Advances in Capillary Chromatography *

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Abstract Capillary columns are used in both capillary liquid chromatography and capillary electrochromatography. The design for capillary liquid chromatography is discussed in comparison with capillary gas chromatography. The difference of diffusion coefficient in gas and liquid phase is a key role. The study for obtaining a high performance capillary liquid chromatography is discussed. Capillary electrochromatography is recently interesting for its instinct ability to realize a high performance chromatography. Capillary electrochromatography with and without pressurized flow is reviewed briefly. Instrumentation for capillary electrochromatography with pressurized flow is described. The port of splitting and gradient elution of both solution and potential are described. The new findings of both the variation of column resistance and capacity factor according to the value of applied electric voltage are also discussed.

Key words capillary liquid chromatography, pressurized flow, electrochromatography, capillary column, split injection, effect of electric field, variation of electric resistance

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1 Capillary columns in liquid chromatography

1.1 Size of flow channel necessary to be designed

At date of 1970 \[ E \pi \text{ capillary gas chromatography had a highest efficiency in chromatographic field. People would like to have also such a high efficient tool in liquid chromatography. What the design of capillary liquid chromatography should be} \]

From the comparative study between gas chromatography and liquid chromatography \[ E \pi \text{ the key factor is mass transfer term} \]

that is mainly related diffusion coefficient \[ E \pi \text{. Average outer reach} \]

\[ s \text{ distance from a certain place} \]

\[ t \text{ for a certain period} \]

\[ t \text{ is given by the following equation by Einstein} \]

\[ d^2 = 2D t \]

\[ E \pi \]

Therefore the outer reach \[ s \text{ distance in liquid phase is about one} \]

- one hundredth of that in gas phase \[ E \pi \] which is derived from equation 1. In those days \[ E \text{ the inner diameter of capillary column used in gas chromatography was in the range of} \]

250 \( \mu \text{m} \) to 500 \( \mu \text{m} \). From the comparative study \[ E \text{ we needed to construct a capillary column with inner diameter of} \]

2.5 \( \mu \text{m} \). It was almost impossible to make such a capillary column of a small inner diameter. In other choice we can extend the period of stay of a solute in a theoretical plate. When we set 10 times longer period of the stay \[ E \text{ the outer reach} \]

\[ s \text{ distance} \]

\[ \text{comes to be} \]

3.3 times larger. The longer stay in a theoretical plate is equal to slower flow velocity of mobile phase. In this condition we can use the capillary with 7.5 \( \mu \text{m} \) inner diameter for open-tubular capillary liquid chromatography \[ E \pi \]. The capillary column with such a small inner diameter was still not possible to accept in those days.

1.2 Trial experiments started

In gas chromatography there are four types of capillary column \[ E \pi \] namely wall coated open tubular, porous layer open tubular, support coated open tubular and packed microcapillary columns \[ E \pi \]. Capillary liquid chromatography would have similar kinds of design as those of capillary gas chromatography. Packed microcapillary column is different from other types of capillary column \[ E \pi \] that the adsorptive material is drawn inside of capillary during the process of capillary drawing. The state of packing is rather loosely \[ E \] and the values of ratio of particle diameter to inner diameter of capillary are 0.2 to 0.5 \[ E \] whereas conventional packed column is well below 0.1. The flow channel in packed capillary column comes to be small \[ E \]
because the inside room is occupied mostly by packed materials.

Tsuda and Novotny have presented the first adaptation of this method at 1978. Activated alumina of 30 μm in particle diameter was loosely packed in a microcapillary column of 75 μm inner diameter and 29 m in length. The cross sectional view is shown in Fig. 1. In this case flow channel is supposed to be about 5 μm-10 μm. A very high theoretical number of 85 000 for quinoline was obtained by using a packed microcapillary column although its retention time was 100 min. Relative short retention time and high theoretical plate number have been achieved by using a packed microcapillary column of 10 μm particle, namely 15 min and 68 000 for dimethyl phthalate respectively under a linear velocity of mobile phase 4.2 cm/s and k' 4.84 respectively shown in Fig. 2. The value of flow resistance parameter $E_0$ for packed microcapillary column is about 80 to 120. The values of $E_0$ for open tubular capillary column and conventional packed column are 32 and 900 respectively. Therefore packed microcapillary has a very small flow resistance. Several applications with high efficiency have been demonstrated. The highest theoretical plate number obtained is up to 300 000. Although the production of packed microcapillary column is not easy it is necessary to avoid any introduction of moisture during its drawing process. The character is quite good and gives a very high efficiency.

The first investigation of open-tubular capillary liquid chromatography was reported by Nota et al. at 1976. They used a capillary column of 230 μm inner diameter. Owing to relatively large column diameter the separation was poor even though the separation was taken for 5 hours. By using open tubular capillary column with 60 μm inner diameter and 3 m in length aromatics were separated in 20 min-60 min with a theoretical plate number of about 600-1 000.

Although the inner diameter used was still far larger compared to that demanded theoretically less than 10 μm the chromatogram obtained was almost similar to those chromatograms presented at the early developing stage of high performance liquid chromatography. The stationary phases used were physically coated with silicone grease and chemically bonded with octadecyl silane. We worked for both reducing the inner diameter of open tubular capillary column and improving stationary phases to obtain a small value of the mass transfer term in mobile and stationary phase respectively. The smallest inner diameters tried were down to 5 μm-10 μm and 2 μm. The best chromatogram obtained by using an open tubular capillary column of 10 μm inner diameter is 30 cm in length and chemically bonded stationary phase γ-aminopropylsilane shown in Fig. 3. Theoretical plate number for peak 9 in Fig. 3 is 38 000. The high theoretical plate number obtained by open tubular capillary liquid chromatography is up to 50 000. This number is less than those obtained by capillary gas chromatography. At present the inner diameter smaller than 7 μm is not practical because it is easily clogged up by an introduction of small dust particles.

**Fig. 1** Electron micrograph of cross section of a packed microcapillary column

B is a part of A. Magnification of A and B are 1 500 x and 7 500 x respectively.

**Fig. 2** Chromatogram obtained by capillary liquid chromatography using a packed microcapillary column

Column 10.3 m × 47 μm i. d. Inlet pressure 49 MPa, 500 kg/cm² linear velocity 4.2 cm/s. Sample 1, didecyl, 2, dimethyl, 3, diheptyl, 4, dicyclohexyl, 5, dibutyl, 6, dipropyl, 7, diethyl, 8, dimethyl phthalate.
into the capillary column. When we would like to operate a capillary liquid chromatographic column with very small inner diameter such as less than 7 μm, we need a clean room for its operation. In the near future we may have a really high efficient capillary liquid chromatographic column.

1.3 Formation of stationary phase of a large surface area

The thickness of stationary phase in capillary gas chromatography is 0.3 μm or more. In stationary phase the mass transfer terms in GC and LC are governed by diffusion coefficient in liquid-liquid. Generally the operational temperature in GC is 100 centigrade or more, instead of room temperature commonly used for LC. As diffusion coefficient depends on temperature the difference of 70 centigrade increases diffusion coefficient two times compared to that at room temperature. The term of mass transfer in liquid phase would be given by period necessary for mass transfer in stationary phase

$$d_i^2/2D_i$$

where $d_i$ and $D_i$ are the film thickness of stationary phase and diffusion coefficient in liquid phase respectively. Therefore the film thickness in capillary liquid chromatography might be less than 0.2 μm on the basic consideration of comparative study between GC and LC. The other characteristic point demanded to stationary phase is that the surface area should be large enough to attain instantly the equilibrium derived molecular movement. The large surface area increases also the loading capacity of solute in the stationary phase.

When we use particles such a way of either loosely packing in the capillary or loading on its inner wall they give a relatively large surface area and give a good loading capacity. But in case of open-tubular capillary column without particle supports we need to modify the inner glass surface chemically. It is possible to employ the several methods used in capillary gas chromatography with minor alteration.

The treatments of inner glass capillary tubing are as follows: surface dissolution and silica-network frame-formation by sodium hydroxide and ammonium hydrogen fluoride, deposition of small particle of activated alumina or silica gel on the inner glass surface.

Concerning the thickness of stationary phase it is not difficult to attain ideal thin film condition. In the case of chemically bonded stationary phase its thickness is around 10 to 40 angstrom if chemical bonding is performed in the state of monolayer. Although the dispersion of liquid such as β-dipropionitrile on the etched glass surface was not well under microscopic observation it showed a good chromatographic performance. But highly viscous liquids such as polyethylene glycol or silicone grease did not work well compared to β-dipropionitrile. The reason may be due to the difference of the values of diffusion coefficient in it.

Consequently one of the key important factors in open-tubular capillary liquid chromatography is to obtain a stationary phase having a high surface area.

2 Capillary electrochromatography

The application of electric field is one of the most exciting topics in science today. The introduction of electric field in chromatography offers the prospect of remarkable advances with its application in the area of separation science. Electrochromatography is a unique separation method with high selectivity and efficiency. Capillary electrochromatography in which electric field is applied along the column is a combined form of liquid chromatography and electrophoresis. There are several mode of capillary electrochromatography such as with and without a pressurized flow or the use of...
pressurized reservoirs at both ends of a column for pressure-assisted chromatography.

Original papers concerning capillary electrochromatography were published by J. W. Jorgenson and K. D. Lukacs at Tsuda et al. at 1982. The chromatogram obtained is shown in Fig. 4. In electrophoresis and electroosmosis nearly plug like flow profile of electroosmosis is nearly plug like. Namely, the central flow velocity is almost equal to the edge of cross-section. Therefore the broadening in mobile phase comes to less than one-thirty of that in Poiseuille flow. After the late of 1980s fused silica capillary tubing has been used for both open tubular and capillary liquid chromatography and capillary electrophoresis for obtaining a high surface area on the inner wall of fused silica capillary have been pursued again.

An excellent chromatogram with 10 μm open tubular capillary column was obtained for a capillary column with ODS-modified porous silica layer and on-column detection.

2.2 Slurry-packed capillary columns in electrophoresis

Typical chromatograms in early days are shown in Fig. 5 and Fig. 6 for the separations of aromatic acids and o-phthalaldehyde derivatives of polyamines with a glass capillary column packed with 3 μm ODS-silica under applied voltage. In slurry-packed capillary column the contribution of electroosmotic flow profile for band broadening in mobile phase is quite few. However, in particular in the condition of a small capacity factor such as less than 2. So, very fine separation became possible. As electroosmosis is generated by the action of molecules in medium, the flow does not cause an increase of pressure as far as the space is not limited. Therefore we can operate capillary electrophoresis by using a column packed with sub-micrometer particles. Further more we can operate capillary electrophoresis with high linear velocity that is high speed analysis. We need to make device for the use of these instinctual nature of electroosmosis. One of the possible approaches is to perform chromatography with a very high linear flow velocity which is not possible to be realized by pressure flow.

3 Pressurized flow driven capillary electro-chromatography

In this section we review briefly the temporal art of the instrumentation of capillary electrochromatography with pressurized flow. As nomenclature there are two names for pressurized flow driven capillary electrophoresis and pseudo-electrochromatography. Fortunately both abbreviations are same as pressurized flow.

Sample movement in a column under applied voltage is shown schematically in Fig. 7. The direction of the flow velocity
of a solute is the result of the summation of three flow velocities: flow velocity derived electrophoretic mobility, electroosmotic velocity and pressurized flow velocity.

There are two methods of generating a pressurized flow. The first uses a modern LC pump and the second uses gravity. With LC pump it is easy to set a relatively high flow velocity in a column. Therefore an analysis time of 10 min can be attained usually. Analysis time in electrochromatography by using a gravity pressure for forcing an effluent into a column takes much longer period (0.5 h-10 h) owing to a slow apparent flow velocity. Electrochromatography with gravity methods is mostly used for preparative purposes.

3.1 Instrumentation for pressurized flow driven electrochromatography

Schematic diagrams of the apparatus for capillary electrochromatography with pressurized flow are shown in Fig. 8.

The injector used is the same as that in liquid chromatography and it is always combined with splitting port because the sample volume loaded in the injector is too much for total injection in a capillary column of CEC. We are now developing a new injector with NL injection volume and it will be directly connected to a column without splitting.

3.2 Splitting port

There are two types of splitting ports shown in Fig. 9. These splitting ports were designed to exclude the bubble generated at electrode to avoid the contamination by the products generated at the surface of electrode and to minimize the interfacing volume as follows.

A stainless-steel guide inserted in the split port was coated with gold electrolytically. The alignment tube in the tee used. The splitting port is one of the keen parts for obtaining a reproducible injection. Any dust happened to be in the tee may deteriorate an inserted tube or geometrical change between the inserted tube and column head may cause the flow velocity in the port to vary by variation of the split ratio for sample injection. Device cost much for making gold coating and device has a weak point concerning toughness due to the geometrical change of PEEK tube in a long period. By using a split-injection the PEC system becomes tough and feasible to automatic operation.

![Image of OPA-Sperm...](image)

**Fig. 6** Chromatogram obtained by capillary electrochromatography using a slurry-packed capillary column

Capillary column 0.2 mm i.d. and 20 cm in length, packed ODS silica mobile phase 70% ethanol solution containing 0.1% ethylenediamine and 0.1% Brij35 as applied voltage 20 kV. Sample OPA derivatives of polyamines.

![Image of OPA-Putrescine](image)

**Fig. 7** Movement of solute in a packed column under high applied voltage along the column

$E_{\text{pres}}$, $E_{\text{osm}}$, and $E_{\text{elec}}$ are pressurized flow velocity, electroosmotic flow velocity and flow velocity generated by electric field $E_{\text{elec}}$, respectively.
Fig. 8 Electrochromatographic system with a capillary column and split injection

Fig. 9 Two different devices of split port

3.3 Gradient elution

In capillary zone electrophoresis, there are some attempts for gradient mode. An organic modifier was added into the electrode vessel in a programmed way and the resulting solvent was sucked into capillary by electroosmotic flow. In this arrangement two electronically controlled pumps were used. The other attempt was that a modifying electrolyte was added into an electrode vessel by a syringe pump. These devices for gradient mode are rather primitive compared to
those adopted in the modern liquid chromatographic system. Tsuda tried to use LC gradient system directly for CZE. In pressurized capillary electrochromatography gradient elution is performed always with the same apparatus used for liquid chromatographic system. This mode has been also tried by other researchers and will be common in CEC in near future.

Another gradient mode in CEC is potential gradient. This electrical gradient mode is very unique and has a lot of possibility to use. When we use a potential gradient mode the system should be reliable and tough because you may have occasionally a problem of bubble formation during the run. Pressurized driven capillary electrochromatography could use this mode without any problem.

3.4 Chromatographic effect induced by pressurized flow

We can use both pressurized flow and electroosmotic flow for carrying a solute in the column. The flow profiles of pressurized flow and electroosmosis are parabolic pattern and plug like respectively. The flow profile of a solute due to electrophoretic migration may also be plug like. When the capacity factor of a solute is relatively small pressurized flow profile contributes to broaden a peak width of a solute that is expressed as an theoretical plate height because the ratio of band broadening in mobile phase come to be larger at an apparent slow flow velocity.

The value of the column inlet pressure generated by an ordinary liquid chromatographic pump does not correspond linearly to the pressurized flow velocity. Schmeer et al. used the inlet pressure of 16 MPa and 8 MPa and found that the apparent flow velocity did not depend on the inlet pressure as these two pressures gave the same pressurized flow velocity. Eimer et al. demonstrated separation of polar and nonpolar analytes with liquid chromatography and PEC by using 4.8 MPa and the latter gave the remarkable improvement of solute peak shapes. Although most of pressurized flow driven electrochromatography are operated by using the column inlet pressure in the range of 5.05 MPa to 20.20 MPa but some of the separations were done under 5.05 MPa in our and other laboratories. under low pressure such as 1.01 MPa we could minimize the effect of Poiseuille flow and obtained chromatograms with very high theoretical plate numbers.

3.5 Manipulating a solute with two selective hands electric field and pressurized flow

When we operate PEC we can apply the voltage in either way that we like. As we can use a pressurized flow as the power of carrying a solute to the end of column it is not necessary to worry too much about the direction of electroosmosis generated in the column. In CEC operated with electroosmotic flow only we need to select the composition of an effluent that generates the electroosmotic flow velocity appropriately. However in PEC we can handle three flows pressurized flow electroosmotic flow and electrophoretic mobility of a solute. We can manipulate a solute both with pressurized flow and electric field. We can keep the solute in the column we can change the sample elution in reverse order as shown in Fig. 10 and we can shorten the elution time of the sample. PEC is also applied to an enantioseparation. When both partitioning and electrophoretic migration produce positive effects high overall selectivity can be obtained. PEC is also applicable to the estimation of electrophoretic mobility of solutes and also of the dissociation constant for unreacted silanol groups on the surface of silica particle.

3.6 Advantages of pressurized flow capillary electrochromatography

PEC offers the possibility to manipulate the separation process to improve the selectivity and to speed up the analysis without modifying the composition of the mobile phase. It is easy to set up gradient mode of programming the composition of effluent. There are also not much troubles when we try the combination of CEC/MS. In CEC/
Fig. 10  Electrophoregrams of mixture of sulfate ion\(\text{SO}_4^{2-}\) a\(\text{HSO}_4^{-}\)thiosulfate ion\(\text{S}_2\text{O}_3^{2-}\) and thiosulfate ion\(\text{S}_2\text{O}_4^{2-}\)

Column length and its inner diameter are 22 cm. Total capillary length is 30.4 cm and 50 \(\mu\)m, respectively. Packing material is TSK IC-Anion-SW. Effluent is 100% of 5 mmol/L phthalic acid and 5 mmol/L hexamethylenediamine aqueous solution containing 0.15% HEPES and 10% methanol. UV detection at 210 nm.

MS-EC can choose any effluent without worrying the electrosomotical flow direction of its power.

One of the basic concepts of pressurized flow driven chromatography is that the operation of electrochromatography can be done without bubble formation problem. This concept leads to pressure-assisted CEC. The apparatus for pressurized reservoir set at both ends of column is now available commercially. It can work very fine. But when you want to condition the column and change the medium in the column, it is better to use LC pump connected to one of the ends of the column. When you would like to search an optimum CEC condition, you need to change the component of the medium often. It may save time if you use PEC instead of capillary electrochromatography with just electroosmotic flow. After you get an optimum separation condition, you may try CEC without pressurized flow.

PEC is a practical analytical method and will be used more often in the near future.

4  Chromatographic phenomena induced by applied electric field

4.1  Variation of capacity factor by the application of electric field

In electrochromatography, the capacity factor is affected by applied voltage and this phenomenon is used for the analysis of the component of effluent. The period of the alternation of column after the beginning of high voltage application was about 20 min. This phenomenon was found at the early days of electrochromatography by Tsuda. Unger et al. also found that longer period is necessary for obtaining constant elution time such as more than 3 h to 5 h. The relationship between capacity factor and applied voltage depends on the sign of surface charge of stationary phase. Namely the relationship at negative charge is a reverse tendency to that at positively charged stationary phase.

An application of electric field on ion exchange resin packing induces the release of solutes from it. When a pulsed electric voltage applied on the column, an increase of pulsed concentration was observed in the mobile phase. Using a tiny packed capillary column with 0.7 mm inner diameter and 1 mm long, pulsed application of electric voltage causes a peak corresponding to its strength as shown in Fig. 11. By using this method it is possible to analyze the adsorptive component in the effluent under its continuous flowing.

4.2  Variation of electric resistance of column under applied electric field

We found that the electric resistance of cation exchange and Fluorinated-Bonded Silica columns varied with applied voltage. It is certainly supposed that this new phenomenon correlates directly to the relationship between capacity factor and applied electric field. The surface on the packing material is altered by the application of electric voltage. This surface chemistry is not well known until now.

The above studies are very interesting and some of them are newly found. For obtaining these phenomena repeated...
experiments are always necessary and a good reproducibility of experiment is also demanded. Pressurized flow capillary electrophoresis is a very reliable method and easy to run repeatedly. Therefore capillary electrophoresis is a new tool for the study in this field.

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References

EY Giddings J C. Dynamics of chromatography. New York: Marcel Dekker Inc. 1965
EY Tsuda T, Nakagawa G. J Chromatogr. 1983, 268, 369-374
EY Halasz J, Heine E. Adv Chromatogr. 1967, 7, 207-263
EY Tsuda T, Novotny M. Anal Chem. 1978, 50, 832-834
EY Tsuda T, Tanaka T, Nakagawa G. Anal Chem. 1998, 70, 249-1 252
EY Knox J, H-Gilbert M T. J Chromatogr. 1999, 768, 405-418
EY Tsuda T, Tanaka T, Nakagawa G. J Chromatogr. 1992, 629, 249-255
EY Hirata Y, Novotny M. J Chromatogr. 1979, 181, 807-1 909
EY Tsuda T, Novotny M. Anal Chem. 1978, 50, 832-834
EY Hirata Y, Novotny M. J Chromatogr. 1979, 186, 21-528
EY Tsuda T, Tsuhkoi K, Nakagawa G. J Chromatogr. 1990, 569, 249-258
EY Hibi K, Ishii D, Tsuda T. J Chromatogr. 1990, 569, 249-258
EY Ishii D, Tsuda T, Takeuchi T. J Chromatogr. 1993, 629, 99-75
EY Jorgenson J W, Guthrie E J. J Chromatogr. 1993, 255, 335-348
EY Tsuda T. Electric field applications in chromatography—industrial and chemical processes. Weinheim: CHF. 1995
EY Tsuda T. Anal Chem. 1988, 60, 675-680

Fig. 11 Typical phenomenon induced by application of electric voltage

Column: glass capillary tubing 0.7 mm i.d. and 1 mm in length packed with anion exchange gel. TSKgel IC-ANION-SW. Particle diameter 5 mm. These peaks were obtained by an application of a pulsed voltage of ~10 V to ~5 V for a period of 6 s. Effluent was the mixture of 0.1 mmol/L benzenesulfonic acid sodium salt aqueous solution and 0.01 mmol/L benzoic acid potassium salt aqueous solution.
E129EY Tsuda T. LG iGC IntEl+992EL 9E086-36
E130EY Bruni C G MÉ•+Tock P P ÍE•+Knaak J CÉ•+ et al. J ChromatogrE+990E517857-572
E131EY Tsuda T. J Chem Soc of JapanE+986E937-942
E133EY Lurie I SE•+Mayer R PE•+Conver T S. Anal ChemE+998E70E255-3 260
E134EY Kitagawa SE•+Tsujii AE•+Watanabe HE•+et al. J Microcol SepE+997E9E347-356
E135EY Verheijj E RE•+Tjaden U RE•+Niessen W M AE•+et al. J ChromatogrE+991E554339-349
E136EY Hugener ME•+Tinke A PE•+Niessen W M AE•+et al. J ChromatogrE+993E647375-385
E137EY Dekkers S E GE•+Tjaden U RE•+van der Greef J. J Chromatogr AEE+995E712E201-209
E138EY Taylor M RE•+Teale P. J Chromatogr AE+997E9E89-95
E139EY Dittmann M. Lecture at 2nd Inter. Symposium on Capillary Electrochromatography. San Francisco USAEE+998EAug. 25
E140EY Saito YE•+Yang F JE•+Sawada KE•+et al. 47th Annual Meeting of Japan Society for Analytical Chemistry. GifE•JapanE+s.n.i E+998. 149
E141EY Eimer TE•+unger K KE•+Tsuda T. Fresenius J Anal ChemE+995E352B49-653
E142EY Eimer TE•+unger K KE•+an der Greef J. Trends in AnalChemE+996E15E63-648
E143EY Schmer ME•+Behnke BE•+Mayer E. Anal ChemE+995E7E656-658
E144EY Kitagawa SE•+Watanabe HE•+Tsuda T. ElectrophoresisE+999E20E17
E145EY Kitagawa SE•+Tsuda T. Anal SciE+999E4E371-575
E146EY Kitagawa SE•+Tsuda T. J Microcol SepE+994E9E91-96
E147EY Deng YE•+Zhang JE•+Tsuda TE•+et al. Anal ChemE+998E9E858-4 593
E150EY Saso LE•+Silverstrini DE•+Cheng C Y. Anal BiochemE+993E212E15-324
E151EY Tsuda TE•+Muneshige ME•+Tanigawa Y. Chemico New Product’s NewsE+999E-DE1©
E152EY Powel AE•+Sepaniak M J. J Microcol SepE+990E2E78-284
E153EY Foret FE•+Tanali SE•+Bocek P. J ChromatogrE+990E516E19-222
E154EY Tsuda T. Anal ChemE+992E74E886-390
E155EY Tsuda TE•+Kedlo ME•+Jones GE•+et al. J ChromatogrE+993E832E201-207
E156EY Kitagawa SE•+Tsuda T. J Microcol SepE+995E9E69-64
E157EY Chaiyasut CE•+Tsuda TE•+Kitagawa SE•+et al. J Microcol SepE+999E11E990-595
E158EY Kitagawa SE•+Tsuda T. Anal SciE+998E4E371-575