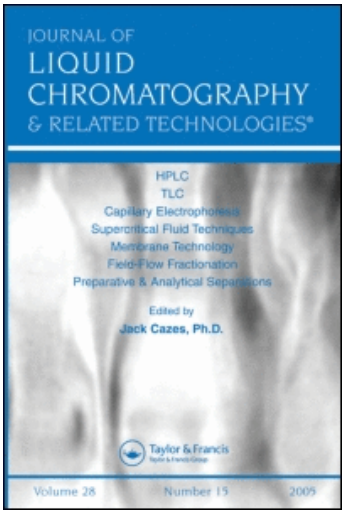

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Determination of Organolead and Organotin Compounds in Water Samples by Micellar Electrokinetic Chromatography

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DETERMINATION OF ORGANOLEAD AND ORGANOTIN COMPOUNDS IN WATER SAMPLES BY MICELLAR ELECTROKINETIC CHROMATOGRAPHY

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Abstract

Micellar electrokinetic chromatography separation of organolead and organotin compounds was investigated. The effects of surfactant concentration and electrolyte buffer pH on the peak efficiencies and resolution were studied. Enrichment of the organolead and organotin species in water samples by liquid-liquid extraction and solid phase extraction using C_{18} membrane disk was performed. 1000-40,000 fold preconcentration for lead and tin species was obtained using solid phase extraction. The detection limits for organolead and organotin compounds were in the range of 1.1-5.2 parts per billion. The levels of these compounds in the collected water samples were determined.

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Introduction

Great attention has been paid to the speciation of organolead and organotin compounds since they permeate many aspects of human society and exert great effects on the economy and the environment. Both organolead and organotin have been widely applied in industrial, agricultural, forestrial and maritime fields. Tetraalkyllead (R_4Pb) compounds have been extensively used as petrol additives, although such use is diminishing, which have contributed significantly towards the problem of environmental pollution [1]. Various organotin compounds have been used as polyvinylchloride plastic stabilizer (dibutyltin or dioctyltin), antifouling agent in marine paint (tribulyltin), wood preservatives (triethyltin) and agricultural fungicide (triphenyltin). Mono- and tetra-organotin have little commercial use up to now, whereas di-and tri-organotin have been the main resources of environmental tin pollution [2-6].

In the past years, the successful determination and speciation of organolead and organotin species have been carried out by coupling separation techniques such as HPLC [7-16] and GC [17-28] with element-specific detectors, i.e. atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICPAES), microwave induced plasma-atomic emission spectrometry (MIPAES), and particularly the recent work of coupling supercritical fluid chromatography (SFC) and extraction [29-33] to inductively coupled plasma mass spectrometry [29] and ICPAES [32] for organotin speciation. For the determination of organolead and organotin compounds, GC methods are generally considered superior to HPLC because of the higher efficiency and the availability of more sensitive detectors. However, in most cases, it is necessary to convert the organolead and organotin into volatile forms by hydride-generation or Grignard reagent derivatization before GC separation can be performed because of the thermal instability of organolead and organotin compounds. These reactions sometimes maybe difficult and non-quantitative, and the by-products and the contaminants may cause interference in

subsequent determinations [31]. As for SFC, the poor solubility of organometallic compounds in common supercritical fluids prevent its wide application. Furthermore, customed-built interfaces for the on-line coupling of chromatography with spectrometry are not routinely available.

Capillary zone electrophoresis (CZE) and its modification in the form of micellar electrokinetic chromatography (MEKC) are newly developed separation methods, based on electrokinetic migration and chromatographic principles [34,35]. CZE and MEKC have demonstrated their enormous capacity and potential for separating ionic and neutral solutes due to the simplicity and high efficiency. CZE method has been recently used for aluminum [36] and arsenic [37] speciation, but there have been hardly any report dealing with the separation and speciation of organolead and organotin compounds by CZE and MEKC. It could be expected that, to separate organolead and organotin compounds, CE and MEKC would be preferred over HPLC due to the better efficiency, and over GC due to the lower temperature used, thus avoiding the derivatization steps.

It should be noted that the injection volume for CE is often several nanolitres, with a typical absolute detection limit of pg solute when conventional HPLC UV detector is used [34]. On the other hand, concentration in the peak is relatively high, e.g., more than 1 ppm for a common solute. This concentration detection ability is not sensitive enough for determining organolead and organotin in environmental samples, in which lead and tin exist at parts per trillion to low parts per billion level, unless preconcentration procedure is performed. Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are the most commonly used methods for sample enrichment. LLE is a successful method but with recognized disadvantages: being laborious, time consuming, and also subject to problems such as the emulsification of the samples during extraction and the disposal of large volume of toxic solvents. In SPE extraction, water samples

are passed through a small cartridge packed with sorbent. Analytes are trapped by the sorbent and then are eluted with a small volume of suitable solvent. In many ways, SPE is superior to LLE methods by overcoming the problems in LLE and has been widely used in HPLC [38,39] and FIA [40,41] techniques. In the past few years, an alternative technique based on the principle of SPE but with a piece of sorbent membrane disk to replace the SPE cartridge has been reported [42]. This disk can be used as the filter membrane in a conventional HPLC filtration apparatus. Because the sorbent disk has larger contacting area than a SPE cartridge, larger flow rates are permitted, and therefore the extraction for large volume (1L or more) samples can be performed with much shorter times than with SPE cartridges. This disk extraction method has been used for the extraction of organic compounds in water samples [42-44]. Evans et al [46] also gave the first report on extracting tributyltin compounds in sea water using SPE disks.

The objectives of this investigation are (i) to develop a simple MEKC method for the separation of the most commonly encountered organo-lead and -tin compounds in environmental samples and (ii) to demonstrate the possibility of determining the organolead and organotin in real samples after disk SPE extraction.

Experimental

Chemicals and Materials

Trimethyllead chloride, triethyllead chloride, trimethyltin bromide, tributyltin bromide and dibutyltin dichloride were analytical grade and purchased from Aldrich Co. (Milwaukee, WI,

USA). *Ca.* 10 mg/ml stock solutions of the above organometallic compounds were prepared by dissolving accurately weighed amounts of the individual compounds in methanol [Caution: alkyllead and alkyltin compounds are highly toxic, and should be handled with great care]. The stock solutions were stored in refrigerator at 4 °C for one month without degradation. External standard solutions were prepared fresh daily. Sodium dodecylsulfate, sodium dihydrogen phosphate and disodium tetraborate from Merck (Germany) were used to prepare different electrolyte buffers, which were filtered with 0.45 μm membrane and degassed by ultrasonication before use. Sodium diethyldithiocarbamate, used as a complexing reagent, was obtained from Merck (Germany). All the other chemicals and solvents were analytical or better grade. Water purified with a Millipore-Q system was used throughout the experiments.

Instrumentation

The home-made electrophoretic system consisted of a Spellman model RHR30PN10/RVC high voltage D.C. power supply with a maximum voltage of 30 kV (Plainview, NY, USA), a piece of silica capillary separation column with dimension 550 or 600 mm length and 0.05 mm i.d. dipped in a pair of buffer reservoirs in which platinum electrodes were placed, and a model UVIS20 micro UV detector operated at 200 nm (Carlo Erba, Italy). Two capillary columns of 450 and 500 mm in effective length, i.e. from the anode to the detection window, were used to perform the separation of organolead and organotin. On-line detection was carried out through a window made by burning off 2 mm of the polyimide coating from the capillary. Samples were introduced into the anodic end of the column hydrodynamically by raising the sample reservoir to a height of 10 cm above the cathode end for 10 or 20 seconds. Electropherograms were recorded and processed with a Model DP-700 integrator (Carlo Erba, Italy). A standard 47 mm filtration apparatus purchased from Whatman (Maidstone, Kent, England) were used to perform membrane extraction. The C_{18} membrane disk with 47 mm diameter and 0.5 mm thickness,

containing 500 mg of 10 μm particle size and 60 Å pore size C_{18} bonded stationary phase, was manufactured by 3M (St. Paul, MN, USA) under the trademark Empore. A vacuum gauge was connected into the hose line between the vacuum pump and the filtration bottle to control the flow rates.

Water sampling and pretreatment

The rain water was collected during a heavy rain. The drainage water was taken from a drainage ditch besides a highway just after a rain. The water samples were passed through 0.45 μm filters, and high purity HNO_3 was added to the water sample to give a pH 1.5. These water samples were used for membrane extraction.

Procedure of C_{18} membrane extraction

1 litre water sample was added to 2.0 ml 5 M acetic acid, and the pH of the sample was adjusted to 8.2 with concentrated ammonia. 1.0 gram sodium diethyldithiocarbamate (NaDDC) was added to the sample and shaken until NaDDC dissolved completely. In some experiments, the samples were spiked with standard organolead and organotin compounds. The samples were then further shaken for another 10 minutes. The C_{18} membrane disk was placed on the disk holder in the Millipore filtration apparatus, the disk was conditioned using *ca.* 10 ml acetone, 10 ml hexane, and 10 ml acetone by applying a slight vacuum. This conditioning step was necessary to remove the accumulated contaminants due to the exposure to the environment and from the manufacturing process. After drawing air through the disk for several minutes, 10 ml methanol was added and drawn slowly through the disk until only a thin layer of methanol remained on the disk (the disk must not be allowed to become dry from then on until finishing the extraction). The disk was then washed with 100 ml Millipore water to remove any residual methanol. The water sample was added to the sample reservoir to start the membrane extraction.

During the extractions, the vacuum was adjusted to allow 1 litre sample to pass through the membrane disk in *ca.* 40 - 45 min. The disk was washed with 20 ml Millipore water, which was adjusted to pH 3.5 with high purity nitric acid, to remove water soluble matrix and complexing reagent trapped after the completion of the extraction. A full vacuum was applied to draw air through the disk for ten minutes. 4 × 2 ml methanol was used to elute the trapped organolead and organotin into an accurately calibrated tapered glass vial. In each elution, 2 ml methanol was added and a slight vacuum was applied to draw off *ca.* half of the methanol, the vacuum was interrupted at this point to allow the solvent to soak the disk for 2-3 minutes. The remaining portion was then drawn through. The eluted samples were kept in a fume cupboard overnight to evaporate the solvent to 0.5 to 1.0 ml. In some experiments, a small N_2 current was passed through the top of the sample vials to speed up the evaporation of the collecting solvent. The duration of evaporation was shortened to 3 to 4 hours by this method which allowed the determination to be carried out on the same day as extraction was done. Finally, the sample solutions were passed through a 0.45 μm filter prior to MEKC analysis.

Solvent extraction procedure given by Chakraborti *et al* [18] was modified as follows to extract organolead and organotin compounds as comparison. 200 ml water sample was transferred into a 250 ml separation funnel. 0.5 ml 5 M acetic acid was added to the sample and the pH was adjusted to 9.0 with 5 M ammonia. 0.25 gram NaDDC was then added and the sample was shaken until NaDDC dissolved completely. Next, 5 ml hexane was added and the sample was further shaken for another 15 minutes. After phase separation, the lower layer was run off. The organic phase was washed with 5 ml 1 M HCl by gently shaking the separation funnel for 5 minutes. The organic phase was transferred to a 5 ml tapered sample vial. The sample was dried by evaporating the solvent. Accurate 200 μl methanol was added to dissolve the sediment. The sample was passed through a 0.45 μm membrane for MEKC determination.

Results and Discussion

MEKC separation of organo-lead and -tin compounds

It has been demonstrated that MEKC has many advantages compared with CZE for separating ionic and neutral solutes [34]. In our preliminary experiments, no organolead and organotin peaks could be observed in the electropherogram obtained using CZE. This could be due to the decomposition of the organolead and organotin in the aqueous buffer. Another explanation was that the solutes were irreversibly adsorbed onto the column wall due to reaction with surface silanol groups. By adding the surfactant sodium dodecylsulfate (SDS) into the buffer, the MEKC separation of organolead and organotin was readily achieved. The effect of SDS concentration on the migration time of lead and tin species is shown in Figure 1. The migration times of the lead and tin species increased with increase of SDS concentrations, suggesting that interaction between organolead and organotin species and SDS micelles occurred. With the increase of SDS concentration, the solubilities of organolead and organotin in the micellar phase were increased, thus the migration times of all the lead and tin species increased. The change of the migration time for trimethyltin was not so remarkable. This could be explained by the weak interaction of trimethyltin with the micelles. Since trimethyltin has relatively small molecular size and large polarity, trimethyltin species are not so readily dissolved by the micelles and had the fastest migration. The migration order of lead and tin was dominated by the distribution ratios of the solutes in the micellar phase, i. e. the hydrophobicities of the solutes. For organolead and organotin species, the hydrophobicity were mainly attributed to their polarities which could be estimated from the ratio of central atom charges to the whole molecule size. Obviously, trimethyltin has the largest polarity and the fastest migration. In contrast, tributyltin has the same central atom but three large butyl groups. Therefore it has weak polarity and strong hydrophobicity. As a result, it has the slowest migration. The slower migration of trimethyllead than its tin counterpart could be explained by the fact that a central lead atom has a larger ion

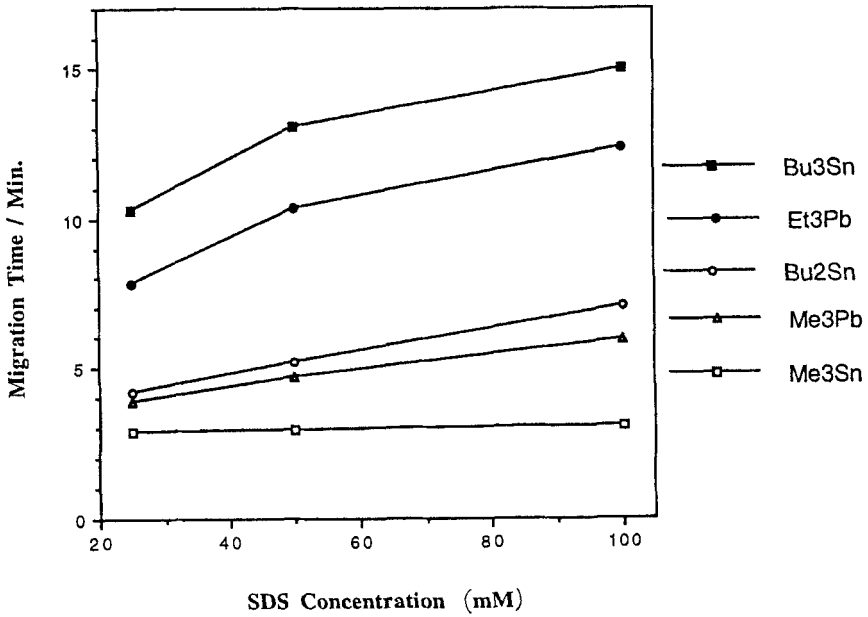

Fig. 1 Effect of the SDS concentration on the migration time of organolead and organotin compounds. MEKC conditions: micellar solution, different SDS concentrations in 0.025M $Na_2B_4O_7$ buffer (pH=9.30); separation column, 550 mm x 0.05 mm i. d. fused silica capillary tube; applied voltage, 20 KV.

radius than a tin atom does in the molecule. Thus trimethyllead had relatively lower polarity and stronger hydrophobicity [47], and its solubility in SDS micellar phase was relatively larger than trimethyltin.

Figure 2 shows the effects of applied voltage on migration of the organolead and organotin species. Generally, sharper peaks for lead and tin species were obtained when higher voltages were applied. The resolutions had also been improved due to the sharp peak shape. This observation was consistent with previous work [48]. The migration time of organolead and organotin compounds decreased with the increased applied voltages. This could be explained by

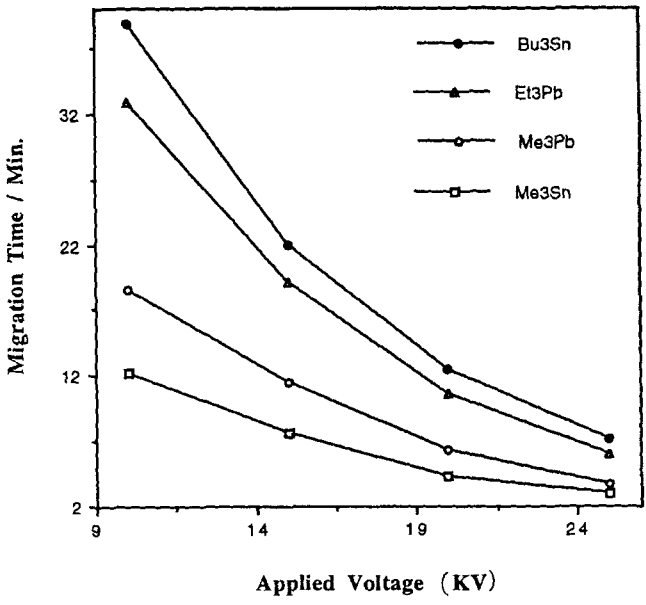

Fig.2 Effect of applied voltage on the migration time of the organolead and organotin compounds. MEKC conditions: micellar solution, 0.050 M SDS in 0.015 M $Na_2B_4O_7$-0.030 M NaH_2PO_4 (pH=7.65). Other conditions as in Fig. 1.

the fact that the organolead and organotin compounds had faster migration at higher electric field since the electroosmotic and electrophoretic flows are directly proportional to the applied voltage. The total separation time of *ca.* 40 min. for the chosen lead and tin species at 10 KV was shorten to 7.2 min. at 25 KV applied voltage. However, a high voltage resulted in a higher baseline noise level. Thus a poorer signal to noise ratio would be expected. It was also subjected to the danger of solutes decomposition at high voltages due to the Joule heat. In the present investigation, an optimum applied voltage of 20 KV was found to give satisfactory results.

The buffer pH affected the separation of organolead and organotin species significantly. The observation was attributed to the fact that these compounds could be partially ionized [18,32]

depending on the pH conditions. In addition, it was found that the buffer pH not only affected the resolution of organolead and organotin species by changing the electrokinetic migration of the solutes and micelles but also affected the detection sensitivities of organolead and organotin by changing the stability of lead and tin species. Figure 3 presents the electrokinetic chromatogram of the organolead and organotin species at different pH values. At pH 9.2 or higher trimethyltin had weak interaction with SDS. It was not separated from methanol completely, and therefore it would be impossible to determine trimethyltin quantitatively above pH 9.2 because of its overlap with the methanol peak. Dibutyltin had a narrow optimum pH range of 8.0 to 10.2 to give stable peaks. It partly overlapped with trimethyllead species at pH 9.2, but could be separated from trimethyllead at higher or lower pH values. Tributyltin and both organolead species gave good separation from other compounds at the pH range of 6.5 to 10.2, but with significant changes in migration times and sensitivities (Figure 3). When pH > 11.2, noisy baseline and unstable electropherogram were obtained, possibly due to the decomposition of organolead and organotin by hydrolysis. In most cases, the separations were carried out in the pH range of 7 to 9.

C_{18} membrane disc extraction of organo-lead and -tin in water samples

Kadokami et al [45] and Junk and Richard [49] reported the extraction of alkyltin species using cartridge extraction methods. Evans *et al* [46] described a method for the direct extraction of tribulytin from simulated water samples using C_{18} disks. These methods typically involve the use of acidified ethyl acetate with or without tropolone to elute alkyltin compounds from the cartridges or discs. Although different alkyltin species have been successfully extracted, it has been found that the extraction of alkyllead compounds exhibits low extraction efficiency without adding complexing reagent [6]. Our extraction procedure showed low extraction efficiencies for all the organo-lead and -tin compounds if no complexing reagent was added to the samples, but the extraction efficiencies were greatly improved when sodium diethyldithiocarbamate (NaDDC)

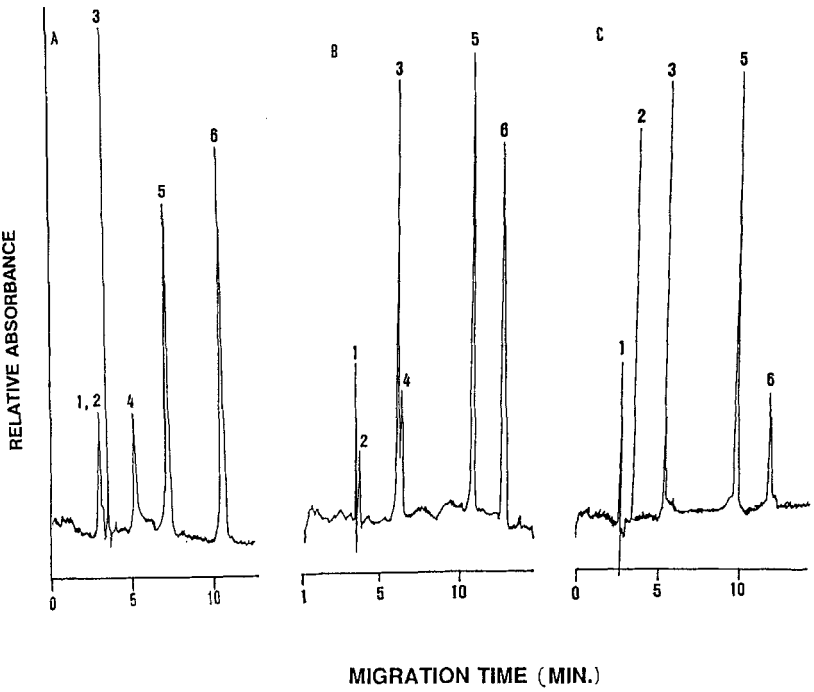

Fig. 3 MEKC separation of the organolead and organotin compounds at various buffer PH values. (A) pH = 10.2 (B) pH = 9.3 (C) pH = 7.65 Peak identification: 1 = methanol, 2 = trimethyltin, 3 = trimethyllead; 4 = dibutyltin, 5 = triethyllead, 6 = tributyltin. MEKC conditions: micellar solution, 0.05 M SDS in different ratios of 0.025M $Na_2B_4O_7$ - 0.075 M NaH_2PO_4 buffer. Other conditions as in Fig.1.

as complexing reagent was added to water samples. NaDDC has been widely used as complexing reagent for metal ion extraction using LLE and cartridge methods. Chau *et al* [6] demonstrated that alkyllead species could be extracted into organic phase using NaDDC as complexing reagent. Since organolead and organotin often exist in ionic forms in aqueous media [18, 32] , obviously, the extraction of alkyllead and organotin with addition of NaDDC was superior to the direct extraction method because of its applicability to both ionic and neutral forms of lead and tin species.

To achieve a high extraction efficiency, two key steps must be carried out effectively. The first is sample loading, which should allow the weak matrix compounds to pass through the membrane and only trapping the solutes of interest. The second step to consider is the elution of the organo-lead and -tin species from the disk. This step should be performed using a solvent with an appropriate polarity which is strong enough to elute the solutes while leaving strong matrix on the disk.

Different sample loading rates, i.e. 30, 60 and 120 min. per litre of sample, were used for the extraction of lead and tin species. It was found that the efficiencies were not affected by the loading rates. This was due to the fact that the membrane has a relatively large contacting area compared with SPE cartridges. Although the flow rates in disk extraction was larger than in the cartridge method, the linear velocity of solutes passing through the disk and the contacting time were comparable with those of the cartridge method. The problem often encountered using disc extraction was the plugging of the disk by the particles in real water samples, even after the water samples had been filtered with 0.45 μm membrane. Hagen *et al* [42] has also encountered this problem and suggested to acidify the samples to overcome this problem. However, this method was not suitable for the extraction of organolead and organotin. Therefore, the samples were passed through double 0.45 μm membranes before C_{18} disk extraction.

The pH dependence of extraction efficiency of alkyllead and alkyltin compounds using liquid-liquid extraction has been investigated by Chakraborti *et al* [18]. In the present study, extraction performed at pH 6.0 and 8.2 using C_{18} disks showed similar efficiencies. Since dithiocarbamate complexes are not stable in acidic medium, the extraction was carried out around pH 8. A high pH may result in C18 stationary phase deterioration and possible hydrolysis of alkyllead and alkyltin compounds.

As solvents to elute the trapped alkyllead and organotin from C_{18} disk, methanol, ethanol, acetone and hexane were compared. Acetone and hexane were strong enough to elute the organolead and organotin species from the disk, but large portion of matrix trapped was also eluted which formed precipitation after evaporization of the solvent. This precipitation made further sample handling (redissolving and filtration) difficult, and also caused potential interference for the following MEKC determination. Methanol and ethanol could elute organolead and tin with less companion matrix and therefore were considered as eluting solvents. Methanol was preferred over ethanol due to the low boiling point and fast evaporation after elution. To determine the volume of methanol needed to elute lead and tin species from C_{18} disks, the organolead and organotin eluted by several portions of 4 ml methanol were determined. It was found that 8 ml methanol could completely eluted organolead and organotin species. In practice, elution was performed using 4×2 ml or 3×3 ml methanol.

Figure 4 presents the electropherogram of the extracts from 1 litre of rain water samples. Since rain water often has a simple matrix, no interferences were encountered and the electropherogram was quite simple. Figure 5 is the electropherogram of the C_{18} disk extracts from 1 litre drainage water sample. This sample had more complicated matrix than rain water. A large matrix peak was detected at ca. 12 min, and tributyltin was masked by the matrix. Figure 6 is the electropherogram of extracts from the same water sample by liquid-liquid extraction method. An even larger matrix peak had been detected at the end of the electropherogram, in which triethyllead and tribulyltin had been masked. From the comparison of Figure 5 and Figure 6, it can be seen that C_{18} disk extraction had relatively lower interference than solvent extraction. The low interferences by C_{18} disk extraction could be explained by the selective separation of solutes from the matrix by the C_{18} disk. The weak matrix such as the main inorganic components, alkali and alkaline earth metals, in common water samples were not retained in the C_{18} stationary phase, whilst stronger main matrix

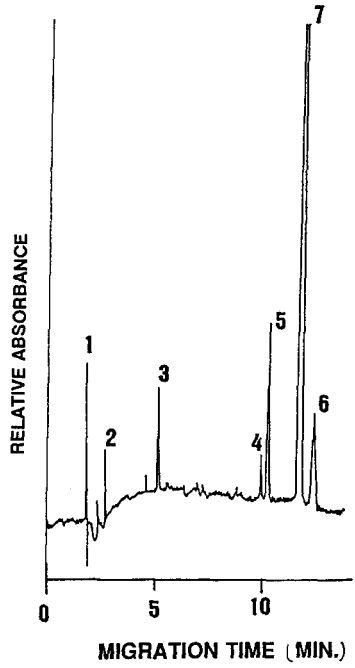

Fig. 4 MEKC electropherogram of C_{18} disc extracts from 1 litre rain water. Peak identification: 1 = methanol, 2 = trimethyltin (49.8 ng/ml), 3 = trimethyllead (18.4 ng/ml), 4 = unknown, 5 = triethyllead (50.0 ng/ml), 6 = tributyltin (28.8ng/ml), 7 = NaDDC + unknown. MEKC conditions: separation column, 600 mm x 0.05 mm i .d. fused silica capillary tube; applied voltage, 20 kV. Other conditions as in Fig. 2.

compounds could be left on the C_{18} disk by choosing a suitable solvent to elute only the solutes of interest with as little matrix as possible. Hagen *et al* [42] and Barcelo *et al* [44] have demonstrated that membrane extraction has lower interference than solid-phase cartridge extraction for pesticides in water samples with enrichment factors of 1000 to 10,000 folds.

Figure 7 shows the electropherogram of C_{18} membrane extracts from tap water with a large enrichment factor of 40,000 folds, i.e. 4 litre water sample was passed through the C_{18} disk and

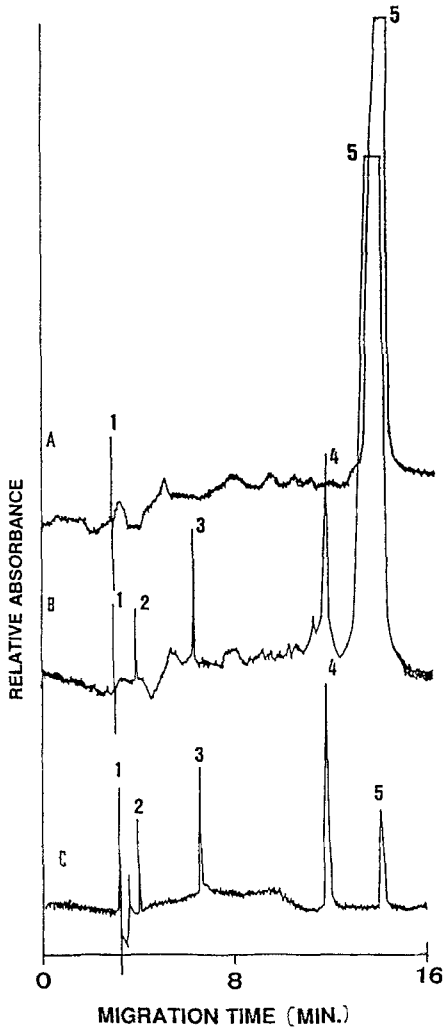

Fig. 5 Electropherogram of the extracts from 1 litre drainage water using C_{18} disc extraction. (A) drainage water sample.(B) same water sample spiked with organolead and organotin species. Peaks: 1 = methanol, 2 = trimethyltin (59.0 ng/ml), 3 = trimethyllead (18.4 ng/ml), 4 = triethyllead (49.3 ng/ml), 5 = tributyltin (14.4 ng/ml) + metrix. (C) direct injection of organolead and organotin species. Peaks: 1 = methanol, 2 = trimethyltin (49.8 μg/ml, 428 pg), 3 = trimethyllead (18.4 μg/ml, 158 pg), 4 = triethyllead (49.3 μg/ml, 423 pg), 5 = tributyltin (28.8 μg/ml, 247 pg). The injection volume for MEKC was 8.6 nl.

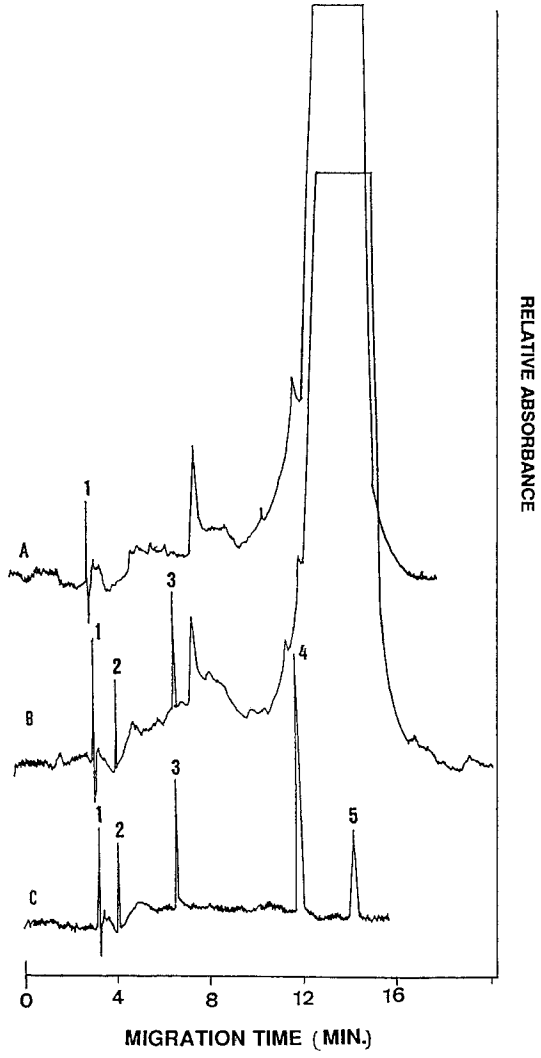

Fig. 6 Electropherogram of extract from drainage water using solvent extraction. Symbols, peaks and concentrations as in Fig. 6. MEKC conditions as in Fig. 5.

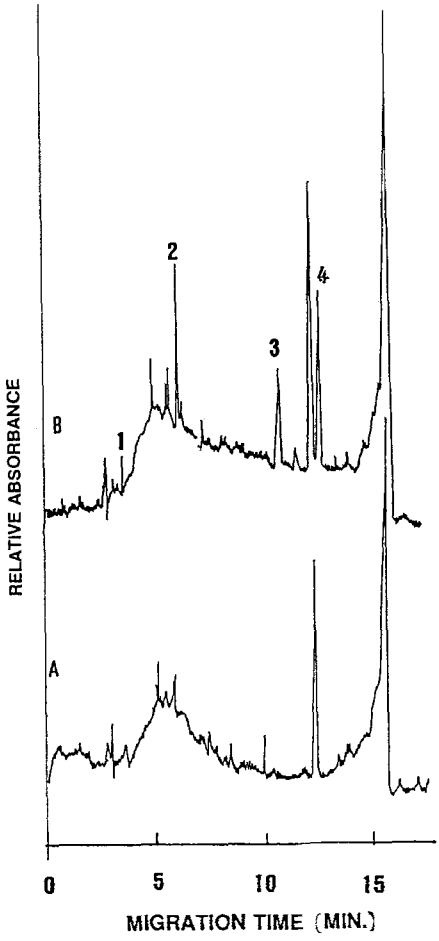

Fig. 7 Electropherogram of C_{18} disk extracts from 4 litres tap water samples. (A) Tap water extracts, (B) same tap water spiked with organolead and organotin species. Peaks: 1 = trimethyltin (2.4 ng/ml), 2 = trimethyllead (0.46 ng/ml), 3 = triethyllead (1.2 ng/ml), 4 = tributyltin (0.72 ng/ml). MEKC conditions as in Fig.5.

Table I. Recovery and precision for the determination of organolead and organotin compounds by CZE

		Me_3Sn	Bu_2Sn	Me_3Pb	Et_3Pb
Added (ppb)		49.8	28.8	18.4	49.3
Recovery (%)	(1)[a]	49.7	88.3	92.7	93.6
	(2)[b]	36.0	ND[c]	91.0	88.0
RSD (%)	(1)[a]	11.0	7.5	4.9	7.8
	(2)[b]	8.4	15.1	9.2	12.0

a: mean value of 5-6 extractions with C_{18} discs followed by MEKC determination.
b: mean value of 3-4 extraction with solvent extraction, followed by MEKC determination.
c: not determined.

a final volume of 100 μl sample was obtained. Although the matrix effects were stronger than the previous extraction with 1000 fold enrichment, the organolead and organotin peaks were still clearly identified. This indicated that the C_{18} disk extraction method may be more suitable than other preconcentration techniques such as solvent extraction and solid phase cartridge extraction for large volume and/or large enrichment factor extraction, provided that the samples had relatively weak matrix. In addition, MEKC method was found to be applicable to the analysis of organolead and organotin compounds due to its very small volume for sample injection.

Table I presents the recoveries of the organolead and tin species in water samples using C_{18} disk extraction. C_{18} disk extraction and solvent extraction gave similar recoveries for lead and tin species. For trimethyltin extraction, low recoveries were obtained. The reason for this is not yet known. A possible explanation is that the polarity of trimethyltin was relatively higher than the other lead and tin species, and the interaction with NaDDC was weak and hence a weak retention in C_{18} disk was expected. For organolead compounds, recoveries of close to 100 percent could be obtained. Table II shows the linear ranges and the detection limits for the

Table II. Linear range and detection limits of organolead and organotin compounds

	Concentration range (ppb)	Detection limits[a] (ppb)[b]	(pg)[c]
Me_3Sn	25.0-200	5.2	42.1
Bu_3Sn	8.2-100	1.1	15.5
Me_3Pb	9.2-100	1.9	22.4
Et_3Pb	14.0-200	1.5	17.2

a: S/N = 3
b: based on extraction from 1 litre of sample using C_{18} disc.
c: based on direct injection of 8.6 nl to MEKC.

determination of organolead and organotin compounds. The detection limits given in Table II were low enough for the determination of organolead and organotin compounds at parts per billion level concentration in environmental samples. For sub parts per billion level lead and tin species determination, larger factor enrichments must be performed, by using larger sample volume and longer extraction time.

Conclusions

MEKC was used to separate several organolead and organotin species most often encountered in environmental samples. MEKC has the advantages that the reactions between alkyltin and the stationary phase as observed in HPLC [23] can be eliminated and much better efficiencies than those of HPLC can be obtained. Unlike in most GC techniques, MEKC separations are carried out at low temperatures, thus avoiding the derivatization step which may introduce problems such as contamination, interference and difficulty in quantitation [24]. Membrane disk extraction was used to overcome the problem encountered in solvent extraction and solid-phase cartridge

extraction, such as emulsification, larger labour requirement and time consumption. The method developed in this work has the advantages of simplicity and rapidity. The potential applications of MEKC and membrane disk extraction for organo-lead and -tin in environmental analysis have been demonstrated.

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