



Simultaneous Determination of Pyridine-Triphenylborane Anti-Fouling Agent and Its Degradation Products in Paint-Waste Samples Using Capillary Zone Electrophoresis with...

Kaewchuay, Netnapit ; Fukushi, Keiichi ; Tsuboi, Ai ; Okamura, Hideo ; Saito, Keiitsu ; Hirokawa, Takeshi

(Citation)

Analytical Sciences, 28(12):1191-1196

(Issue Date)

2012-12

(Resource Type)

journal article

(Version)

Version of Record

(Rights)

©2012 The Japan Society for Analytical Chemistry

(URL)

<https://hdl.handle.net/20.500.14094/90002788>



Simultaneous Determination of Pyridine-Triphenylborane Anti-Fouling Agent and Its Degradation Products in Paint-Waste Samples Using Capillary Zone Electrophoresis with Field-Amplified Sample Injection

Netnapit KAEWCHUAY,* Keiichi FUKUSHI,*† Ai TSUBOI,* Hideo OKAMURA,* Keiitsu SAITO,** and Takeshi HIROKAWA***

*Graduate School of Maritime Sciences, Kobe University, 5-1-1 Fukaeminami-machi, Higashinada, Kobe 658-0022, Japan

**Graduate School of Human Development and Environment, Kobe University, 3-11 Tsurukabuto, Nada, Kobe 657-8501, Japan

***Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-hiroshima, Hiroshima 739-8527, Japan

We proposed a capillary zone electrophoresis (CZE) procedure using field-amplified sample injection (FASI) for the simultaneous determination of pyridine-triphenylborane (PTPB) and its degradation products: diphenylborinic acid (DPB), phenylboronic acid (MPB), and phenol. The LODs for PTPB, DPB, MPB, and phenol were, respectively, 0.85, 0.88, 44, and 28 $\mu\text{g L}^{-1}$. The RSDs ($n = 4$) for the analytes listed above were in respective ranges of 6.2 – 14, 5.9 – 10, and 0.49 – 0.62% for the peak area, peak height, and migration time. The compounds were extracted from paint-waste samples collected from shipyards using a siliga-gel column. The extract was dissolved with acetonitrile containing 1% (v/v) pyridine. The samples were then analyzed using CZE, revealing respective concentrations of 0.076 – 0.53, 0.015 – 0.36, 1.7 – 22, and 1.2 – 13 $\mu\text{g g}^{-1}$. The proposed FASI-CZE method is a simple and promising procedure that is expected to be useful for the determination of PTPB and its degradation products in paint wastes.

(Received July 30, 2012; Accepted October 12, 2012; Published December 10, 2012)

Introduction

Over the past decades of successful development, capillary electrophoresis (CE) has matured as an established separation technique in several application areas with recognized advantages of simplicity, separation efficiency, minor sample and solvent consumption. However, CE has a low concentration sensitivity from minute sample volumes (at the nL level), and a short optical path length (typically 25 – 100 μm) available with UV detection.¹ Different types of in-line sample concentration techniques have been proposed to enhance the CE sensitivity: large volume sample stacking,² large-volume sample stacking with an electroosmotic flow (EOF) pump (LVSEP),^{3,4} sweeping,⁵⁻⁷ dynamic pH junction,^{8,9} field-amplified sample injection (FASI),¹⁰⁻¹⁵ two-end field amplified sample injection (TE-FASI),¹⁶ acetonitrile (ACN)-mediated stacking,¹⁷ isotachopheresis (ITP) and transient ITP,¹⁸⁻²⁰ electrokinetic supercharging (EKS),²¹⁻²³ counter-flow electrokinetic supercharging (CF-EKS),²⁴ pressure-assisted injection techniques,^{25,26} and simultaneous electrokinetic and hydrodynamic injection (SEHI).^{27,28} These procedures are useful, but some were somewhat complicated in their application to real samples.

FASI is a popular and simple online enrichment technique by which samples are prepared in highly diluted background electrolyte (BGE) or water. A sample is introduced into the capillary using hydrodynamic or electrokinetic injection (EKI). Furthermore, the injection of a short plug of water into the column before sample introduction with EKI was proposed to insure proper field amplification (FASI with water plug).¹⁰ This procedure is expressed hereinafter as just FASI. Analytes are stacked at the interface between the water plug and the BGE because of the higher electric field strength in the water plug than that in the BGE. Similar procedures were also developed using a plug of organic solvent, such as methanol, ACN, and their mixture instead of the water plug.¹³

An anti-fouling agent, pyridine-triphenylborane (PTPB), is usually applied to ship hulls to prevent unnecessary fuel consumption resulting from the buildup of marine organisms, such as barnacles and bivalves. Over time, they adhere to ship hull surfaces. However, anti-fouling agents are harmful to non-target marine organisms.²⁹ The characteristics of an ideal anti-fouling agent are that it be long-lasting, but easily degradable to less toxic compounds for marine organisms shortly after dissolving in seawater. Developing an analytical method for these compounds is important to elucidate their degradation products and their toxicities to marine organisms. Reportedly, PTPB can degrade to diphenylborinic acid (DPB), phenylboronic acid (MPB), phenol, and other materials.

† To whom correspondence should be addressed.
E-mail: fukushi@maritime.kobe-u.ac.jp

Conventionally, HPLC has been used for the determination of PTPB.³⁰⁻³² According to a procedure described by Takahashi *et al.*,³² the four analytes listed above are detectable, but DPB and MPB were not separable.²⁹ Although PTPB and DPB were simultaneously detectable using HPLC, another analytical condition, including the use of a different column had to be used for the simultaneous determination of MPB and phenol.³³ Consequently, no analytical method is available for the simultaneous determination of PTPB, DPB, MPB, and phenol, except for our previous methods.^{34,35}

We previously developed a capillary zone electrophoresis (CZE) with direct UV detection for the simultaneous determination of PTPB, DPB, MPB, and phenol.³⁴ Furthermore, a novel hybrid sample injection mode (HSIM) that presents the combination of FASI and vacuum injection was proposed to enhance the detection sensitivity.³⁵ In fact, HSIM cannot be used for some commercial instruments: EKI and vacuum injection modes are inapplicable simultaneously. Moreover, when the HSIM is applied to the analysis of real samples, such as paint wastes, its separation efficiency might be degraded because of coexisting substances in the samples and the sample solvent introduced simultaneously. Presumably, FASI is advantageous compared to HSIM from the standpoint of its extensive utility and separation efficiency for real samples. Therefore, this study used FASI for applications to real samples. The analytical conditions, time of water plug injection, time, and voltage of sample introduction were examined and optimized. Boer and Ensing,³⁶ and Hirokawa *et al.*^{37,38} reported that the efficiency of EKI and EKS is strongly related to the electrode configurations. Therefore, we investigated the effects of the distance between the tip of the electrode and a capillary end (D_{ec}) on the peak heights for the analytes listed above using FASI. Biocide-based anti-fouling paints are an important localized source of trace elements (particularly copper and zinc) and organic biocide in water.³⁹ The procedure established in this study was therefore applied to the determination of PTPB, DPB, MPB, and phenol in paint wastes obtained from shipyards around Osaka Bay in Japan. This is the first reported attempt to use FASI-CZE as a simple and sensitive procedure for the analysis of PTPB and its degradation products in real samples, such as paint wastes.

Experimental

Reagents and chemicals

All reagents were of analytical-reagent grade and used as received. PTPB, DPB, and MPB were obtained from Hokko Chemical (Tokyo, Japan). Phenol was the product of Nacalai Tesque (Kyoto, Japan). Individual stock solutions (1000 mg L⁻¹) of PTPB, DPB, MPB and phenol were prepared in ACN purchased from Nacalai Tesque. To keep the stability of the stock solutions for a long time, 1% (v/v) pyridine (Nacalai Tesque) was added (except for phenol), and the solutions were then covered with an aluminum foil and kept at 4°C to prevent their degradation. Standard solutions used for the examination of analytical conditions and building-up the calibration graphs were prepared by serial dilutions of the stock solutions with ACN. Hexane, dichloromethane, ethyl acetate, and methanol obtained from Wako Pure Chemical Industries (Osaka, Japan) were used as extracting reagents for paint-waste samples. The extracted solutions were passed through a silica-gel column (MEGA BE-SI: 1 g, 6 mL; Varian Inc., Palo Alto, CA) for clean-up and preconcentration. The pH of the BGE (a 20 mM solution of sodium tetraborate) was adjusted to 9.8 using 1 M

NaOH (Nacalai Tesque). The BGE was filtered through a 0.45- μ m membrane filter (Advantec Toyo Kaisha, Tokyo, Japan) before use. Distilled, deionized water, obtained from an automatic still (WG220; Yamato Kagaku) and a Simpli Lab-UV high-purity water apparatus (Merck Millipore, Tokyo, Japan) were used throughout.

Apparatus

The CE apparatus used throughout this study was equipped with a UV-vis absorbance detector (270A-HT; Perkin-Elmer, Foster City, CA). The rise time for the detector was set at 0.5 s. A polyimide-coated fused-silica capillary was used (75 μ m i.d. \times 375 μ m o.d.; GL Sciences, Tokyo, Japan). The total length of the capillary was 72 cm; its effective length was 50 cm. The peak area, peak height, and migration time were measured using a Chromato-Integrator (D-2500; Hitachi, Tokyo, Japan). The pH measurements were carried out using a pH meter (F-22; Horiba, Kyoto, Japan). PTPB and its degradation products were extracted from paint-waste samples using a shaker (RECIPRO SHAKER SR-25; Taitec, Saitama, Japan), a centrifuge (KUBOTA 3700; Kubota Seisakusho, Tokyo, Japan), and a rotary evaporator (RE300; Yamato Kagaku, Tokyo, Japan).

Sample preparation

Three paint-waste samples were obtained from shipyards along the coast of the Osaka Bay, located in Osaka city (wastes I and II) and in Aioi city (waste III) in Japan. When ship hulls were sandblasted with high pressure in docks, some fragments came off. They were collected, and served as the samples after drying. The ingredients of these samples could be dissolved into the sea when ships were on a voyage, at anchor, or in port. PTPB and its degradation products were extracted from the paint-waste samples according to the following procedure.⁴⁰ The sample (2.5 g) in 25 mL of dichloromethane was shaken at 200 rpm for 6 h. The resultant solution was centrifuged at 2000g for 10 min. The supernatant solution in an eggplant-shape flask was evaporated to dryness *in vacuo* below 40°C. The residue in the eggplant-shape flask was dissolved with 5 mL of hexane, and the solution was passed through the silica-gel column pre-cleaned using 5 mL of methanol, ethyl acetate, dichloromethane, and hexane. Then, 5 mL of dichloromethane, ethyl acetate, and methanol were separately added to the eggplant-shape flask in this order. Each solution was passed through the column successively to elute the analytes. Each eluate was dried up by blowing a nitrogen stream. The residue was dissolved with 2 mL of ACN containing 1% (v/v) pyridine. From preliminary experiments, it was found that all analytes were detected in the ethyl acetate fractions. Phenol was detected in both the dichloromethane and methanol fractions, but the concentrations were less than the ethyl acetate fractions. In this study, the ethyl acetate fractions were analyzed to evaluate the applicability of the proposed method to paint-waste samples. The resultant solutions of the ethyl acetate fractions were diluted 50 times for waste I, 20 times for waste II, and 300 times for waste III with ACN to avoid interference from coexisting anions derived from substances present in the paint wastes. The diluted samples and those added with 5 - 200 μ g L⁻¹ of PTPB, DPB, MPB, and phenol, were analyzed using the method. The concentrations of these compounds in the paint wastes were calculated using the standard addition procedure and calibration graphs.

CZE procedure

New capillaries were pretreated by flushing with 1 M NaOH for 40 min and then with water for 10 min. The following

optimum analytical conditions were established. Before the first analysis of each day, the capillary was washed with water for 5 min, 1 M NaOH for 5 min, and water for 10 min. The capillary was thermostated at 30°C. The detection wavelength was set at 200 nm as the signal-to-noise ratios for all compounds had maximum values.³⁴ A BGE, 20 mM sodium tetraborate was adjusted to pH 9.8 with 1 M NaOH. Between runs, the capillary was flushed with 0.1 M NaOH for 3 min. It was then filled with the BGE for 3 min. Subsequently, water was injected by the application of a vacuum (16.9 kPa) for 2 s (corresponding to 42 nL), and the sample solution was injected into the capillary using FASI (5 kV for 6 s, at the sample inlet side as the cathode). The vertical distance between the tip of electrode and the capillary end (D_{ec}) was set at 0.5 mm as a default D_{ec} . The electrode tip was kept higher than the capillary end. Each step was run automatically. After each analysis, a constant volume of the sample (600 μ L) was newly filled in the vial. The BGEs of the sample inlet side and the detector side were renewed for every two and four injections, respectively. The capillary was flushed with water for 5 min to fill the capillary with water at the end of the day. Calibration graphs were prepared using synthetic standards.

Results and Discussion

Strategy for separation and sensitivity enhancement

We adopted the FASI procedure to separate and to enrich the low concentrations of analytes in paint-waste samples because of its higher separation efficiency and simplicity, as described in Introduction. The same BGE, adjusted to pH 9.8, as used in our previous study,³⁵ was adopted here so that the all analytes would exist as anions in the alkaline BGE. The sample inlet side must be set as the cathode to inject the analytes into the capillary using FASI. However, the EOF works to push the analytes back to the sample vial. That is to say, the amount of injected analytes depends on the difference between the magnitude of electrophoretic migration of the analytes and that of EOF: higher mobility of analytes can be introduced more than lower mobility of analytes in the same magnitude of EOF. Therefore, the applied voltage and the time for sample introduction must be optimized. It is also important to ascertain the optimum injection time for a water plug, since the sensitivity and reproducibility were reportedly improved by injecting the water plug into the capillary.¹⁰

Hirokawa *et al.*³⁷ described the effectiveness of prolonging the vertical distance between the tip of electrode and the capillary end (D_{ec}) to obtain high sensitivity in EKS-CZE. The amount of sample injected into the capillary can be increased by extending D_{ec} . It might be worthwhile to use long D_{ec} in this study. Dawod *et al.*²⁴ used a hydrodynamic counter-flow to minimize the introduction of the sample matrix into the capillary, thus allowing longer injections to be performed in EKS-CZE. The direction of the counter-flow was from the outlet to the inlet vials to balance the reversed EOF while applying the negative potential to inject the sample into the capillary. Meighan *et al.*²⁶ similarly applied positive pressure to allow long EKI to be performed. A negative potential was applied to inject the sample into the capillary with a positive pressure towards the anode (the outlet vial) to balance the EOF. These are attractive procedures to determine low concentrations of analytes. However, the hydrodynamic counter-flow proposed in the former procedure was inapplicable in the CE apparatus used in the present study. The latter procedure was apparently similar to the HSIM proposed previously.³⁵

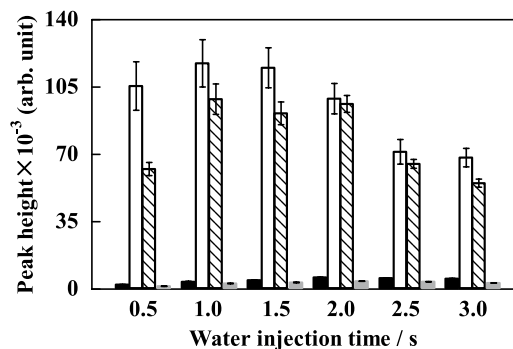


Fig. 1 Effect of the injection time of water plug on the peak height. Bars, respectively, correspond to phenol, PTPB, DPB, and MPB from left to right. Sample injection: 5 kV for 6 s. CZE conditions: capillary, 50/72 cm \times 75 μ m i.d.; BGE, 20 mM sodium tetraborate adjusted to pH 9.8 with 1 M NaOH; voltage, 15 kV; wavelength for detection, 200 nm. Sample, 0.5 mg L⁻¹ of each analyte in ACN ($n = 4$).

Effect of water plug

A mixture of 0.5 mg L⁻¹ PTPB, DPB, MPB, and phenol was analyzed using FASI (sample injection, 5 kV for 6 s) with default D_{ec} (0.5 mm). The vacuum injection time for the water plug was varied between 0.5 and 3 s. The results are depicted in Fig. 1. The peak height for PTPB increased with the injection time up to 1 s, leveled off to 1.5 s, and then decreased. The peak height for DPB increased to 1 s, leveled off to 2 s, and then decreased. The peak heights for MPB and phenol increased when going to 2 s and then decreased slightly. The tendency presented above is explainable as follows. The water plug provided a higher electric field because of its lower conductivity, which facilitated sample stacking. However, a further increase of the water plug would cause diffusion of the analyte zones.¹³ The optimum injection time of the water plug depends on the analyte. For 2 s, the maximum peak heights were obtained for DPB, MPB, and phenol, except for PTPB. When the injection time was 2 s, the RSDs of peak heights for PTPB, DPB, MPB, and phenol (2.6 – 16%) were smaller than those for 0.5 s (11 – 24%) and 1 s (12 – 19%) and similar to those for 1.5 s (7.4 – 18%), 2.5 s (2.9 – 18%), and 3 s (5.9 – 15%). Therefore, the optimum injection time of the water plug adopted in the subsequent experiments was 2 s.

Effect of the sample-injection voltage and time

The sample-injection voltage was varied between 3 and 7 kV using FASI with the sample-injection time for 6 s. The same sample as that described in the former section was used. As apparent in Fig. 2A, the peak heights for PTPB, DPB, MPB, and phenol increased concomitantly with increasing injection voltage up to 5 kV, and then decreased. The maximum peak heights were obtained for all analytes when the voltage was set at 5 kV. The RSDs of the peak heights for all analytes (2.6 – 18%) were almost identical for the injection voltages. Therefore, 5 kV was used further as the optimum injection voltage.

The sample-injection time was varied between 4 and 8 s, with the injection voltage set at 5 kV using the same sample as in the former section. The results are portrayed in Fig. 2B. The peak height for PTPB increased with the injection time up to 7 s, and then decreased. The peak heights for DPB, MPB, and phenol increased concomitantly with increasing injection time up to 6 s, and then decreased. The maximum peak heights were obtained for DPB, MPB, and phenol, except for PTPB when the

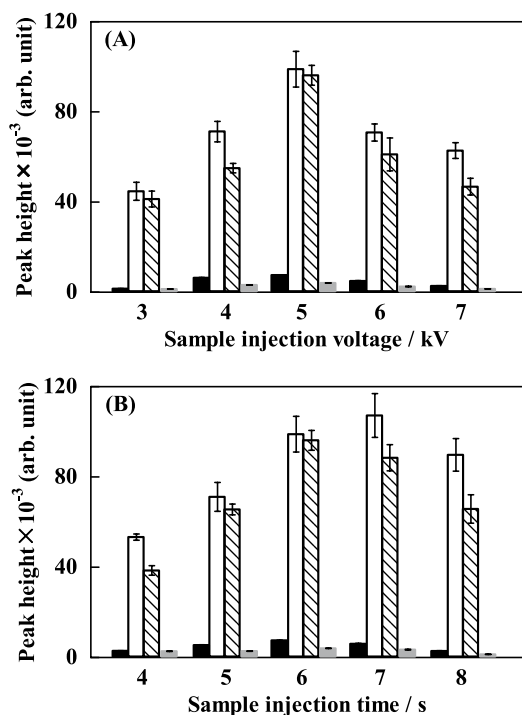


Fig. 2 Effect of the sample-injection voltage and time on the peak height. (A) Sample-injection voltage. (B) Sample-injection time. The water plug was vacuum injected for 2 s (42 nL) before sample introduction. CZE conditions, sample, and bar assignments are as shown in Fig. 1.

sample-injection time was 6 s. The RSDs of peak heights for all analytes (2.6 – 19%) were almost identical among the injection times. Therefore, 6 s was chosen as the optimum sample-injection time.

A mixture of PTPB, DPB, MPB, and phenol was analyzed using FASI under the optimum conditions (injection time of the water plug, 2 s; sample injection, 5 kV for 6 s) to compare the results obtained using EKI (5 kV for 6 s). The peak heights for PTPB and DPB using the FASI (Fig. 3A) were, respectively, 16 and 58 times higher than those obtained using the EKI. The chemical form of PTPB detected was supposed to be triphenylborane because of the migration order of the four compounds and the description in the reference.³¹ However, the commercial triphenylborane is produced as pyridinyl complexes. Therefore, the second peak was assigned as PTPB instead of TPB. No peaks for MPB and phenol were observed in the case of the EKI (Fig. 3B). A stronger electric field strength was necessary to introduce MPB and phenol into the capillary because the electrophoretic mobility for MPB and phenol in ACN are probably less than those for PTPB and DPB. The results show that the FASI performed on-column concentration for PTPB, DPB, MPB, and phenol.

Effect of the electrode configurations

The effects of the vertical distance between the tip of electrode and the capillary end (D_{ec}) on the peak heights for the analytes were examined using optimum FASI conditions (water plug, 2 s; sample injection, 5 kV for 6 s), and the same samples as those described in the section “Effect of water plug”. The D_{ec} was set at 0.5 mm as a default D_{ec} or 8 mm (referred hereinafter as long D_{ec}). The electrode was moved upward to achieve the possible longest distance of 8 mm, at which the electrode

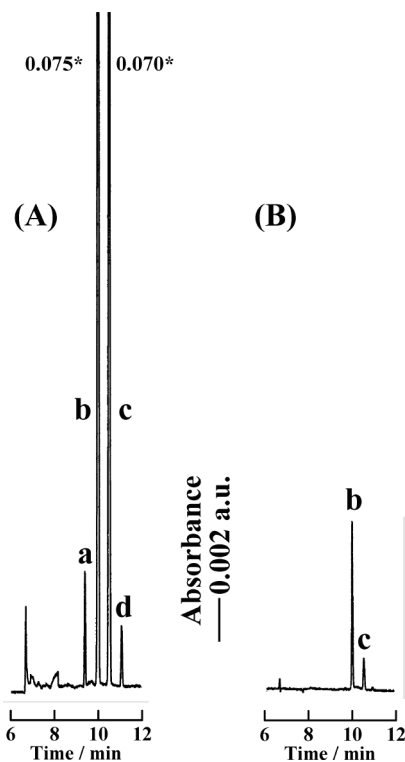


Fig. 3 Effect of the water plug for FASI on the peak height. (A) FASI, the water plug was vacuum injected for 2 s before sample introduction (5 kV for 6 s); *, absorbance values. (B) EKI, 5 kV for 6 s. CZE conditions and sample are as presented in Fig. 1. Peak identification: a, phenol; b, PTPB; c, DPB; d, MPB.

remained situated in the 600 μ L sample solution at a given vial volume 700 μ L. The electrode tip was kept higher than the capillary end. Using a long D_{ec} (8 mm), the peak heights for PTPB and DPB were, respectively, 2.2 and 1.2 times higher than those obtained using the default D_{ec} (0.5 mm). The peak heights for MPB and phenol were, respectively, 0.41 and 0.40 times lower than those obtained using the default D_{ec} . Hirokawa *et al.*³⁸ determined atmospheric electrolytes using EKS-CZE with a default D_{ec} (1.1 mm) and a long D_{ec} (19.5 mm). The LODs obtained using the long D_{ec} were improved *ca.* five times in comparison with those by the default D_{ec} . In their procedure for anions, the pH of the BGE was 6.1 and the EOF was suppressed using hydroxypropyl cellulose. During sample introduction, less analyte was moved back to the sample vial. In contrast, in our procedure, more analyte was moved back to the sample vial because of a strong EOF. This tendency for MPB and phenol was probably stronger than that for PTPB and DPB. A significant improvement was not obtained using the long D_{ec} . Therefore, the default D_{ec} was used further as the electrode configuration.

Calibration graphs

The calibration graphs for PTPB, DPB, MPB, and phenol were linear using both the peak area and the peak height as the analytical response. Regression equations relating the height response (y) to the concentration for PTPB, DPB, MPB, and phenol (x , 0 – 300 μ g L⁻¹) are shown in Table 1, which also presents the RSDs and LODs for the four analytes using the proposed FASI-CZE method. The RSDs of the peak area for PTPB, DPB, MPB, and phenol were obtained as 6.2 – 14%, for peak heights of 5.9 – 10%, and for migration times of

Table 1 Precision, LODs, and regression equations of PTPB, DPB, MPB, and phenol

| Analyte | RSD, % ^a | | | LOD/ $\mu\text{g L}^{-1}$ ($S/N = 3$) | | Regression equation ^b (r , correlation coefficient) | Standard deviation | |
|---------|---------------------|--------|------|--|--------------------|--|--|----------------------------|
| | Area | Height | Time | FASI | HSIM ³³ | Area (upper) and height (lower) | Slope | Intercept |
| PTPB | 6.2 | 5.9 | 0.62 | 0.85 | 0.88 | $y = 9.72 \times 10^5 x - 4.69 \times 10^2$ ($r = 0.9968$) $y = 2.79 \times 10^3 x - 2.01 \times 10^1$ ($r = 0.9978$) | 4.91×10^4 1.74×10^4 | 3.60×10^2 1.61 |
| DPB | 14 | 10 | 0.56 | 0.88 | 1.0 | $y = 4.05 \times 10^5 x + 5.14 \times 10^2$ ($r = 0.9926$) $y = 2.28 \times 10^5 x + 7.82 \times 10^1$ ($r = 0.9927$) | 2.08×10^4 1.27×10^4 | 1.92×10^2 10.7 |
| MPB | 8.4 | 7.5 | 0.50 | 44 | 21 | $y = 1.46 \times 10^4 x + 1.03 \times 10^2$ ($r = 0.9983$) $y = 4.76 \times 10^3 x - 4.88 \times 10^1$ ($r = 0.9745$) | 1.97×10^2 3.24×10^3 | 32.2 7.13 |
| Phenol | 9.6 | 6.8 | 0.49 | 28 | 23 | $y = 2.12 \times 10^4 x - 1.02 \times 10^2$ ($r = 0.9967$) $y = 7.74 \times 10^3 x - 9.83 \times 10^1$ ($r = 0.9970$) | 6.43×10^2 1.41×10^2 | 30.5 5.18 |

a. Sample: $30 \mu\text{g L}^{-1}$ of PTPB, DPB, and $300 \mu\text{g L}^{-1}$ of MPB and phenol in ACN; $n = 4$. CZE conditions as in Fig. 3A. b. In the regression equation, the x value is the concentration of analytes ($0 - 30 \mu\text{g L}^{-1}$ of PTPB, DPB, and $0 - 300 \mu\text{g L}^{-1}$ of MPB and phenol) and the y value is the peak area or height.

Table 2 Analytical results for PTPB, DPB, MPB, and phenol in paint-waste samples obtained from shipyards^a

| Sample | Concentration/ $\mu\text{g g}^{-1} \pm$ standard deviation ($n = 3$) | | | | | | | |
|-----------|--|-------------------|-------------------|-------------------|---------------|---------------|---------------|----------------|
| | PTPB | | DPB | | MPB | | Phenol | |
| | SA ^b | WC ^c | SA | WC | SA | WC | SA | WC |
| Waste I | 0.076 ± 0.010 | 0.048 ± 0.002 | ND ^d | ND | 1.7 ± 0.2 | 2.3 ± 0.2 | 2.8 ± 0.2 | 3.6 ± 0.1 |
| Waste II | ND | ND | 0.015 ± 0.001 | 0.021 ± 0.001 | ND | ND | 1.2 ± 0.1 | 1.6 ± 0.02 |
| Waste III | 0.53 ± 0.10 | 0.41 ± 0.04 | 0.36 ± 0.02 | 0.48 ± 0.01 | 22 ± 2 | 26 ± 1 | 13 ± 2 | 9.3 ± 0.2 |

a. CZE conditions are as in Fig. 3A. b. Concentrations were calculated using the peak height and standard addition procedure. c. Concentrations were calculated using the peak height and the working curves. d. Not detected.

0.49 - 0.62%. The LODs obtained using the FASI-CZE were similar to those obtained using the HSIM-CZE;³⁵ the LODs of PTPB and DPB were *ca.* 30 times lower than those for the vacuum injection procedure, but the LODs of MPB and phenol were similar to those for the vacuum injection procedure.³⁴ The LOD for PTPB obtained using our method ($0.85 \mu\text{g L}^{-1}$) was superior to the LOD in the HPLC method by Oda *et al.* ($810 \mu\text{g L}^{-1}$)³⁰ and the LOD in the HPLC-MS method by Hanada *et al.* ($12 \mu\text{g L}^{-1}$)³¹ although inferior to the LOD in the LC/MS/MS method by Tanaka *et al.* (68pg L^{-1}).⁴¹ However, the LODs for MPB and phenol were 30 - 50 times higher than those for PTPB and DPB. Great room for improvement exists for the LODs for the former analytes.

Applications

The proposed procedure was applied to the determination of PTPB, DPB, MPB, and phenol in the paint-waste samples obtained from shipyards. Figure 4 displays electropherograms of the analytes extracted from the paint wastes. Phenol, PTPB, and MPB were detected in waste I (Fig. 4I), phenol and DPB were detected in waste II (Fig. 4II), and all analytes were detected in waste III (Fig. 4III) with the baseline separation. The electropherograms obtained for waste I, waste II, and waste III added with the standard of analytes are also shown (Figs. 4IA, IIA, and IIIA). Table 2 presents analytical results for the analytes listed above in the samples using the standard addition method and the working curves. The former results agreed with the latter results. As a preliminary experiment, when a different paint-waste sample was analyzed using CZE with vacuum injection and HPLC,²⁹ the concentration of PTPB ($3.8 \mu\text{g g}^{-1}$) found using the former agreed with that ($3.8 \mu\text{g g}^{-1}$) using the latter.

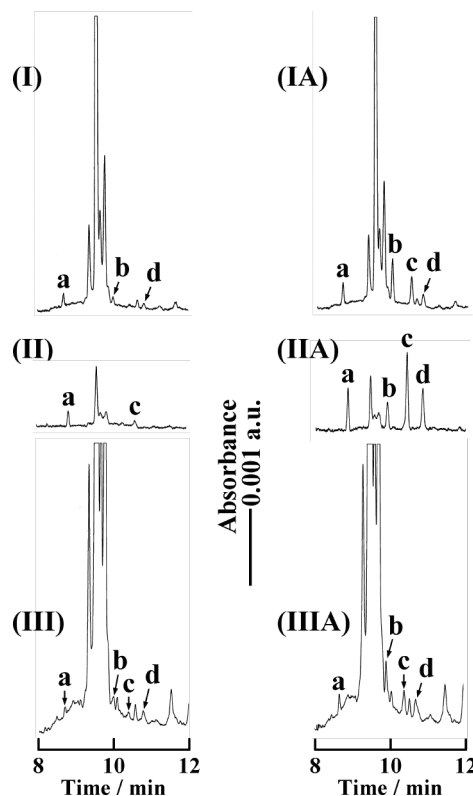


Fig. 4 Electropherograms of paint-waste samples. (I) Waste I, (IA) waste I added with $5 \mu\text{g L}^{-1}$ PTPB, DPB, $50 \mu\text{g L}^{-1}$ MPB, and phenol; (II) waste II, (IIA) waste II added with $10 \mu\text{g L}^{-1}$ PTPB, DPB, $100 \mu\text{g L}^{-1}$ MPB, and phenol; (III) waste III, (IIIA) waste III added with $5 \mu\text{g L}^{-1}$ PTPB, DPB, $50 \mu\text{g L}^{-1}$ MPB, and phenol. CZE conditions and peak identification are as presented in Fig. 3A.

Conclusions

We developed a FASI-CZE method for the simultaneous determination of PTPB, DPB, MPB, and phenol in paint wastes. This simple proposed method appears to be promising for the determination of PTPB and its degradation products in paint-waste samples. Further improvements of the LODs for MPB and phenol are expected to make the method more useful.

References

1. Z. Xu, A. R. Timerbaev, and T. Hirokawa, *J. Chromatogr., A*, **2009**, *1216*, 660.
2. I. S. L. Lee, M. C. Boyce, and M. C. Breadmore, *Food Chem.*, **2012**, *133*, 205.
3. T. Kawai, K. Sueyoshi, F. Kitagawa, and K. Otsuka, *Anal. Chem.*, **2010**, *82*, 6504.
4. T. Kawai, M. Watanabe, K. Sueyoshi, F. Kitagawa, and K. Otsuka, *J. Chromatogr., A*, **2012**, *1232*, 52.
5. J. P. Quirino and P. R. Haddad, *J. Sep. Sci.*, **2011**, *34*, 2872.
6. I. Maijó, F. Borrull, C. Aguilar, and M. Calull, *Chromatographia*, **2011**, *73*, 83.
7. C. C. Wang, C. C. Chen, S. J. Wang, and S. M. Wu, *J. Chromatogr., A*, **2011**, *1218*, 6832.
8. J. Jaafar, Z. Irwan, R. Ahamad, S. Terabe, T. Ikegami, and N. Tanaka, *J. Sep. Sci.*, **2007**, *30*, 391.
9. A. A. Kazarian, E. F. Hilder, and M. C. Breadmore, *J. Sep. Sci.*, **2011**, *34*, 2800.
10. R. L. Chien and D. S. Burgi, *J. Chromatogr.*, **1991**, *559*, 141.
11. X. Hu, S. Cui, and J. Q. Liu, *Chromatographia*, **2010**, *72*, 993.
12. X. Hai, T. Nauwelaers, R. Busson, E. Adams, J. Hoogmartens, and A. V. Schepdael, *Electrophoresis*, **2010**, *31*, 3352.
13. L. Xu, C. Basheer, and H. K. Lee, *J. Chromatogr., A*, **2010**, *1217*, 6036.
14. B. Claude, R. Nehmé, and P. Morin, *Anal. Chim. Acta*, **2011**, *699*, 242.
15. H. W. Liao, S. W. Lin, U. I. Wu, and C. H. Kuo, *J. Chromatogr., A*, **2012**, *1226*, 48.
16. X. Hou, D. Deng, X. Wu, Y. Lv, and J. Zhang, *J. Chromatogr., A*, **2010**, *1217*, 5622.
17. L. S. Yu, X. Q. Xu, L. Huang, J. M. Lin, and G. N. Chen, *Electrophoresis*, **2009**, *30*, 661.
18. M. C. Breadmore, *J. Chromatogr., A*, **2010**, *1217*, 3900.
19. J. P. Quirino, *J. Sep. Sci.*, **2011**, *34*, 1020.
20. J. P. Quirino and M. C. Breadmore, *J. Sep. Sci.*, **2012**, *35*, 60.
21. M. Dawod and D. S. Chung, *J. Sep. Sci.*, **2011**, *34*, 2790.
22. Z. Xu, K. Kawahito, X. Ye, A. R. Timerbaev, and T. Hirokawa, *Electrophoresis*, **2011**, *32*, 1195.
23. Z. Xu, K. Nakamura, A. R. Timerbaev, and T. Hirokawa, *Anal. Chem.*, **2011**, *83*, 398.
24. M. Dawod, M. C. Breadmore, R. M. Guijt, and P. R. Haddad, *J. Chromatogr., A*, **2009**, *1216*, 3380.
25. H. Zhang, J. Gavina, and Y. L. Feng, *J. Chromatogr., A*, **2011**, *1218*, 3095.
26. M. M. Meighan, M. Dawod, R. M. Guijt, M. A. Hayes, and M. C. Breadmore, *J. Chromatogr., A*, **2011**, *1218*, 6750.
27. F. Oukacine, J. P. Quirino, L. Garrelly, B. Romestand, T. Zou, and H. Cottet, *Anal. Chem.*, **2011**, *83*, 4949.
28. J. P. Quirino and A. T. Aranas, *Anal. Chim. Acta*, **2012**, *733*, 84.
29. X. Zhou, H. Okamura, and S. Nagata, *Chemosphere*, **2007**, *67*, 1904.
30. T. Oda, M. Sugawara, and S. Nishino, *Annual Report of the Sapporo City Institute of Public Health*, **1998**, 82.
31. Y. Hanada, T. Tanizaki, M. Koga, H. Shiraiishi, and M. Soma, *Anal. Sci.*, **2002**, *18*, 445.
32. K. Takahashi, E. Yoshikawa, M. Akiyama, K. Kitaori, and S. Masuoka, *J. Jpn. Soc. Colour Mater.*, **2005**, *78*, 50.
33. C. L. W. Hsu and T. L. White, *J. Chromatogr., A*, **1998**, *828*, 461.
34. K. Fukushi, Y. Yakushiji, H. Okamura, Y. Hashimoto, and K. Saito, *J. Chromatogr., A*, **2010**, *1217*, 2187.
35. N. Kaewchuay, Y. Yakushiji, K. Fukushi, K. Saito, and T. Hirokawa, *Electrophoresis*, **2011**, *32*, 1486.
36. T. de Boer and K. Ensing, *J. Chromatogr., A*, **1997**, *788*, 212.
37. T. Hirokawa, E. Koshimidzu, and Z. Xu, *Electrophoresis*, **2008**, *29*, 3786.
38. Z. Xu, E. Koshimidzu, and T. Hirokawa, *Electrophoresis*, **2009**, *30*, 3534.
39. G. Cognetti and F. Maltagliati, *Mar. Pollut. Bull.*, **2012**, *64*, 175.
40. Supelco Solid Phase Extraction Products, Compilation prepared by Supelco Analytical, SIGMA-ALDRICH, <http://www.supelco.com.tw/C-2%20%20150-163%20.New.pdf>.
41. H. Tanaka, T. Hano, K. Kono, T. Inoue, in Proceedings of the 21st Annual Symposium of Japan Society for Environmental Chemistry, **2012**, Matsuyama, 438.