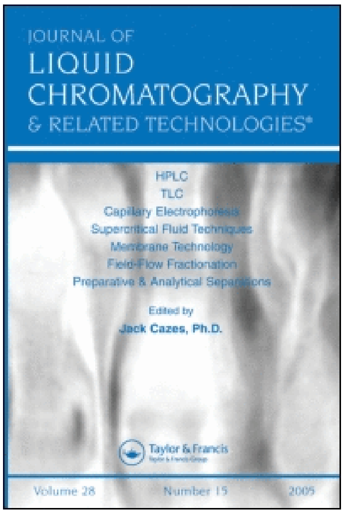

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OPTIMIZATION OF SAMPLE PREPARATION TECHNIQUES FOR THE DETERMINATION OF 4-NONYLPHENOL IN WATER AND SEDIMENT

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ABSTRACT

Sample preparation techniques for the determination of 4-nonylphenol in water and sediments were optimized using two-level orthogonal array design (OAD). Comparison between the use of cartridge-based solid-phase extraction and membranous disk-based extraction was made for water samples. For sediment samples, microwave-assisted solvent extraction (MASE) was employed. A comparison between MASE and classical soxhlet extraction of spiked samples was also carried out. 4-Nonylphenol was determined using high performance liquid chromatography (HPLC) coupled to both ultraviolet and fluorescence detection

INTRODUCTION

The focus in trace organic pollutant analysis has shifted from analytical instrumentation to sample preparation.[1,2] Sample preparation is a critical stage in the entire experimental procedure. It is both time-consuming and tedious as two-thirds of the analysis time is typically spent on it. The method detection limits for the determination of many organic pollutants are greatly dependent on the sample preparation conditions used. Loss of samples at this stage of the experiment is usually inevitable, e.g. adsorption of analytes onto the glassware, inadequate transfer of samples, inefficient extraction of compounds from the samples and matrix effects. However, sample losses can be largely avoided or at least minimized by careful selection of optimum sample preparation conditions derived from appropriate optimization procedures.

Recently, orthogonal array design (OAD) has been used as a chemometric method for the optimization of analytical procedures.[3-9] OAD is a sophisticated and cost-effective optimization strategy that is used to assign factors to a series of experimental combinations whose results can then be analyzed by using a common mathematical process. e.g. analysis of variance (ANOVA). The main effects of the factors and two-variable interactions can be considered separately as different factors and estimated by OAD along with the corresponding linear graphs or triangular tables.[10-11]

During the last 40 years, 4-nonylphenol (4-NP) has been widely used for the production of non-ionic surfactants, e.g. nonylphenol ethoxylates (NPE) in industrial detergents formulations. The biodegradable non-ionic surfactants had replaced the non-biodegradable synthetic types which were responsible for severe environmental problems such as foaming. However, the former surfactants themselves are of concern owing to their release into the environment through industrial runoff. The biodegradability of the NPE under laboratory and natural conditions has been well studied.[12-14] During anaerobic sewage treatment, NPE is degraded to its refractory metabolite, 4-NP, and concern has arisen owing to the recognition of the increased aquatic toxicity of this species over that of the parent surfactants. The toxicity of this hydrophobic metabolite towards marine organisms is well-documented.[15-18] Due to their hydrophobicity, 4-NP can associate with suspended matter and eventually with sediments. Recently, Soto and co-workers found that nonylphenol is strongly oestrogenic in cultured human breast cells and in rodents.[19] The occurrence and potential hazardous effects of 4-NP or other alkyphenols have thus stimulated research on their presence in environmental samples.[20-23]

For the extraction of 4-NP from water and sewage effluent, liquid-liquid partition using methylene chloride is usually used.[15] Recently, solid-phase extraction (SPE) using C_{18}-packed cartridges has been used for the trace enrichment of nonylphenols in water.[19]

For extracting 4-NP from sediment and sewage sludge, soxhlet extraction is the most common technique. Different extracting solvents including methanol,[15] dichloromethane[16] and hexane[18] have been used. Recently, microwave-assisted solvent extraction (MASE) has been applied for the extraction of several classes of organic compounds (pesticides, polyaromatic hydrocarbons, acidic/neutral/basic organics, biological compounds and stabilizers) from solid matrices such as soil, sediment, plant and animal tissues, and polymers.[24-30] Through microwave irradiation, the temperatures of the extracting solvents can be increased by more than 100^0 C above their normal boiling points, thus allowing much shorter extraction times (minutes, compared to >16 hours for soxhlet extraction). The desorption process during the irradiation does not cause breakdown of organic compounds of interest, thus further enhancing the usefulness of this method of extraction. The reduction in extraction time and solvent consumption in MASE are obvious advantages over soxhlet extraction as the latter technique requires 16-24 hours and 200-300 mL of organic solvent in order to extract one sample. The parameters which can be optimized for the MASE of 4-NP in sediment samples include types of extracting solvents, extraction temperature and duration of extraction.

In the present study, 2 two-level orthogonal array designs using an OA_8 (2^7) matrix is used to optimize conditions for three sample preparation procedures, namely C_{18}-packed cartridge SPE, C_{18}-impregnated disk SPE and MASE, in the determination of 4-NP in water and sediment.

MATERIALS AND METHODS

Instrumentation and Chemicals

The microwave-assisted solvent extraction was carried out using a microwave extraction system (Model MES-1000, CEM, Matthews, NC, USA), equipped with a solvent detector, a safety feature. The MES-1000 is able to extract 12 solid samples at a time.

HPLC analysis was performed on a Waters (Milford, MA, USA) Powerline system comprising the Waters 600E system controller, Waters 486 tunable absorbance detector, Waters 470 scanning fluorescence detector and Waters 700 Satellite WISP autosampler. The Maxima 825/Baseline 815 Powerline HPLC software was used to control the system. The HPLC conditions used were: initial eluent of 80%:20% acetonitrile:water; programmed linearly to 100% acetonitrile over 20 min at a flow rate of 1.2

mL/min. Chromatographic separation was achieved on a 25 cm x 4.6 cm I.D. (5-µm particle size) Spherex C_{18} column (Phenomenex, Torrance, CA, USA). For UV detection, the wavelength was set at 225 nm. For fluorescence detection, the excitation (E_x) wavelength was 224 nm and emission (E_m) wavelength 308 nm.

All pesticide-grade and HPLC-grade organic solvents were purchased from Fischer Scienific (Pittsburgh, PA, USA). The water used was taken from a Milli-Q purification system (Millipore, Bedford, MA, USA). Technical grade 4-NP was purchased from Tokyo Kasei Kyogo (Tokyo, Japan). A standard solution of 4-NP containing 1000 ppm was prepared in methanol. Appropriate dilutions were made from this stock solution for calibration and spiking purposes. Analytical-grade sodium chloride and sodium dodecyl sulphate were purchased from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), respectively.

Bakerbond Spe-500 cartridges (C_{18}-bonded silica gel containing 16% carbon) used in the present optimization procedure were purchased from J.T. Baker (Philipsburg, NJ, USA). 47-mm Empore (3M, St. Paul's, MN, USA) membranes with Bakerbond (J.T. Baker) C_{18}-bonded silica were used for disk extraction.

Optimization Strategy

On the basis of previously published information relating to the sample preparation techniques for 4-NP in water and sediment,[23] two different experiments were designed for optimization. All the parameters and their possible interactions in these two experiments were examined by two-level orthogonal array design with an $OA_8(2^7)$ matrix. Details on the assignment of factors and their interactions in the two-level OAD have been described elsewhere.[3-6] In the application of OAD, prior knowledge of the parameters most likely to be influential in the analysis is very helpful as certain two-variable interactions can be neglected.

The first experiment was designed to optimize the extraction of 4-NP using C_{18} cartridges. Three parameters likely to affect the extraction efficiency include: eluting solvent (Factor A), concentration of sodium chloride (Factor B) assignment of the factors and their levels is shown in Table 1. For a more direct and concentration of sodium dodecyl sulphate (SDS) (Factor C). The comparison between the membranous C_{18} disk and SPE cartride in terms of extraction efficiency, the optimum SPE conditions for cartridge extraction

Table 1

Assignment of Factors and their Levels Using an OA_8 (2^7) Matrix for the Extraction of Water

	Column*							Response
Trial No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**PR**
1	Methanol	0		0				70.5
2	Methanol	0		$1x10^{-4}$				88.7
3	Methanol	10		0				90.5
4	Methanol	10		$1x10^{-4}$				96.5
5	Acetonitrile	0		0				69.0
6	Acetronitrile	0		$1x10^{-4}$				83.6
7	Acetronitrile	10		0				84.0
8	Acetronitrile	10		$1x10^{-4}$				88.0

---

*Column 1 is assigned to eluting solvent (Factor A); column 2 is assigned to the concentration of sodium chloride (Factor B) [0-10% (v/v)]; column 3 is the interaction between Factor A and Factor B (AxB); column 4 is assigned to concentration of sodium dodecyl sulphate (Factor C) [0-$1x10^{-4}$M]; column 5 is the interaction between the Factor A and Factor C (AxC); column 6 is the interaction between Factor B and Factor C (BxC) and column 7 is unassigned.

were also used for disk-based extractions.

In the second experiment, the following parameters affecting the extraction efficiency of 4-NP present in sediment by MASE were selected: extracting solvent (Factor D), extraction temperature (Factor E) and duration of extraction (Factor F). The duration of extraction was defined as that from whence the pre-set temperature was reached. The microwave power was not considered for optimization because it was dependent upon the number of samples in one run. In this second experiment, the power was maintained at 50% and the temperature of the extracting solvent reached the required level within 5 minutes. The assignment of factors and their levels are provided in Table 2.

The percentage recovery (PR) of 4-NP was used as the response function in both experiments because it is convenient and time-saving especially when considering the effect of changes the parameters have on the extraction

Table 2

Assignment of Factors and their Levels Using an OA_8 (2^7) Matrix for the Extraction of Water

	Column*							Response
Trial No.	1	2	3	4	5	6	7	PR
1	Methylene chloride	100^{0}C		5				95.4
2	Methylene chloride	100^{0}C		15				86.1
3	Methylene chloride	120^{0}C		5				80.2
4	Methylene chloride	120^{0}C		15				80.0
5	Acetone/ Petroleum ether	100^{0}C		5				79.2
6	Acetone/ Petroleum ether	100^{0}C		15				75.0
7	Acetone/ Petroleum ether	120^{0}C		5				69.0
8	Acetone/ Petroleum ether	120^{0}C		15				72.0

---

*Column 1 is assigned to the extracting solvents (methylene chloride and acetone/petroleum (1:1, v/v) (Factor D); column 2 is assigned to extraction temperature (100^{0}C to 120^{0}C) (Factor E); column 3 is the interaction between factor D and factor E; column 4 is assigned to the duration of extraction (Factor F); column 5 is the interaction between the factor D and factor F; column 6 is the interaction between the factor E and factor F; column 7 is unassigned.

efficiency. The PR results relating to extraction of 4-NP in water and in sediment are shown in Tables 1 and 2, respectively.

Sample Preparation

Solid phase extraction of water

SPE of 4-NP was carried out in a Supelco (Bellefonte, PA, USA) vacuum manifold. 0.5 μg of 4-NP was spiked into 0.5 L of Milli-Q water. Prior to use, SPE cartridges were conditioned with 5 mL of the eluting solvents, followed by 5-mL aliquots of their respective aqueous media as shown in the experimental design (Table 1) for washing. The vacuum was applied at 68kPa, gauge reading. After spiked samples had been processed, the sorbent was air dried for 1 min. The adsorbed analyte was then eluted with one aliquot of 4 mL of the appropriate solvents. 20 μL of the extract was injected for HPLC analysis. The procedure was identical for disk extraction except that a solvent filtration apparatus was used.

Soxhlet extraction

5 g of sediment samples were carefully weighed and quantitatively transferred into an extraction thimble pre-rinsed with methylene chloride. The sample was extracted in a soxhlet apparatus with 300 mL of methylene chloride for 16 hours.

Microwave-assisted solvent extraction of sediment

5 g samples were accurately weighed out and quantitatively transferred into Teflon-lined extraction vessels of the MES-1000. The volume of extracting solvent was 30 mL. The operating conditions are given in Table 2.

Real sample analysis

Different types of water samples (tap water, sea water and wastewater) were extracted using the optimum SPE conditions established from the OAD exercise. Sediment was sampled from locations *ca.* 1 km from the shore of the primary industrial areas (Jurong and Tuas regions) of Singapore. The samples were extracted using the optimum MASE conditions and the extracts then analyzed with HPLC/fluorescence.

RESULTS AND DISCUSSION

Linear Range, Detection Limits and Precision

The linearities of the calibration graphs for 4-NP were in the range 50-5000 ng for UV detection and 0.5-100 ng for fluorescence detection. Fluorescence

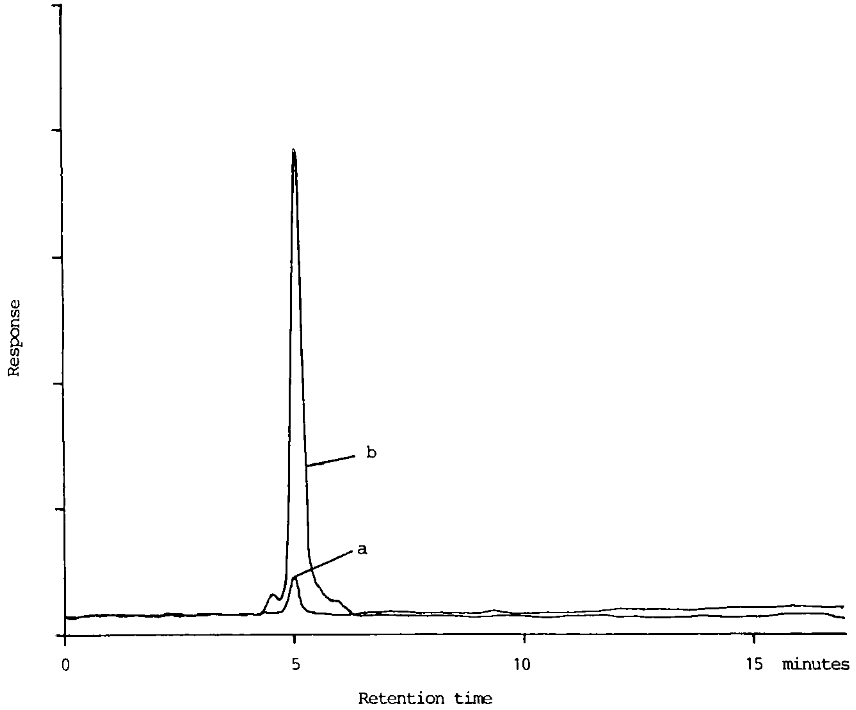

Figure 1. Superimposed high performance liquid chromatograms of a standard solution of 4-nonylphenol using (a) UV detection and (b) fluorescence detection. (See text for conditions).

detection exhibited at least 100-fold greater sensitivity than UV detection. Thus, quantitation for 4-NP was carried out with this mode of detection. The detection limits were determined based on a signal-to-noise ratio of 3. The detection limits for the 4-NP with fluorescence and UV detection were 0.02 ng and 25 ng, respectively. The retention time reproducibility was 0.05%. Figure 1(a) shows a liquid chromatogram of a standard solution of 4-NP in methanol using UV detection while Figure 1(b) gives that with fluorescence detection.

Optimization of Analytical Conditions for 4-NP

A total of 16 experimental trials pre-designed according to the 2-level OA_8 (2^7) matrix for the two optimization experiments were carried out. Corresponding chromatograms were subsequently obtained to derive percentage recoveries (PRs) based on peak areas. The PRs obtained for water and sediment are tabulated in Tables 1 and 2 respectively. Based on the method presented previously[3], the results of the sum of squares (SS) for PRs for different variables and so-called two-variable interactions in both experiments were first calculated (see Tables 3 and 4, respectively). Three possible two-variable interactions are assigned to columns 3, 5 and 6 by using associated triangular tables[3]. Column 7 is unassigned to any variable or two-variable interaction in this optimization exercise. Thus, it is not necessary to carry out repetition of any experimental trials. However, data from previous publications and also the computed results of SS given in the ANOVA table (Table 3) indicate that 2 two-variable interactions assigned to columns 3 and 5 are negligible except for interaction BxC (column 6). In the case of the second experiment, interactions assigned to columns 5 and 6 are ignored. Finally, columns 3, 5 and 7 for the first experiment, and columns 5, 6 and 7 for the second experiment have been treated as dummies amd the error variance must be pooled from the SS for the total of the respective columns in each experiment.

From the ANOVA Table 3, it is seen that variable B (concentration of NaCl), variable C (concentration of SDS), variable A (eluting solvents) and interaction BxC are statistically significant at $P<0.05$ in the first experiment. (Variable B was the most significant factor ($P<0.005$) in the first experiment). Both variables B and C have been found previously to have significant influence on the recoveries of 4-NP during SPE[23]. Marcomini and his co-workers have mentioned that at least 3% NaCl (w/w) or 3×10^{-3} M SDS was necessary to prevent losses occurring in the filtration step during sample preparation.[23] In their work, recoveries of above 82% were obtained during SPE of water and industrial effluent spiked with 4-NP in the presence of 8% NaCl (w/w) or 7×10^{-3} M SDS. A relatively higher recovery was observed when NaCl instead of SDS was added. The same observation has also been made by Marcomini and his coworkers.[23] In our present work, the use of 10% (w/w) of NaCl and 1×10^{-4} M SDS during extraction of water gave good recoveries of 4-NP in the range of 83.6-96.5%. Thus, the optimum conditions for SPE of 4-NP are A_1, B_2 and C_2, namely, methanol as the eluting solvent, 10% (w/w) of sodium chloride and 1×10^{-4} M of SDS. It is affirmed that the above conclusion from ANOVA is the same as that from the direct observation method, which indicates that optimum conditions were obtained from experimental trial no. 4 in the first experiment.

In the case of the second experiment (MASE), only variable D (extracting solvent) and interaction DxE were statistically significant above $P<0.05$ (ANOVA Table 4). For the MASE of 4 - NP, methylene chloride is a better extracting solvent compared to 1:1(v/v) acetone/petroleum ether. The

Table 3

An ANOVA Table for Results Obtained in the Extraction of Water

Source	Sum of Squares	Degrees of Freedom	Mean Square	F ratio[a]	Significance
A (Solvent)	58.3	1	58.3	13.6	*P<0.05
B (NaCl)	278.5	1	278.5	64.8	***P<0.005
C (SDS)	229.0	1	229.0	53.1	**P<0.01
BxC	65.0	1	65.0	15.1	*P<0.05
Pooled Error[b]	12.9	3	4.3		
Total	643.7	7			

---

[a] The critical F ratio is 55.55 (***P<0.005), 34.12 (**P<0.01) and 10.13 (*P<0.05).

[b] Pooled error result from the pooling negligible effects from columns 3 and 5 (AxB and AxC) and unassigned column effect (column 7).

influence of the solvent on the extraction of organics has also been mentioned previously.[26,30] With the help of microwave irradiation, temperatures of the extracting solvents can be raised 100^0 C above their respective boiling points. The importance of interaction between the extracting solvent and the extraction temperature on the recoveries of 4-NP can only be an observation here. The extraction temperature from 100^0C to 120^0C and duration of extraction from 5 to 15 mins were not statistically significant to affect the recoveries of 4-NP from sediment samples. Similarly, the optimum conditions for SPE of 4-NP are D_1, E_1 and F_1, namely, methanol as extracting solvent, extraction temperature of 100 C and duration of extraction of 5 mins (experimental trial no. 1 in the second experiment).

Analytical Results of Real Samples

Using the optimum conditions obtained in the optimization procedures, analysis of genuine samples was carried out and the results tabulated in Tables 5 and 6.

Table 4

An ANOVA Table for Results Obtained in the Extraction of Sediment

Source	**Sum of Squares**	**Degrees of Freedom**	**Mean Square**	**F ratio**[a]	**Significance**
D (Solvent)	270.3	1	270.3	18.8	$^{**}P<0.025$
E (Temp)	14.6	1	14.6	1.0	
F (Duration)	8.0	1	0.6		
DxE	147.9	1	10.3		$^{*}P<0.05$
Pooled Error[b]	43.2	3	14.4		
Total	484.0	7			

---

[a] The critical F ratio is 17.44 ($^{**}P<0.025$) and 10.13 ($^{*}P<0.05$). [b] Pooled error results from the pooling negligible effects from column 5 & 6 (DxF and ExF) and unassigned column effect from column 7.

For the analysis of different types of water, a comparison between cartridge extraction and disk extraction of 4-NP using identical optimum conditions was carried out. Table 5 shows that both methods gave comparable recoveries for different types of spiked water samples. However, lower recoveries were obtained for unfiltered sea water and untreated industrial wastewater samples. Losses of 4-NP during extraction may be due to adsorption to the particulate matter present in these water samples. The high sedimentation observed in the untreated industrial wastewater may be the cause of the low recovery of 4-NP from this matrix. Basically, the problem of clogging of the SPE sorbents by particulate matter is also another possible reason for the lower recoveries in these water samples. However, this problem was less significant when disks, which are less prone to clogging, were used with the result that relatively higher recoveries were obtained from sea water and wastewater samples. Thus, in summary, membranous disk is more suitable for the extraction of high volumes of 'dirty' water samples.

Chromatograms of extracts of an untreated industrial wastewater sample and its spiked counterpart are shown in Figures 2(a) & (b).

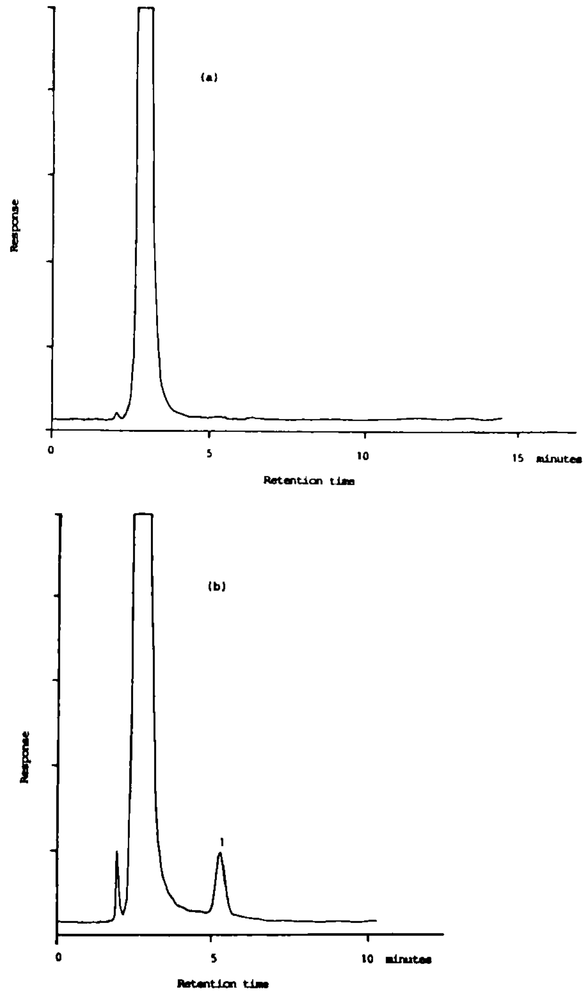

Figure 2. High performance liquid chromatogram with fluorescence detection of extract of (a) untreated wastewater extracted with C_{18} SPE cartridges and (b) spiked untreated wastewater with 50 ppb of 4-nonylphenol and extracted with C_{18} SPE cartridges. Peak 1 = 4-nonylphenol (retention time: 5.1 minutes). (See text for conditions.)

Table 5

Percent Recoveries of 4-nonylphenol Spiked into Different Water Samples using Conditions Optimized by OAD

Sample	Recovery (%)[a] A*	Recovery (%)[a] B
Distilled water	96.5±2.5	95.±3.0
Tap water	96.0±2.5	96.3±4.1
Seawater (unfiltered)	85.5±7.1	89.3±6.9
Seawater (filtered)	89.0±4.7	91.0±3.7
Wastewater (pH2)	82.9±8.4	84.0±7.1

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[a] Mean %RSD (n=4)

*Method A: optimum SPE conditions using SPE C_{18} cartridges. Method B: same optimum SPE conditions using membranous C_{18} disks

Table 6

Comparison of Percent Recoveries Between Optimum MASE Conditions and Soxhlet Extraction for 4-Nonylphenol Spiked into Marine Sediments at 0.5 μg Levels

Sample[b]	Recovery (%)[a] MASE	Recovery (%)[a] Soxhlet Extraction
Sediment (A)	95.4±3.0	92.3±6.1
Sediment (B)	89.6±4.1	87.9±3.0
Sediment (C)	85.1±8.3	80.8±11.6

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[a] Mean %RSD (n=4)

[b] Genuine sediment samples collected from different coastal region around Singapore, A=east coast (minimal industrial activities), B=Straits of Johore (some industrial activities) and C=Jurong (heavy industrial activities)

Table 6 shows the recoveries of 4-NP spiked into different marine sediment samples, using MASE and soxhlet extraction. Both techniques gave satisfactory and comparable results for the recovery of 4-NP from marine sediment samples collected from several coastal locations. Recoveries were in the range 85.1-95.4% (%RSD 3.0-8.3) for MASE, and 80.8-92.3% (%RSD 3.0-11.6) for soxhlet extraction. Lower recoveries were observed for 4-NP spiked in marine sediments sampled from a heavy industrial area in Jurong to the west of Singapore island. On the other hand, higher recoveries were obtained from marine sediments sampled near the east coast of the island, a recreational area with minimal industrial activity. It was observed that the levels of recoveries might be affected by the quality of marine sediment in terms of the level of organics present in the sediment samples, e.g. organic carbon and humic acid. One possible reason may be the adsorption of 4-NP to the organic carbon present within the sediment particulates. Using the optimum conditions for MASE, no 4-NP was detected in the marine sediments sampled in this study. In summary, based on recovery studies of spiked samples, MASE is a better extraction technique, in terms of time and costs, when compared to soxhlet extraction as the latter requires the consumption of large volumes of hazardous organic solvents and prolonged hours of extraction time for one sample. With MASE, one may carry out extraction for 12 samples in one run and with minimal losses of the compound of interest.

CONCLUSION

This paper is concerned with the optimization of the sample preparation procedures using OAD for the determination of 4-NP in water and sediment. All three factors under consideration for solid phase extraction of 4-NP from water samples, namely concentration of sodium chloride, concentration of SDS and eluting solvents were found to be statistically significant. In the case of MASE of 4-NP in sediment, only the type of extracting solvent and its interaction with extraction temperature were found to be statistically significant. In this study, two-level OAD was used as a testing strategy for screening all factors and their interactions using fewer experimental trials so as to achieve the optimum analytical conditions without affecting the quality of the results. However, it should be emphasized that adequate judgement and pre-experience is necessary in identifying the factors and their levels, and output reponse for a given sample preparation procedure, and this procedure is normally subject to a case-by-case consideration. Under the optimum conditions for both sample preparation procedures, good recoveries of above 80% can be obtained for 4-NP in water and sediment. A preliminary survey of some areas of the Singapore marine environment indicated that there was no contamination of water and sediment samples by 4-NP.

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