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Determination of formaldehyde by capillary electrophoresis in the presence of a dihydroxyacetone matrix

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Abstract

A capillary electrophoretic (CE) method was developed that allows the trace determination of formaldehyde in the presence of an excess of dihydroxyacetone (DHA). As formaldehyde is an uncharged molecule with no electrophoretic mobility and a low response in UV detection, the conditions for a direct CE trace determination are not promising. After derivatisation with dansylhydrazine, a charged formaldehyde dansylhydrazone was obtained which has a very good UV response at 214 nm. Owing to the high separation efficiency of CE, it was possible to separate and determine formaldehyde dansylhydrazone in the presence of a 100 000-fold excess of DHA dansylhydrzone.

Keywords: Formaldehyde; Dihydroxyacetone

1. Introduction

Dihydroxyacetone (DHA) (1,3-dihydroxypropan-2-one) is used as an intermediate for the production of, e.g., tanning agents, emulsifiers, plastifiers, alkyd-type resins and X-ray contrast agents. Owing to its self-tanning properties on the human skin, it is used as component in the cosmetics industry. The problem with this special application is the stability of DHA. During its decomposition, many different reactions may occur. One degradation product is formaldehyde, which has been reported to act as an allergen or even as a carcinogen. Therefore, the amount of formaldehyde has to be determined during the production, storage and processing of DHA. This paper describes the development of a method based on the high separation efficiency of capillary electrophoresis [1].

2. Experimental

2.1. Reagents

Most of the reagents (buffer salts, methanol, water) and DHA ("for cosmetic use" grade) were obtained from Merck (Darmstadt, Germany). For the derivatisation procedure, dansylhydrazine from Fluka (Buchs, Switzerland) was used.

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2.2. Instrumentation

The CE system employed was a Beckman P/ACE System 2100 equipped with a UV detector and deuterium lamp. For data acquisition a Siemens–Nixdorf 486-CPU computer with Beckman System Gold software (Version 8.0) was used.

2.3. Derivatisation procedure

Approximately 6 g/l of dansylhydrazine were dissolved in methanol–water mixture (80:20, v/v) adjusted to pH 3.0 with sulfuric acid (0.05 mol/l), then 0.5 g of DHA was allowed to react with 4 ml of this dansylhydrazine solution (Fig. 1). After reaction for 25 min the maximum formaldehyde dansylhydrazone peak area was obtained. Further experiments showed that the derivatisation reaction is incomplete with reaction times of less than 20 min and at reaction times longer than 30 min we observed a slight decrease in the formaldehyde dansylhydrazone peak area.

2.4. CE separation conditions

Starting with a CE separation system comparable to that described previously [2], which is even able to separate the *Z*- and *E*-isomers of acetaldehyde and propionaldehyde dansylhydrazones (Fig. 2), we optimized the separation conditions for the interesting pair of formaldehyde and dihydroxyacetone dansylhydrazones. In the first step of the optimization experiments, the pH range 5–8 at intervals of one pH unit was examined. The concentration of the buffer was 75 m*M*. To avoid a molarity change during the pH adjustment, two buffers were prepared: 75 m*M* sodium dihydrogenphosphate and 75 m*M* disodium hydrogenphosphate solutions. The disodium hydrogenphosphate buffer solution was titrated with the sodium dihydrogenphosphate buffer solution to the final pH value. Fine optimization of the pH value in the running buffer is shown in Fig. 3.

Fig. 4 shows the effect of organic modifier variations. The percentage of methanol was optimized in order to obtain a good peak resolution between the trace component formaldehyde dansylhydrazone and the excess of dihydroxyacetone dansylhydrazone. According to Fig. 4, a methanol content of 30% should be the optimum, but in a series of experiments we observed a decrease in the migration time for the analyte peak. At a modifier concentration of 20% this effect was tolerable.

The optimization experiments resulted in the CE separation conditions shown in Fig. 5.

3. Results and discussion

A method was developed that allows the determination of formaldehyde in the presence of a dihydroxyacetone matrix. The basic calibration was carried out with aqueous formaldehyde solutions covering the concentration range 67–1333 μg/l, resulting in a linear calibration graph which also gave the blank:

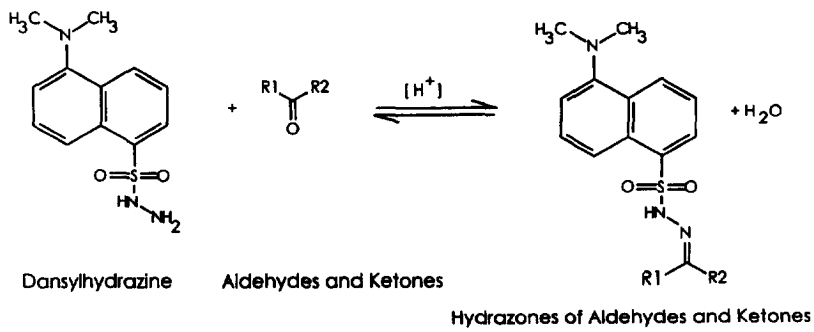

Fig. 1. Reaction of dansylhydrazine with carbonyl compounds.

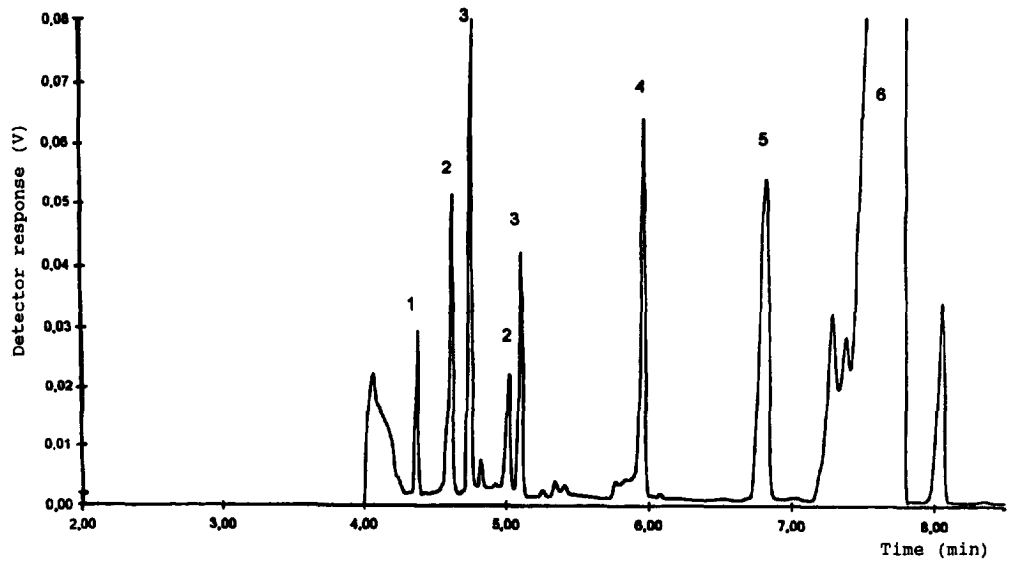

Fig. 2. Electropherogram of a carbonyl standard mixture. CE conditions: buffer = 20 m*M* $Na_2B_4O_7$–10 m*M* Na_3PO_4 (pH 7.0, adjusted with 0.5 *M* H_2SO_4)–10% methanol. Peaks: dansylhydrazones of: 1 = acetone; 2 = propionaldehyde; 3 = acetaldehyde; 4 = formaldehyde; 5 = methylglyoxal; 6 = reagent peak.

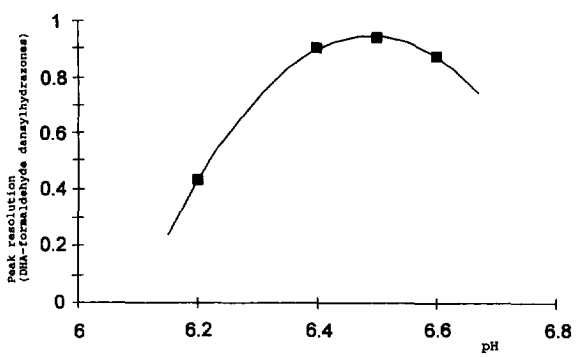

Fig. 3. pH optimization of the running buffer.

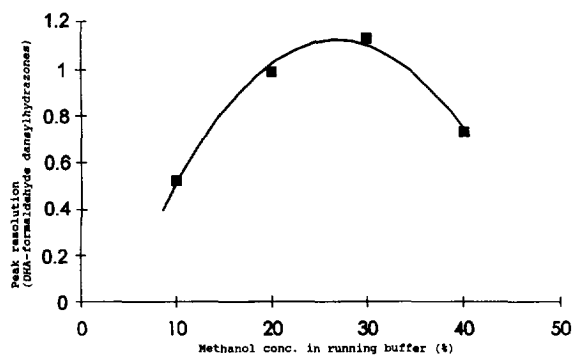

Fig. 4. Optimization of organic modifier concentration.

$$y = 6.929 \cdot 10^{-4}[V(\mu g/l)] \cdot x + 0.6475V$$

As our systematic statistic investigations showed, incompleteness of the reaction between formaldehyde and dansylhydrazine in the presence of the DHA matrix is the main shortcoming of the method. To overcome the problem of this proportional systematic deviation, we selected the standard addition technique for quantification of formaldehyde. As expected, the slope of the calibration curve with DHA matrix was different, i.e., $2.957 \cdot 10^{-4}$.

The yield of the derivatisation reaction is given as the ratio of the slopes according to the following equation:

$$U = b_A \cdot 100\% / b = 43\% \quad \text{with} \quad b_A = 2.957 \cdot 10^{-4}$$

and $b = 6.929 \cdot 10^{-4}$.

The formaldehyde content of a real sample was calculated according to the equation

$$c_{FA} = y_0 - (y_b U)/b_A$$

where y_0 = axis segment of the standard addition calibration function and y_b = blank of the reagent solution. In a real sample 238 μg/l of formaldehyde was found, i.e., with a sample

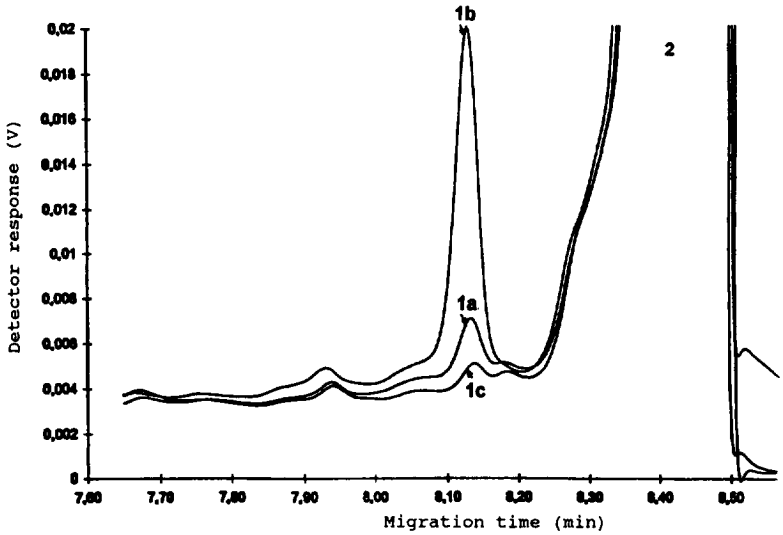

Fig. 5. Electropherogram of derivatized dihydroxyacetone with spiked formaldehyde. Separation conditions: Buffer, 75 m*M* NaH_2PO_4–Na_2HPO_4 (pH 6.5)–20% (v/v) methanol; capillary, 50 μm I.D. × 50 cm to detector, total length 57 cm; voltage, 25 kV; current, 30 μA; detection, UV at 214 nm; injection, hydrodynamic (15 s); temperature, 24°C. Peaks: 1 = formaldehyde dansylhydrazone peaks; 1a = 10 ppm formaldehyde added; 1b = 100 ppm formaldehyde added; 1c = real dihydroxyacetone sample without spiked formaldehyde; 2 = DHA dansylhydrazone peak.

concentration of 0.5 g CHA in 4 ml, a formaldehyde content of 1.9 ppm in the original DHA sample.

The limit of detection was calculated from the calibration function according to [3]

$$X_N = x_p$$

if $0.5x_1 < x_p < x_1$. With this equation we found a detection limit of 200 ppb.

GC cannot be used in this special case for formaldehyde determination owing to the thermal lability of DHA. When heated, DHA decomposes and generates many components. One of these degradation products is formaldehyde, which could be verified during stress experiments with DHA (i.e. treatment of DHA at 40°C). Compared with other chromatographic techniques, e.g. HPLC, determination after derivatization with 2,4-dinitrophenylhydrazine CE is faster, easier and less reagent consuming.

References

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