ELSEVIER

Journal of Chromatography A, 979 (2002) 409–416

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Laser-induced fluorescence and UV detection of derivatized aldehydes in air samples using capillary electrophoresis

Elisabete Alves Pereira[a], Emanuel Carrilho[b], Marina F.M. Tavares[a,*]

[a]*Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05508-900 São Paulo, SP, Brazil*

[b]*Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil*

Abstract

In this work, two capillary zone electrophoresis methodologies using UV absorption detection (214 nm) and laser-induced fluorescence detection (He/Cd laser, 325 nm excitation, 520 nm emission) of selected aldehydes (formaldehyde, acetaldehyde, propionaldehyde and acrolein) derivatized with dansylhydrazine (DNSH, 5-dimethylaminonaphthalene-1-sulfohydrazide) were proposed and validated. The aldehydes react with DNSH to form negatively charged molecules in methanolic medium. In both methodologies, nine DNSH-derivatives, including isomers of acetaldehyde, propionaldehyde and acrolein and two impurities were baseline separated in 20 mmol l^{-1} phosphate buffer at pH 7.02, in less than 9 min. The limits of detection for the UV and LIF methodologies ranged from 1.1–9.5 μg l^{-1} and 0.29–5.3 μg l^{-1}, respectively. The applicability of both methodologies to contemplate real samples was confirmed in the analysis of aldehyde–DNSH derivatives in indoor and outdoor air samples.

Keywords: Air analysis; Derivatization, electrophoresis; Aldehydes; Ketones; Volatile organic compounds; Dansylhydrazine

1. Introduction

Low molecular mass aldehydes are among the most abundant volatile organic compounds (VOCs) in the atmosphere. The C_1–C_5 aldehydes are produced from many sources such as industrial activities, incomplete combustion of fossil fuels and biomass. The smaller aliphatic aldehydes are produced from photooxidation of both anthropogenic and biogenic hydrocarbons, ethers, alcohols, and other organic compounds [1,2]. Plastics, foam insulations, cosmetics and lacquers are sources of aldehydes and ketones indoors [3].

Aldehydes have long caused a great deal of concern due to their deleterious impact on the environment. They are important precursor compounds of photochemical smog and their chemistry has been associated to the generation of harmful free radicals, peroxyacetylnitrate (PAN) and ozone [4,5]. Examples of the adverse effects of aldehydes on health include: formaldehyde and acrolein are well-known irritants of the respiratory tracts of animals and humans [6], formaldehyde has been regulated for its carcinogenic properties as it inhibits protein active sites [7,8] and acetaldehyde has also shown a strong chemical reactivity [8].

Environmental measurements of aldehydes have been conducted in polluted urban air and remote areas [9–13]. Indoor air pollution has been disclosed lately as an important issue because individuals

*Corresponding author. Tel.: +55-11-3091-2056; fax: +55-11-3815-5579.

E-mail address: mfmtavar@iq.usp.br (M.F.M. Tavares).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01258-X

spend large fractions of their time in indoor environments. Indoor measurements of aldehydes have been reported in office buildings [14], residential houses [14] and libraries [15].

Due to the development of modern analytical techniques, the number of aldehyde species identified and measured in environmental samples has increased considerably. Conventional methods for measuring aldehydes are usually based on spectrophotometry and chromatography [16]. In both cases, aldehydes must be derivatized for detection.

A multitude of different derivatizing agents has been used for the analysis of aldehydes [17]. All aldehyde-specific reagents promote a condensation reaction between the reagents and the analytes yielding a colored and/or fluorescent derivative. The most commonly used derivatization agents for aldehydes are hydrazine-based reagents. They react with aldehydes and ketones with formation of the respective hydrazones. The hydrazones are typically detected by UV–Vis or fluorescence spectroscopies, with or without preliminary liquid chromatographic separation [17]. Spectrophotometric methods are, in most cases, not sensitive enough for environmental samples and because they lack specificity, only total aldehydes can be computed [17,18]. Reported disadvantages of chromatographic methods include large amounts of solvents, long analysis time, and extensive purification of reagents and solvents are required [18].

In the last few years, capillary electrophoresis has been introduced in the analysis of aliphatic aldehydes, derivatized with bissulfite [19], 4-hydrazinobenzosulphonic acid [20], 2,4-dinitrophenylhydrazine [19,21,22] and dansylhydrazine (DNSH) [21–23]. The greatest advantage of the latter reagent, DNSH, is that there is no need for purification procedures prior to electrophoretic analysis since the migration of the reagent and its impurities does not interfere with the migration of the aldehyde-derivatives.

This work describes two alternative methodologies for determination of aldehydes derivatized with DNSH (reaction depicted in Fig. 1), using both UV absorbance and fluorescence detection in capillary electrophoresis (CE). The reactional medium and the electrolyte system were optimized for the application to real indoor and outdoor air samples. Additionally, both methodologies were validated with respect to linearity, limit of detection and quantification, precision (migration time, peak area and peak height within-day repeatabilities) and robustness.

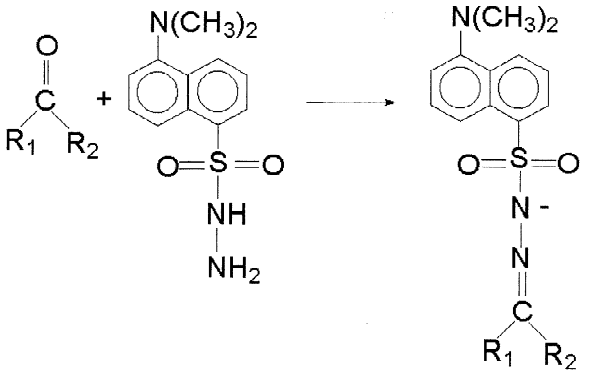

Fig. 1. Derivatization reaction of a carbonyl with DNSH.

2. Experimental

2.1. Instrumentation

All experiments were conducted in a P/ACE 5510 capillary electrophoresis system (Beckman Instruments, Fullerton, CA, USA) equipped with a diode array detector, set at 214 nm and a temperature control device that maintained the capillary holder cartridge at 29 °C. The data acquisition and treatment software was supplied by the manufacturer (Beckman P/ACE System Gold Software). The laser-induced fluorescence (LIF) detection was performed by coupling a He–Cd laser (Ohmnichrome, Melles Griot, Carlsbad, CA, USA) with a UV-transparent quartz optic fiber to a second P/ACE unit. The 325-nm laser line was used for excitation and a 520-nm bandpass filter (Oriel, Stratford, CT, USA) was used to collect the fluorescent light. Fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) of 58 cm (50 cm effective length)×75 μm I.D.×375 μm O.D. were used. Samples were injected hydrodynamically at 34 mbar (1 mbar=100 Pa) during 2 s. The electrophoresis system was operated under normal polarity and constant voltage conditions of +20 kV.

2.2. Reagents and solutions

All reagents and solvents were of analytical grade and used with no further purification. Formaldehyde, acetaldehyde, acetone and 5-dimethylaminonaphthalene-1-sulfohydrazide (dansylhydrazine, DNSH) were obtained from Sigma (St. Louis, MO, USA). Propionaldehyde and acrolein were obtained from Riedel-Haën (Seelze, Germany). Aldehyde stock solutions at 1000 mg l^{-1} concentration were prepared by dissolving appropriate amounts of the selected standards in deionized water (Milli-Q, Millipore, Bedford, MA, USA). The hydrazones were prepared by adding 50 μl of the aldehyde stock solution to 5-ml methanol (or acetonitrile) solution containing 345 μg ml^{-1} dansylhydrazine. The reactional medium was allowed 24 h to ensure complete derivatization. The optimal electrolyte solution for electrophoresis was 20 mmol l^{-1} phosphate buffer, pH 7.02, however, a 10 mmol l^{-1} tetraborate–5 mmol l^{-1} phosphate buffer, pH 7.20 was also investigated.

2.3. Analytical procedure

The electrolyte solution was prepared fresh daily. At the beginning of each day, the fused-silica capillary was conditioned by flushing 1 mol l^{-1} NaOH solution (5 min), followed by a 5-min flush of deionized water and electrolyte solution (40 min). In between runs, the capillary was just replenished with fresh electrolyte solution (3-min flush). Specific electrophoretic conditions and separation electrolytes are stated in the figure legends.

2.4. Sample collection and preparation

Air samples were collected using octadecylsilica modified cartridges. The cartridges were conditioned with acetonitrile, followed by deionized water. After conditioning, the cartridges were loaded with 10 ml of the reagent solution (0.4 mg ml^{-1} dansylhydrazine containing 0.4 mg ml^{-1} of trichloroacetic acid in methanol), and dried with nitrogen at a flow-rate of 500 ml min^{-1} for 3 min. Samples were collected by passing air through the dansylhydrazine–trichloroacetic acid pretreated cartridge at a rate of 1.0 l min^{-1} during 2 h and 15 min. After the sample was collected, the cartridges were sealed in a glass tube and placed in an oven at 60 °C for 10 min. The compounds were eluted from the cartridges with 2 ml methanol. The eluate was then evaporated to dryness at 50 °C under reduced pressure and the residue was dissolved in 200 μl of a 95% methanolic solution, prior to analysis.

3. Results and discussion

3.1. UV absorbance detection methodology

The use of DNSH as derivatizing agent for aldehydes in CE separations was introduced by Bächmann et al. [23]. In this original paper, a study of the separation buffer pH was conducted in which a mixture of tetraborate–phosphate was employed in the pH range from 8.5 to 6.3. When the buffer pH was adjusted to 7.1, baseline separation of 11 aldehyde derivatives was accomplished in less than 8 min. In subsequent articles, where applications of this system to an environmental sample and a cosmetic product were described [24,25], the conditions in which the derivatizing reaction was conducted varied as well as a few buffer organic additives being employed during separation. Since the methodology parameters seemed to be optimized according to the nature of the sample, we decided to explore in better detail the effect of solvents in the reactional medium and the buffer composition, before applying the DNSH derivatization to the analysis of aldehydes in indoor and outdoor air samples.

Considering the experimental difficulty to adjust tetraborate–phosphate buffers at pH 7 and since phosphate buffers present optimal buffer capacities at ~pH 2.5, 7, and 12, it occurred to us to test simply a phosphate buffer for the separation of aldehyde–DNSH derivatives. Comparative results of the two buffer systems are presented in Fig. 2. Small variations of signal intensity and column efficiency are observed and the overall analysis time is longer when phosphate buffer is employed. It is interesting to notice that all aldehydes but formaldehyde yielded two geometric isomers, while acrolein produced three derivatives.

Since the organic solvent used in the reaction

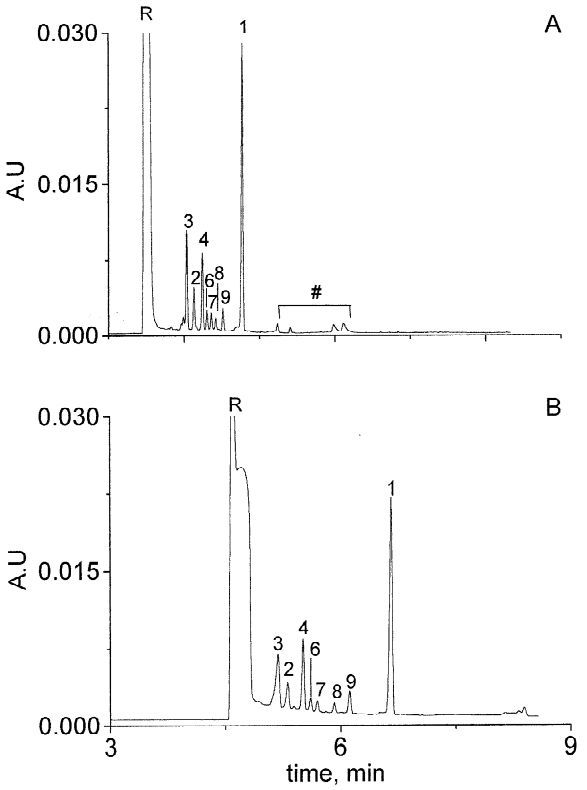

Fig. 2. Effect of the buffer electrolyte composition in the separation of aldehyde–DNSH derivatives prepared in acetonitrile (UV absorbance detection method). (A) 15 mmol l^{-1} tetraborate buffer containing 5 mmol l^{-1} phosphate, pH 7.2 and (B) 20 mmol l^{-1} phosphate buffer, pH 7.02. Concentration of each aldehyde was 5 mg l^{-1}. Separation conditions, fused-silica capillary, 57 cm total length (50 cm to detector)×75 μm I.D.×360 μm O.D.; separation voltage, 20 kV; hydrodynamic injection, 2 s at 34 mbar; UV absorbance detection at 214 nm. Peak identification: 1, formaldehyde; 2 and 7, acetaldehyde; 3 and 6, propionaldehyde; 4, 8, and 9, acrolein; 5, acetone; R, excess reagent; ≠, impurities.

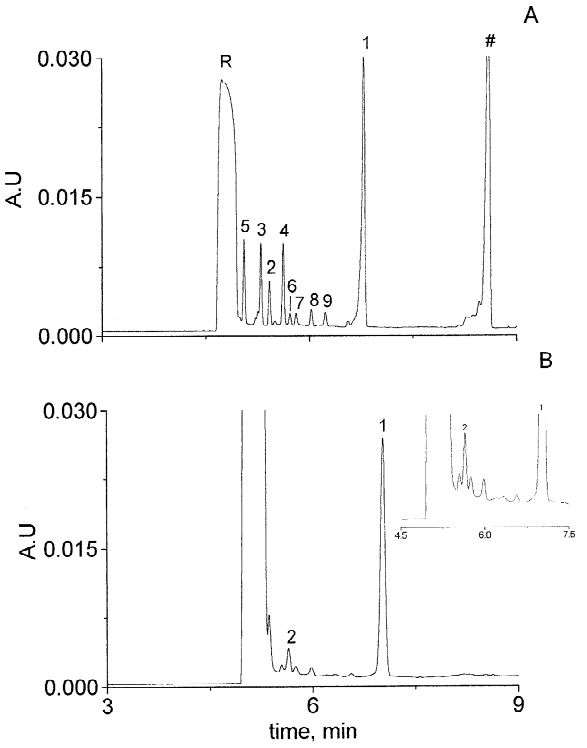

Fig. 3. Separation of aldehyde–DNSH derivatives prepared in MeOH by the UV absorbance detection method (214 nm). (A) Standard mixture of each aldehyde–DNSH derivative at 5 mg l^{-1} concentration and (B) a typical *indoor* air sample (141 l) collected at the laboratory. Electrophoretic conditions and peak labels as in Fig. 2B.

medium can affect considerably the reaction yield, and consequently, the method sensitivity, the solvent type seemed to be a reasonable variable for further investigation. Methanol was evaluated during the labeling procedure and the resulting aldehyde–DNSH derivatives were analyzed in a pH 7.0 phosphate buffer. The results are depicted in Fig. 3A. All derivatives were baseline separated in less than 7 min. Additionally, a slightly better resolution as well as an improvement in signal intensity were observed when methanol replaced acetonitrile (Fig. 2B) in the reactional medium.

It is well-known that acetone is not derivatized by dansylhydrazine in favorable yield if the medium is not acidulated appropriately [26]. On the other hand, the reagent itself can be degraded in acidic medium. Therefore, a careful control of the medium acidity is indicated if acetone is to be determined. In this work, the reaction medium was not acidulated. However, during sample collection, a cartridge impregnated with DNSH in trichloroacetic acid was used as a means to minimize interference from water vapor [27]. Nevertheless, a close inspection of Figs. 2 and 3 indicates that acetone was not detectable when

acetonitrile was the medium solvent. However, when methanol, a better proton donor solvent, was used, acetone could be readily visualized.

3.2. Laser-induced fluorescence detection methodology

The use of DNSH as a derivatization reagent brings about the possibility to use either absorbance or fluorescence detection since it presents both high molar absorbtivity and good fluorescence quantum yield. Fluorescence is inherently a high-sensitivity technique. Detection limits using laser-induced fluorescence detection (LIF) are one to three orders of magnitude lower than those obtained with absorbance detection. However, the fluorescence detection in CE can eventually be less sensitive than UV detection if fluorescence quenching occurs caused by the buffer.

In order to evaluate possible quenching effects, the LIF detection for the DNSH–aldehyde derivatives in phosphate buffer was investigated. The results are shown in Fig. 4. As observed, the signal of acetone and propionaldehyde relative to acetaldehyde decreased, suggesting that a structure-related fluorescence suppression might be occurring.

3.3. Method validation

Based on the results presented herein, methanol was selected for the derivatization reactional medium and a pH 7.0, 20 mmol l^{-1} phosphate solution was used as the CE separation buffer for both UV and LIF detection of the aldehyde–DNSH derivatives under investigation in this work.

Tables 1 and 2 present a few validation parameters for the UV detection methodology, as well as the estimates of the limit of detection (LOD) with respect to each single aldehyde. Within-day repeatability of migration times was better than 1.1% whereas peak area measurements, in general, were more precise than peak height (Table 1). For quantitative purposes, calibration curves based on peak area were built (Table 2). The limit of detection for all aldehydes under investigation was in the range of 1.1 to 9.5 μg l^{-1}.

Tables 3 and 4 present validation parameters for the LIF detection based methodology. Within-day repeatability of migration times was better than 0.90% whereas peak height measurements were more precise than peak area (Table 3). For quantitative purposes, calibration curves based on the peak height were built (Table 4). The limit of detection for all aldehydes investigated in this work were in the range of 0.29 to 5.3 μg l^{-1}. This represents roughly a twofold sensitivity improvement over the UV-detection methodology.

Despite the fact that phosphate buffer was a suitable electrolyte for the separation, the gain in

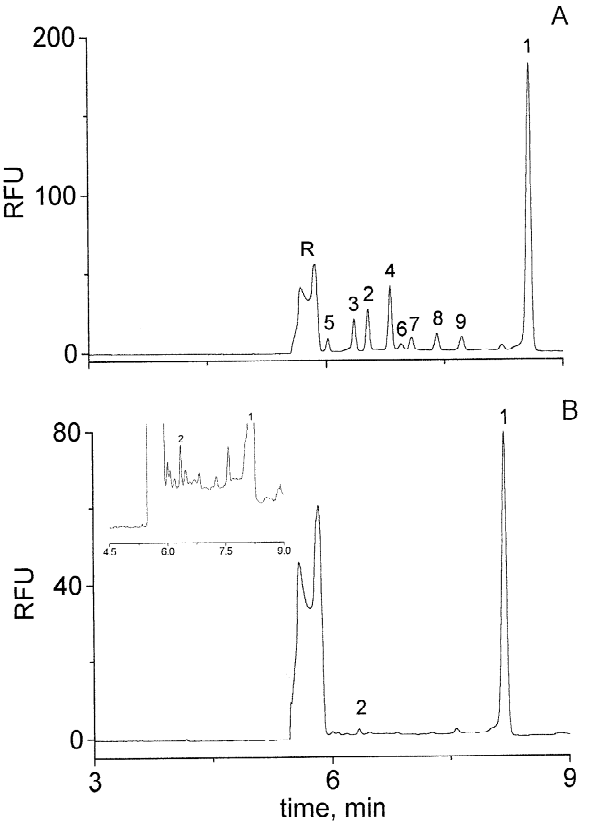

Fig. 4. Separation of aldehyde–DNSH derivatives prepared in MeOH by the LIF detection method (excitation at 325 nm; emission at 520 nm). (A) Standard mixture of each aldehyde–DNSH derivative at 5 mg l^{-1} concentration and (B) a typical *outdoor* air sample (150 l). Electrophoretic conditions and peak labels as in Fig. 2B.

Table 1
Method validation regarding within-day repeatability for the UV absorbance detection methodology

Aldehyde–DNSH derivative	Migration time (min)	RSD (%, $n=5$)		
		Time	Peak area	Peak height
Formaldehyde	6.79	1.1	2.0	5.4
Acetaldehyde	5.42	0.66	5.0	8.3
	5.81	0.76	6.0	15
Propionaldehyde	5.29	0.52	3.5	8.8
	5.72	0.83	3.1	8.2
Acrolein	5.62	0.78	5.7	8.9
	6.03	0.78	4.8	7.0
	6.23	0.97	5.1	7.2
Acetone	5.05	0.85	3.5	6.6

Table 2
Statistical parameters of the calibration curves and estimates of limits of detection (LOD) and quantification (LOQ) of single aldehydes for the UV-absorbance detection methodology

Aldehyde–DNSH derivative	Calibration curve equation[c]	R^2	LOD[a] ($\mu g\ l^{-1}$)	LOQ[b] ($\mu g\ l^{-1}$)
Formaldehyde	$y = 64.4x + 1925$	0.9997	1.1	3.6
Acetaldehyde	$y = 13.4x + 236$	0.9995	7.6	25
Propionaldehyde	$y = 9.98x + 98.9$	0.9999	9.5	32
Acrolein	$y = 12.9x - 1.84$	0.9987	9.3	31
Acetone	$y = 3.13x - 6.78$	0.9999	9.5	32

[a] Refers to the free aldehyde; calculated from interpolation of y in the calibration curve ($y - y_b = 3s_b$, where y_b is the intercept and s_b is the error associated to its estimate).
[b] $S/N = 10$, refers to the free aldehyde.
[c] Adduct concentration interval from 100 to 1000 $\mu g\ l^{-1}$; based on peak area.

sensitivity when the LIF detector replaced the UV-detector was not as impressive, suggesting that a fluorescence quenching effect must be occurring to some extent. Moreover, if Tables 1 and 3 are closely observed, there is a shift in migration time for all aldehyde–DNSH derivatives. Considering that the LIF detector was assembled in a different CE unit, and the LIF analysis was conducted in a different

Table 3
Method validation regarding within-day repeatability for the LIF detection methodology

Aldehyde–DNSH derivative	Migration time (min)	RSD (%, $n=5$)		
		Time	Peak area	Peak height
Formaldehyde	8.57	0.90	4.4	2.0
Acetaldehyde	6.52	0.54	4.4	3.1
	7.08	0.77	5.3	3.3
Propionaldehyde	6.35	0.43	4.8	3.9
	6.95	0.71	3.8	4.2
Acrolein	6.81	0.64	4.2	2.3
	7.40	0.73	6.7	3.0
	7.72	0.77	3.9	2.2
Acetone	6.02	0.16	20	8.4

Table 4
Statistical parameters of the calibration curves and estimates of limits of detection (LOD) and quantification (LOQ) of single aldehydes for the LIF detection methodology

Aldehyde–DNSH derivative	Calibration curve equation[c]	R^2	LOD[a] ($\mu g\ l^{-1}$)	LOQ[b] ($\mu g\ l^{-1}$)
Formaldehyde	$y = 0.09434x - 9.566$	0.9977	0.29	0.98
Acetaldehyde	$y = 0.01075x - 1.104$	0.9975	3.2	11
Propionaldehyde	$y = 0.00875x - 0.9287$	0.9976	5.3	18
Acrolein	$y = 0.01866x - 2.268$	0.9953	3.9	13
Acetone			$>464\ \mu g\ l^{-1}$	

[a] Refers to the free aldehyde; calculated from interpolation of y in a calibration curve ($y - y_b = 3s_b$, where y_b is the intercept and s_b is the error associated to its estimate), with adduct concentration interval from 40 to 100 $\mu g\ l^{-1}$.
[b] $S/N = 10$, refers to the free aldehyde.
[c] Adduct concentration interval from 250 to 2500; based on peak height.

day, the observed shifts in migration time can actually be used to evaluate the method robustness. Therefore, if we compute the migration time of each single aldehyde in different days and different equipment, a day-to-day repeatability of 10% is obtained.

3.4. Applications

Fig. 3B shows a typical electropherogram of an indoor air sample (laboratory) collected in a DNSH-modified cartridge, using the proposed UV absorbance detection methodology. As demonstrated, formaldehyde and acetaldehyde are the only detectable aldehyde components in the sample. Rough estimates of their concentrations are 2.2 and 0.67 ppb (v/v), respectively. The predominance of formaldehyde over acetaldehyde can be attributed to the unique source of this compound indoors. Formaldehyde is emitted from construction materials (e.g. wood products such as particle board) and furniture [14]. Other sources include coatings, plastics, paper products, foam insulation, textile materials, cleaning agents, cosmetic products, etc. [28]. Thus, a significant level of formaldehyde is expected to be found indoors.

Outdoor air samples were collected in the vicinity of the laboratory, which is located in the second floor of a two-storey building. In Fig. 4B, a typical electropherogram of an outdoor air sample is depicted. The concentration of formaldehyde in this particular sample was found to be 0.96 ppb (v/v). Traces of acetaldehyde were also found, 0.19 ppb (v/v). In general, formaldehyde predominates in urban areas [29]. Brazil faces a unique atmospheric problem because of the widespread use of ethanol as fuel for internal combustion engines. Partial oxidation of ethanol in vehicular exhaust leads to higher levels of acetaldehyde compared to formaldehyde, which has been reported in Brazilian urban air [30]. The discrepancy found in the level of acetaldehyde in the outdoor air sample suggests that the sampling location was not representative. The sample was collected near our laboratory, which is located in a very arboreal and scarcely populated area, thus minimizing the pollution effects from high-traffic avenues.

4. Conclusion

The applicability of DNSH as derivatization reagent for the trace analysis of aldehydes in capillary electrophoresis has been established. The procedures presented herein for the determination of aldehydes, using both UV and LIF detection schemes, are rapid and simple. Excellent limits of detection were found, making CE eligible for the analysis of environmental samples.

Acknowledgements

The authors wish to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) of

Brazil for fellowships (FAPESP 97/12433-4, CNPq 301201/94-3) and financial support (FAPESP 00/04414-4 and 98/12385-2).

References

[1] T.E. Graedel, Atmospheric Chemical Compounds: Sources, Occurrence and Biossay, Academic Press, Orlando, FL, 1986.
[2] P. Carlier, H. Hannachi, G. Mouvier, Atmos. Environ. 20 (1986) 2079.
[3] L. Nondek, R.E. Milofsky, J.W. Birks, Chromatographia 32 (1991) 33.
[4] B.J. Finlayson-Pitts, J.N. Pitts Jr., Science 276 (1997) 1045.
[5] W.C. Trogler, J. Chem. Educ. 72 (1995) 973.
[6] National Research Council, Formaldehyde and Other Aldehydes, National Academic Press, Washington, DC, 1981.
[7] M.O. Amdur, Air pollutants, in: Casarett na Doull's Toxicology: the Basic Science of Poisons, Pergamon Press, New York, 1991, p. 866, Chapter 5.
[8] T. Sakai, H. Nagasawa, H. Nishikwa, Talanta 43 (1996) 859.
[9] D. Grosjean, Environ. Sci. Technol. 16 (1982) 254.
[10] D. Grosjean, R. Swanson, C. Ellis, Sci. Total Environ. 29 (1983) 65.
[11] K. Kuwata, M. Uebori, H. Yamasaki, Y. Kuge, Anal. Chem. 55 (1983) 2013.
[12] L. Haszpra, I. Szilagyi, A. Demeter, T. Turanyi, T. Berces, Atmos. Environ. 25A (1991) 2103.
[13] P. Schulam, R. Newbold, L.A. Hull, Atmos. Environ. 19 (1985) 623.
[14] J. Zhang, Q. He, P.J. Lloy, Environ. Sci. Technol. 28 (1994) 146.
[15] G. Fantuzzi, G. Aggazzotti, E. Righi, L. Cavazzuti, G. Predieri, A. Ranceshelli, Sci. Total Environ. 193 (1996) 49.
[16] A. Vairavamurthy, J.M. Roberts, L. Newman, Atmos. Environ. 26A (1992) 1965.
[17] M. Voge, A. Büldt, U. Karst, Fresenius J. Anal. Chem. 366 (2000) 781.
[18] X. Zhou, K. Mopper, Environ. Sci. Technol. 24 (1990) 1482.
[19] E.A. Pereira, A.A. Cardoso, M.F.M. Tavares, J. AOAC Int. 82 (1999) 1562.
[20] S. Takeda, S. Wakita, M. Yamane, K. Higashi, Electrophoresis 15 (1994) 1332.
[21] S.-L. Zhao, T.-Y. Dai, Z. Liu, F.-S. Wei, H.-F. Zou, X.-B. Xu, Chemosphere 35 (1997) 2131.
[22] A. Asthana, D. Bose, S. Kulshrestha, S.P. Pathak, S.K. Sanghi, W.Th. Kok, Chromatographia 48 (1998) 807.
[23] K. Bächmann, I. Haag, K.Y. Han, R.Q. Schimitzer, Fresenius J. Anal. Chem. 346 (1993) 786.
[24] A. Mainka, K. Bächmann, J. Chromatogr. A 767 (1997) 241.
[25] K. Fige, T. Ried, K. Bächmann, J. Chromatogr. A 730 (1996) 333.
[26] L. Nondek, D.R. Rodler, J.W. Birks, Environ. Sci. Technol. 26 (1992) 1174.
[27] D.R. Rodler, L. Nondek, J.W. Birks, Environ. Sci. Technol. 27 (1993) 2814.
[28] G. Fantuzzi, G. Aggazzotti, E. Righi, L. Cavazzuti, G. Predieri, A. Franceschelli, Sci. Total Environ. 193 (1996) 49.
[29] E.A. Pereira, P.K. Dasgupta, Int. J. Environ. Anal. Chem. 66 (1997) 201.
[30] D. Grosjean, A.H. Miguel, T.M. Tavares, Atmos. Environ. 24B (1990) 101.