Journal of Chromatography A, 1499 (2017) 190–195

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

High performance separation of quaternary amines using microchip non-aqueous electrophoresis coupled with contactless conductivity detection

Roger Cardoso Moreira[a], Marilia Sousa Lopes[a], Iris Medeiros Junior[b], Wendell K.T. Coltro[a,c,*]

[a] Instituto de Química, Universidade Federal de Goiás, Campus Samambaia, 74690-900, Goiânia, GO, Brazil
[b] Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello (CENPES), 21040-000, Rio de Janeiro, RJ, Brazil
[c] Instituto Nacional de Ciência e Tecnologia de Bioanalítica, 13084-971, Campinas, SP, Brazil

ARTICLE INFO

Article history:
Received 3 January 2017
Received in revised form 22 March 2017
Accepted 23 March 2017
Available online 27 March 2017

Keywords:
Capillary electrophoresis
Corrosion inhibitors
Electrochemical detection
Integrated microfluidic platform
Organic solvents
Petroleomics

ABSTRACT

This study describes the development of an analytical methodology for the separation of quaternary amines using non-aqueous microchip electrophoresis (NAME) coupled with capacitively coupled contactless conductivity detection (C^4D). All experiments were performed using a commercial microchip electrophoresis system consisting of a C^4D detector, a high-voltage sequencer and a microfluidic platform to assemble a glass microchip with integrated sensing electrodes. The detection parameters were optimized and the best response was reached applying a 700-kHz sinusoidal wave with 14 V_{pp} excitation voltage. The running electrolyte composition was optimized aiming to achieve the best analytical performance. The mixture containing methanol and acetonitrile at the proportion of 90:10 (v:v) as well as sodium deoxycholate provided separations of ten quaternary amines with high efficiency and baseline resolution. The separation efficiencies ranged from 8.7×10^4 to 3.0×10^5 plates/m. The proposed methodology provided linear response in the concentration range between 50 and 1000 μmol/L and limits of detection between 2 and 27 μmol/L. The analytical feasibility of the proposed methodology was tested in the determination of quaternary amines in corrosion inhibitor samples often used for coating oil pipelines. Five quaternary amines (dodecyltrimethylammonium chloride, tetradecyltrimetylammonium bromide, cetyltrimethylammonium bromide, tetraoctylammonium bromide and tetradodecylammonium bromide) were successfully detected at concentration levels from 0.07 to 6.45 mol/L. The accuracy of the developed methodology was investigated and the achieved recovery values varied from 85 to 122%. Based on the reported data, NAME-C^4D devices exhibited great potential to provide high performance separations of hydrophobic compounds. The developed methodology can be useful for the analysis of species that usually present strong adsorption on the channel inner walls.

1. Introduction

Quaternary amines are surfactants widely used in industrial applications due to their capacity to form coating films to prevent common problems associated with corrosion in multiphase petroleum/water pipelines [1–4]. The presence of a polar hydrophilic head and a non-polar hydrophobic tail makes the use of these compounds quite attractive to be anchored on the surface of pipelines, which are often composed of iron or steel. The physical adsorption or the chemisorption of these quaternary amines on metal surfaces grant their inhibitory action against corrosion [5,6]. The effects promoted by corrosion certainly represent high costs to the oil industry and, if do not properly treated, it can generate huge problems related to water disposal and consequently environmental pollution. In addition, the corrosion virtually affects all of the oil fields levels including the extraction at the bottom surface, the processing steps as well as the transport through oil pipelines [7–10]. For this reason, the development of analytical methods for determination of quaternary amines is of paramount relevance.

Chromatographic methods coupled to mass spectrometry have been often used to determine these compounds [11,12]. However, these methods present some drawbacks to be overcome including long analysis time and strong adsorption of analytes on

* Corresponding author at: Instituto de Química, Universidade Federal de Goiás, Campus Samambaia, 74690–900, Goiânia, GO, Brazil.
E-mail address: wendell@ufg.br (W.K.T. Coltro).

http://dx.doi.org/10.1016/j.chroma.2017.03.062
0021-9673/

the stationary phase [13]. On the other hand, non-aqueous capillary electrophoresis (NACE) has appeared recently as a promising approach for analysis of these kinds of compounds [14,15]. In this electrophoretic mode, the running electrolyte and the samples are prepared using organic solvents to ensure better solubility of hydrophobic compounds. The use of organic media minimizes the adsorption between analytes and the capillary inner walls, thus providing higher separation efficiencies. As observed by all the scientific community, the miniaturization of electrophoretic systems has become globally a current trend [16,17]. Microchip electrophoresis (ME) devices offer some advantages including low sample consumption, high throughput capability, short analysis times and portability [16–19]. Due to their attractive features, the development of methods based on non-aqueous microchip electrophoresis (NAME) may result in the feasibility of rapid, simple and reliable methods for the determination of quaternary amines. However, this strategy is still not well explored for analysis of quaternary amines. In 2003, Wang and Pumera reported the separation of tetramethylammonium bromide (TMA), tetrapropylammonium chloride (TPA), tetrabutylammonium perchlorate (TBA) and N,N-dimethyldodecylamine (DMDA) using NAME-C^4D devices [20]. The authors achieved complete separations within 2 min with efficiencies between 93 680 and 127 680 plates/m.

Since the pioneering reports [18,19], glass substrate has been the most widely selected platform for applications involving ME devices. The choosing of this material is associated with some advantages like low chemical reactivity, low thermal conductivity, great similarity with fused silica capillaries and optical transparency [18,19,21]. While this latter property makes easy the integration of glass chips with optical detectors, the electrochemical detection on microchips has received considerable attention in the last years [22–26]. Among the different electrochemical detection modes, capacitively coupled contactless conductivity detection (C^4D) has emerged as a powerful tool to monitor separations on these devices [27–30]. The increasingly popularity is attributed to the possibility to minimize bubble generation, electrode surface fouling and electrical interferences usually associated with the high voltage applied to electrophoresis [31]. Another interesting feature makes reference to the possibility to use any conductive material [32–37], or even ionic solutions [38,39], as sensing electrodes. In addition, due to the compatibility of microfabrication technologies, sensing electrodes may be easily integrated with electrophoresis channels in a single substrate enabling the production in large scale and, consequently, its commercialization as fully integrated analytical platforms.

In this context, this study aims to report the development and optimization of an analytical methodology based on NAME-C^4D for the separation of quaternary amines. The effect of the electrolyte composition was thoroughly investigated to ensure separations with high selectivity and efficiency. As proof-of-concept, the developed methodology was successfully explored for the analysis of quaternary amines in real samples containing corrosion inhibitors collected from oil pipelines.

2. Materials and methods

2.1. Chemicals

Methanol (MeOH), acetonitrile (MeCN), N,N-dimethyl-formamide (DMF), dimethyl sulfoxide (DMSO), tetraethylammonium hydroxide (TEAOH), hexyltrimethylammonium (HTAB), trimethyloctylammonium bromide (TOMB), dodecyltrimethylammonium chloride (DTAC) tetradecyltrimetylammonium bromide (TTAB), trimethyloctadecylammonium bromide (TODAB), tetraoctylammonium bromide (TOAB), cetyltrimethylammonium bromide (CTAB), tetradodecylammonium bromide (TDAB), tetramethylammonium bromide (TMAB), sodium cholate hydrate (NaCH), deoxycholic acid (DCHA), sodium L-lactate (NaLa), sodium deoxycholate (NaDCHA), 2,6-dihydroxybenzoic acid (2,6-DHBA), 2-(N-Morpholino)ethanesulfonic acid sodium salt (NaMES), 3-(Cyclohexylamino)-2-hydroxy-1-propanesulfonic acid sodium salt (NaCAPSO) and 3-(N-Morpholino)propanesulfonic acid hemisodium salt (NaMOPS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All reagents were analytical grade and used as received.

2.2. Instrumentation

Experiments were performed using a Quad HV microchip electrophoresis system (model ER455) supplied by eDAQ (Denistone East, NSW, Australia). Electrophoretic separations were carried out on a commercial glass microchip model ET190 from Micronit Microfluids (Enschede, Netherlands). For the experiments involving non-aqueous electrophoresis, the cover of the microfluidic platform provided by eDAQ was replaced by an adapted support prepared in a polyacetal substrate by a local (MS Máquinas Goiânia, GO, Brazil) to better support the use of organic solvents. Fig. S1, available in Electronic Supplementary Material (ESM), displays optical images comparing the commercial and the adapted covers as well as the assembling with HV cables. The electrophoresis chip layout (see Fig. S2 in the ESM) was composed of two channels arranged in a double-T geometry with gap of 100 μm. The sampling and separation channels (100 μm wide and 10 μm deep) were 7.0 mm and 85 mm, respectively. Two pairs of sensing electrodes (200 μm wide × 500 μm long × 200 nm thick spaced by 250 μm) were positioned at 70 mm from the channel intersection. Further details about the device and electrode geometries were recently reported [40,41]. The high voltage values were controlled using eDAQ Sequencer software (version 1.3.3). PowerChrom software version 2.7.9 was used for data acquisition and processing.

2.3. NAME and C^4D procedures

All channels were preconditioned with 0.1 M NaOH during 10 min followed by rinsing steps with ultrapure water and running electrolyte during 5 and 10 min, respectively. To ensure better injection-to-injection reproducibility, the channels were rinsed with running electrolyte for 5 min between each analysis. Aliquots (100 μL) of sample or electrolyte were added on sample (SR); sample waste (SW), electrolyte (ER) and electrolyte waste (EW) reservoirs (see chip layout presented in Fig. S2) using a micropipette. Sample was introduced inside microchannels through gated injection protocol. For this purpose, voltages of 2.7 kV and 3.0 kV were applied to the SR and ER, respectively, keeping the other reservoirs grounded. It is important to note that higher voltages were not applied due to the limitation of the high voltage sequencer. To introduce discrete sample plugs, the voltage applied to ER was floated during 1 s and immediately reestablished to avoid sample leakage. For C^4D measurements, the operational frequency and the excitation voltage amplitude were initially optimized and the best response was achieved applying a 700-kHz sinusoidal wave with excitation voltage of 14 V_{pp}. For all recorded electropherograms, the baseline was corrected using Microcal™ Origin™ software (Microcal,Northampton, MA, USA).

2.4. Solution preparation

Stock solutions of each quaternary ammonium (10 mmol/L each) were prepared in methanol. Working solutions were diluted at desired concentrations using the same solvent. Different run-