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Elemental speciation studies in capillary electrophoresis ——New trends for trace elements analysis

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Abstract: Speciation of elements could provide valuable information for chemistry, environment, medicine and life science. As a new separation technique, capillary electrophoresis offers a number of important attributes including: high separation efficiency, short analysis time, and low sample consumption. The development in the elemental speciation analysis by capillary electrophoresis is reviewed with 56 references. Various CE separation modes (e. g., capillary zone electrophoresis, micellar electrokinetic capillary chromatography, capillary isoelectric focusing, capillary electrochromatography) and detection techniques (e. g., UV - Vis, fluorescence, electrochemistry, inductively coupled plasma - mass spectrometry) applied are discussed. Further, some issues concerning the limitations and the future of CE with regard to speciation studies are also discussed.

Key words: capillary electrophoresis; speciation analysis; trace element; review

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0 Introduction

Environmental pollutants are a significant hazard to human health; among them trace elements have beneficial and harmful effects depending on their quantities and chemical species in living organisms. In addition to the common elements (sodium, calcium, magnesium, etc.), a number of trace elements (selenium, zinc, molybdenum, manganese, etc.) are considered essential with specific biological functions at relatively low levels. However, when present in excess, these elements can be harmful. The elements present in biological and environmental materials are distributed among various chemical forms which include inorganic salts, organic and bio-metallic or bio-metalloid compounds. Determination of total elemental concentration is of limited value, as this information cannot be directly related to the chemical, biological and toxicological activity of a particular element. Oxidation state and/or chemical form of trace elements determine their toxicological effects or nutritional benefits. Analytical elemental speciation has been defined as the separation, identification and quantification of the different chemical forms or species of a particular element in a given sample. Information on elemental speciation in environmental and clinical material is vital in studies on possible mechanisms of element transport and/or degradation in the environment, element bioavailability and on possible metabolic pathways within living organisms. The growing interest in elemental speciation is reflected in the number of recent publications in the literature, and it can be easily justified by a strong demand for analytical tools adequate for determination of elemental speciation in various fields, including environmental and life sciences. In the development of any analytical procedure for elemental speciation, it is necessary to consider: (a) the species /form to be detected; (b) the need to preserve the natural composition and distribution of species in the sample during the procedure; and finally; (c) the selectivity and detection capability of the analytical technique for quantification.

Since usually more than one elemental species exists in a sample, a separation step is necessary. A variety of separation techniques have been used. Of these techniques, gas chromatography (GC) and liquid chromatography (LC) are most commonly used, as indicated by the numerous reviews and proce-

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dures published[1,2]. Capillary electrophoresis (CE) is a comparatively new separation technique. Applicability of using CE as an alternative way for speciation analysis has been explored in recent years[3]. Among the separation techniques previously mentioned, CE offers a number of important attributes including: high separation efficiency, short analysis time, low sample consumption and low operating cost. CE become now a well-established analytical method and is used as an alternative or complementary technique to HPLC. Since separation in CE is mainly governed by difference in charge-to-size of analytes, this technique is extremely powerful in chemical speciation purposes[4].

In 1998, Dabek-Zlotorzynska et al[5]. comprehensively reviewed the state-of-the-art of CE for metal speciation analysis. Later on, several excellent reviews of elemental speciation analysis in CE have been presented in the literature [4,6-10]. This review presents the developments of elemental speciation analysis in CE. Various separation modes and detection methods are discussed. The principal limitations and further outlook are also described.

1 Separation in capillary electrophoresis

CE is an instrumental approach to electrophoresis in which sample components placed between two buffer solutions are separated in an open-tubular capillary with an inside diameter ranging from 2 to 200 μm and a length usually between 10 and 100 cm. The separation is based on the electrophoretic mobility of the analyte species induced by the large potential (10～30 kV) applied across the capillary. This migration takes place under the combined effects of electrophoretic and electroosmotic flows (EOF) generated by applying an electric field across the capillary. The successful approach for speciation analysis depends on two factors: selectivity (to be sure of determining the proper species) and sensitivity (to match the analyte's level in the sample). This section briefly reviews the separation modes applied in elemental speciation analysis to date.

CE separations can be accomplished with various modes, including the popularly employed capillary zone electrophoresis (CZE), micellar electrokinetic capillary chromatography (MEKC), capillary isoelectric focusing (CIEF), capillary electrochromatography (CEC) etc.

CZE-based separation is the most widely used operation mode in speciation analysis. CZE can be divided into two subdirectories: (i) counter-electroosmotic flow CZE; (ii) co-electroosmotic flow CZE. Recently, a comprehensive investigation on separation of organic and inorganic arsenic species by capillary electrophoresis using direct spectrophotometric detection was demonstrated by Sun et al[11]. In that article, both counter- and co-electroosmotic flow CZE were utilized. A separation of nine arsenic species was performed by the counter-EOF mode. For the co-EOF mode, poly(diallydimethylammonium chloride) (PDDAC) was used for dynamic coating of the capillary and to provide a stable and reproducible reversed EOF. It can be seen from the results that the co-EOF mode is more rapid and provides sharper peaks.

Neutral compounds will co-migrate under the classic CZE conditions. Terabe et al[12]. successfully developed a MEKC separation mode to resolve this problem. In MEKC mode, surfactant with concentration over its critical micellar concentration (CMC) is necessary to be added in the carrier electrolyte to form micelle as the pseudostationary phase. The prominent advantage of MEKC is its ability to separate both neutral and ionic species. MEKC have also been widely used in the speciation of elements, especially for the speciation of various organometallic compounds. At an early stage of the development of speciation analysis by CE, Ng et al [13] probed the applicability of MEKC to the separation of organoselenium and organolead compounds. The simultaneous resolution of individual lead, mercury and selenium species, overall 9-10 organic and inorganic analytes, was attained as a result of combining pre-column derivatization and differential micellar solubilization principles[14].

Capillary isoelectric focusing (CIEF) has continuously been an attractive separation technique for biologically important ampholytes, i.e., proteins and peptides. Isoelectric focusing is characterized by high resolution and spontaneous focusing of analytes. In CIEF system, the ampholytes are employed to offer a pH gradient along the capillary when applying an electric field. Species with different isoelectric points (pI values) will move to and be focused on their individual pI, and then be separated from each other. Michalke and Schramel[15] proposed a separation of six inorganic and organic Se species with CIEF. Because the authors utilized an online coupling inductively coupled plasma mass spectrometry (ICP-MS) detector, the formation of metal complexes was not necessary. The detection limits were around 10～30 μg Se/L. The method was applied to standard mixtures and body fluids like human milk and serum. Selenium carrying glutathione (GSSeSG) and selenocystine (SeC) in serum was identified by standard additions procedure. Scapolan et al[16]. studied in detail the chemical behavior of uranium in biological medium by using CZE and CIEF with time-resolved laser induced florescence (TRLIF) detection. By using CIEF, different uranium complexes were separated as a function of their pIs. Very low level of different uranyl complexes were identified in virtue of the utilization of TRLIF detection scheme. The author investigated the results obtained

in various inorganic chemical and biological systems.

Capillary electrochromatography combines the high efficiency of CZE and the high selectivity of HPLC and has received increasingly more attention. Compared with CZE and MEKC, seldom report concerning speciation analysis of elements by CEC has been published. A bonded phase capillary column containing macrocyclic polyamine, 1, 15-dioxa-4, 8, 12, 18, 22, 26-hexaazacyclooctaeicosane ([28]ane - N_6O_2) was used for the electrophoretic separation of arsenic ($HAsO_4^{2-}$ - Ph_4As^+), chromium (CrO_4^{2-} - Cr^{3+}) and selenium (SeO_4^{2-} - SeO_3^{2-}) species[17]. A simple device interfacing capillary electrochromatography systems to ICP-MS is described. Concentration detection limits for these metal ions were in the low ppb range. In addition, the matrix effect of the established system with the bonded phase was found smaller than that with the bare fused silica.

2 Detection techniques

A variety of CE detectors, including UV-Vis, fluorescence, electrochemistry, X-ray emission, chemiluminescence, electrospray ionization - MS and ICP-AES/MS etc., have been utilized in the speciation studies to date. This section will briefly describe their applications.

UV detection has been extensively used in speciation analysis because of their simplicity and versatility. Since most metal species are transparent in UV - Vis region, the derivatization steps using suitable chromophore is required prior to separation. The complexing regents CDTA[18] used in CE speciation, which form absorbing complexes with metal ions in different oxidation states. Besides the direct detection, indirect UV detection modes were also widely used in this research field[19]. Indirect detection is based on the detection of a nonabsorbing analyte that produces interference or suppression of a given background signal; the analyte is detected indirectly as an inverted peak. Several cationic and anionic co - ions such as imidazole and chromate have been used in the indirect UV detection of element speciation. The main disadvantages of UV detection method is lack of adequate sensitivity, usually with the detection limits of only 10^{-5}～10^{-6} mol/L limited by the short path length (2～100 μm) through the column. Various attempts have been made to improve the sensitivity of UV-Vis detectors by increasing the optical path length, including the use of Z - shaped and multireflection detection cell, but with some sacrifice in resolution and design simplicity. Generally, UV-Vis detectors are not ideal for the speciation determination because they suffer from poor selectivity and are not very sensitive.

Less sophisticated and more affordable detectors, such as fluorescence, and amperometric detector, can be employed in elemental speciation. For instance, laser - induced fluorescence (LIF) detection was used to characterize humic substances and their interactions with metal ions in CE. Additionally, indirect fluorescence detection was also applied in the speciation analysis of tin[20]. A technique based on capillary electrophoresis and amperometric detection (CE - AD) has been developed for the speciation of mercury at ng/mL concentration levels[21]. Controlling the reduction potential applied on the microelectrode attains selective detection of these electrochemically active species. The detection limits of 0.1 ng/mL for Hg^{2+} and 3 ng/mL for CH_3Hg^+ are potentially attractive for the monitoring of mercury contamination in sediments[22]. However, there is still a call for further efforts on the implementation of these detectors for practical use.

To date, chemiluminescence (CL) is one of the less developed detection systems for CE, yet there are several features in this method, which bring it closes to a sensitive detection system. CL detection system is characterized by a simple cheap optical system requiring no light sources, avoiding the efforts of stray light and the instability of the light source, and thus providing low background noise with excellent sensitivity. In terms of sensitivity, CL perhaps represents the ultimate detection scheme. Some reports have shown that CL is an alternative promising detection procedure for CE. Recently, our group has made continuing efforts in ultrasensitive CL detection of metal ions by CE[23～25]. Recently, speciation of vanadium was also carried out in CE with CL detection[26], it was found that V(Ⅳ) has excellent catalytic behavior for the chemiluminescence (CL) reaction of luminol and hydrogen peroxide. The detection limit for V(Ⅳ) is 2.4×10^{-17} mol/L. Up to now, this could be the highest sensitivity for metal ions analysis. In addition, the separation of 1.3×10^{-16} mol/L V(Ⅳ) and 6.7×10^{-5} mol/L V(Ⅴ) has been performed successfully. As far as we know, this is the first report on speciation of elements by CE-CL. Most recently, Zhang's group[27] carried out the ultrasensitive speciation analysis of Cr(Ⅵ) and Cr(Ⅲ) by CE-CL. Based on in - capillary reduction, chromium (Ⅵ) can be reduced by acidic sodium hydrogensulfite to form chromium (Ⅲ) while the sample is running through the capillary. The limits of detection (DL) of Cr(Ⅲ) and Cr(Ⅵ) were 6×10^{-13} and 8×10^{-12} mol/L (S/N = 3), respectively. The mass DL for Cr(Ⅲ) and Cr(Ⅵ) were 1.2×10^{-20} mol (12 zmol) and 3.8×10^{-19} mol (380 zmol), respectively.

Recently, great efforts have been devoted to interfacing CE with element - selective detectors including inductively coupled plasma (ICP) atomic emission spectrometry (AES) and MS. The interface between the end of the electrophoresis capillary and the ICP is key to the success of the CE - ICP technique.

The considerable advantages of ICP-MS as a detector include (i) the very low detection limits (<1μg/L); (ii) direct element information and element quantification is possible; (iii) all buffer systems and stacking procedures fit well to the detector; (iv) no compromises between separation and detection. On the other hand, there are some limitations: (i) detection of only the element is possible; (ii) unknown species cannot be identified; (iii) m/z signals can be interfered by polyatomic interferences, resulting in pseudo element signals. A review on this topic of CE-ICP-MS has been published recently[7].

Olesik et al[28] first used CE-ICP-AES for the elemental speciation analysis including separation of Fe(II) and Fe(III). Deng et al[29] developed a simple interface for CE-ICP-AES. The interface is relatively simple to build and is easy to set up to couple a commercial capillary electrophoresis to the ICP spectrometer. The separation and detection of Cr^{3+}/$Cr_2O_7^{2-}$ and Cu^{2+}/Cu-$EDTA^{2-}$ was achieved with the detection limits of Cr and Cu are ~5 ng/mL. The combination of high separation efficiency of CE with the high sensitivity of ICP-MS detection provides a valuable technique for elemental speciation.

Recently, metal speciation was carried out by on-line hyphenation of capillary electrophoresis with mass spectrometry via an electrospray ionization (ESI) interface[30]. The Se species were sufficiently separated from each other with the detection limits were calculated as 1~6 mg/L for the organic Se species. Electrospray is a soft ionization technique. The ionization process does not alter their structure and they will mostly be detected as singly charged molecular ions. Therefore, ESI-MS is best suited for the speciation of covalent organometallic compounds. Generally, CE-ESI-MS can provide maximum information, i.e. direct determination of the element in its specific form; CE/ICP-MS directly yields elemental information. Michalke et al.[30] compared the two hyphenated systems (CE-ESI-MS and CE-ICP-MS) for three selenium speciation investigations. CE-ICP-MS detection provides considerably improved the detection limits compared to CE-ESI-MS.

As a remarkable feature of CE, on-line pre-concentration by field-amplified sample injection (FASI) or isotachophoretic electrostacking of the sample injected into the capillary can be applied in measuring the trace levels of various ions[14,31]. By simple field-amplified stacking, occurring when the conductivity of the sample is lower than that of the surrounding electrolyte, sensitivity can be improved effectively. Simultaneous speciation of lead, mercury, and selenium was carried out by CE[14]. FASI was performed in order to improve the detection sensitivity. Up to 1500-fold on-line enrichment and down to sub-nanogram per-milliliter detection limits were obtained for the analytes under the optimal stacking conditions. The method was applied successfully in the determination of Pb(II) and Se(IV) in seawater samples.

A novel hyphenated technique, on-line coupling of capillary electrophoresis to atomic fluorescence spectrometry (AFS), was developed by Yan's group[32] for speciation analysis of four environmentally significant and toxic forms of arsenic: arsenite, arsenate, monomethylarsenic acid, and dimethylarsenic acid. Baseline separation of the four arsenic species was achieved by capillary electrophoresis using a 20 mmol/L phosphate buffer (pH 6.5). A hydride generation (HG) technique was employed to convert the arsenic species from the CE effluent into their respective hydrides. The precision (RSD) ranged from 2.1% to 3.1% for migration time, from 2.8% to 4.2% for peak area response, and from 2.0% to 4.1% for peak height response for the arsenic species at the 1 mg/L (as As) level. The detection limits were in the range of 9~18 μg/L (as As). The recoveries of the four arsenic species in locally collected water samples and urine sample ranged from 91% to 115%. The developed technique was successfully applied to the speciation of the water-methanol extractable arsenic in a sediment sample. Later on, the same group[33] developed a novel method for speciation analysis of mercury by on-line hyphenating capillary electrophoresis with atomic fluorescence spectrometry. The four mercury species of inorganic mercury Hg(II), methymercury MeHg(I), ethylmercury EtHg(I), and phenylmercury PhHg(I) were separated as mercury-cysteine complexes by CE using a mixture of 100 mmol/L of boric acid and 12% v/v methanol (pH 9.1) as electrolyte. The precisions were in the range of 1.9%~2.5% for migration time, 1.8%~6.3% for peak area response, and 2.3%~6.1% for peak height response for the four mercury species. The detection limits ranged from 6.8 to 16.5 μg/L (as Hg). The recoveries of the four mercury species in the water samples were in the range of 86.6%~111%. The developed technique was successfully applied to speciation analysis of mercury in a certified reference material (DORM-2, dogfish muscle).

3 Applications in elemental speciation analysis

Nowadays, capillary electrophoresis with various detection techniques, including UV-Vis, fluorescence, electrochemistry, chemiluminescence, electrospray ionization-MS and ICP-AES/MS etc., have been utilized in the speciation studies of elements as follows: As[34~37], Se[38,39], Pb[3,14], Hg[3,21,40], Fe[41,42], Cr[27,43], V[26,44], Sb[45,46], Al[47], platinum-group elements[48,49], even more sulfur[50], nitrogen[51], chlorine[52], bromine[52,53] and iodine[54] etc. inorganic anions. Table 1 and Ta-

ble 2 listed some applications of speciation analysis of arsenic, selenium and other elements, respectively.

Tab. 1 Some applications of arsenic and selenium speciation analysis in CE (DL, the detection limit)

Species Analyzed	Sample	Buffer	Detection	DL	Ref
As(III), As(V), MMA, DMA, AsB, AsC	Test solution	20 mM CAPS-40 mmol/L CD (pH 10)	ICP-SFMS	0.3-6.0 μg/L	[34]
As(III), As(V), MMA, DMA, AsB	Soil extracts	0.5 mmol/L chromate-0.5 mmol/L TTAB (pH 11.2)	ICP-MS	HYD: 6-17 μg/L ELM: 0.08-0.26 μg/L	[35]
As(III), As(V), DMA	Test solution	90 mmol/L K_2HPO_4-10 mmol/L NaCN (pH 6.5)	ICP-TOF-MS	1-20 pg for 20 nl	[36]
Se(IV), SeC, e(VI), SEM	Human milk	Na_2CO_3-NaOH (pH 11.5), 100 mmol/L NaOH-H_3PO_4 (pH 2～10)	ICP-MS	10-30 μg/L for inorganic Se; 10-20 μg/L for organic Se	[38]
Se(IV), PSC, DPS	Standard	25 mmol/L SDS-2.5 mmol/L NTA (pH 7)	Direct UV	Se(IV) 120, PSC 260, DPS 10 μg/L	[3]
PS(II), Se(IV)	Sea water	2.5 mmol/L TTHA-2 mmol/L SDS-40 mmol/L phosphate-boric acid (pH 7.5)	Direct UV	Se(IV) 0.3367, PS 2.022 μg/L	[14]

MMA, monomethylarsinate; DMA, dimethylarsinate; NA, arsanilic acid; PhA, phenylarsonic acid; AsB, arsenobetaine; AsC, arsenocholine ion; SeC, selenocystine; SeM, selenomethionine; PSC, henylselenium chloride; DPS, diphenylselenium; PS, phenylselenium; HYD: hydrodynamic injection; ELM: electromigration injection.

Tab. 2 Some applications of metal elements speciation analysis in CE (DL, the detection limit)

Species Analyzed	Sample	Buffer	Detection	DL	Ref
Pb(II), TEL, TML, DPL	Standard	25 mmol/L SDS-2.5 mmol/L NTA (pH 7)	Indirect UV	Pb(II) 110, TEL 40, TML 80 DPL 100 (μg/L)	[3]
TEL, DPL, Pb(II)	Sea water	2.5 mmol/L TTHA-2 mmol/L SDS-40 mmol/L phosphate-boric acid (pH 7.5)	Direct UV	No stated	[14]
Hg^{2+}, Hg^{+}, PMA	Standard	25 mmol/L SDS-2.5 mmol/L NTA (pH 7)	Direct UV	Hg^{2+} 130, Hg^{+} 310, PMA 90 (μg/L)	[3]
Hg^{2+}, $CH^{3}Hg^{+}$, $C_2H_5Hg^{+}$	Sediments	0.1 mol/L creatinine-acetic acid (pH 4.8)	Amperometeric	Hg^{2+} 0.2, CH_3Hg^{+} 3 (μg/L)	[21]
Hg^{2+}, $CH^{3}Hg^{+}$, $C_2H_5Hg^{+}$	Lenses solutions	20 mmol/L Na2CO_3-SDS-cysteine (pH 11)	ICP-MS	Hg^{2+} 170, CH_3Hg^{+} 80, $C_2H_5Hg^{+}$ 100 (μg/L)	[40]
Fe(II), Fe(III)	Aerosols	100 m mol/L borate	Direct UV	1×10^{-6} mol/L Fe(II)	[41]
Fe(II), Fe(III)	Standard	250 mmol/L borate-1 mmol/L phen -1 mmol/L CDTA (pH 9.0)	ICP-AES	Comparison three different digestion/dissolution methods	[42]
Cr(III), Cr(Vi)	rinse water	4.5 mmol/L histidine (pH 3.4)	contactless conductometric	Cr(III) 10, Cr(VI) 39 (μg/L)	[43]
Cr(II), Cr(VI)	Standard	0.02 mol l^{-1} acetate-1mmol l^{-1} EDTA (pH 4.7)	CL	Same Ref. 66	[36]
V(V), V(IV)	Standard	0.1 mol/L monochloroacetate buffer (pH 2.2)	Direct UV	V(V) 5×10^{-7}, V(IV) 2×10^{-7} mol/L	[44]
Sb(III), Sb(V), TMSb	Fouling and sewage sludge	Na_2HPO_4/NaH_2PO_4, 20 mmol/L (pH 5.6)	ICP-MS	0.1-0.7 μg/L	[45]
Sb(III), Sb(V)	Standard	1.2 mmol/L fluorescein (pH 9.5)	Indirect fluorescence detection	μmol/L	[46]
Al^{3+}, fluoride Al	Tea, canal water, tap water	nicotinamide (pH 3.2)	Indirect UV	No stated	[47]
Pt(II), Pt(VI) and other platinum-group elements	Standard	60 mmol/L KCl (pH 3.1)	Direct UV	0.1-0.6 ppm	[48]
Rh species	standard	0.1 mol/L HCl	Direct UV	Comparison the mechanism of catalytic kinetic reactions in Rh species	[49]

Recently, a new approach for the speciation of metallothioneins (MT) in human brain cytosols is described[55]. The analysis is performed by application of a newly developed coupling of CE with inductively coupled plasma - sector field mass spectrometry (ICP - SFMS). The analytical procedure developed has been used for the first time in comparative studies of the distributions of MT-1, MT-2, and MT-3 in brain samples taken from patients with Alzheimer's disease and from a control group. This work demonstrate for the first time that the CE - ICP - MS technique is suitable for the separation and identification of metals bound to metalloprotein in real-world samples such as human cell cytosols. The same group[56] analyzed MT isoforms in a natural cytosol pH environmental by using surface - modified capillaries with CE - ICP - MS. The separation of nine MT isoforms from rabbit liver were improved by applying surface - modified capillaries, and the metal composition of MTs also has been

characterized by subsequent ICP - SFMS. Indeed, an understanding of the mechanisms controlling the essentiality and toxicity of trace elements in biological systems at the molecular level depends critically on the possibility of the identification, characterization, and quantification of chemical forms of these elements involved in life processes.

4 Conclusions

It is believed that the elemental speciation analysis is one of the most difficult tasks of analytical chemistry. The continuing efforts by many research groups have led to rapid progress in CE separation with various detection techniques. Despite the significant advantages, there are a number of limitations and challenges in speciation by CE. It suggests based on the recent literature that further development in speciation by CE be as described as follows: (1) more effort should be focused on new detectors that are instrumentally simpler, less expensive and versatile that offers the ability to detect various types of analytes at trace levels; (2) sample preparations and separations that produce the smallest possible perturbation on element species will be the focus of future studies; (3) broaden its applications to various factual samples.

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毛细管电泳中的形态分析
——微量元素分析新方向

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摘 要:元素的形态分析可为化学、环境科学、医学和生命科学提供重要的信息.作为一种新型的分离技术,毛细管电泳具有分离效率高、速度快、样品耗量少等优点.本文评述了毛细管电泳在元素形态研究中的进展,包括区带电泳、胶束电动色谱、毛细管电色谱等分离模式和紫外、电化学、电感耦合等离子体质谱及化学发光等检测手段的应用.讨论了该领域存在的问题和未来的发展趋势.引用文献 56篇.

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