**DETERMINATION OF LOWER ALIPHATIC CARBONYL COMPOUNDS
IN STACK GAS AS THEIR 2,4-DINITROPHENYLHYDRAZONES BY MICELLAR
ELECTROKINETIC CHROMATOGRAPHY**

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ABSTRACT

A method for the determination of lower aliphatic carbonyl compounds in stack gas was described. Carbonyls were sampled with 2,4-dinitrophenylhydrazine (DNPH). The sorbent was extracted with carbon disulfide, and the hydrazones were determined by micellar electrokinetic chromatography (MEKC) with UV detection at 214 nm. Under the optimized MEKC conditions, the DNPH derivatives of the three carbonyls (formaldehyde, acetaldehyde and acetone) were completely separated from one another. The method was validated over the range of 10-500 mg/L of carbonyl-DNPH. The detection limit of the method was 2.0 mg/L, which is suitable for the determination of carbonyls in stack gas samples.

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INTRODUCTION

Carbonyl compounds have received much attention in air pollution studies because of their toxicity and potential to react with other pollutants to form carcinogens. Carbonyls including aldehydes and ketones are produced by industrial plants, incinerators, automobiles and are even formed in the atmosphere by photochemical reactions. There is much interest in the identification and determination of these partially oxidized hydrocarbons, since they have a high specific activity in photochemical smog formation, and specifically, the unsaturated aldehydes are known as eye, nose and throat irritants. The method widely proposed to determine carbonyls in polluted airs is to form their 2,4-dinitrophenylhydrazones (DNPH) derivatives and determine the derivatives by gas chromatography or liquid chromatography [1-7].

MEKC, developed by Terabe et al. [8, 9], has many advantages, such as brevity, high separation efficiency, minimal sample, reagent and solvent consumption, etc. Takeda et al. proposed a MEKC method for the analysis of lower aliphatic aldehydes in waters [10]. This paper reports a MEKC procedure for

determining lower aliphatic carbonyls (formaldehyde, acetaldehyde and acetone) in stack gas of an organic chemical plant.

EXPERIMENTAL

Apparatus and Reagents

MEKC was performed with a P/ACE 5010 electrophoresis system (Beckman, USA). Gold software was used for data processing.

All reagents and solvents were of analytical grade. Formaldehyde, acetaldehyde, acetone and 2,4-dinitrophenylhydrazine were obtained from Beijing Chemical Plant (Beijing, China). Sodium dodecyl sulfate (SDS) and methanol were obtained from Sigma (St. Louis, MO, USA). Distilled water was purified with Milli-Q (Millipore, MA, USA).

Preparation of Sampling Solution and Running Buffer

The sampling solution for collecting the carbonyls in stack gas was prepared by dissolving 1.56 g of the DNPH (20% H₂O) in 500 mL of 2 N HCl with the aid of a magnetic stirrer. An SDS solution was prepared by dissolving 0.05 M SDS in a 0.02 M sodium tetraborate solution adjusted to pH 9.0.

Preparation of Carbonyl-DNPH Derivatives

The 2,4-dinitrophenylhydrazones of the carbonyl compounds studied were prepared by a standard method [11]. The precipitates formed were isolated by filtration, washed with 2N HCl, water and cold ethanol and dried over silica gel in a vacuum desiccator. After this treatment, the derivatives were sufficiently pure for MEKC analysis.

Sample Collection and Analytical Procedure

Five liters of stack gas sample were absorbed at 1 L/min through two impingers in series with 100mL sampling solution. The two sampling solutions were combined and extracted twice with 5 mL of carbon disulfide. The extracts were combined, washed with 20 mL of 2N hydrochloric acid, then washed with 20 mL of distilled water, and finally concentrated under gentle heating at reduced pressure. The dried sample was dissolved in 50 mL of methanol and then analyzed by MEKC.

RESULTS AND DISCUSSION

MEKC Conditions and Separation of Carbonyl-DNPH Derivatives

A fused-silica capillary tube (50 μ m i.d. $\times$ 470 mm, Yongnian, Hebei, China) was used as the separation tube. Running buffer was 0.02 mol/L borate solution containing 0.05 mol/L SDS (pH = 9.0). UV detection wavelength was 214 nm. The samples were injected by pressure (0.5 psi $\times$ 2 s). The injection

volume of a sample was 2.4 nL. Voltage and temperature were set at 30 kV and 25°C, respectively, throughout all experiments. The separation of the three carbonyl-DNPH derivatives by MEKC under the optimized conditions was shown in Figure 1.

Fig. 1 Electrophoretograms of the standard mixture and the sample

(a) the standard Mixture (b) the sample

Peaks: 1. Formaldehyde-DNPH, 2. Acetaldehyde-DNPH, 3. Acetone-DNPH

As shown in Figure 1, the DNPH derivatives of the carbonyls studied were completely separated from one another. The migration times and their relative standard deviations (RSD) are listed in Table 1. The RSDs of the peak areas and the peak heights are shown in Table 2. Peak areas were used for quantitative analysis of the carbonyls because of their good reproducibility.

Table 1 Migration times and their RSDs of the DNPH-carbonyls.

	Mean migration time	RSD
	(min)	(%, n = 6))
Formaldehyde-DNPH	5.25	0.34
Acetaldehyde-DNPH	6.32	0.34
Acetone-DNPH	7.07	0.34

Table 2 Reproducibility of peak areas and peak heights of the DNPH-carbonyls (n = 6).

	RSD of peak area (%)	RSD of peak height (%)
Formaldehyde-DNPH	5.46	8.06
Acetaldehyde-DNPH	4.76	7.53
Acetone-DNPH	2.99	7.34

Linearity and Detection Limit

The calibration graph equations of peak area versus the concentration of analytes, correlation coefficients and detection limits are shown in Table 3. The detection limits are based on the quantity required to give a response that is thrice the noise level. The results showed excellent linearity over the range of 10-500 mg/L.

Table 3 Calibration graph equations, correlation coefficients and detection limits.

	Calibration graph equation	Correlation coefficient	Detection limit* (mg/L)
Formaldehyde-DNPH	$Y = 2.114X + 0.0269$	0.9991	2.0
Acetaldehyde-DNPH	$Y = 2.194X + 0.0021$	0.9998	2.0
Acetone-DNPH	$Y = 2.180X - 0.0174$	0.9997	2.0

* Signal-to-noise ratio = 3.

Table 4 Concentration of carbonyl compounds in stack gas

Sample number	Formaldehyde (ppm, v/v)	Acetaldehyde (ppm, v/v)	Acetone (ppm, v/v)
1	66.3	230.2	20.5
2	86.8	221.2	20.4
3	107.6	243.8	18.1
4	110.1	255.8	42.1

Determination of Carbonyls in Stack Gas

The developed MEKC procedure was applied for the determination of carbonyls in 4 stack gas samples, collected from an organic chemical plant in Qingdao city, China. The concentrations of the carbonyls in these samples are given in Table 4.

CONCLUSIONS

The results of this study indicate that the monitoring of lower aliphatic carbonyls in stack gas samples can be achieved by selective sampling with DNPH reagent and subsequent hydrazone analysis by MEKC. Detection limits of 2 mg/L were achieved for all the DNPH derivatives of the carbonyls studied. This level of detectability is adequate enough for almost all the stack gas samples. Using more sensitive detection, MEKC may prove to be even more useful for the monitoring of lower aliphatic carbonyls in environmental samples.

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REFERENCES

1. Y. Hoshika and Y. Takata, Gas chromatographic separation of carbonyl compounds as their 2,4-dinitrophenylhydrazones using capillary columns, *J. Chromatogr.* **120**, 379-389 (1976).
2. V. P. Uralets, J. A. Rijks and P. A. Leclercq, Syn-anti isomerisation of 2,4-dinitrophenylhydrazones of volatile carbonyl compounds in capillary gas chromatographic-mass spectrometric analysis, *J. Chromatogr.* **194**, 135-144 (1980).
3. K. Kuwata, M. Uebori and Y. Yamasaki, Determination of aliphatic and aromatic aldehydes in polluted airs as their 2,4-dinitrophenylhydrazones by high performance liquid chromatography, *J. Chromatogr. Sci.* **17**, 264-268 (1979).
4. R. K. Beasley, C. E. Hoffmann, M. L. Rueppel and J. W. Worley, Sampling of formaldehyde in air with coated solid sorbent and determination by high performance liquid chromatography, *Anal. Chem.* **52**, 1110-1114 (1980).
5. K. Kuwata, M. Uebori, H. Yamasaki and Y. Kuge, Determination of aliphatic aldehydes in air by liquid chromatography, *Anal. Chem.* **55**, 2013-2016 (1983).

6. L. Nondek, D. R. Rodier and J. W. Birks, Measurement of sub-ppbv concentrations of aldehydes in a forest atmosphere using a new HPLC technique, *Environ. Sci. Technol.* **26**, 1174-1178 (1992).
7. A. C. Geng, Z. L. Chen and G. G. Siu, Determination of low-molecular-weight aldehydes in stack gas and automobile exhaust gas by liquid chromatography, *Analitica Chimica Acta* **257**, 99-104 (1992).
8. S. Terabe, K. Otsuka, K. Ichikawa, A. Tsuchiya and T. Ando, Electrokinetic separations with micellar solutions and open-tubular capillaries, *Anal. Chem.* **56**, 111-113 (1984).
9. S. Terabe, K. Otsuka, and T. Ando, Electrokinetic chromatography with micellar solution and open-tubular capillary, *Anal. Chem.* **57**, 834-841 (1985).
10. S. Takeda, S. Wakida, M. Yamane and K. Higashi, *Electrophoresis* **15**, 1332-1334 (1994).
11. R. L. Shriner, R. C. Fuson and D. Y. Curtin, *The Systematic Identification of Organic Compounds- A Laboratory Manual* (4th Edn), p219. Wiley, New York (1956).