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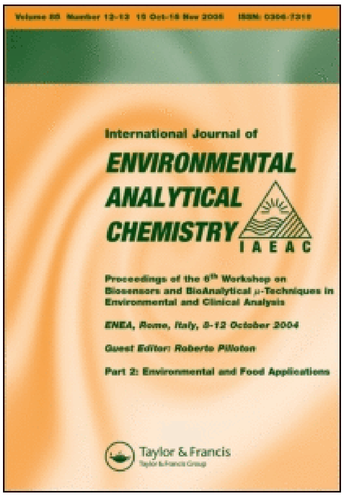

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CAPILLARY ELECTROPHORETIC DETERMINATION OF DISODIUM ETHYLENE BISDITHIOCARBAMATE (NABAM) AND SODIUM DIETHYLDITHIOCARBAMATE (NADDC)

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A simple and sensitive capillary elecrophoretic method has been developed for the separation and determination of Nabam and NaDDC in boric acid buffer by direct UV absorbance detection at 254 nm. The separation is dependent on pH and nature of the buffer. In this method the detection limits (S/N = 3) are 1.56×10^{-6} mol/L and 2.48×10^{-6} mol/L and the linear calibration range is three orders of magnitude for Nabam and NaDDC, respectively. The method has been successfully applied for the analysis of wheat samples spiked with Nabam.

Keywords: Nabam; NaDDC; capillary electrophoresis; environmental samples

INTRODUCTION

Dithiocarbamates have found variety of applications in agriculture as pesticides and in rubber industry as vulcanisation accelerators and anti-oxidants. Dithiocarbamates are generally determined on the basis of their decomposition by hot mineral acids to amine and carbon disulfide [1]. Dithiocarbamates have also been determined in vegetable food-stuffs using spectrophotometry [2], high-performance liquid chromatography [3], extraction voltammetry [4] flow injection fluorimetry [5] and titrimetry [6]. Gas chromatographic methods, including head space analysis [7] and liquid chromatographic methods [8] have also been used to determine dithio-carbamate residues. Dithiocarbamates are also determined by the

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methods which do not use acid decomposition include indirect titration with EDTA [9], polarography [10] and determination of the metallic component of the fungicides [11]. However, all these methods suffer from the following disadvantages:

a) Methods other than gas chromatography are indirect, time consuming and sensitivity is low

b) Gas chromatographic methods are sensitive but suffer from lack of the selectivity since all dithiocarbamate pesticides evolve carbon disulphide on acid hydrolysis.

c) Spectrophotometric methods suffer the interference of various ions.

Capillary electrophoresis [12,13], is a microvolume separation technique increasingly achieving recognition for its use in the separation of inorganic and organic compounds. The key features of this technique are its very short analysis time and small sample volumes in the nanoliter and picoliter range. The sensitivity of LC (and GC) procedures is better than that of CE (with its limited sample introduction), but CE is an interesting alternative separation procedure. Capillary electrophoresis has been used for the determination of sodium dimethyldithiocarbamate using sulphonic acid polymer coated capillary columns at pH 6.5 using sodium phosphate buffer [14].

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As sodium diethyldithiocarbamate and Nabam are present as anions in solutions and unwanted neutral species and cations are screened from the analysis due to applied reverse-polarity electrical field. The all aspects of the inorganic anions and small organic anions analysis have been discussed by Jones and Jandik [13]. This report is concerned with the the investigation of the potential of capillary electrophoresis in the separation of Nabam and NaDDC. Nabam is an effective fungicide. The maximum residue limits [5] for dithiocarbamates (based on carbon disulfide) which are being considered by the European Union are 2–7 mg kg^{-1}As will be demonstrated in this report, capillary electrophoresis with its precision instrumentation and small sample requirements is well suited for the determination of these dithiocarbamates. The methodologies developed in this study can be applied for the determination of other dithiocarbamates.

EXPERIMENTAL

Instrumentation

The CE system consist of the high voltage power supply and the modulart injector (SpectraPHORESIS 100, ThermoQuest, Eggelsbach, Germany), system equipped with an UV absorbance detector. Fused silica capillary of 100 μm i.d and 75 cm long (45 cm to the detector) were used. The solutes were injected in the hydrodynamic mode by vacuum for 2 second. TSP 1000, software was used for the data acquisition. Detection was performed by direct UV absorbance at a wavelength of $\lambda = 254$ nm. All experiments were conducted at 25±1°C.

Reagents and solutions

All chemicals used were of analytical-reagent grade and doubly distilled water was used for the preparation of solutions and all dilutions. Nabam was obtained from Riedel-de Haën (Germany) and NaDDC was obtained as sodium diethylditiocarbamate trihydrate (Fluka, Germany) were used as received. Stock solutions (200 mg l^{-1}) of these dithiocarbamates were prepared by dissolving 20 mg of each compound in doubly distilled water and diluting to 100 ml in a calibrated flask. Working solutions of lower concentrations were prepared by appropriate dilution with water.

Electrophoretic buffer solution was prepared from boric acid 1.25 mM and by adding 0.1 M NaOH solution to adjust the dersired pH (9.2).

PROCEDURES

Basic procedure

The capillary was rinsed with 1 M NaOH, 0.1 M NaOH and water for 2 minutes, respectively, then equilibrated with the carrier electrolyte for 2 min. Between all electrophoretic separations the capillary was rinsed for 2 min with carrier electrolyte. All electrolyte solutions were filtered through a 0.45 μm membrane filter.

Preparation of standard calibration graph

A series of standard solutions of Nabam and NaDDC were injected into the capillary under the optimised conditions to test the linearity of the calibration graph. The linear equations found for Nabam and NaDDC are $Y = 24.42x + 0.1135$ and $Y = 18.074x - 0.5512$; respectively. The characteristics of the calibration curves corresponding to these two analytes are summarized in Table I.

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TABLE I Features of the calibration graphs for the determination of Nabam and NaDDC

Characteristic	*Nabam*	*NaDDC*
Linear regression	Y= 24.42x+0.1135	Y = 18.074x-0.5512
Correlation coefficient	0.9999	0.9942
Detection limit (S/N= 3)	0.39 mg/kg	0.56 mg/kg
RSD[a] (%)	2.76	3.78

a. Concentration of Nabam 0.08 mM and NaDDC 0.03mM, (5 experiments).

RESULTS AND DISCUSSION

Nabam and NaDDC exhibits UV absorption at a wavelength of $\lambda = 254$ nm, so it was well suited for their analysis using capillary electrophoresis. In order to determine the best separation conditions (peak efficiency, analysis time) borate, phosphate and acetate buffer of pH 9.0, 7.0 and 4.5, respectively of 1.25 – 50 mM were investigated and compared. It was observed that below pH 7.0 in phosphate and acetate buffer good peak were not observed. Well defined peaks were obtained in between 1.25 – 50 mM borate buffer of pH 9.0. It was observed that the migration time was more at the higher concentrations of the borate buffer. Above 25 mM concentration of borate buffer there was a considerable increase in the migration time of the both analytes, resulting in an increase in the analysis time due to more electrostatic repulsions between the analytes and the buffer. Therefore, 1.25 mM of borate buffer concentration was preferred. The influence of the applied voltage was also studied by increasing the applied voltage. The separation speed increases with increasing voltage. Therefore, +30 V was applied to get the shortest time for the separation.

Figure 1 illustrates typical electropherogram of the separation of the two dithiocarbamates at pH 9.0. Both compounds, show sharp peaks with base line resolution.

APPLICATIONS

Determination of Nabam in grains

About 10 g of accurately weighed wheat grains were sprayed with 5 ml of an aqueous solution with different amounts of Nabam of 0.1% solution. The sam-

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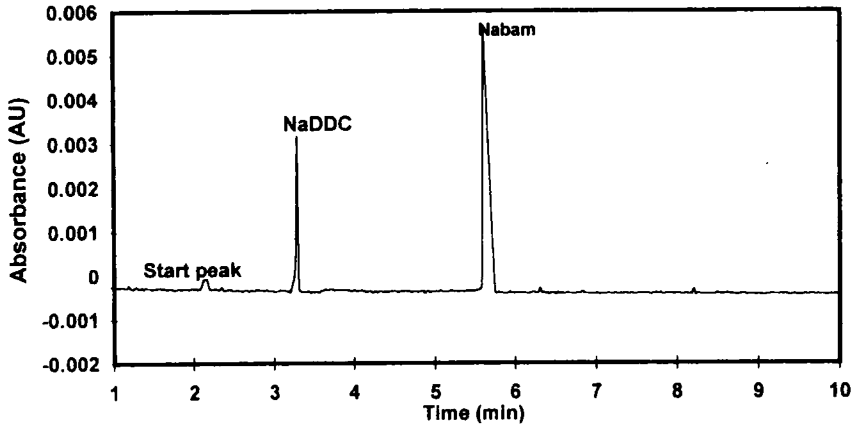

FIGURE 1 Capillary electropherogram of Nabam (0.08 mM) and NaDDC (0.03mM) using 1.25 mM boric acid buffer (pH 9.0) as the carrier electrolyte, voltage applied 30 kV, detection by UV absorbance at a wavelength of λ = 254 nm

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ples were then allowed to dry in the sun for 1 h and thereafter, in the shade for 24 h to remove extraneous moisture. For each determination a blank assay was carried by spraying the same amount of grain with 5 ml of water. The previously ground samples were treated with 50 ml of 0.1 M NaOH. Fortified for 10 min and centrifuged at 2000 rpm for 5 min. Aliquots of the resulting solutions were filtered and analysed by the general procedure. Results of the determinations are given in Table II. Using this method it is possible to estimate 0.39 μg/ml (0.39 mg/kg) of Nabam and 0.56 μg/ml (0.56 mg/kg) of NaDDC, which is better than Nitowski et al. [14] (1.0 μg/ml with stringent analysis controls and routinely 10 μg/ml) method using sulphonic acid polymer-coated capillary columns. Thus the detection limit is quite comparable with the existing methods and is less than that of the regulation of the European Union (2 –7 mg/kg).

TABLE II Recovery of Nabam from treated wheat grain samples

Added (μg/g)	*Found[a] (μg/g)*	*Recovery (%)*
5.0	4.7 ± 0.20	94
10.0	9.6 ± 0.27	96

a. average of three experiments.

CONCLUSION

Capillary electrophoresis technique thus provides an important tool in the hand of the analytical chemists for the analysis and the separation of dithiocarbamates. The simplicity, small sample volume requirement and selectivity makes it advantageous to other chromatographic techniques. Thus the usefulness of capillary electrophoresis as a tool for checking the amount of the dithiocarbamates is successfully demonstrated.

Acknowledgements

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