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Use of Dynamically Coated Capillaries for the Routine Analysis of Methamphetamine, Amphetamine, MDA, MDMA, MDEA, and Cocaine using Capillary Electrophoresis*

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ABSTRACT: A rapid, accurate, precise, reproducible, economical, and environmentally gentle method using capillary electrophoresis (CE) is presented for the routine analysis of methamphetamine, amphetamine, MDA, MDMA, MDEA, and cocaine in seized drugs.

The methodology uses a 32 cm by 50 μm capillary (length to detector 23.5 cm) with a commercially available buffer kit and diode array UV detection. Dynamic coating of the capillary surface is accomplished by flushing with base for 1 min, a proprietary polycation for 1 min, and then a proprietary polyanion for 2 min. This approach provides a relatively high and stable electroosmotic flow (EOF), even at low pHs. The background electrolyte (BGE) contains 75 mM phosphate buffer (pH 2.5) with the same polyanion as above.

Using this methodology, amphetamine, methamphetamine, MDA, MDMA, MDEA, and an internal standard (*n*-butylamphetamine) are baseline resolved in less than 5 min. The run-to-run migration time %RSDs and peak area %RSDs are typically $<0.3\%$ and $<2.1\%$, respectively. The day-to-day and capillary-to-capillary migration time %RSDs are $<1.5\%$ and $<2.1\%$, respectively. The %RSDs of the relative migration times compared with the internal standard on a day-to-day and capillary-to-capillary basis are $<0.2\%$ and $<0.06\%$, respectively. The linear dynamic range using peak areas range from 0.003 to 0.10 mg/mL. The correlation coefficients are >0.9998, with all calibration curves passing at or near the origin. Similar data are obtained for cocaine and its internal standard henyltoloxamine.

None of the compounds usually encountered in illicit samples interfere with the target compound (e.g., methamphetamine and cocaine) or the internal standard. Quantitative results for synthetic mixtures and seized exhibits are in good agreement with actual values, and also with results obtained from other techniques. The relatively high EOF for the dynamically coated capillary system allows for the screening of basic, acidic, and neutral adulterants in drug seizures; identification is facilitated by the use of automated UV library searches.

KEYWORDS: forensic science, forensic drug analysis, capillary electrophoresis, dynamically coated capillaries, amphetamine, methamphetamine, MDA, MDMA, MDEA, cocaine

For the quantitation of seized drugs such as the various phenethylamines or cocaine, precise, accurate, and reproducible methodology is required. Chromatographic techniques such as gas chromatography (GC) (1–4) and high performance liquid chromatography (HPLC) (4–7) have traditionally been used for this purpose. Recently, two variants of capillary electrophoresis (CE), micellar electrokinetic capillary chromatography (MECC) (1,3,5,8) and capillary zone electrophoresis (CZE) (2,4–5,9,10), have also been shown to be viable for these analyses. CE is advantageous versus GC by virtue of its ability to handle thermally labile, highly polar and nonvolatile solutes without prior derivatization and/or prior extraction. CE also provides considerably higher peak efficiencies compared with HPLC, resulting in faster and improved separations.

An important goal of any analytical technique is to maximize precision and reproducibility. Precision refers to short-term (run-to-run) changes while reproducibility relates to long-term (day-to-day and capillary-to-capillary) changes. Some of the precision and reproducibility problems found in CE separations arise from failure to follow good laboratory practice (such as not routinely changing run buffer vials). Buffer depletion and electrolysis can lead to pH changes in the background electrolyte (BGE), resulting in variations of the electroosmotic flow (EOF) and, consequently, changes in migration times and peak areas. Fouling of the capillary surface by components of the run buffer or sample can also lead to EOF changes. Operating at low pH (where the EOF is minimal), performing capillary conditioning between injections, or using coated capillaries, can minimize these effects. Another source of imprecision is the presence of organic solvents in the BGE. Evaporation of these solvents (which can occur even in capped vials) can lead to changes in EOF. Selectivity can also be affected when additives such as micelles and cyclodextrins are used.

Since the pKa values of most basic drugs are quite high, operating at pH 2.5 ensures that these solutes will be fully ionized, even

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if subtle changes occur in the BGE due to inconsistent preparation. As a result, variations in migration times and peak areas due to changes in mobility with pH will be minimized. However, at this low pH, the diminutive EOF precludes screening for acidic and some weakly basic and neutral adulterants. Neutral and uncharged adulterants would, of course, have a mobility equal to the EOF, and therefore migrate as one peak.

Permanently or dynamically modified capillaries are used to limit unwanted adsorption of buffer or sample components to the capillary surface. Typically, the capillaries are permanently modified by covalently bonding functional groups (11) or by adsorbing polymers (12–13), which greatly reduce, eliminate, or reverse the EOF. Unfortunately, the stability of many of these coatings is questionable. Dynamically coated capillaries, where the capillaries are coated with additives from the BGE, give more consistent phases due to their continuous regeneration. In addition, since the coatings can be regenerated before each run, unwanted adsorbed solutes are removed from the capillary wall.

Chevigne and Janssens developed a novel coating procedure in which the bare fused-silica capillary is first coated with a polycation followed by a polyanion (14). The first step coats the capillary with an excess of positive charges. This coated surface is then treated with a polyanion to form a modified capillary wall that now contains excess negatively charged sites; this gives rise to a stable and enhanced EOF over a wide pH range. A similar approach was reported by Graul and Schlenoff (15). In their procedure, the BGE contains both the appropriate buffer and the polymeric additive. Inclusion of the polymer in the BGE helps maintain a stable EOF. The feasibility of the first approach for the reproducible separation of seized drugs has been previously demonstrated (16,17).

This paper describes the qualitative and quantitative analysis of amphetamine, methamphetamine, MDA, MDMA, MDEA, and cocaine in seized drugs, using a commercially available kit containing a pH 2.5 BGE which is based on the Chevigne and Janssens approach (14) for dynamically coating capillaries. For several of these analytes, a direct comparison with CZE using uncoated capillaries is also presented.

Methods

Instrumentation

For capillary electrophoresis, a Hewlett-Packard Model HP^{3D}CE Capillary Electrophoresis System (Waldbronn, Germany) was used for all studies. Bare-silica 32 cm (23.5 cm to detector window) by 50 μm i.d. capillaries obtained from Polymicro Technologies (Phoenix, AZ) were used.

A Hewlett-Packard 6890 Gas Chromatograph (Wilmington, DE) operating in the split mode with an FID detector was used for the quantitation of methamphetamine exhibits. The capillary (J & W Scientific, Folsom, CA) was a fused silica, cross-linked and bonded DB-1 30 m by 0.2 mm i.d. column with a 0.25 μm film thickness. The carrier gas was hydrogen (zero grade) with a linear velocity of 42 cm/s; the auxiliary gas was nitrogen. The injector temperature was 230°C, while the detector temperature was 280°C. The oven program consisted of an initial temperature of 150°C for 2 min, followed by a 5°C/min ramp to 190°C, and finally a 0.1 min hold. A 1 μL injection volume was used with a 20:1 split ratio.

Quantitative analysis of methamphetamine exhibits was performed using a Varian Unity 500 MHz NMR (Palo Alto, CA.). Weighed samples and internal standard (methenamine) were dissolved in deuterochloroform, and placed in the NMR. A 5 mm indirect detection probe was used with the following settings: computer automated deuterium solvent lock, automatic shimming of Z1 and Z2, computer adjusted receiver gain, pulse width of 10.0 microseconds (90 degree pulse width of 16.0 microseconds), spectral width of 4668 Hz (approximately 9 ppm with 1 ppm on each side of spectrum), filter band set to twice the spectral width (9400 Hz), delay between acquisitions of 30 s (greater than 5 times T1 maximum allowing full relaxation of observed nuclei), 32 K data points (acquisition time of 3.5 s), 2 steady state, nonacquired transients prior to acquisition of 16 transients, and unweighted Fourier transform with zero filling, phase, drift and baseline correction.

Materials

CElixir Reagent A and CElixir Reagent B (pH 2.5, MicroSolv Technology Corporation, Eatontown, NJ) were used as received. Sodium phosphate (monobasic), phosphoric acid, and sodium hydroxide were reagent grade. Deionized water was obtained from a Millipore Milli-Q Gradient A10 water system (Bedford, MA). All drug standards used in this study were obtained from the reference collection of the Special Testing and Research Laboratory (McLean, VA).

Procedures

Prior to first use, the bare-silica capillaries were conditioned with 0.1 *N* sodium hydroxide for 5 min, water for 2 min and BGE for 2 min. For experiments using dynamically coated capillaries, the columns were conditioned prior to first use with 0.1 *N* sodium hydroxide for 5 min, water for 2 min, CElixir Reagent A for 1 min, and CElixir Reagent B (pH 2.5) for 2 min.

The BGE for the studies using uncoated capillaries consisted of 75 mM phosphate (monobasic) adjusted to pH 2.6 with phosphoric acid. The capillaries were rinsed with BGE for 2 min between injections. Separations were performed at 15°C at a voltage of 7.5 kV. For certain experiments, a 1 min prewash with 0.1 *N* sodium hydroxide or 0.1 *M* phosphoric acid was also used prior to flushing with BGE.

The BGE for the studies using dynamically coated capillaries consisted of 75 mM phosphate, pH 2.5, containing a proprietary polyanion (CElixir Reagent B, pH 2.5). Between injections, the capillaries were flushed with either 0.1 *N* or 1.0 *N* sodium hydroxide for 1 min, then flushed with CElixir Reagent A for 1 min, and finally flushed with CElixir Reagent B (pH 2.5) for 2 min. The separations were performed at 15°C at a voltage of 10.0 kV. For overnight storage, the capillaries were first washed with water for 3 min and then flushed with air for 1 min.

Experiments comparing uncoated and dynamically coated capillaries were performed as follows: standard drug substances were dissolved in the BGE at a concentration of 0.1 mg/mL (except cocaine and related compounds, 0.05 mg/mL; *cis*- and *trans*-cinnamoylcocaine were from a cocaine sample at a concentration of 0.10 mg/mL). Pressure injection of 35 millibar seconds (mbs) was employed (cocaine and related compounds, 20 mbs.). Run-to-run, day-to-day and capillary-to-capillary precision studies on the dynamically coated capillaries were assessed using the phenethylamines dissolved in 3.5 mM phosphate buffer, pH 3.2. The injection buffer was prepared by diluting the BGE used for uncoated capillaries by a factor of twenty with water. Solute concentrations were approximately 0.05 mg/mL, except for *n*-butylamphetamine (0.10 mg/mL). The injection size was 100 mbs.

Quantitative analysis by CE was performed using internal standards. Standards of phenethylamines were prepared at concentrations of approximately 0.05 mg/mL in the injection buffer. A 100 μL aliquot of internal standard (*n*-butylamphetamine, 1 mg/mL dissolved in injection buffer) was added to 1 mL of standard. An

appropriate amount of sample was dissolved in an applicable volume of injection solvent to give a solute concentration within the linear range of the method. Internal standard was added to a 1 mL aliquot of sample as above. For cocaine, the standards were prepared at a concentration of approximately 0.10 mg/mL in the injection buffer. The cocaine internal standard, phenyltoloxamine, 1 mg/mL, was added as noted above. Samples were prepared as for the phenethylamines. Samples and standards were filtered through an SRI 0.5 μm Nylon 66 filter (Eatontown, NJ), and 100 mbs injections were employed.

All CE runs were carried out with UV detection at 195 nm with a bandwidth of 10 nm except for those performed on a standard mixture of amphetamine, methamphetamine and related basic compounds (200 nm with a bandwith of 20 nm).

For quantitative analysis of methamphetamine by GC, a standard solution was prepared at a concentration of 2.0 mg/mL in water. A 3.0 mL quantity of a 1.0 mg/mL of the internal standard solution (*n*-butylamphetamine dissolved in chloroform) was added to a 2.0 mL aliquot of standard solution and 2–3 mL of 0.5 *M* potassium hydroxide. After shaking, the chloroform layer was removed and the aqueous layer extracted twice more with 2 to 3 mL of chloroform. The 3 chloroform fractions were combined and dried over sodium sulfate, then diluted with additional chloroform to a total volume of 10.0 mL. Internal standard was added to 2.0 mL of sample, as above.

Methamphetamine was quantitated using NMR by dissolving an appropriate amount of sample in approximately 1 mL of internal standard solution (an accurately weighed amount of 1 mg/mL methenamine in deuterated chloroform containing tetramethylsilane as internal reference) to give a solute concentration within the linear range of the method (0.35 mg/mL–58.74 mg/mL.) The sample was then filtered through a Whatman micro fiber filter (Clifton, NJ) and transferred to an NMR sample tube.

Results and Discussion

Uncoated Versus Dynamically Coated Capillaries

A comparison of uncoated versus dynamically coated capillaries for analyses of amphetamine, methamphetamine, and related basic compounds is shown in Fig. 1. With the exception of procaine, the resolution for the solutes is similar by either technique; however, the time for separation is about 50% shorter using the coated capillary. The shorter migration times are due to the higher voltage used with the coated capillary (10 kV versus 7.5 kV) and the considerably higher EOF present in the latter system (1.2×10^{-4} versus 3.2×10^{-5} cm^2/Vs). The voltages were optimized for both systems using an Ohm's Law plot. The voltages that provided approximately a 5% positive deviation from linearity for the current were selected as optimal for each system.

Procaine (a seldom encountered adulterant in amphetamine and methamphetamine exhibits (18) undergoes a significant change in selectivity from uncoated versus dynamically coated capillaries. In the absence of the coating reagent, procaine co-migrates with amphetamine. When the coating reagent is used, it co-migrates with methamphetamine. This indicates that the coating is not inert, and that some solutes may interact with it. This is not surprising, as similar findings were observed using a form of CE known as "Ion-Exchange Electrokinetic Chromatography" in 1990 (19). In that technique, polymeric ionic reagents (similar to those used here) were used to modify selectivity.

When applying dynamic coating reagents to new separations, it is important to check for selectivity changes. Table 1 shows the effective mobilities for the drug substances reported in this work. The mobilities for nicotinimide and procaine decrease slightly when the coated capillary is used, while all of the other drug substances show slight increases in their mobilities. These changes in mobility,

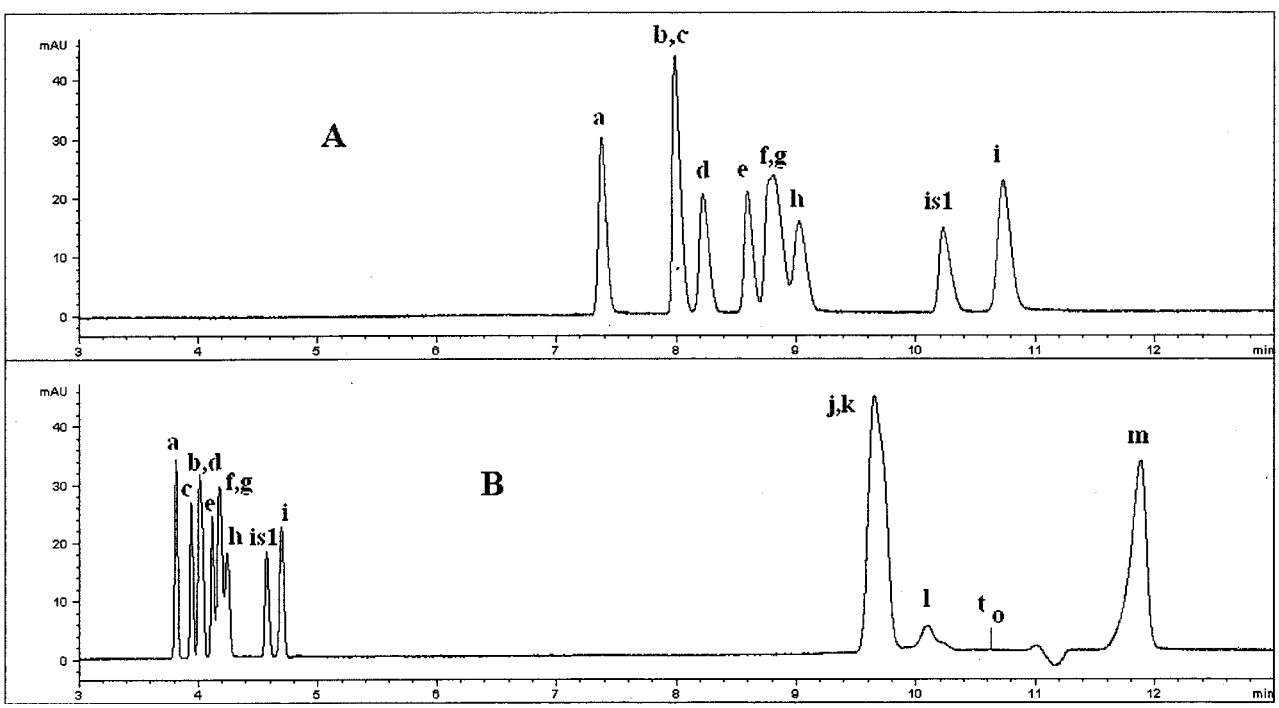

FIG. 1—*CZE separation of a standard mixture of amphetamine, methamphetamine and related compounds using* A*) uncoated capillary and* B*) dynamically coated capillary. Experimental conditions are described in the methods sections. Peaks: nicotinamide (*a*), procaine (*b*), amphetamine (*c*), methamphetamine (*d*), norpseudoephedrine (*e*), pseudoephedrine (*f*), norephedrine (*g*), ephedrine (*h*), n-butylamphetamine (is1), lidocaine (*i*), caffeine (*j*), acetaminophen (*k*), P2P (*l*), and aspirin (*m*).*

though slight, are sufficient to affect the co-migration of procaine as noted above.

CZE analyses in uncoated capillaries at low pH, i.e., 2.6, is generally not used for the separation of uncharged substances found in seized exhibits. Some form of secondary equilibrium is required to effect a separation for these solutes. In addition, the low EOF in bare silica at pH 2.5 (t_0 = 50 min) results in lengthy separation times. With dynamically coated capillaries, it is possible to separate neutral acidic substances and nonionic solutes in the presence of cationic (basic) drugs (Fig. 1*B*). The basic drugs elute in approximately 4 min. Caffeine (neutral) and acetominophen (anionic) coelute, but are separated from phenylacetone (P2P) just ahead of the EOF marker (t_0 = 10.5 min), while aspirin elutes after the EOF marker. These interesting selectivity effects could be explained by ion-pairing or hydrophobic interactions of the solutes with the charged polymers in the run buffer, as previously described by Terabe (19).

A comparison of a separation of cocaine and related compounds using an uncoated capillary versus a dynamically coated capillary is shown in Fig. 2. Similar results were found as reported above for the amphetamines. Note that benzoylecgonine (which has low mobility relative to the other compounds at low pH, due to the partial ionization of the carboxylic acid group) shows a three-fold decrease in migration time when the coated capillary is used. This effect is primarily due to the increased EOF in the latter system. Since the other solutes show a two-fold decrease in migration time, the coating is not totally inert towards the solutes, even though no changes in selectivity are noted (unlike the amphetamine separation). Phenyltoloxamine is a reasonable internal standard, and this separation can be applied towards the separation of acidic and neutral solutes present in seized cocaine exhibits.

TABLE 1—*Effective mobilities for an uncoated versus a dynamically coated capillary system.*

Solute	μ_{ep} Uncoated Capillary	μ_{ep} Coated Capillary
Nicotinimide	2.15×10^{-4}	2.11×10^{-4}
Procaine	1.98×10^{-4}	1.93×10^{-4}
Amphetamine	1.98×10^{-4}	2.02×10^{-4}
Methamphetamine	1.92×10^{-4}	1.96×10^{-4}
Norpseudoephedrine	1.84×10^{-4}	1.88×10^{-4}
Pseudoephedrine	1.79×10^{-4}	1.83×10^{-4}
Norephedrine	1.79×10^{-4}	1.83×10^{-4}
Ephedrine	1.75×10^{-4}	1.80×10^{-4}
n-Butyamphetamine	1.53×10^{-4}	1.58×10^{-4}
Lidocaine	1.46×10^{-4}	1.50×10^{-4}
DMSO (neutral marker)	3.2×10^{-5} (μ_{eo})	1.21×10^{-4} (μ_{eo})

A comparison, using both coated and uncoated capillaries, of the run-to-run migration time precision for nicotinamide, methamphetamine, and n-butylamphetamine (internal standard) is shown in Table 2. Regardless of whether a prewash step was used for the uncoated capillary, or the type of prewash step, the dynamically coated capillary exhibited improved migration time precision. For the uncoated capillary, the best precision was obtained using a 0.1 *M* phosphoric acid prewash (% RSD range: 0.35 to 0.54%), which was considerably poor compared with that obtained with the coated capillary (%RSD range: 0.24 to 0.26%). A comparison of the run-to-run migration time precision for procaine, cocaine and benzocaine is shown in Table 2 for an uncoated capillary with a 0.1 *M* phosphoric acid prewash versus the coated capillary. For these solutes, there is an even greater improvement in precision using the coated capillary %RSD range: 0.83 to 1.61% versus (%RSD range: 0.17 to 0.38%). Since peak areas for a given solute are proportional to migration times, improved migration time precision usually provides better area precision (and therefore better relative area precision). Relative area precision depends on how well a reference compound compensates for any changes occurring to the target solute.

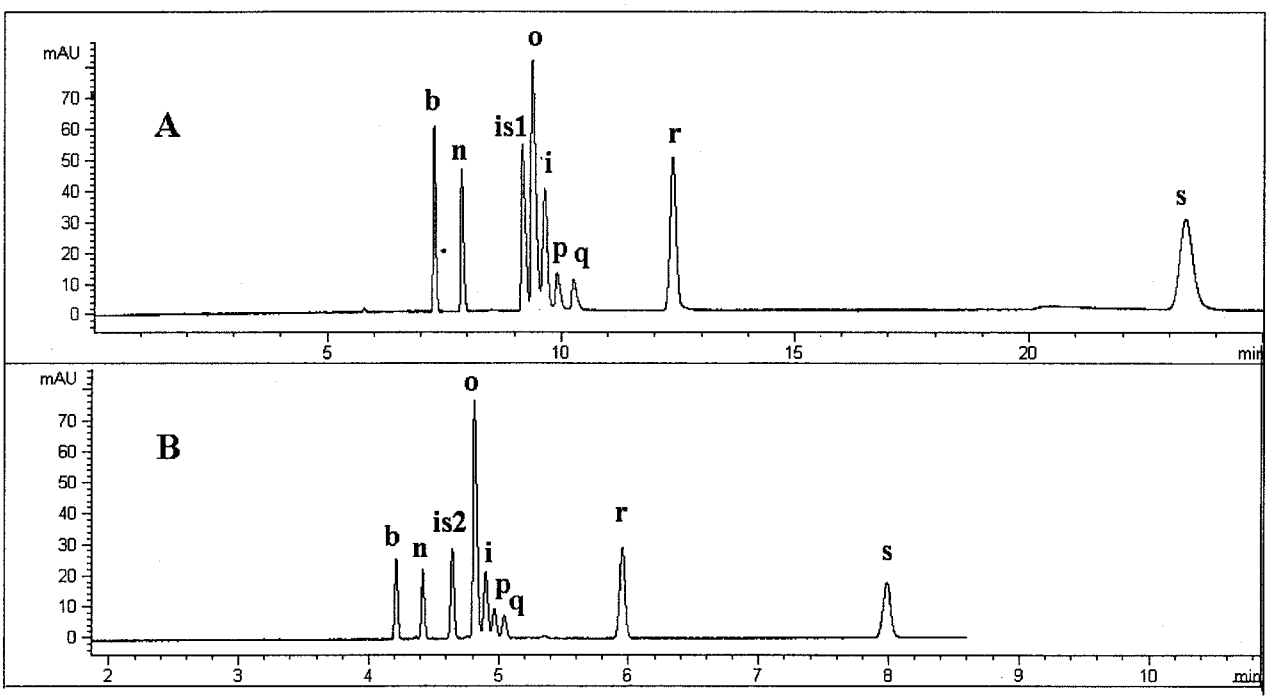

FIG. 2—*CZE separation of a standard mixture of cocaine and related compounds using* A*) uncoated capillary and* B*) dynamically coated capillary. Experimental conditions are described in the methods sections. Peaks: tetracaine (*n*), cocaine (*o*), cis-cinnamoylcocaine (*p*), trans-cinnamoylcocaine (*q*), benzocaine (*r*), benzoylecgonine (*s*), and phenyltoloxamine (is2). Other peaks as in Fig. 1.*

TABLE 2—*Run-to-run migration time precision (%RSD),* n = *8 using a dynamically coated versus an uncoated capillary system.*

Solute	Dynamically Coated*	Uncoated†	Uncoated‡	Uncoated§
Nicotinimide	0.24	0.74	0.54	0.45
Metham-phetamine‖	0.24	0.74	0.35	0.40
n-butylam-phetamine	0.26	0.91	0.44	0.55
Procaine	0.17	0.83	…	…
Cocaine	0.32	…	1.01	…
Benzocaine	0.38	…	1.61	…

*Prewash 0.1 *M* sodium hydroxide.
†Prewash 0.1 *M* sodium hydroxide.
‡Uncoated capillary (prewash 0.1 *M* phosphoric acid).
§Uncoated capillary (no prewash).
‖Amphetamine for dynamically coated capillary.

TABLE 3—*Run-to-run relative area (relative to* n*-butylamphetamine) precision (%RSD),* n = *8 using a dynamically coated versus an uncoated capillary system.*

Solute	Dynamically Coated*	Uncoated†
Nicotinimide	0.44	0.71
Methamphetamine‡	0.48	1.10
Lidocaine	0.46	0.95

*Prewash 0.1 *M* sodium hydroxide.
†Prewash 0.1 *M* phosphoric acid.
‡Amphetamine for dynamically coated capillary.

The relative peak area precision for nicotinamide, methamphetamine, and lidocaine is shown in Table 3. Once again, the coated capillary provided superior results (%RSD range: 0.44 to 0.48% versus %RSD range: 0.71 to 1.10%, relative to *n*-butylamphetamine). For cocaine, the %RSD ($n = 8$) relative area (relative to phenyltoloxamine) is 0.81%.

Precision, Reproducibility, Linearity, Selectivity and Accuracy for Dynamically Coated Capillaries

The precision (run-to-run on different days) and reproducibility (day-to-day and capillary-to-capillary) for the dynamically coated capillaries was studied using a test mixture of amphetamine, methamphetamine, MDA, MDMA, MDEA, and *n*-butylamphetamine (see Fig. 3). The precision for methamphetamine and MDA on 5 different days is shown in Table 4. Excluding the first series of runs on Day 2, excellent precision values for migration times (%RSD range: 0.10 to 0.26%), relative migration times (%RSD range: 0.00 to 0.11%) and relative areas (%RSD range: 0.39 to 2.09%) were obtained for methamphetamine and MDA. Although excellent migration time precision was obtained using a 0.1 *N* sodium hydroxide wash between injections (see Tables 2 and 4), the use of a stronger base wash appears to be a better option (see Table 4). On Day 1 (as in previous experiments), the capillary was washed between injections with 0.1 *N* sodium hydroxide. However, on Day 2, there was an approximate 5-fold increase in the migration time %RSD. On this same day, the superior precision of the previous day's work was restored by using a 1 *N* sodium hydroxide wash between injections. This implies that it is better to condition the capillary with 1 *N* sodium hydroxide before first use.

As shown in Table 5, good day-to-day reproducibility for migration time (%RSD range: 1.27 to 1.48%), and relative area

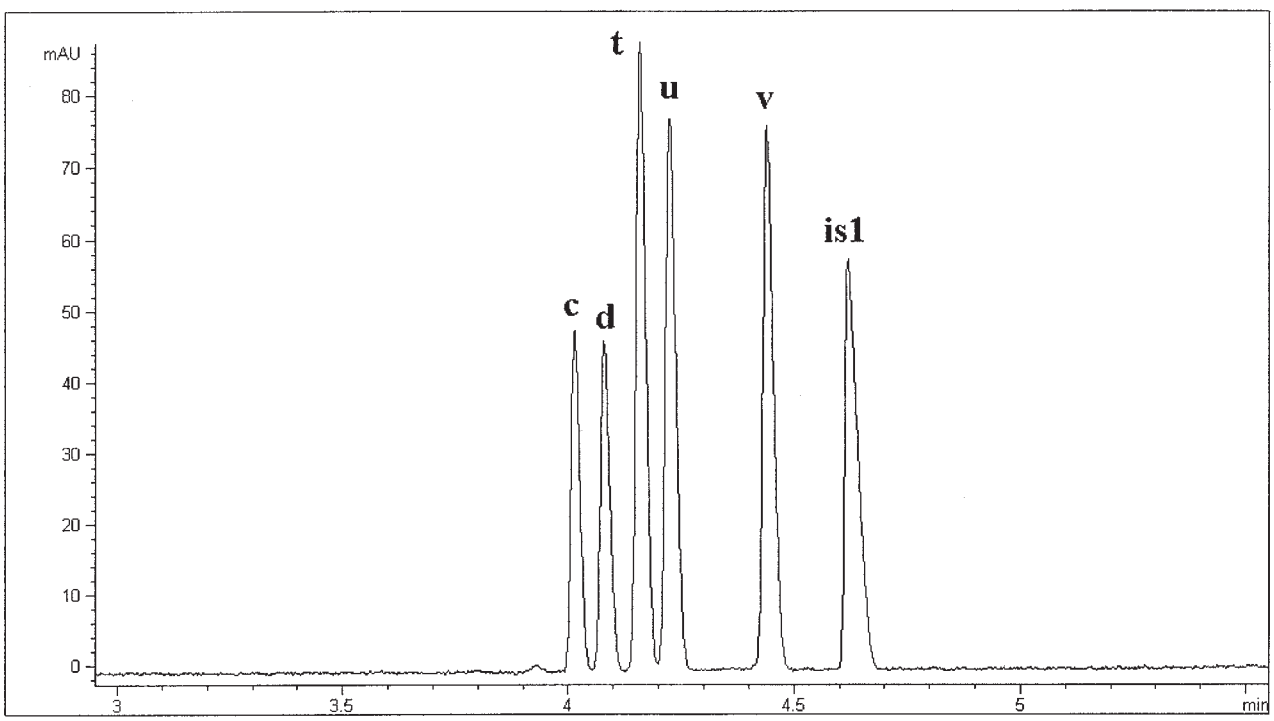

FIG. 3—*Electropherogram of a test mixture of phenethylamines using CZE with a dynamically coated capillary. Experimental conditions are described in the methods sections. Peaks: MDA (t), MDMA (u), and MDEA (v). Other peaks as in Fig. 1.*

(%RSD range: 0.57 to 3.2%), and excellent day-to-day reproducibility for relative migration time (%RSD range: 0.05 to 0.21%) were obtained for the test mixture solutes which were separated. Similarly, as shown in Table 6, good capillary-to-capillary reproducibility for migration time (%RSD range: 1.88 to 2.07%), and relative area (%RSD range: 1.17 to 4.21%), and excellent day-to-day reproducibility for relative migration time (%RSD range: 0.00 to 0.06% were found for these same compounds. For analytical purposes, the relative migration time is the most critical parameter, since it indicates the ability to reproduce the separation.

The linearity ranges and equations of the regression plots for solutes including amphetamine, methamphetamine, MDA, MDMA, MDEA, and cocaine are shown in Table 7. Good linearity was obtained for each of these compounds ($1.0000 \geq R2 \geq 0.9998$), with plots of area standard/area internal standard versus concentration passing near the origin. However, although linearity was preserved, band broadening was observed for the various solutes at higher concentrations (≥0.10 mg/mL), presumably due to electrodispersion (20.) For the above solutes, at the lowest concentration within the linearity range (approximately 0.003 mg/mL), good precision was obtained for relative area (%RSD range: 1.88 to 3.32%). At the upper concentration range (approximately 0.05 mg/mL for the phenethylamines and 0.10 mg/mL for cocaine), excellent precision for these solutes was achieved for relative area (%RSD range: 0.66 to 0.92%).

Relative migration times (relative to *n*-butylamphetamine) of amphetamine, methamphetamine, MDA, MDMA, MDEA, cocaine, and related compounds are shown in Table 8. There are no

TABLE 4—*Run-to-run precision (%RSD),* n *= 6 on different days for migration time (MT), relative migration time (RMT) and relative area (*R *area) using a dynamically coated capillary system. Data relative to* n-*butylamphetamine.*

Solute	Pre-wash	Day	MT	RMT	*R* Area
Methamphetamine	0.1 M NaOH	1	0.25	0.11	0.39
		2	1.20	0.09	0.68
		4	0.10	0.00	0.96
	1.0 M NaOH	2	0.15	0.11	0.86
		3	0.12	0.00	0.96
		5	0.10	0.05	1.43
MDA	0.1 M NaOH	1	0.26	0.06	2.09
		2	1.26	0.06	1.12
		4	0.11	0.05	0.59
	1.0 M NaOH	2	0.16	0.06	0.71
		3	0.12	0.00	0.41
		5	0.10	0.06	1.77

TABLE 5—*Day-to-day reproducibility (%RSD),* n *= 5 for migration time (MT), relative migration time (RMT) and relative area (*R *area) using a dynamically coated capillary system (prewash 1.0* M *sodium hydroxide.) Data relative to* n- *butylamphetamine.*

Solute	MT	RMT	*R* Area
Amphetamine	1.27	0.21	0.69
Methamphetamine	1.30	0.17	0.57
MDA	1.37	0.09	2.94
MDMA	1.37	0.12	3.20
MDEA	1.44	0.05	2.99
n-Butylamphetamine	1.48	0.00	0.00

TABLE 6—*Capillary-to-capillary reproducibility (%RSD),* n *= 5 for migration time (MT), relative migration time (RMT) and relative area (*R *area) using a dynamically coated capillary system (prewash 1.0* M *sodium hydroxide.) Data relative to* n-*butylamphetamine.*

Solute	MT	RMT	*R* area
Amphetamine	2.07	0.06	1.29
Methamphetamine	1.88	0.06	1.17
MDA	2.06	0.06	3.40
MDMA	2.06	0.06	4.21
MDEA	2.06	0.00	3.99
n-Butylamphetamine	2.06	0.00	0.00

TABLE 7—*Results for linearity study.*

Solute	Linearity Range (mg/mL)	Correlation Coefficient (R^2)
Amphetamine	0.00318–0.10	0.9998
Methamphetamine	0.00316–0.10	0.9999
MDA	0.00322–0.10	1.0000
MDMA	0.00318–0.10	1.0000
MDEA	0.00316–0.10	1.0000
Cocaine	0.00314–0.40	0.9999

TABLE 8—*Relative migration times (RMT) using a dynamically coated capillary system. Data relative to* n-*butylamphetamine.*

Solute	RMT
Doxylamine	0.765
Chlorpheniramine	0.784
Quinine	0.804
beta-Phenethylamine	0.807
Chlorquinine	0.812
Nicotinimide	0.836
Amphetamine	0.868
Methamphetamine	0.883
Procaine	0.883
MDA	0.900
Norpseudoephedrine	0.906
MDMA	0.914
Norephedrine	0.917
Pseudoephedrine	0.919
Tetracaine	0.927
Ephedrine	0.932
Phenylephrine	0.951
MDEA	0.961
Ketamine	0.962
Phenyltoxylamine	0.971
n-Butylamphetamine	1.00
Dextromethorphan	1.00
Cocaine	1.01
Lidocaine	1.03
cis-Cinnamoylcocaine	1.04
trans-Cinnamoylcocaine	1.06
Benzocaine	1.25
Benzoylecgonine	1.68
Acetominophen	2.11
Caffeine	2.14
Guaifenesin	2.14
P2P	2.24
DMSO (neutral marker)	2.40
Aspirin	2.71
Salicylic acid	4.84

†Relative to *n*-butylamphetamine.

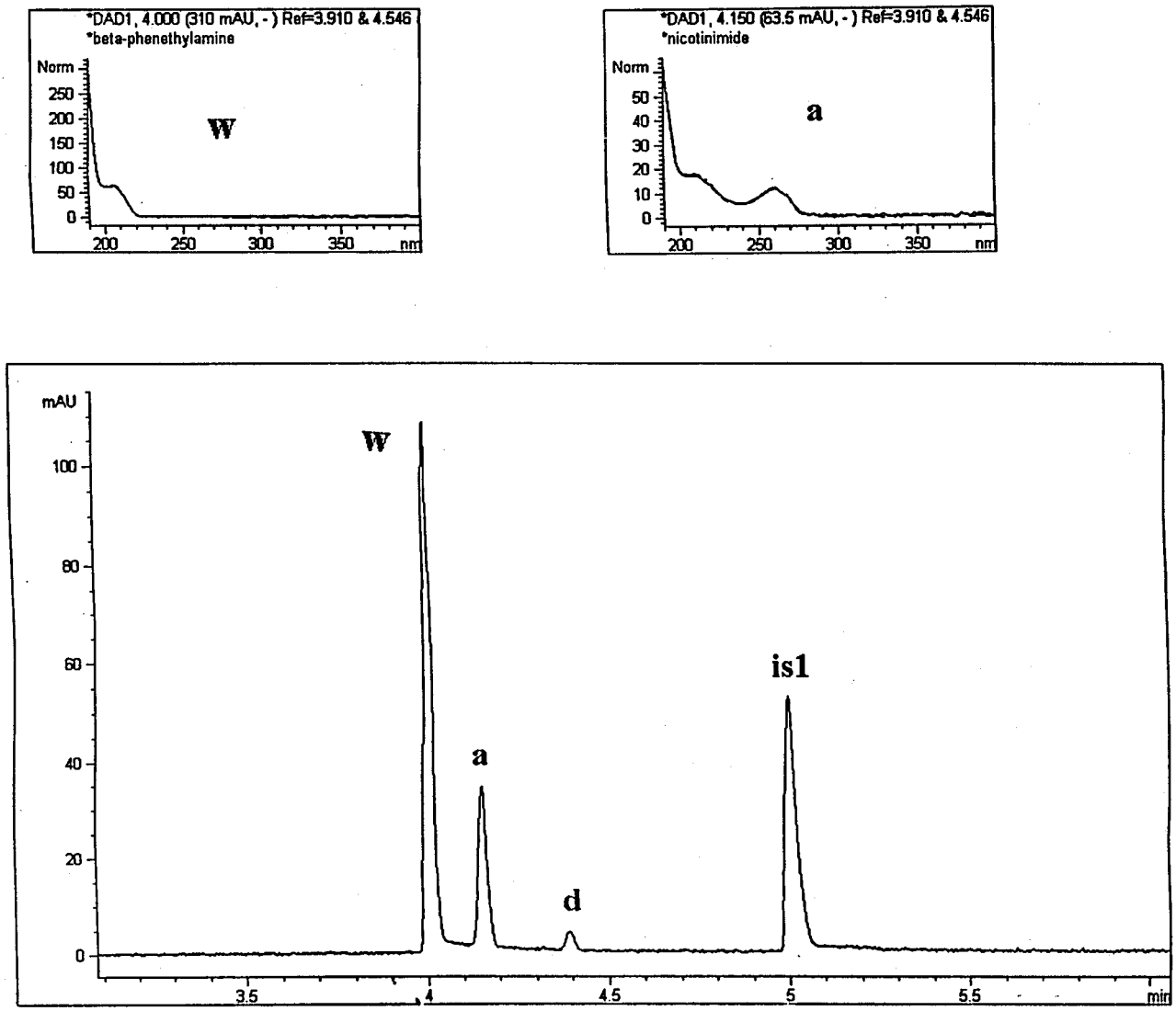

FIG. 4—*An electropherogram using a dynamically coated capillary of seized methamphetamine HCl sample containing* beta-*phenethylamine and nicotinamide and the results of a library search for these compounds. Experimental conditions are described in the methods sections. Peaks:* beta-*phenethylamine (w). Other peaks as in Fig. 1.*

TABLE 9—*Comparison of quantitation of seized methamphetamine exhibits (calculated as % HCl salt) using NMR, capillary GC and a dynamically coated CE.*

Sample	NMR	GC	CE
1	15.5	14.3	14.7
2	99.9	97.9	95.0
3	1.90	1.78	2.07
4	10.7	10.1	10.5
5	5.54	5.36	5.68
6	8.85	8.80	8.89

significant interfering compounds for the quantitation of the compounds of interest. Dextromethorphan overlaps with the internal standard *n*-butylamphetamine; however, although the former compound is occasionally encountered in phenethylamine (18) samples, since these solutes have different UV spectra, diode-array UV detection (which was used in this study) would indicate interference with the internal standard. In addition, procaine co-migrates with methamphetamine; however, mixtures of these solutes are not usually found. In addition, the presence of procaine is easily ascertained by examining the 280 nm signal, which is selective for this solute. Ketamine co-migrates with MDEA; but again, this combination is not likely be encountered (18). Sugars would have migration times at or near t_0, with very weak UV responses (virtually no response at wavelengths higher than 200 nm). MDA precursor compounds such as safrole, isosafrole, piperonal, and 3,4-methylenedioxyphenyl-2-nitropropene would almost certainly have migration times at or near t_0.

As shown in Table 9, good overall agreement was obtained for the quantitation of 6 methamphetamine HCl samples via NMR, capillary GC, and CE (dynamically coated capillary approach). Good recoveries were obtained for amphetamine, methamphetamine, MDA, MDMA, MDEA, and cocaine when cut with varying amounts of mannitol and inositol; (recovery range 96.4 to 102%).

For the analysis of samples, PDA-UV detection was used for peak purity and peak identity. Peak purity was used to determine

the presence/lack of interfering compounds. Automatic UV library searches were also performed, which increased the confidence that the compound being quantitated was correctly identified. In addition, these library searches aided in the identification of adulterants. An electropherogram of a seized methamphetamine HCl sample containing *beta*-phenethylamine and nicotinamide, and the corresponding results of a library search for these compounds, are shown in Fig. 4.

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