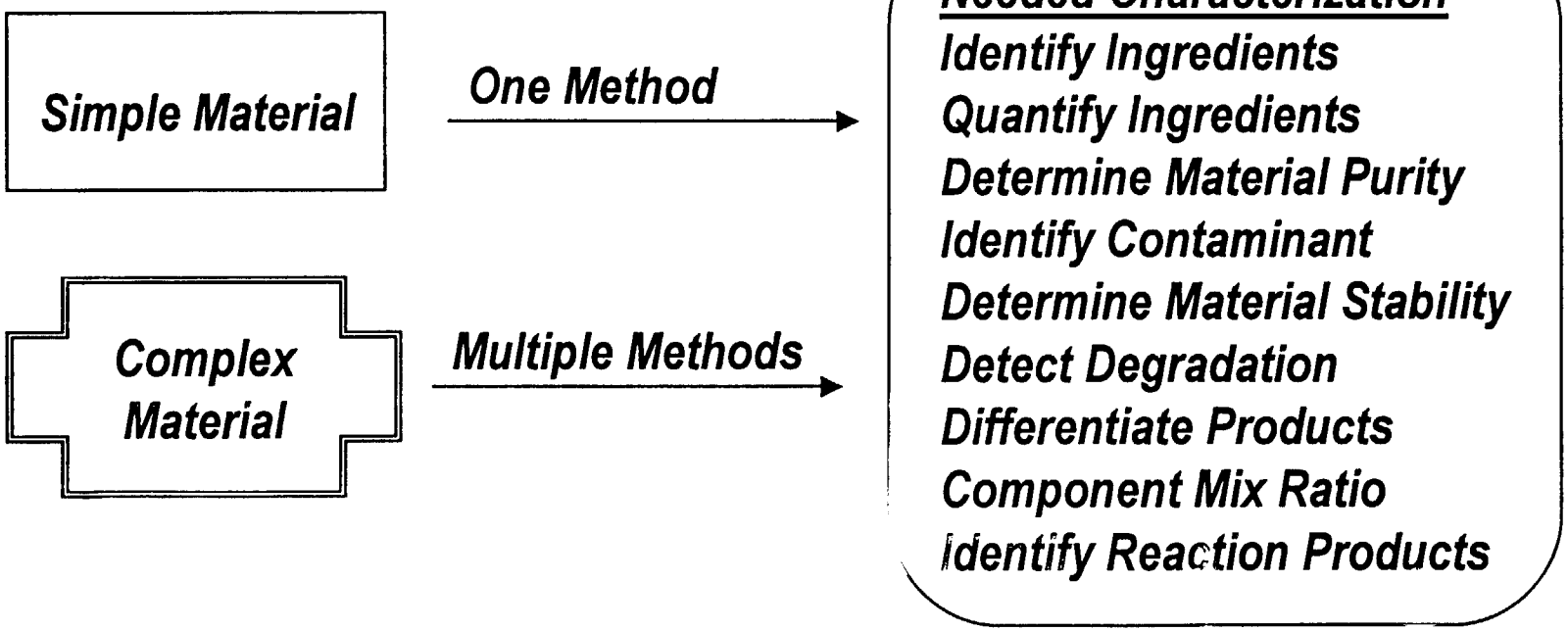
Chemical Fingerprinting



- *Factors that Determine Fingerprinting Approach*
  - *Physical State:* *Solid, liquid, or gas?*
    Homogeneous or distinct phases?
    Sample size?
  - *Chemical Properties:* *Single ingredient or complex mixture?*
    Major, minor, or trace components?
    Organic, inorganic, or combination?
    Masking of one component by another?
    Separation of components required?
  - *Information Required:* *Qualitative or quantitative data?*
    Bulk or surface composition?

Chemical Fingerprinting

- *Fingerprinting: Combination of instrumental analysis methods that diagnostically characterize a material*

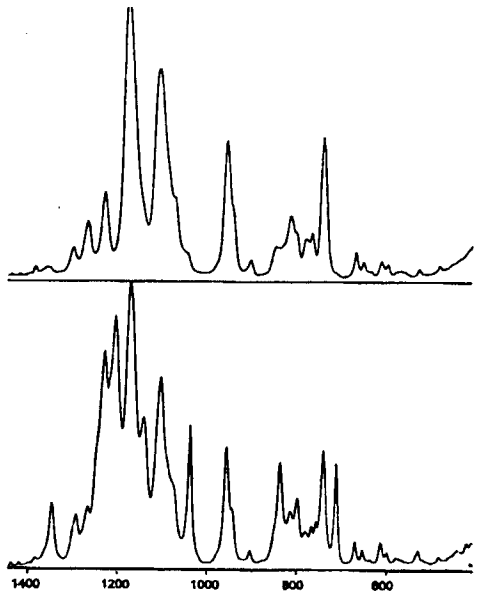


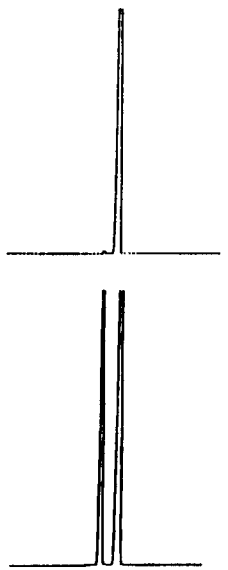
Chemical Fingerprinting

- *Simple Materials and Approach: HCFC-225 and HCFC-225G*

HCFC-225G
Single Isomer
Trace Impurities

HCFC-225
Two isomers
Trace Impurities



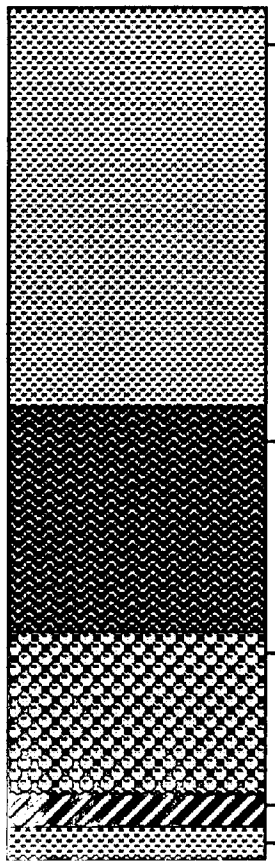


FTIR:
Rapid Differentiation

GC:
Isomer Ratio, % Purity

Chemical Fingerprinting

- *Complex Material Example: Urethane Foam Component*



Polyol
One or several polyols
Aromatic and/or non-aromatic
Polyesters and/or polyethers
Concentration ~5 - 65 %

Blowing Agent
CFC, HCFC, third generation
Concentration ~15-35%

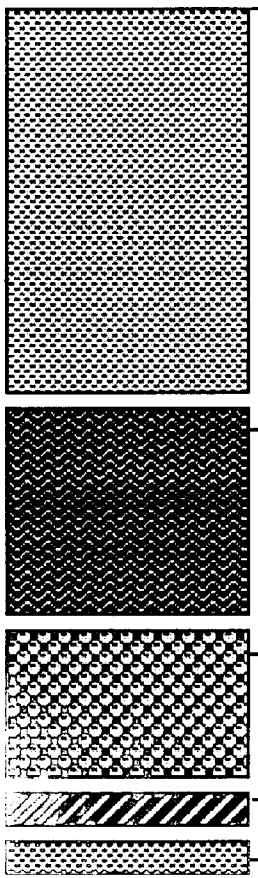
Flame Retardant
One or several flame retardants
Phosphorus- and/or halogen-based
Concentration ~1-20%

Catalyst
One or several catalysts
Organic amine and/or organometallic
Concentration ~0.5-4%

Surfactant
Silicone copolymer
Concentration ~1-2%

Chemical Fingerprinting

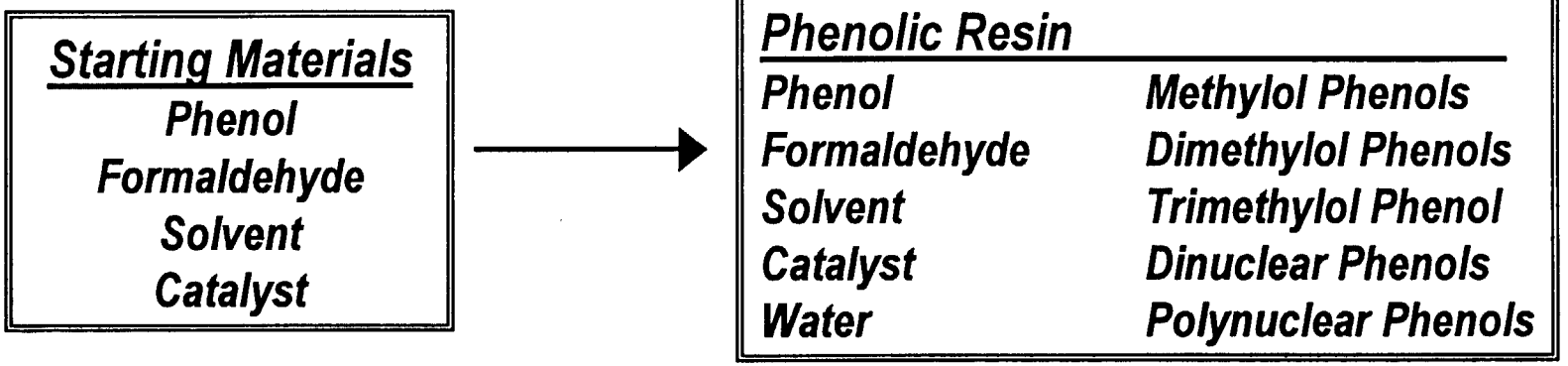
- *Complex Material Approach: Urethane Foam Component*



Polyol	FTIR:	Functional groups, polyol type
	GC:	Polyol conc. based on volatile portion
	HPLC:	Detectable polyol concentration
	GPC:	Molecular weight distribution
Blowing Agent	GC:	Blowing agent concentration
	GC/MS:	Blowing agent degradation
	FTIR:	Rapid blowing agent identification
Flame Retardant	ICP/AES:	Phosphorus concentration
	GC:	Phosphorus-based flame ret. conc.
	HPLC:	Halogen-based flame retardant conc.
	GC:	Concentration of polyol diluent
Catalyst	ICP/AES:	Tin, lead concentration (organometallic)
	GC:	Volatile amine catalyst concentration
Surfactant	ICP/AES:	Silicon concentration

Chemical Fingerprinting

- *Complex Material and Approach: Phenolic Resin*



HPLC:	*Phenol and methylol phenol concentrations*
GC:	*Solvent concentrations*
GPC:	*Molecular weight distribution (resin advancement)*
FTIR:	*Functional groups (resin advancement)*
ICP/AES:	*Concentration of metal due to metal hydroxide catalysts*
IC:	*Ammonium hydroxide catalyst concentration*
Titrations:	*Formaldehyde and water concentrations*

Chemical Fingerprinting

- *Supplier Partnership is Vital Element in Fingerprint Program*

Material Suppliers:

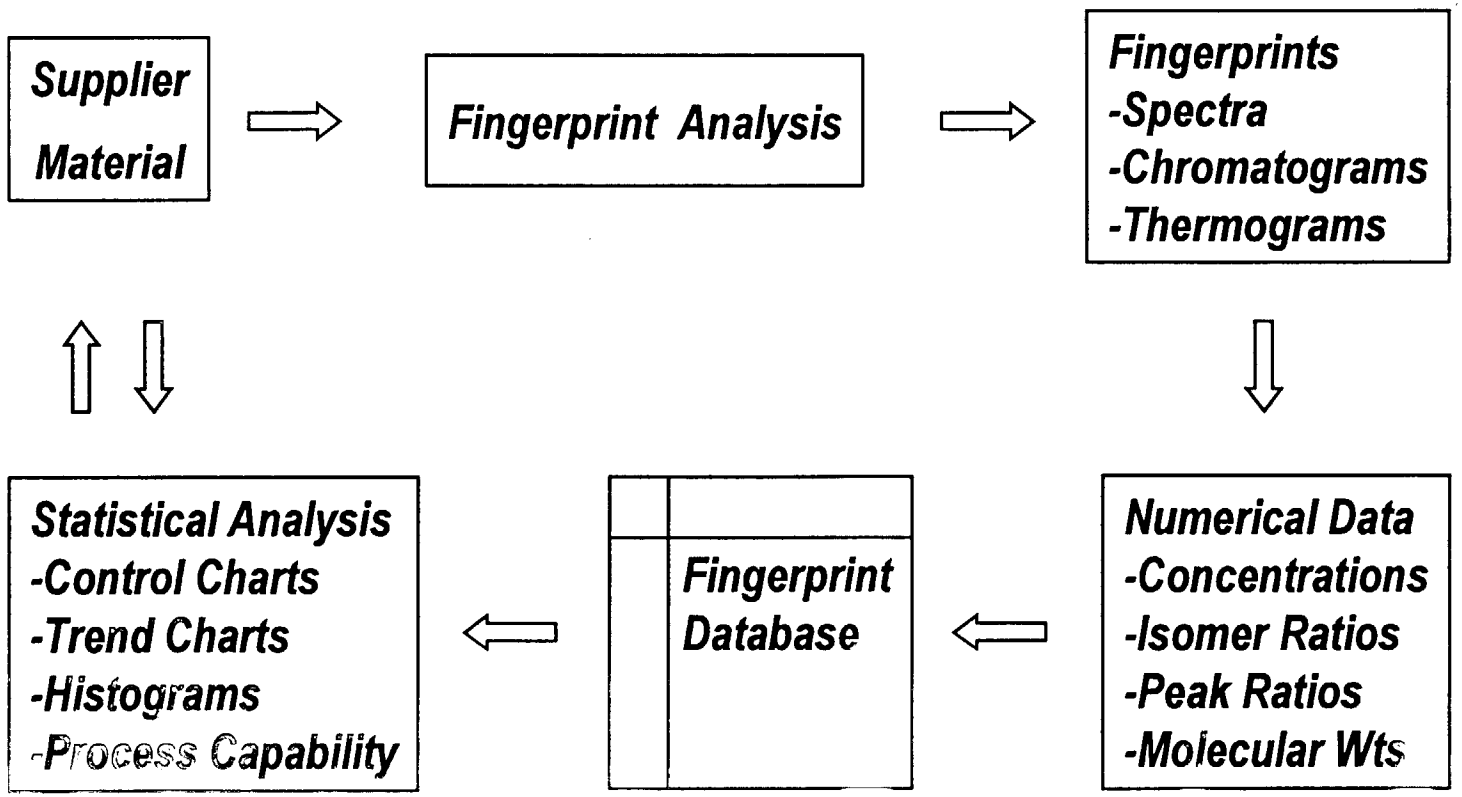
- Provide information on formulation and chemistry
- Supply samples of formulation ingredients
- Avoid changes to material formulation when possible
- Notify us of necessary changes to material

Fingerprinting Program:

- Use information to understand material's chemistry and threats to availability
- Use information and samples to develop fingerprint methods
- Supply fingerprint data
- Safeguard proprietary information

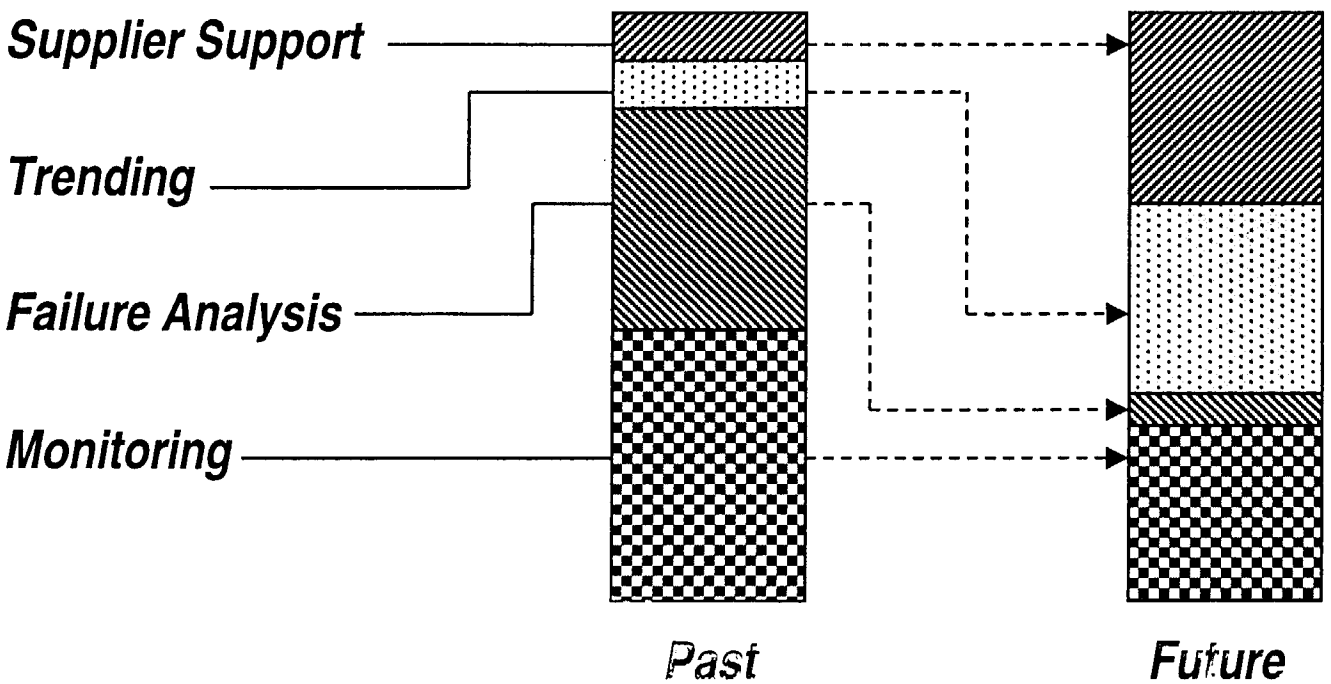
Chemical Fingerprinting

- *Fingerprint Databases & Trending to Detect Material Variations*



Chemical Fingerprinting

- *Evolving Role of Fingerprinting in Aerospace Industry*



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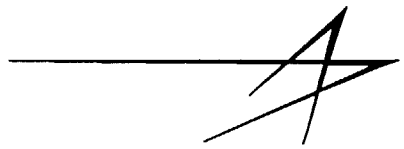
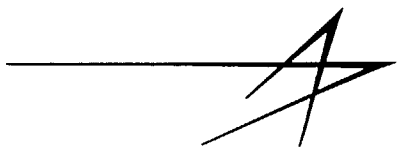


- *Benefits: Fingerprinting provides benefits in the areas of receiving acceptance, failure investigations, new material development, and alternate material qualification*
  - *Multipurpose methods with diagnostic capability*
  - *Quantitative databases and reference libraries*
  - *Increased material reliability*
  - *Ensured future replication of successful materials*
  - *Expeditious problem resolution*
  - *Automated sample analysis*
  - *Reduced cost of material requalifications*
  - *Increased supplier communication*

Chemical Fingerprinting



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