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Short communication

Capillary electrophoretic determination of ferric dimethyldithiocarbamate as iron(III) chelate of EDTA

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Abstract

A simple and sensitive capillary electrophoretic method with UV detection has been developed for the determination of Ferbam (ferric dimethyldithiocarbamate) in boric acid buffer after its acidic decomposition and complexation with EDTA as $Fe–EDTA^-$ complex. The determination is dependent on the pH and the nature of the buffer solutions. In this method the detection limit ($S/N=3$) is $1.8\cdot10^{-6}$ mol/L (0.7 mg/kg) of Ferbam. The relative standard deviation for the analysis of 50 μg/ml was found to be 2.9%. The method was successfully applied for the analysis of wheat grain samples spiked with Ferbam. The applicability of capillary electrophoresis as a useful tool for the analysis of Ferbam is demonstrated.

Keywords: Dithiocarbamates; Ferbam; Carbamates; Pesticides; Metal chelates

1. Introduction

Ferbam [iron(III) dimethyldithiocarbamate] is a well known dithiocarbamate effective fungicide widely used against a variety of plant pathogenic fungi. Ferbam is generally determined by the carbon disulphide evolution method based on its decomposition by hot mineral acids to amine and carbon disulfide using different approaches [1]. Ferbam is also determined by converting it into moybdenum [2], copper [3] and 1,10-phenanthroline [4] complexes. McLeod and McCulley [5] determined dithiocarbamate fungicides by headspace gas chromatography of the carbon disulphide evolved in controlled conditions from foodstuffs and similar methods were also given by the Committee for Analytical Methods [6]. 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 fungicides evolve carbon disulphide on acid hydrolysis.

(c) Spectrophotometric methods suffer the interference of various ions.

Capillary electrophoresis [7,8], 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. Capillary electrophoresis has been used for the determination of sodium dimethyldithiocarbamate

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using sulphonic acid polymer coated capillary columns at pH 6.5 using sodium phosphate buffer [9]. Liang et al. used diode array detection and factor analysis for the determination of dithiocarbamates [10]. In another approach, solid-phase extraction was used to separate dithiocarbamates with other pesticides [11]. The extensive studies of metal–aminopolycarboxylate complexes are reviewed by Timerbaev [12].

This report is concerned with the investigation of the potential of capillary electrophoresis in the determination of Ferbam. As will be demonstrated in this report, capillary electrophoresis with its precision instrumentation and small sample requirements is well suited for the determination of Ferbam.

Here, we present a relatively simple and selective capillary electrophoretic method by converting Fe(III) present in Ferbam into Fe(III)–$EDTA^{-}$ complex. The chemical structure of Ferbam is as follows: $[(CH_3)_2–NC(S)_2]_3Fe$.

2. Experimental

2.1. Instrumentation

Separations were performed on a Thermo Separation Products 100 CE-system equipped with an UV absorbance detector. Fused silica capillaries of 75 cm long (45 cm to the detector)×100 μm I.D. were used. The solutes were injected in the hydrodynamic mode by vacuum injection for 2 s. TSP 1000 software was used for the data acquisition. Detection was performed by direct UV absorbance at 254 nm. All experiments were conducted at 25±1°C.

2.2. 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.

2.2.1. Ferbam solution

Ferbam was obtained from Riedel-de Haën (Germany) and used as received. Ferbam solution was prepared by decomposing its 20 mg with concentrated nitric acid (5–10 ml) and heated till all the fumes were ceased (almost to dryness) and dissolved the residue in 1–2 ml of concentrated HCl and diluted upto 30–40 ml and pH adjusted in the range 2–3 using dilute NaOH and finally diluted to 100 ml in a calibrated flask. The recovery of iron(III) from Ferbam was checked by titrating it using Variamine Blue B as indicator [13]. Working solutions of lower concentrations were prepared by appropriate dilutions with distilled water.

2.2.2. EDTA solution

Stock solution of EDTA (0.5 m*M*) as disodium salt was prepared in distilled water.

2.2.3. Buffer solution

Electrophoretic buffer solution was prepared from boric acid 50 m*M* and adjusting the desired pH by adding 0.1 *M* NaOH solution.

2.3. Procedures

2.3.1. Basic procedure

The capillary was rinsed with 1 *M* NaOH, 0.1 *M* NaOH and water for 2 min, 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.

2.3.2. Preparation of standard calibration graph

A series of standard solutions of Ferbam were mixed with EDTA (1 ml) and diluted to 2 ml with distilled water and injected into the capillary under the optimised conditions to test the linearity of the calibration graph.

2.3.3. Determination of Ferbam in grains

The method was applied for the determination of Ferbam from wheat grains. A known amount of Ferbam in acetonitrile was crushed with 10 g of wheat grains and shaken mechanically with chloroform (100 ml) for 1 h. The mixture was filtered and the residue in the funnel was washed with chloroform (3×10 ml). The extracts were evaporated to dryness and solution was prepared as discussed above and determined by the general procedure. Untreated samples were taken as reference and the

Table 1
Recovery of Ferbam from spiked grain samples

Added (μg)	Found (μg)[a]	Recovery (%)
5.0	4.70	94
10.0	9.60	96
20.0	19.60	98
50.0	49.50	99

[a] Average of five experiments (RSD = 2.6–3.5%). Amount of grains = 10 g.

results indicated good recoveries in all cases. The results of the determinations are given in Table 1.

3. Results and discussion

A typical capillary electropherogram of Ferbam at pH 9.0 is shown in Fig. 1. It shows a sharp peak with baseline resolution. In order to determine the best experimental conditions (peak efficiency, analysis time) borate, phosphate and acetate buffer of pH 9.0, 7.0 and 4.5, respectively of 1.25–50 m*M* were investigated and compared. It was observed that below pH 7.0 in phosphate and acetate buffer good peak were not observed. A well defined peak was obtained in between 25 and 50 m*M* 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 m*M* 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. Therefore, 25 m*M* of borate buffer concentration was preferred. The influence of the

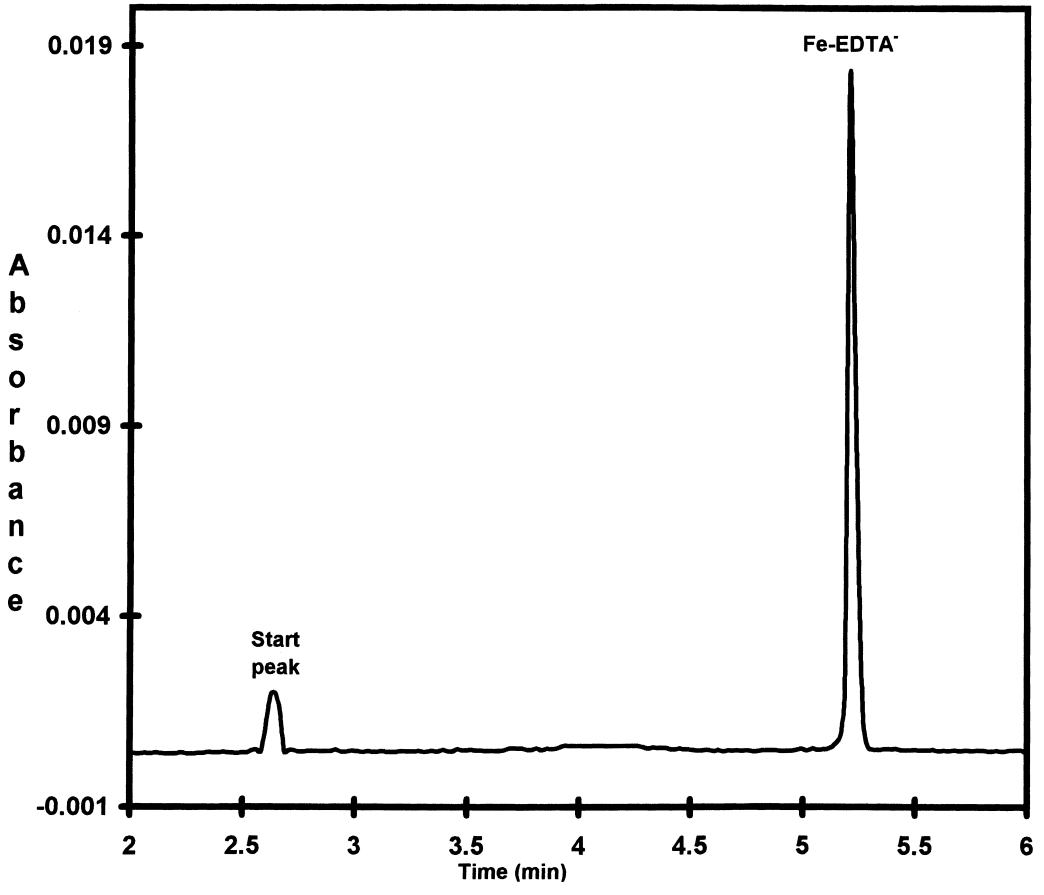

Fig. 1. Capillary electropherogram of Ferbam as Fe–EDTA^{-} complex; Ferbam (50 μg), EDTA (0.25 m*M*); boric acid buffer (25 m*M*; pH 9.0) as the carrier electrolyte, voltage applied +30 kV, detection by UV absorbance at 254 nm.

applied voltage was also studied by increasing the applied voltage. The retention time decreases with increasing voltage. Therefore, +30 kV was applied to get the shortest time. A linear relationship between peak height and concentrations were obtained in the range 3.5–500 μg/ml with an correlation coefficient of 0.9994. The linear regression equation for the calibration curve is $y=0.0001x+0.0003$. Aliquots containing 50 μg/ml of give a relative standard deviation of 2.9% in analysis. Ferbam, if present with other water soluble dithiocarbamates such as nabam, metham, sodium diethyldithiocarbamate, etc., can easily be separated by extraction with chloroform; Nabam and others will remain in the aqueous phase which can then be analysed by the basic procedure [14]. Furthermore, our experiments have shown that Ferbam can be determined directly in the presence of metal ions like Co(II), Zn(II), Cu(II) and Ni(II) without any interference, whereas, these metal ions strongly interfere in the spectrophotometric methods [2,3]. These results are similar to as reported by earlier workers [12,15].

4. Conclusions

Capillary electrophoresis provides an important tool in the hands of the analytical chemists for the determination of Ferbam. The detection limit ($S/N=3$) using this method is 0.7 μg/ml (0.7 mg/kg) of Ferbam which is better than 1 μg/ml of Nitowski et al.'s [9] method reported for dimethyldithiocarbamate using sulphonic acid polymer-coated capillary columns. As most of the cations and anions do not interfere in the determination of Ferbam, moreover, the simplicity and small sample volume requirements makes it advantageous to other chromatographic techniques. Thus, the usefulness of capillary electrophoresis as a tool for checking the amount of Ferbam is successfully demonstrated.

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