Large-volume sample stacking for the analysis of low molecular mass amines in steam water by CE using novel highly absorbing probe for indirect UV detection

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ABSTRACT

A rapid, simple, sensitive and ultrafast capillary electrophoretic method – large-volume sample stacking (LVSS) without a polarity switching step has been developed in this study for determining ammonia and 9 amines, including ethanolamine, cyclohexylamine, hydrazine, morpholine, triethanolamine, and dimethylamine in steam water and their degradation products, such as methylamine, ethylamine, diethanolamine, and ammonia. The background electrolyte (BGE) containing acridine as a probe was firstly used for indirect UV detection. Acridine was shown to be very beneficial for the determination of low molecular mass amines due to its high electrophoretic mobility and at the same time high molar absorption coefficient (ε_{252}) of $1.7 * 10^5$. No laborious sample preparation was needed. Separation and detection was achieved in about 8.5 min for BGE containing acridine per sample. Limits of detection (LOD) using acridine were as low as 0.003 mg/L. The calibration plots showed good linearity over the concentration range from 0.01 to 1 mg/L for ammonia and the amines of interest for nuclear and thermal power plants. The proposed method was successfully applied to the determination of ethanolamine and cyclohexylamine in steam water samples obtained from thermal power plant and the analytical results were in good agreement with those obtained by reference ion chromatography (IC) method.

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1. Introduction

The determination of amines is of considerable interest as these compounds are widely used in industrial processes as corrosion inhibitors in the steam-water cycles of the power plants [1]. Almost all steam generators in steam power plants use some type of amines or a blend of amines to prevent corrosion in the secondary water system. For plants, in which carbon steel and copper alloys and impurities in feed water are simultaneously present, a corrosion of steam generators, turbines, condensers, piping, etc. may occur. In this case, alternate amines like morpholine, or ethanolamine can be selected to manage corrosion of carbon steel and decrease corrosion transport [2]. Power plants in different countries also use ammonia, hydrazine, dimethylamine, cyclohexylamine, triethanolamine [3,4]. These reagents are usually added to the feedwater to raise the pH of the condensate, feedwater, and drainwater to the level of 9.0–9.5. Typical concentrations of amines usually used as corrosion inhibitors are between 0.1 and 10 mg/L [3,5–7]. While ammonia is thermally stable, other amines (morpholine, ethanolamine and cyclohexylamine) decompose at about 300 °C. Ammonia, and the

organic amines such as methylamine, ethylamine, and diethanolamine were identified as the major degradation products [8]. Degradation of amines leads not only to corrosion inhibitor losses, but may also contribute to operational problems such as foaming, corrosion and fouling. Therefore, the screening and quantification of amines are very essential in determining the appropriate amounts to use for maximum protection at nuclear and thermal plants.

There are several analytical methods to detect amines in water, such as HPLC [9–11], gas chromatography (GC) [12–16] and ion-exchange chromatography [17]. However, in some cases these methods may be complicated and time consuming, especially if laborious preconcentration method is used.

Capillary electroporesis (CE) is known as a powerful tool in the separation and determination of various species, and is also used to determine low chain amines. However, the derivatization is usually used for direct detection using capillary electrophoresis [18–20] and detection sensitivity is a problem because of small injection volumes and short optical path length associated with on-column UV detection. An obvious solution to achieve better concentration limits is to improve the detection system. However, such alternative techniques as laser-induced fluorescence or indirect fluorescences and the installation of a Z-shaped cells are either expensive or cumbersome and complicated to implement. Some authors have used CE at $\mu g * L^{-1}$ levels with different
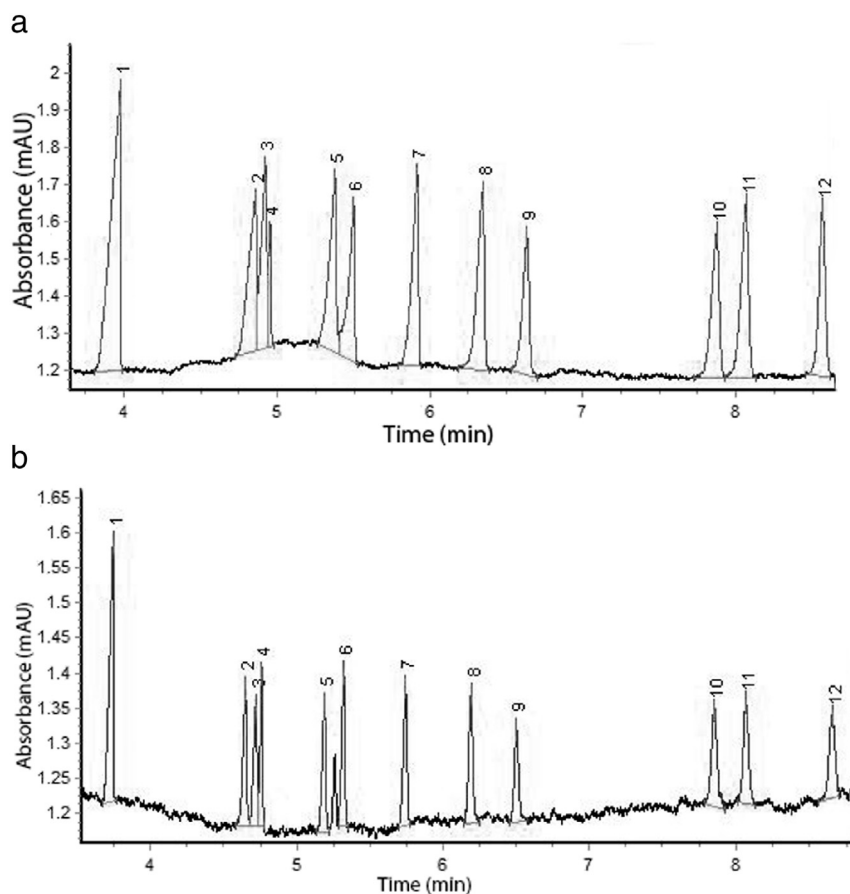
Fig. 1. a Electrophoregram of a mixture of organic amines with possible degradation products at 0.1 mg/L. Electrolyte: 2 mM/L acridine, 20 mM/L acetic acid, 0.05% Tween 20, pH 3.3, LVSS method, detection: indirect UV detection (254 nm), injection: by pressure 99 mbar for 18 s, peak 1 – NH_4^+, 2 – methylamine, 3 – K^+ (from DI water), 4 – hydrazine, 5 – dimethylamine, 6 – Na^+ (from DI water), 7 – ethylamine, 8 – ethanolamine, 9 – morpholine, 10 – diethanolamine, 11 – cyclohehylamine, 12 – triethanolamine. b Electrophoregram of a mixture of organic amines with possible degradation products at 0.1 mg/L. Electrolyte: 2 mM/L acridine, 20 mM/L acetic acid, 0.05% Tween 20, pH 3.3, detection: indirect UV detection (254 nm), usual injection: by pressure 30 mbar for 10 s, peak 1 – NH_4^+, 2 – methylamine, 3 – K^+ (from DI water), 4 - hydrazine, 5 – dimethylamine, 6 – Na^+ (from DI water), 7 – ethylamine, 8 – ethanolamine, 9 – morpholine, 10 – diethanolamine, 11 – cyclohehylamine, 12 – triethanolamine.

preconcentration methods such as on-column concentration: solid phase extraction (SPE) inside the capillary [21], SPE in-line with the capillary [22,23], on-line coupling of isotachophoresis with CE [24,25], transient isotachophoresis [26], sweeping [27,28], and field-amplified methods [29–31], and large-volume sample stacking (LVSS) [32–35]. In sample stacking with hydrodynamic injection, long injections of sample solutions prepared in low conductivity matrices or water (large-volume sample stacking, LVSS) are better in order to maximize the obtainable sensitivity enhancements.

At the same time, when using capillary electrophoresis with indirect UV detection, where BGE contains a probe, good result can be achieved in determination of amines [36]. Most widely used compounds as probes used when determining cations and amines are imidazole, benzimidazole, [37] pyridine, benzylamine, 4-aminopyridine [38], Cu(II) [39], histidine [40–42].

Previous papers disclose the use of probes having high molar coefficients, and having high molecular mass for indirect UV detection [43], for example, chrysoidine [44], methyl green [45], tetrazolium violet [46], etc. However, these large probes are not optimal for the determination of small ions with high electrophoretic mobilities like low chain amines. For example, electrophoretic mobility (μ_{ep}) of ethanolamine is $3.83 * 10^{-4}$ cm^2 V^{-1} s^{-1}, μ_{ep} of cyclohexylamine is $3.46 * 10^{-4} cm^2 V^{-1} s^{-1}$ [47]. When indirect detection is applied, sensitivity is determined by both molar coefficient of extinction of the probe ion and so-called transfer ratio [43]. These two factors are controversial when analytes are fast as strongly UV-probes are usually large and slowly migrating that lead to low transfer ratio and high

electrodispersion. Electrophoretic mobility of large ions could be relatively high only when the probe ion is highly charged, but multiple charge of the probe ion also reduces the transfer ratio [43]. In other words, optimal probe for the determination of small ions like amines should be small fast-migrating ion with a single charge and high molar coefficient of extinction [39,41,48,39]. Acridine is a rare case of a probe that meets these requirements. It has a unique combination of properties as a probe ion for indirect UV detection of small cations: extremely high molar coefficient of (ε_{252}) $1.7 * 10^5$ [49,50] and relatively

Table 1
Analytical figures of merit of the proposed LVSS method for the determination of amines and ammonia.

Analytes	Calibration range, mg/L	t_{min}	rRSD (%)	R^2	LOD, mg/L	LOQ, mg/L
Ammonia	0.01–1	3.97	4.2	0.9969	0.003	0.010
Methylamine	0.01–1	4.85	3.7	0.9986	0.003	0.009
Hydrazine	0.01–1	4.92	2.5	0.9987	0.004	0.012
Dimethylamine	0.01–1	5.33	3.6	0.9997	0.005	0.015
Ethylamine	0.01–1	5.91	2.3	0.9998	0.003	0.010
Ethanolamine	0.01–1	6.34	1.2	0.9999	0.003	0.011
Morpholine	0.01–1	6.64	1.4	0.9999	0.005	0.015
Diethanolamine	0.01–1	7.88	1.9	0.9996	0.005	0.015
Cyclohexylamine	0.01–1	8.07	3.0	0.9998	0.004	0.012
Triethanolamine	0.01–1	8.56	3.2	0.9998	0.003	0.010