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Potentiometric detection of aliphatic amines by flow injection analysis and ion-interaction chromatography with a metallic copper electrode

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Abstract

The detection of aliphatic amines in flow systems with a potentiometric method based on a metallic copper wire electrode is described. The electrode is shown to give sensitive response toward aliphatic amines in flow injection analysis. The parameters affecting the response characteristics of the electrode such as the pH of the carrier, the concentration of an ion-interaction reagent and the injection volume were investigated. The metallic copper electrode was applied to the detection of amines after separation by ion-interaction chromatography with a mobile phase containing a low concentration of octylammonium salicylate in unbuffered solution. Detection limits in the range of 0.5–1.0 nmol were obtained in the presence of 0.3 mM octylammonium salicylate at a pH of 6.0 and a flow-rate of 0.3 ml/min. A comparison of the potentiometric detection with conventional UV is given, showing comparable sensitivities. The potentiometric method offers a low cost, easily constructed detector with some possible applications.

Keywords: Flow injection analysis; Ion-interaction chromatography; Copper electrode; Aliphatic amines; Copper

1. Introduction

The determination of aliphatic amines is of considerable interest as these compounds are used in industry with a variety of applications. They are used as raw material or at an intermediate stage in the production of other chemical, pharmaceutical, polymers, pesticides, dyestuffs and corrosion inhibitors [1]. In the present paper, we report on the feasibility of using potentiometric methods because of their low cost and simple instrumentation required. Other methods have been used for the determination of aliphatic amines, including colorimetry [2], polarog-

raphy [3], flow-injection analysis (FIA) [4], gas chromatography (GC) [5] and high-performance liquid chromatography (HPLC). In liquid chromatography, different detection techniques have been used in detecting trace amount of amines, including conductivity [6], spectroscopy [7] and amperometry [8]. Because most aliphatic amines do not absorb in the ultraviolet region, chemical derivatization techniques are extensively used to increase detectability for spectrophotometric methods, e.g., detection of lower-molecular-mass aliphatic amines by HPLC with fluorimetric detection after derivatization with *o*-phthalaldehyde (OPA) has been described [9]. The reagents such as 9-fluorenylmethyl-chloroformate (FMOC-Cl) and 2-(9-anthryl)ethyl chloro-

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formate (AEOC) were used in pre-column derivatization of the amine, and then separated by using HPLC in conjunction with fluorescence detection [10]. Electrochemical detection techniques, such as amperometric detection, have also been used in conjunction with reversed-phase chromatography for the detection of the low-molecular-mass amines [11].

Potentiometric detection in HPLC has not been successfully used to detect amines in previous reports. Metallic copper electrodes have been successfully used as potentiometric detectors after liquid chromatographic separation methods, including ion-exchange [12], reversed-phase [13], ion-interaction and ion-exclusion [14,15]. From previous studies, it was shown that low detection limits may be achieved depending on the buffer concentration, as well as the complexation of cupric ion with the mobile phase, and the solute at the electrode surface [14]. The lower molecular weight amines were successfully separated by ion-interaction chromatography with octylammonium salicylate eluent with UV detection [16,17]. Electrochemical studies on the corrosion of copper have been shown that the electrode potential change occur at a copper electrode depends on the concentration of corrosion agent such as aliphatic diamine [18]. It appears therefore that there is a possible use of the metallic copper electrode for the potentiometric detection of amines in FIA and HPLC.

The aim of this study is to show that a metallic copper electrode can be used to detect amines. The response characteristics of a copper electrode for aliphatic amines were initially measured in a flow injection analysis (FIA). Some parameters affecting the electrode response were studied to find the optimum operating conditions for the electrode. On the basis of the FIA response characteristics of the electrode, ion-interaction chromatography coupled with a metallic copper electrode detector was found to be a possible method for the detection of aliphatic amines.

2. Experimental

2.1. Instrumentation

Flow injection analysis was used in preliminary studies to evaluate the response of amines on a

metallic copper wire electrode under various conditions. The system was composed of a Millipore-Waters (Milford, MA, USA) Model 510 pump, U6K universal injection valve (Waters) and a flow through potentiometric detector consisting of a metallic copper wire and Ag/AgCl electrode as previously described [14]. A 30 cm length of coiled stainless steel tubing (0.4 mm I.D.) was placed between the injector and detector. The potentiometric response was monitored with a digital pH/mV meter (Orion 701A), and recorded on a linear Model/120 strip-chart recorder and also interfaced to an Apple IIe microcomputer data system.

Chromatography was performed using a Model 510 pump, U6K injection valve and Model 484 tunable absorbance detector. The potentiometric detector was connected in series with the UV detector. A Brownlee Laboratories reversed-phase C₁₈ column was used. The column dimensions were 100×4.6 mm. Chromatograms were recorded with an SE-120 chart recorder. Solution pH readings were measured with an Orion research Model 701A/digital meter fitted with a combination pH glass electrode. The voltage difference between the two electrodes was monitored continuously with a millivolt meter as described for the FIA system.

2.2. Chemicals and solutions

All chemicals were of analytical grade and were used without further purification. Stock 10 mM solutions of mixture of the amines were prepared in Milli-Q water and diluted to the required concentrations before use. The mobile phases were prepared by dissolution of an appropriate amount of octylamine in Milli-Q water and the pH was adjusted with salicylic acid. The solutions were filtered through a Millipore 0.45 μm membrane filter and degassed in an ultrasonic bath prior to use. All water used was distilled and passed through a Milli-Q water purification system.

2.3. Procedure

The treatment of the copper wire electrode prior to use has been described in previous reports [14]. Carrier solution for FIA and mobile phase compositions for HPLC were varied in concentrations of octylammonium salicylate in aqueous solution. In the

flow injection analysis, the carrier solution was continuously pumped through the detector cell at a constant flow-rate. The mobile phases were pumped through the column and the detection cell at a flow-rate of 1.0 ml/min until a stable baseline potential was obtained. The UV detector was operated at 205 nm with a sensitivity setting of 0.01 a.u.f.s. After the measurements were completed, the column was flushed with a 30% MeOH–water mixture for approximately 60 min at a flow-rate of 1.0 ml/min.

3. Results and discussion

3.1. Flow injection measurement

Because of its sensitivity and reproducibility, the metallic copper electrode has found a range of

applications as a potentiometric detector in HPLC and FIA [15,19]. Thus, in preliminary studies, flow-injection measurements were carried out to determine whether the copper metallic electrode could be used in octylammonium salicylate as an ion-interaction reagent for the separation of aliphatic amines. Then the mobile phase was tested in a single-line FIA system using octylammonium salicylate as the carrier solution to determine the electrode performance.

Fig. 1 shows typical peak recordings in the FIA system when responding to aliphatic amines using a metallic copper wire electrode as detector under optimum carrier conditions. It was observed that amines injected gave negative peaks. This indicates that amines form stronger copper complexes than octylammonium salicylate in the carrier solution. The side-reaction coefficient for hydroxide ions with

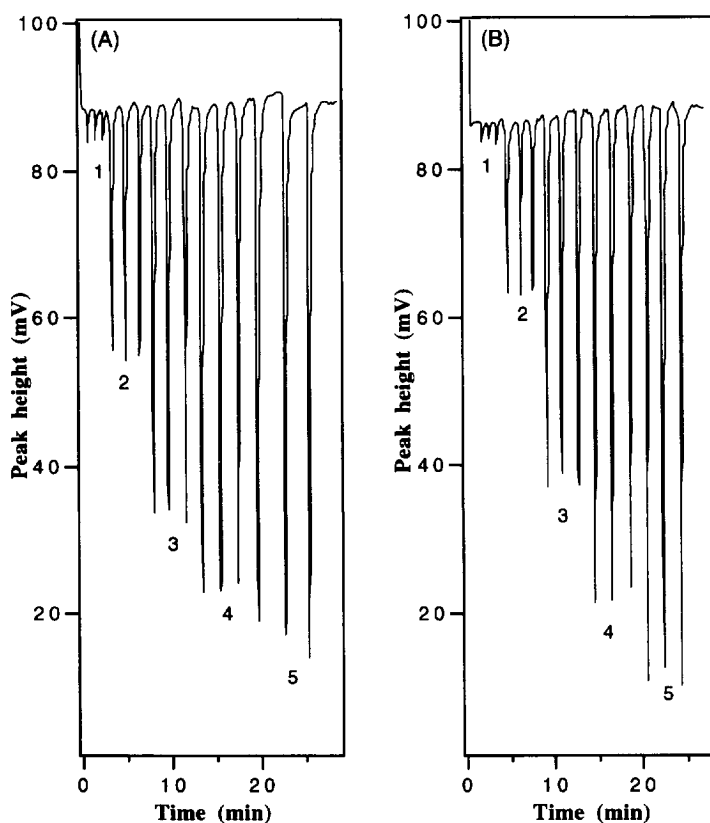


Fig. 1. Typical flow injection peaks for aliphatic amines with the following amounts injected: (A) methylamine: (1) 1 nmol, (2) 5 nmol, (3) 10 nmol, (4) 15 nmol, (5) 20 nmol; (B) Propylamine: (1) 1 nmol, (2) 5 nmol, (3) 10 nmol, (4) 15 nmol, (5) 20 nmol. Carrier solution: pH 5.5, 1 mM octylammonium salicylate; flow-rate: 1.0 ml/min; injected amount: $20 \mu\text{l} \times 10^{-3} \text{ M}$.

Cu^{2+} can be neglected at a $\text{pH} \leq 6$ because complexation of Cu^{2+} with amines is much stronger than with the hydroxyl ion [19].

The copper electrode sensitivity was found to be affected by the carrier pH. This can be attributed to the influence of pH changes on the complexation equilibrium between Cu^{2+} and amines. Using 1 mM octylammonium salicylate as a carrier solution, the peak height increased in peak height by 88–98 mV for the test amines with increasing the pH of the carrier solution from 3.5 to 5.0; after pH 5, the peak height decreased with increasing pH of the solution, for example, the potentiometric response reduced in peak height by 29–34 mV with carrier pH ranging from 5.0 to 6.0. The electrode response decreased at pH is high because of the increasing participation of the copper equilibrium involving hydroxide ions. Similar observations were reported previously for detection of anions and cations in FIA and ion chromatography using a metallic copper electrode as the detector [19]. However, in the view of separation of aliphatic amines by ion-interaction chromatography using octylammonium salicylate as an IIC [16,17], the carrier pH in the range of approximate 5–6 was used in following studies.

The buffer concentration in the carrier solution also influences the response of the copper electrode. Potentiometric detection using a copper electrode is therefore most likely to be successful with a low concentrations of ion-interaction reagent which forms only a weak complex with copper ions at the electrode surface [12,14]. Fig. 2 shows the relationship between the IIR concentration and the electrode response. The peak height decreased in height by 22–27 mV for each tested amine with IIR concentrations ranging from 0.5 to 5 mM. These results are in agreement with those described in previous studies on ion-interaction chromatography using a copper electrode for the detection of carboxylic acids [14].

The effect of injected volume on the electrode response was studied by injecting a standard amine solution in various volumes at constant concentration into the flow system. The response increased as the injected volume increased until an approximate steady state response was achieved at a volume of 50 μl . Maximal complex formation between copper ions and the amines was obtained under steady state

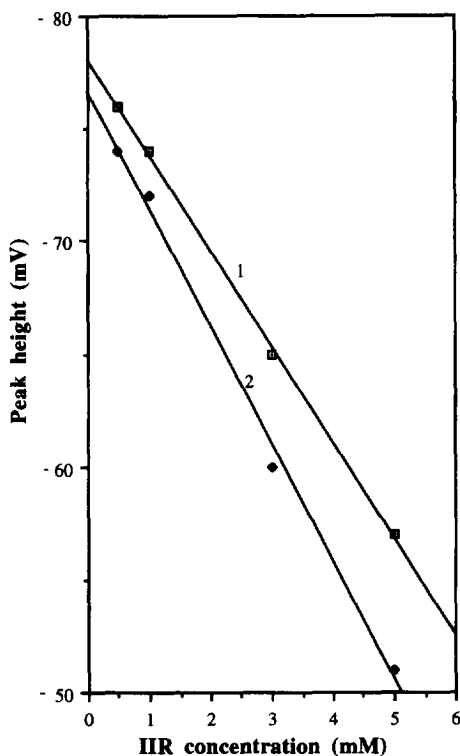


Fig. 2. Effect of the concentration of ion-interaction reagent in carrier solution on the peak height of aliphatic amines: (1) methylamine, (2) propylamine. Conditions as in Fig. 1.

conditions. It was shown that 20–30 μl best suited the situation.

In flow-injection systems with potentiometric detection, optimum sensitivity and linear dynamics are obtained with long sample residence times and low dispersion [20]. The residence time and dispersion can be adjusted by altering some experimental conditions such as flow-rate. When the flow-rate increased from 0.5 and 2.5 ml/min, a reduction in peak height by 25–27 mV for the test amines was observed. This may be attributed to the decreased time period during which the amine sample is in contact with the electrode surface at high flow-rate, as described by Ruzicka et al. [20]. The optimum flow-rate that gives sensitive peak height and fast response was found to be 1.0 ml/min.

The reproducibility of the electrode response was tested by injecting a sequence of 10 replicate samples of methylamine using 1 mM octylammonium salicylate at pH 5.5. The mean value for peak heights

recorded was 50.1 mV with a standard deviation of 1.1 mV (R.S.D. 2.2%) for methylamine. In continuous use, little base line drift was found to occur. After 8 h of continuous exposure to blank carrier solution and test solution, base line drift of less than 3 mV was observed. The noise level recorded for the baseline was about 0.5 mV.

FIA measurements have shown that the metallic copper wire gave a sensitive response to methylamine and ethylamine. However, the electrode is not specific and selective for amines; it is impossible to detect a specific amine in a mixture of amines with an FIA. As the dynamic response behaviour for amines has been shown to be rapid and reproducible in FIA measurements, it would appear that detection of mixed amines in a sample could be achieved by using separation methods such as HPLC coupled with a metallic copper electrode. In addition, the electrode response has been shown to be controlled by some factors such as pH and the IIR concen-

tration in eluent, which are also suitable for reversed-phase or ion-interaction modes for determination of organic compounds. The following studies examined the use of a metallic copper wire electrode coupled with ion-interaction chromatography for the detection of aliphatic amines.

3.2. Ion-interaction chromatography of amines

The possibility of utilizing a metallic copper wire electrode for the detection of amines in ion-interaction chromatography was investigated based on the results of FIA measurements. From the point of view of both the electrode response and chromatographic separation, a short column was used for the separation of the tested solutes to decrease the solute dispersion and increase the electrode response [12,14,19]. Therefore, a 100×4.6 mm C₁₈ column with a 0.3 mM octylammonium salicylate at a pH of 6.0 as an eluent was used. Typical chromatograms

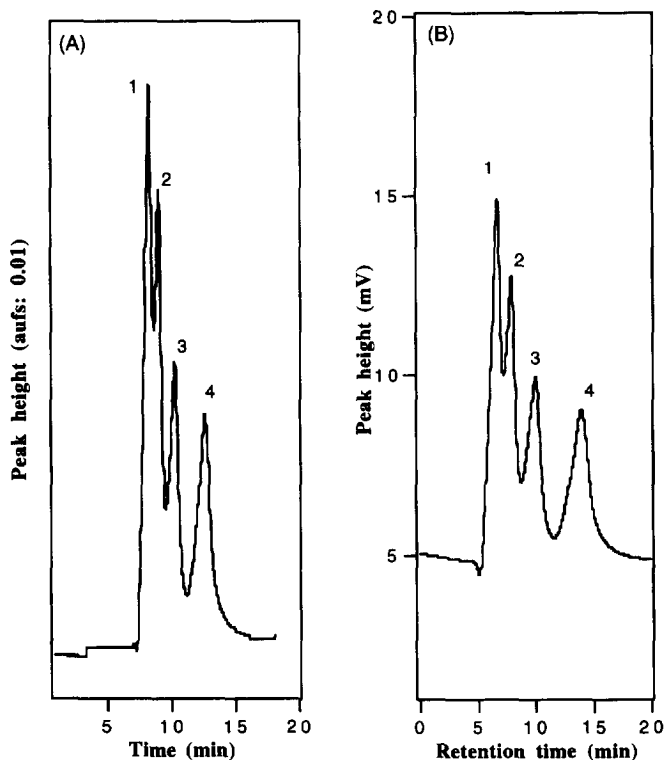


Fig. 3. Chromatograms of a mixture of aliphatic amines separated by ion-interaction chromatography. (A) UV absorbance detector (205 nm, a.u.f.s.: 0.01). (B) Potentiometric detector with a metallic copper wire electrode. (1) Methylamine, (2) ethylamine, (3) *n*-propylamine, (4) *n*-butylamine. Mobile phase: 0.3 mM octylammonium salicylate, pH 6.0; flow-rate: 0.3 ml/min. Injected amount: 30 $\mu\text{l} \times 10^{-3} M$.

showing the separation and detection of four amines using the copper electrode and UV absorbance as detectors are shown in Fig. 3. The amines separated were in order of elution: methylamine, ethylamine, propylamine and butylamine. The retention times were 8.0, 9.0, 10.0 and 13.0 min, respectively. Similar results were observed for UV and conductometric detectors [16,17]. It was found that using only a small ion-interaction reagent concentration in the eluent, without any buffer, a symmetrical peak shape resulted. However, resolution of methylamine and ethylamine was relatively poor due to the short column used [14].

The calibration relationships between peak height and injected amount of amines were linear at low concentrations. The calibration plots for potentiometric detection are shown in Fig. 4. The injections of amine standards covered the working range from 1×10^{-4} to 1×10^{-2} M, and showed the expected

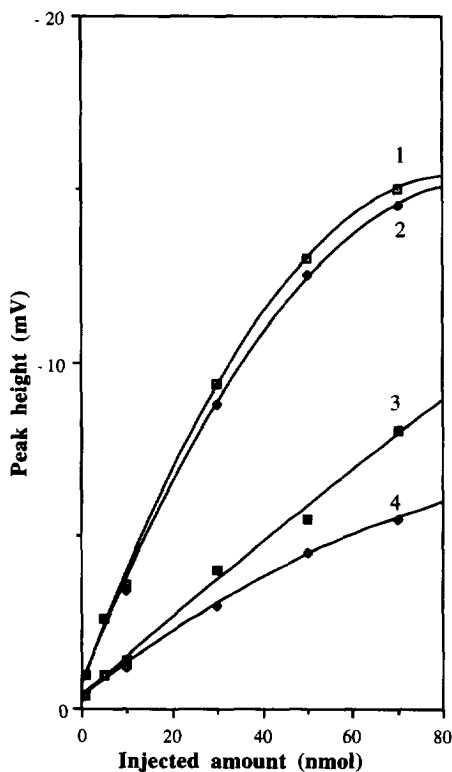


Fig. 4. Calibration relationship between peak height and injection amount for aliphatic amines: (1) methylamine, (2) ethylamine, (3) *n*-propylamine, (4) *n*-butylamine. Conditions as in Fig. 3.

Table 1

Detection limits for UV and potentiometric detectors

Solute	Detection limit	
	UV detector (nmol)	Cu electrode (nmol)
Methylamine	0.10	0.70
Ethylamine	0.30	0.70
Propylamine	1.00	0.80
Butylamine	1.00	0.80

Mobile phase: 0.3 mM octylammonium salicylate, pH: 6.0, flow-rate: 0.3 ml/min.

Nernstian behaviour where the electrode potential begins to level off at higher solute concentration. A plot of electrode potential vs. solute concentrations was linear in the low concentration range. The detection limits obtained for the components of the tested mixture were estimated from the calibration plots. Table 1 lists detection limits for both the UV and potentiometric detectors. It is worth noting that methylamine and ethylamine were detected more sensitively with the UV method, while propylamine and butylamine were detected better with the copper detector under the conditions used.

4. Conclusions

The new sensor for the detection of amines developed in this study has been shown to be useful in both FIA and ion interaction chromatography. The main aim of this work was to demonstrate that the copper electrode sensor responds to amines and to determine optimum experimental conditions for the detection method. The FIA data show excellent speed of response, stable baseline and good sensitivity giving detection limits of the order of nanomoles injected. The HPLC method also compared favourably with UV detection, but was limited due to the short column used. The applications of this method with the copper detector have been proven advantageous in comparison with UV detection or derivatization methods which must be used with fluorometric detection due to the low cost and the simple construction of the flow-through cell. Some real world FIA and HPLC application are envisaged, including analysis of petroleum refinery wastewater [6] and fish freshness [21], and further work is being planned on these aspects.

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