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Short Communication

Determination of volatile fatty acids in landfill leachates by high-performance liquid chromatography

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ABSTRACT

HPLC with UV detection was used to determine the volatile fatty acids in landfill leachates. It successfully determined formic acid, which could not be detected by GC with flame ionization detection. Calibration graphs were linear with very good correlation coefficients ($r > 0.999$). The application of the method is illustrated by the analysis of leachate samples collected from the Taichung sanitary landfill.

INTRODUCTION

In order to find the best conditions for wastewater treatment, a distillation–GC method with flame ionization detection (FID) has been described to determine the volatile fatty acids in landfill leachates [1]. However, FID cannot detect formic acid owing to its combustion products, CO_2 and H_2O [2]. Moreover, problems alway exist because of the high polarity of the acids, which lead to asymmetric peaks or ghosting [3,4]. High-temperature conditioning is often needed to overcome these effects [1]. In general, HPLC appears to be superior to GC for determining organic compounds with high polarity and low volatility. Both reversed-phase and cation-exchange columns have succeeded in separating organic acids, followed by mass spectrometric detection [5,6].

In this paper, the determination of volatile fatty acids in landfill leachates by HPLC–UV detection after distillation is described. From previous studies, a 75% distillate collection after discarding the first 7.5% of light-end distillate was judged to be the best pretreatment of the leachate sample for chromatographic analysis [1]. The performance of the HPLC–UV method was compared with that of the GC–FID method. The samples analysed were leachates from the Taichung sanitary landfill.

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EXPERIMENTAL

Apparatus

A Shimadzu (Kyoto, Japan) LC-9A system equipped with a Rheodyne Model 7125 injection valve (20-μl sample loop) was used. A Spherisorb 5 ODS column (250 mm × 4.6 mm I.D.) (Supelco, Bellefonte, PA, USA) was used to separate the fatty acids. A Soma Model S-3702 UV detector and a Shimadzu C-R6A Chromatopac integrator were used to detect and record the chromatograms. A Radiometer PHM 82 pH meter with a glass electrode was used for pH measurements.

Reagents

Distilled, deionized water was used to prepare all solutions. Stock standard solutions (1000 μg/ml) of formic, acetic, propionic, *n*-butyric and isobutyric acids were prepared from ACS reagent-grade chemicals (Riedel-de Häen, Germany). Working standard solutions of these acids were prepared fresh daily by appropriate dilution of the stock standard solutions with water. The sulphuric acid used in the distillation process and to adjust the pH of eluent was of ultrapure grade from Aldrich (Milwaukee, WI, USA). The chromatographic eluent was prepared from HPLC-grade methanol (Mallinckrodt, St. Louis, MO, USA) and water, the pH being adjusted with 0.05 *M* sulphuric acid. All eluents were filtered through a 0.45-μm PVDF membrane filter and degassed by sonication before use.

Sample pretreatment

Pretreatment of leachate samples was performed by distillation. Sulphuric acid was added to increase the recovery of volatile fatty acids. The assembly of the distillation apparatus and the operating procedures were as described previously [1]. An aliquot of 75 ml of distillate was collected for HPLC-UV analysis after the first 7.5 ml of distillate had been discarded.

HPLC-UV procedure

Elution was performed with a flow-rate gradient to shorten the running time. The eluent was methanol-water (3:97, v/v) of pH 4.0, adjusted with 0.05 *M* sulphuric acid. The flow-rate gradient was initially 1.0 ml/min for 5 min, increased to 2.0 ml/min in 3 min, held for 7 min, and finally decreased to 1.0 ml/min in 3 min.

RESULTS AND DISCUSSION

In the determination of volatile fatty acids by GC, asymmetric peaks and ghosting phenomena often appear because of the high polarity of the fatty acids. These may create difficulties in peak identification and lead to quantitative errors. Unfortunately, GC-FID cannot determine formic acid. In a previous study [1], no formic acid was detected by GC-FID even when the concentration was raised to 2000 μg/ml. In order to overcome the shortcomings of GC-FID in the determination of volatile fatty acids, the HPLC-UV method was examined for this application.

HPLC is a useful technique for separating organic compounds of high polarity and low volatility. For the determination of fatty acids with UV detection, the wavelength should be set at 210 nm, which is the maximum absorption wavelength for fatty acids. However, the baseline was not stable at this wavelength, so 230 nm was selected. Owing to their high polarity, short-chain fatty acids are only briefly retained on the ODS column. However, the separation of formic acid from acetic acid is very difficult with an eluent of relatively high polarity. Based on the pK_a difference between formic acid (3.75 at 20°C) and acetic acid (4.75 at 20°C), an ion-suppression technique was employed to improve the separation. The eluent pH was adjusted to 4.0 (based on calibration of the pH meter in water). Fig. 1 shows the chromatograms of volatile fatty acids obtained for (a) a standard solution and (b) a real sample. Formic acid was separated from acetic acid and was detected by the UV detector, and the isomers of isobutyric and *n*-butyric acid were also separated.

Because the volatile fatty acids do not contain strong UV-absorbing groups, their detection would be poor. However, the concentrations of volatile fatty acids in landfill leachates are generally high. Therefore, the applicability of the HPLC-UV method to the determination of volatile fatty acids in leachates is not affected.

To test the applicability of the method to analysis of real samples for volatile fatty acids, the standard addition method was used. A series of 5-ml volumes of standard acid solutions with different concentrations were added individually to 95-ml landfill leachate samples. After distillation pretreatment and

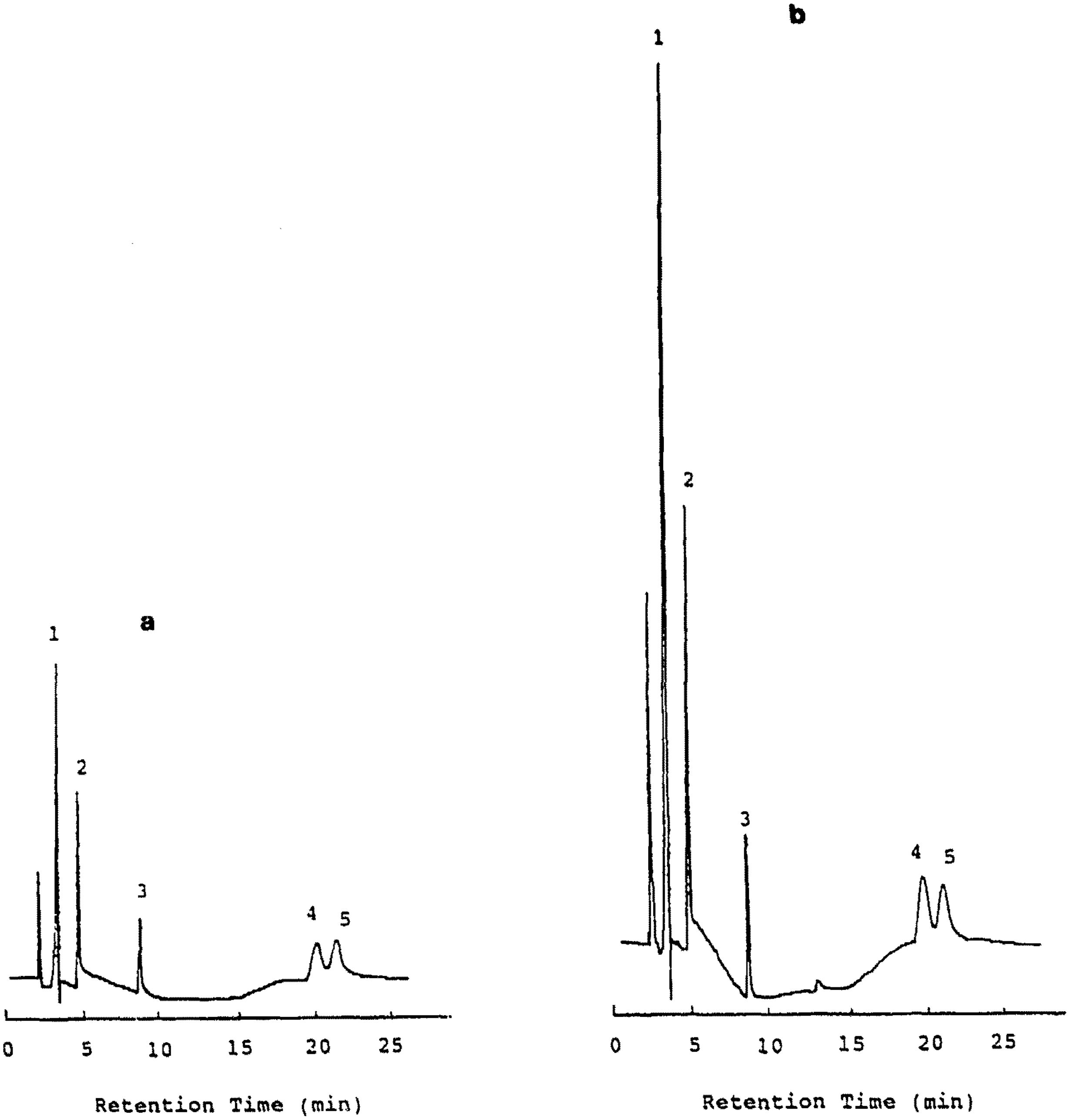

Fig. 1. HPLC of volatile fatty acids under the optimum conditions. (a) Standard solution (500 μg/ml for each acid); (b) landfill leachate sample. Peaks: 1 = formic acid; 2 = acetic acid; 3 = propionic acid; 4 = isobutyric acid; 5 = *n*-butyric acid.

HPLC–UV determination, calibration graphs were constructed for the five volatile acids. They all showed good linearity with correlation coefficients >0.999. These results imply that the HPLC–UV method with an appropriate sample pretreatment can be useful for the determination of volatile fatty acids in landfill leachate.

Results of replicate measurements on leachate samples from the Taichung sanitary landfill are given in Table I. The values obtained and their standard deviations are comparable to those obtained by GC–FID except that the detection of formic acid was impossible by GC–FID. The results confirm

TABLE I

COMPARISON OF THE RESULTS OBTAINED BY GC–FID AND HPLC–UV METHODS

Volatile fatty acid	HPLC–UV		GC–FID	
	Concentration (μg/ml)	R.S.D. (%)[a]	Concentration (μg/ml)	R.S.D. (%)[a]
Formic	680	2.32	–	–
Acetic	728	1.73	713	1.95
Propionic	531	2.14	523	2.44
Isobutyric	548	3.38	560	2.72
n-Butyric	479	1.60	485	2.29

[a] Relative standard deviation for five determinations.

the applicability of the distillation–HPLC–UV procedure to the determination of volatile fatty acids in landfill leachates if a 23-min separation time is acceptable.

CONCLUSIONS

In contrast to the GC–FID method, the HPLC–UV procedure is able to determine formic acid and is free from ghosting, although it is more timeconsuming and has poorer detection limits than GC–FID. The method is suitable for the determination of volatile fatty acids in landfill leachates.

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