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Review

Analysis of natural food pigments by capillary electrophoresis

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Abstract

Lac, cochineal, safflower, gardenia, *Monascus* and elderberry pigments are used as food color additives in Japan. These natural pigments can be analyzed by capillary electrophoresis (CE). CE has several advantages over thin layer chromatography, gas chromatography and high-performance liquid chromatography, such as low capillary cost, reduced operating costs, small sample amounts, low production of waste materials and short analysis time. CE is shown to be a useful technique for the analysis of these natural food pigments and the pigments extracted from commercial food samples by solid-phase extraction method. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Food analysis; *Carthamus tinctorius*; *Gardenia jasminoides*; *Monascus*; *Sambucus nigra*; Pigments; Anthraquinones

Contents

1. Introduction

1.1. Analysis of natural food pigments

Natural food pigments are used extensively as food additives to enhance sensory response and to promote sales. The quantities of the various natural pigments used in Japan in 1994, are shown in Table 1 [1]. Several varieties of natural food pigments (carotenoids, anthocyanins, flavonoids, anthraquinones and others) are used as color additives. When

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Table 1
Amounts of natural food pigments used in Japan in 1994 [1]

Food pigment	Amount (kg)
Carotenoids	1 230 000
Annatto	550 000
Paprika	250 000
Gardenia yellow	350 000
Extracted carotene	80 000
Anthocyanins	385 000
Red cabbage	100 000
Grape skin	100 000
Berry	90 000
Purple corn	50 000
Grape juice	20 000
Red perilla	15 000
Purple sweet potato	10 000
Flavonoids	308 000
Kaoliang	26 000
Onion	50 000
Shea nut	2 000
Cacao	50 000
Safflower	180 000
Anthraquinones	133 000
Cochineal	120 000
Madder	10 000
Lac	3 000
Others	1 195 000
Beet	230 000
Curcumin	150 000
Monascus	700 000
Gardenia blue	100 000
Spirulina	15 000
Total	3 251 000

natural food pigment is utilized to color food, it is a requirement to indicate what is used if the pigment remains in the final products in a detectable amount. Therefore, analytical methods that can detect, identify and quantify the pigments contained in food are required.

Several methods have been developed to analyze the components of natural food pigments: thin-layer chromatography (TLC) [2–7], gas chromatography (GC) [8], high-performance liquid chromatography (HPLC) with a visible light absorbance detector [9–14] or a photodiode array detector [15,16] and HPLC–mass spectrometry (LC–MS) [1,17] are the most powerful analytical separation methods. However, analysis using these methods is difficult because the concentration of the sample recovered from food is often very dilute. In recent years, capillary electrophoresis (CE) has been applied to the analysis of various food ingredients [18–29]. This is because CE utilizes high resolution, short analysis time, and minimal amounts of samples. There are numerous reports on the analysis of synthetic food pigments by CE [30–36] and HPLC [37–41], but only a few manuscripts, including those by the authors [42–46] describe the analysis of natural food pigments using CE. This review describes the CE analysis of several natural food pigments mostly performed in the author's laboratories.

1.2. Capillary electrophoresis

In 1967, the first free zone electrophoresis experiments, employing a rotating glass tube of 3-mm I.D. [47], were reported by Hjertén. Later, 200-μm I.D. capillaries made of glass or PTFE were used successfully, allowing the application of higher electric fields [48,49]. In 1981, Jorgenson and Lukacs, using 75-μm I.D. glass capillaries and on-column fluorescence detection [50], described the potential of CE as an analytical technique. Since that time, the use of CE as a new technique for the separation and analysis of chemical compounds has increased gradually. CE offers simpler method development, minimal sample volume requirements, and less organic solvent waste.

Several separation modes of CE can be classified, each possessing its own characteristic separation mechanism: capillary zone electrophoresis (CZE), micellar electrokinetic chromatography (MEKC), capillary gel electrophoresis (CGE), capillary isoelectric focusing (cIEF), capillary isotachophoresis (cITP) and capillary electrochromatography (CEC). CZE, MEKC, CGE and CEC are zonal types of CE, whereas cIEF is considered a focusing technique, and cITP a moving boundary or displacement technique. Among these separation modes, CZE and MEKC are most effectively employed for the separation of small molecules.

1.3. Capillary zone electrophoresis

CZE is the most widely used mode because it is

applicable to separations of both anions and cations, and from small ions to particles. Application areas of CE include the analysis of amino acids, peptides, proteins and numerous other ionic chemical compounds. In CZE, the capillary is simply filled with a buffer. Separation of both anionic and cationic solutes is possible in one run by CZE due to the strong electroosmotic flow (EOF) under neutral or alkaline conditions. EOF is the bulk flow of liquid inside the capillary and is a consequence of the surface charge on the inside wall of the capillary and an applied electric field. Neutral solutes do not have the electrophoretic mobility and migrate with the EOF. Fig. 1 schematically shows a CZE separation of a model mixture. A sample is injected at the anodic end of the capillary, and a high voltage is applied between the two ends of the capillary. The solutes are separated as zones according to the differences in electrophoretic mobilities, which mainly depend on the charge and mass of the analyte, during migration in the capillary. EOF carries the whole bulk solution through the capillary toward the cathode. To optimize the CZE separation, the pH of the running buffer is the most important factor and the use of additives interacting with analytes is another choice to improve selectivity.

1.4. Micellar electrokinetic chromatography

In 1984, Terabe et al. developed MEKC, a capillary electrophoretic technique at the crossroad of chromatography and electrophoresis [51–55]. The development of MEKC is a major advancement in CE because it has provided a method for separation of electrically neutral compounds. In MEKC, an ionic surfactant is added at a higher concentration than the critical micelle concentration, to the electrolyte solution, forming a pseudo-stationary micellar phase. A schematic representation of the separation mechanism of MEKC using an anionic surfactant is shown in Fig. 2. The separation system consists of an electroosmotically moving aqueous phase and an electrophoretically moving pseudo-stationary micellar phase. When an uncoated fused-silica capillary is employed, the strong EOF transports the bulk buffer solution towards the cathode owing to the negative charge on the capillary surface. The migration order for neutral analytes in MEKC generally is related to the hydrophobicity of the analyte: more hydrophobic analytes migrate slower than less hydrophobic ones. The migration time of the neutral analyte is limited between the migration time of EOF and that of the micelle.

2. Lac and cochineal pigments

Natural pigments for food are classified into several groups according to the fundamental chemical structure, in which the quinone structure constitutes a class of natural pigments. A large number of natural anthraquinones show yellow or red and about 170 species are known as natural pigments. Main commercial anthraquinone pigments are lac and

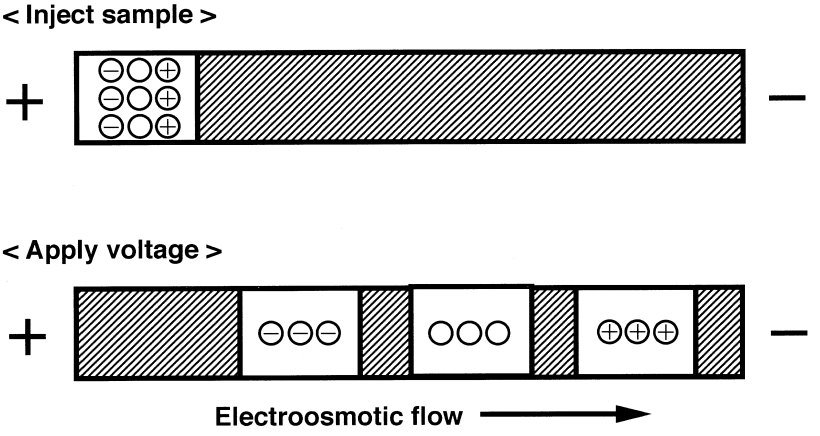


Fig. 1. Schematic separation in CZE with EOF.

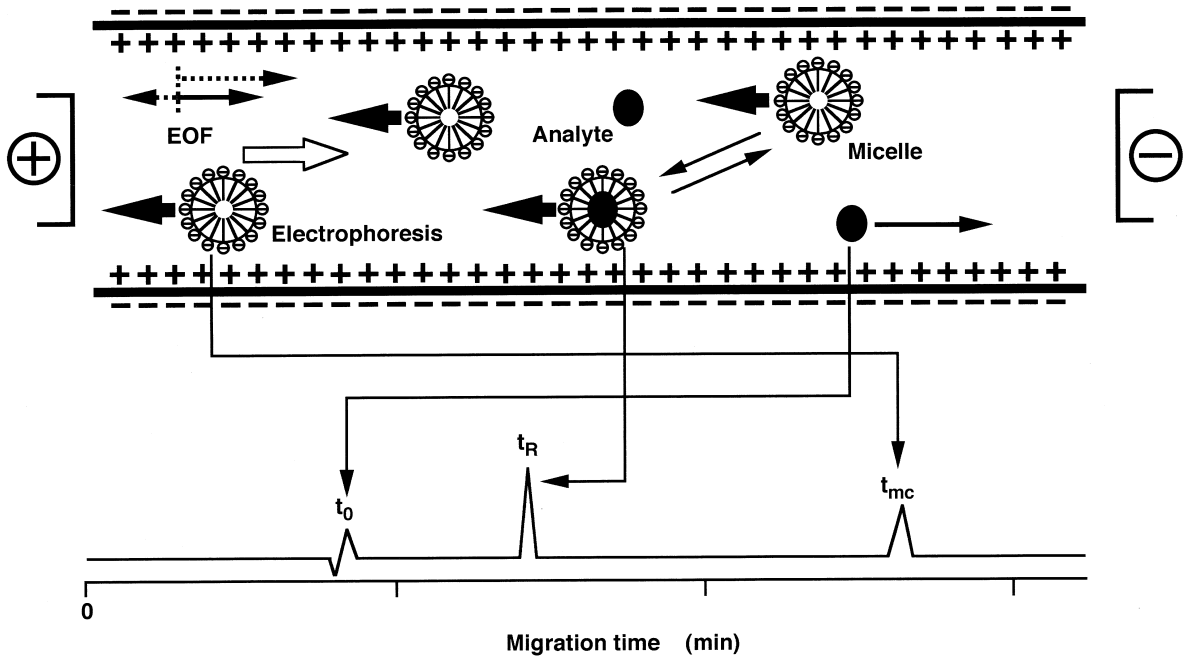


Fig. 2. Schematic principle of MEKC with anionic micelle. t_0=migration time of a neutral 'unretained' solute, t_R='retention' time in MEKC, t_{mc}=migration time of a micellar aggregate.

cochineal pigments in Japan. The lac, *Laccifer lacca* KERR, a resinous material (stick-lac) produced by a female insect, originated in India and Thailand. Red lac pigments are extracted with water from the stick-lac and consist of numerous chemical species, laccaic acid A, laccaic acid B, laccaic acid C and others as the major components, as shown in Fig. 3A [56–62]. An insect, cochineal, living on a cactus originated in Mexico [63]. Cochineal pigments extracted from dried insects are dark red powders and the main component is carminic acid [64–66], as shown in Fig. 3B.

MEKC with a high-molecular-mass surfactant, butyl acrylate–butyl methacrylate–methacrylic acid copolymer sodium salts (BBMA), solution in an ammonium formate buffer at pH 7.0 [67,68], including 1 m*M* ethylenediaminetetraacetic acid sodium salt (EDTA) was successful for separating the lac and cochineal pigments [42]. Addition of EDTA to the BBMA solution markedly improved reproducibil-

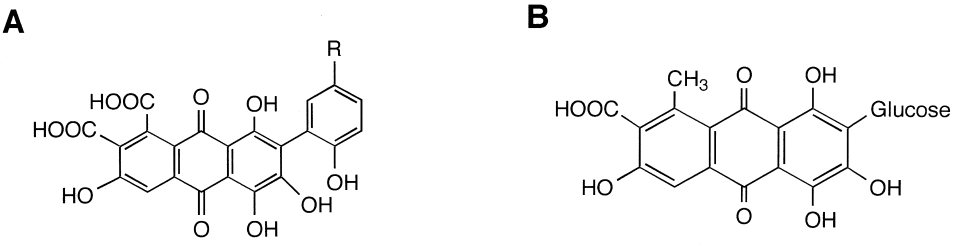


Fig. 3. Structures of the main components of lac (A) and cochineal (B) pigments.

ity probably due to the masking effect of EDTA against metal ions which may form complexes with the anthraquinones. The repeatability of the method was also evaluated for intra-day variability. No significant difference in separation patterns and migration times was observed among the repeated runs for the lac and cochineal pigments. The principal component of the lac pigment isolated by HPLC was measured by fast atom bombardment mass spectrometry (FAB-MS). The molecular mass strongly suggested that the principal component of the red lac pigments was laccaic acid A [42].

3. Safflower pigments

Safflower, *Carthamus tinctorius* L., is indigenous to Egypt and is known as a herb [69]. Its flowers produce red and yellow pigments. Red safflower pigment was originally used as a cosmetic and textile dye, and today is also used as a food colorant [70,71]. The main component of the red pigment is called carthamin [72–76] (Fig. 4A), and due to its low solubility in water, the red pigment is mainly used in colored chocolate in Japan. The yellow safflower pigment, on the other hand, has been used as a natural food colorant for a long time [77], mainly in colored juice, jelly and candy because of its water solubility. The yellow pigment has numerous components [77–81], safflomin A and safflor yellow B being the main ones, as shown in Figs. 4B and 4C.

Since the yellow pigment of safflower has several diol groups, CZE was performed with a borate buffer at various alkaline pH values [43]. Good separation was obtained at pH 9.0, although it needed a long time to complete the separation, as shown in Fig. 5A. However, MEKC with BBMA solution in an ammonium formate buffer at pH 7.0, gave better resolution and short analysis times of the yellow pigment, as shown in Fig. 5B. The red pigment of safflower was also successfully separated by MEKC with the BBMA solution. Mass spectra for the principal component of the yellow safflower pigment isolated by HPLC were measured by FAB-MS. The molecular mass strongly suggested that the principal component of the yellow pigments was safflomin A as suggested in an earlier report [77].

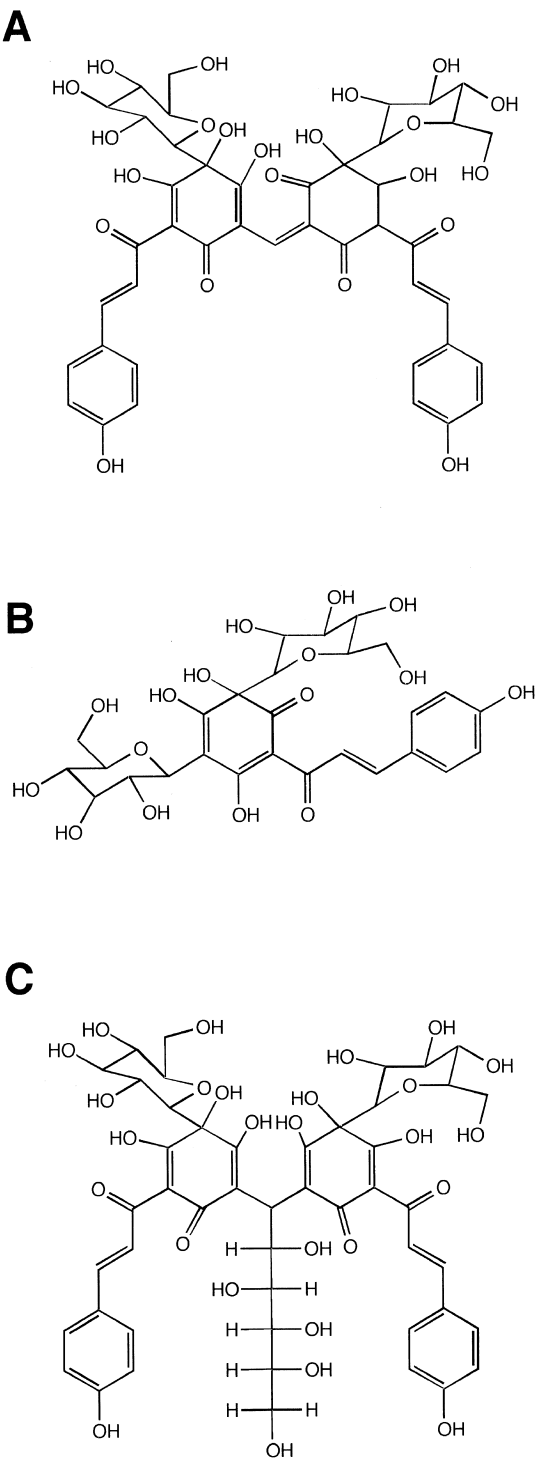


Fig. 4. Structures of red and yellow safflower pigments. A=carthamin, B=safflomin A, C=safflor yellow B.

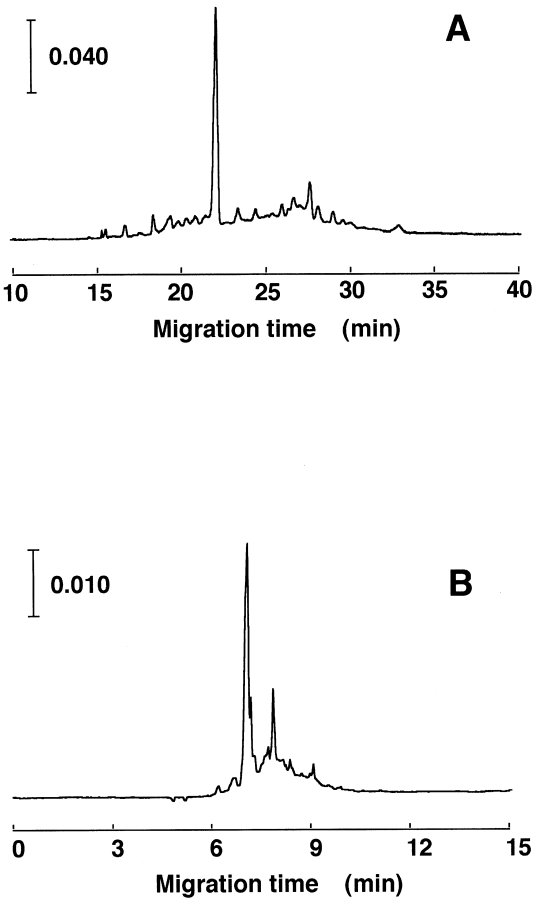


Fig. 5. Separation of the yellow safflower pigments by CZE (A) and MEKC (B) [43]. (A) CZE conditions: capillary: 50 cm×50 μm I.D.; running solution: 300 m*M* borate buffer at pH 9.0; applied voltage: 15 kV; temperature: 20°C; detection: 400 nm. (B) MEKC conditions: running solution: 20 m*M* ammonium formate buffer at pH 7.0 containing 2% BBMA. Other conditions are the same as those in A.

4. Gardenia pigments

The constituents of gardenia fruits, *Gardenia jasminoides* ELLIS, are known as herb medicine and natural dyes in China. The fruits produce yellow carotenoid pigments and iridoid compounds. The two main components in the yellow pigments are called crocin and crocetin, as shown in Fig. 6A [82–84], and the yellow pigments have been used as a natural food colorant for a long time in Japan, mainly in colored juice, jelly, candy and noodles, because of their water solubility. The iridoid constituents of gardenia fruits, which are used as tranquilizers and precursor of gardenia blue pigments, are called geniposide and gardenoside, as shown in Fig. 6B [85]. There are a few reports on the analysis of yellow gardenia pigments [86] and iridoid gardenia constituents [87,88] by HPLC.

MEKC with an SDS solution in a phosphate buffer at pH 7.0, containing acetonitrile was successful for separating the gardenia yellow pigments. In order to check the reproducibility of the separation of gardenia yellow pigments containing mainly crocin, pigments was repeatedly analyzed 15 times by MEKC with the solution containing acetonitrile. No significant difference in the separation pattern and migration time was observed among the repeated runs of the yellow pigments [44].

Crocin and crocetin were successfully extracted from commercial food samples by SPE. The recovery of each pigment by SPE was found to be 82%, which was determined by a decrease in the absorbance of each aqueous solution of the original yellow pigment by SPE. Fig. 7A shows the MEKC separation of the pigments extracted from noodles,

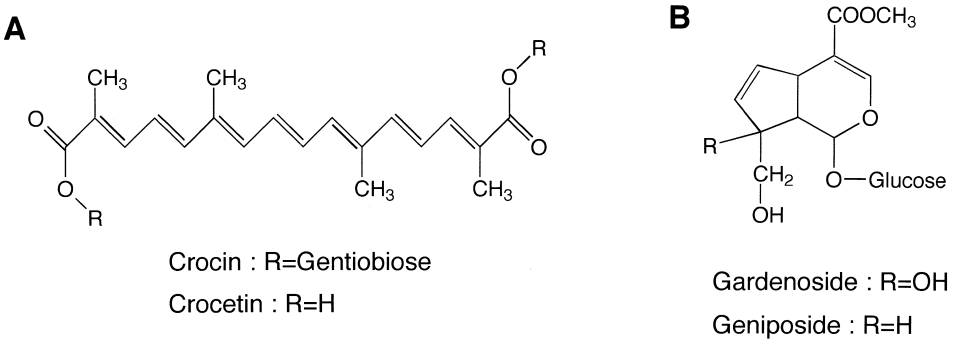


Fig. 6. Structures of carotenoid yellow pigments (A) and iridoid compounds (B) in gardenia fruits.

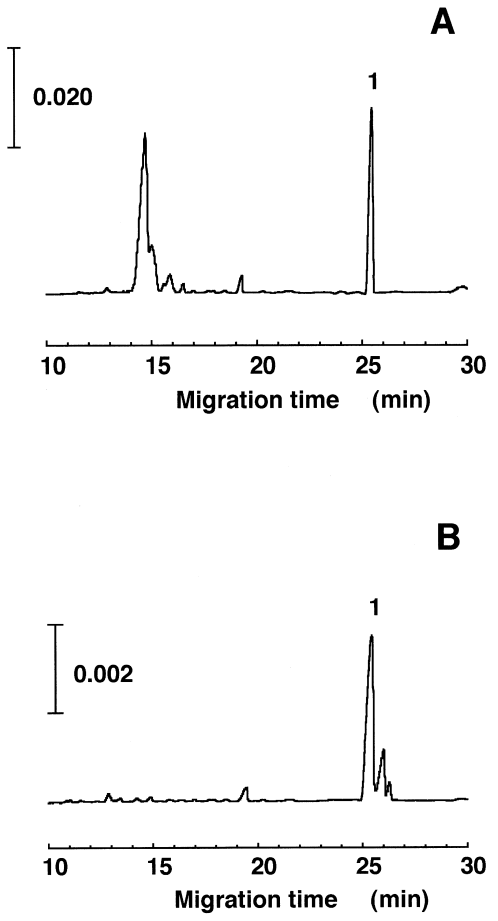


Fig. 7. Separation of yellow pigments extracted from commercial noodle (A) and commercial yellow gardenia pigments (B) [44]. MEKC conditions: (A) capillary: 50 cm×50 μm I.D.; running solution: 20 m*M* SDS solution in 50 m*M* phosphate buffer at pH 7.0 containing 20% acetonitrile; applied voltage: 15 kV; temperature: 20°C; detection: 440 nm. (B) Conditions as in (A). Peaks: 1=crocetin.

and the peak at 25 min was identified as that of crocetin by comparing the electropherogram of the standard pigments (Fig. 7B) [44].

Geniposide and gardenoside were extracted from the shattered gardenia fruit using distilled water. For the separation of geniposide and gardenoside, MEKC with an SDS solution in a borate buffer at pH 8.5, was successful. Compared to the HPLC method, the MEKC method is advantageous due to its low running cost and shorter analysis times. Table 2 shows the contents of geniposide and gardenoside in gardenia fruits from several habitats. Zhejiang, China-grown gardenia fruits contained about 46 mg/g geniposide and 16 mg/g gardenoside (ratio=0.35); however, Korea-grown gardenia fruits contained about 31 mg/g geniposide and 27 mg/g gardenoside (ratio=0.88). Hubei, China-grown gardenia fruits contained the greatest amount of the geniposide, and Taiwan-grown gardenia fruits had the highest content of the gardenoside [44].

Table 2
MEKC determination of the gardenoside and geniposide extracted from gardenia fruit samples [44]

Habitat	Quantitation (mg/g)		Gardenoside/geniposide
	Gardenoside	Geniposide	
Sichuan (China)	27.2	59.1	0.46
Guangxi (China)	28.0	56.2	0.50
Hubei (China)	28.7	76.1	0.38
Zhejiang (China)	16.1	46.4	0.35
Shanghai (China)	17.2	44.5	0.39
Taiwan	30.8	41.2	0.75
Korea	27.2	30.8	0.88

5. Monascus pigments

The fungi *Monascus* is a source of a natural colorant which has been used as ‘red rice’ and ‘red rice wine’ in China, Indonesia, Taiwan and some other oriental countries for hundreds of years. The *Monascus* pigments are composed of red, yellow and purple pigments. The fungi *Monascus* produce six major free pigments: rubropunctatin, monascorubrin, rubropunctatamine, monascorubramine, monascin and ankaflavin and also complexed pigments [89,90]. The free pigments are insoluble in water. However, their complexation with proteins and peptides in the culture medium makes them soluble in aqueous media. According to a recent toxicological study, the *Monascus* pigments were shown to be nontoxic to rats and mice [91]. Then, the red natural coloring material which is produced from *Monascus* species was used as a food additive in Japan. Recently, the mutant strain of *Monascus* was found to produce novel yellow pigments designated as xanthomonasin A and xanthomonasin B [92], as shown in Fig. 8. The yellow pigments were also used as a food additive in Japan.

MEKC with an SDS solution in a phosphate buffer

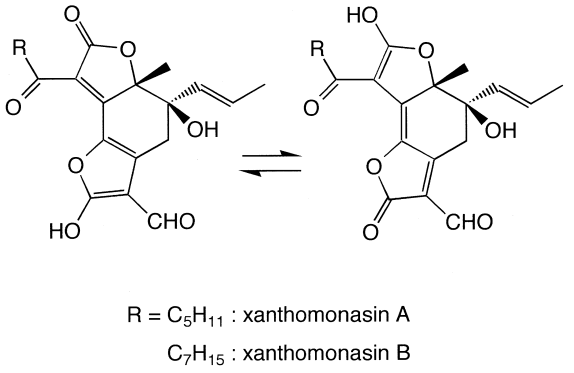


Fig. 8. Structures of *Monascus* yellow pigments: xanthomonasin (A) and xanthomonasin (B).

at pH 7.0, containing 20% acetonitrile or a BBMA solution in ammonium formate buffer at pH 7.0, containing 10% methanol were successful for separating the *Monascus* yellow pigments. The highest peak in either electropherogram was identified as xanthomonasin A and the second highest peak as xanthomonasin B [92], as described later. In order to check the reproducibility of the separation of *Monascus* yellow pigments by the proposed method using the SDS solution containing acetonitrile, *Monascus* yellow pigments were analyzed repeatedly 20 times. No significant difference in the separation pattern and migration time was observed among the repeated runs. The *Monascus* yellow pigments were analyzed also by on-line MEKC–ESI-MS using BBMA as a pseudo-stationary phase. Fig. 9 shows the single ion chromatograms obtained by on-line MEKC–ESI-MS at *m*/*e* 437 and 465. The molecular mass of the xanthomonasin A, first migrating peak, was estimated to be 388 from *m*/*e* 437 peak of MEKC–ESI-MS, and xanthomonasin B, the second migrating peak, was estimated to be 416 from *m*/*e* 465 peak of MEKC–ESI-MS, in Fig. 9, because *m*/*e* 437 peak of xanthomonasin A and *m*/*e* 465 peak of xanthomonasin B were probably due to the addition of methanol (molecular mass 32) and water (molecular mass 18) ions [45].

6. Elderberry pigments

Elderberry, *Sambucus nigra* L., is a brilliant red–purple colored fruit, which is used in Europe to prepare candies, jams, jellies and beverages [93]. The juice squeezed from elderberry fruits contains red–purple pigments. The pigments of elderberry are anthocyanins, and are widely used as safe food colorants in Japan. Brønnum-Hansen et al. [94] reported on the structures of the four main anthocyanins from elderberry pigments: cyanidin-3-sambubioside-5-glucoside (CSG), cyanidin-3-glucoside-5-glucoside (CGG), cyanidin-3-sambubioside (CS) and cyanidin-3-glucoside (CG). The color of the

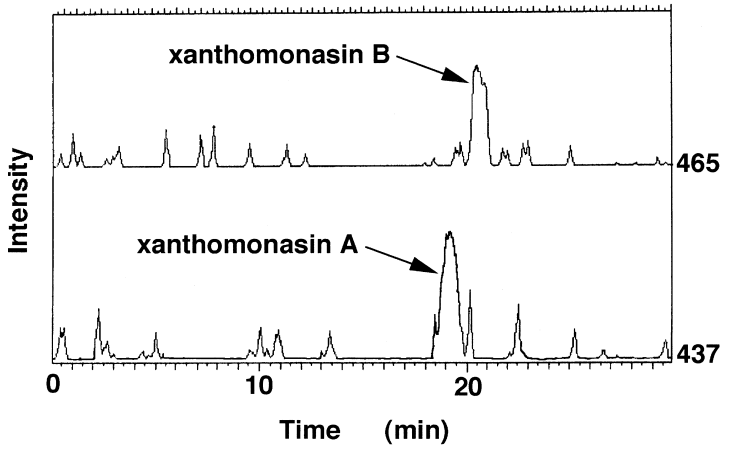
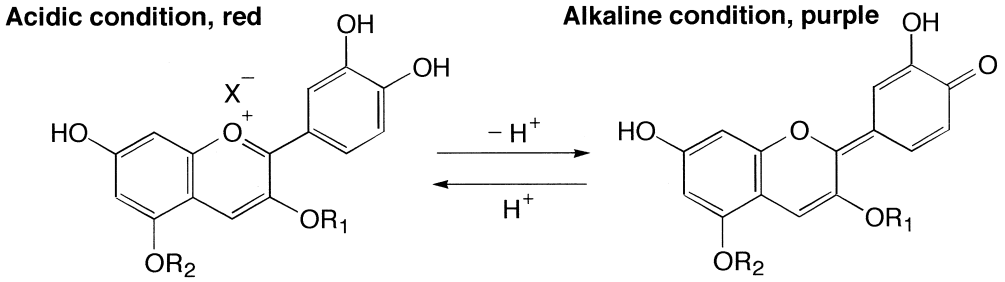


Fig. 9. Single ion chromatograms of xanthomonasin A and xanthomonasin B obtained by MEKC–ESI-MS [45]. MEKC–ESI-MS conditions: capillary: 50 cm×50 μm I.D.; running solution: 2% BBMA in 20 m*M* ammonium formate buffer at pH 7.0 containing 10% methanol; applied voltage: 13 kV; electrospray voltage: 3 kV; sheath liquid: water–methanol–formic acid (50:50:1, v/v/v) at ca. 5 ml/min.



Compounds		R_1	R_2
Cyanidin-3-sambubioside-5-glucoside	(CSG)	Xylopyranosyl-glucopyranoside	Glucopyranoside
Cyanidin-3-glucoside-5-glucoside	(CGG)	Glucopyranoside	Glucopyranoside
Cyanidin-3-sambubioside	(CS)	Xylopyranosyl-glucopyranoside	H
Cyanidin-3-glucoside	(CG)	Glucopyranoside	H

Fig. 10. Structures of elderberry pigments.

Table 3
Analytical results of natural food pigments extracted from commercial food samples [42–46]

Food sample	Pigment	Compound	*n*	Migration time		Quantitation	
				Mean (min)	RSD (%)	Mean (μg/ml)	RSD (%)
Jelly	Lac	Laccaic acid A	4	13.12	0.76	234	2.55
	Cochineal	Carminic acid	4	10.58	0.38	639	0.37
	Elderberry	CSG	3	4.49	0.45		
		CGG	3	4.66	0.43		
		CS	3	6.52	0.37	905	3.24
		CG	3	7.33	0.35	439	4.62
Juice	Cochineal	Carminic acid	4	10.55	0.28	850	0.47
	Safflower	Safflomin A	4	21.33	0.26	427	2.36
Candy	Safflower	Safflomin A	4	21.17	0.45	1253	0.94
	Gardenia	Crocin	3	12.22	0.48	590	2.54
	Monascus	Xanthomonasin A	5	12.88	0.87	105	2.38
		Xanthomonasin B	5	16.47	0.99	76	2.45
	Elderberry	CSG	3	4.48	0.38		
		CGG	3	4.65	0.36		
		CS	3	6.51	0.32	863	2.36
		CG	3	7.32	0.31	421	3.54
Noodle	Gardenia	Crocetin	3	25.24	0.64	67	2.38

elderberry pigments changed from red (acidic condition) to purple (alkaline condition), as shown in Fig. 10.

Brønnum-Hansen et al. [94] reported on the separation of the extracts of anthocyanins from elderberry by HPLC. Bridle et al. [95] reported on the separation of anthocyanins by CZE with a pH 8.0 borate running buffer. However, the color was not stable under alkaline conditions. Separation of anthocyanin pigments must be under acidic or neutral conditions. Therefore, the elderberry pigments were separated by MEKC with an SDS solution in a phosphate–borate buffer at pH 7.0. Elderberry pigments are used for coloration of candy, juice and jelly owing to their acid stability. The recovery of elderberry pigments from food samples containing 0.1% pigments by SPE was found to be from 74.2% to 94.1%, respectively, by HPLC and MEKC analyses. Fig. 11 shows an electropherogram of the pigment extracted from a commercial jelly sample, which was similar to that of the commercial elderberry pigments for food additives [46].

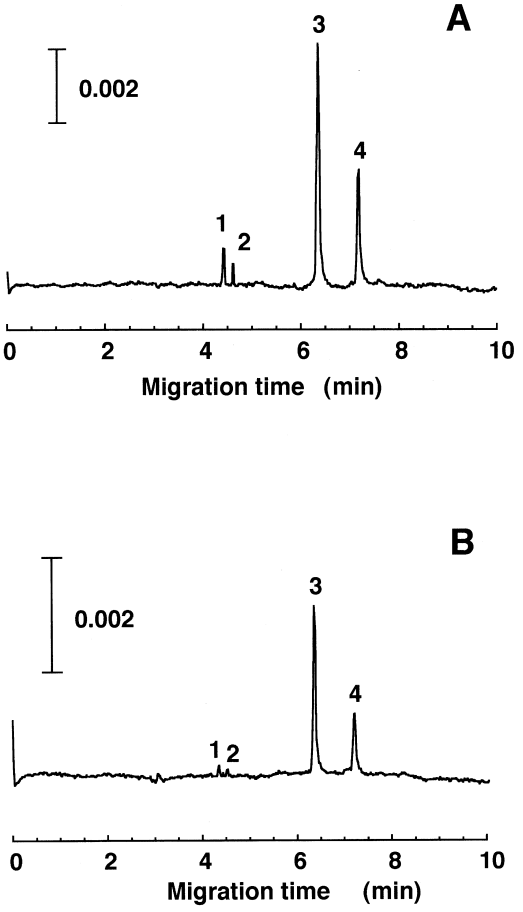


Fig. 11. Separation of elderberry pigments (A) and extraction from a commercial jelly sample (B) by MEKC [46]. MEKC conditions: (A) capillary: 36 cm×50 μm I.D.; running solution: 30 m*M* SDS solution in 30 m*M* phosphate–60 m*M* borate buffer at pH 7.0; applied voltage: 10 kV; temperature: 20°C; detection: 560 nm. (B) Conditions as in (A). Peaks: 1=cyanidin-3-sambubioside-5-glucoside (CSG), 2=cyanidin-3-glucoside-5-glucoside (CGG), 3=cyanidin-3-sambubioside (CS), 4=cyanidin-3-glucoside (CG).

7. Validation of pigments extracted from food samples

Lac, cochineal, safflower, gardenia, *Monascus* and elderberry pigments were extracted by an SPE method from commercial food samples, such as juice, jelly, candy and noodle. Juice with a dark color was analyzed without any pretreatment. The recovery of the pigments by SPE was found to be 65 to 85%, which was determined by a decrease in the absorbance of each aqueous solution of the original pigments by SPE. The analytical results in Table 3 show that natural food pigments extracted from commercial food samples are quantitated with good separation. The intra-day variation was measured by analyzing from three to five times. The detection limit of these pigments was from 0.05 to 0.2 μg/ml. The relative standard deviation (RSD) of the migration times was less than 1.2% and that for quantitation was less than 5.0% [42–46].

8. Conclusions

In conclusion, CE has been proven to be a useful technique for analyzing natural food pigments, such as lac, cochineal, safflower, gardenia, *Monascus* and elderberry. The amount of the sample required for the analysis is very small, and the repeatability of migration times and quantitation is high even for real samples, probably due to the absence of any packing material inside the capillary. Another advantage of the CE method is its low running cost. This CE

method can be applied to quality control analysis in food additives. The CE method will also be widely applicable to the analysis of different food additives.

9. Nomenclature

BBMA	acrylate–butyl methacrylate–methacrylic acid copolymer sodium salts
CE	capillary electrophoresis
CEC	capillary electrochromatography
CG	cyanidin-3-glucoside
CGE	capillary gel electrophoresis
CGG	cyanidin-3-glucoside-5-glucoside
cIEF	capillary isoelectric focusing
cITP	capillary isotachophoresis
CS	cyanidin-3-sambubioside
CSG	cyanidin-3-sambubioside-5-glucoside
CZE	capillary zone electrophoresis
EDTA	ethylenediaminetetraacetic acid sodium salt
EOF	electroosmotic flow
ESI-MS	electrospray ionization mass spectrometry
FAB-MS	fast atom bombardment mass spectrometry
GC	gas chromatography
HPLC	high-performance liquid chromatography
LC–MS	HPLC–mass spectrometry
MEKC	micellar electrokinetic chromatography
PTFE	poly(tetrafluoroethylene)
RSD	relative standard deviation
SDS	sodium dodecylsulfate
SPE	solid-phase extraction
TLC	thin-layer chromatography

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