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Communications

Analysis of Nitrophenols with Gas Chromatography/Mass Spectrometry by Flash Heater Derivatization

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In order to determine trace phenolic compounds in waste water, several studies have been made on the use of capillary gas chromatography[1-3]. Gas chromatographic technique allows good separation of various phenolic compounds with appropriate sensitivity. Because of high polarity and low vapour pressure of nitrophenols, they are eluted as nonsymmetrical peaks in GC analysis due to interaction or adsorption to active OH sites existing in the GC system. To circumvent adsorption to active OH sites and to improve sensitivity the conversion of nitrophenols into less polar derivatives prior to GC is usually employed. Silylation reaction among various derivatizing reactions is popular because a variety of silylating reagents are commercially available, and most of the reactions are designed to introduce the trimethylsilyl groups into analytes for enhancing volatility. Although this type of procedure has often been used in many derivatization methods to improve the GC properties of polar substances, the use of the method[4-8] previously reported was too much time consuming to obtain satisfactory results for acidic and highly polar nitrophenols because of the presence of nitro groups on aromatic ring. The nitro groups appeare to lower nucleophilicity of phenolic OH groups in the course of the derivatization reaction.

We have confirmed that nitrophenols can be easily derivatized in a heated capillary injector (flash-heater derivatization: FHD[9-11]) through the co-injection of silyl derivatizing agent and analytes for the purpose of improving the derivatization yields and of analyzing quantitatively the nitrophenols extracted from waste water in the nanogram range with GC/MS-selected ion monitoring (SIM). We have performed a systematic study of flash heater derivatization of nitrophenols to look for the optimum conditions including the effect of silylation reagents, injection volume and the linearity of derivatization on quantification.

Table 1. Effect of Silylating Reagents on the Flash Heater Derivatization of Nitrophenols Measured in GC/MS-SCAN Mode ($n=4$)

Compound	MSTFA		BSA		BSTFA	
	AR	rsd (%)	AR	rsd (%)	AR	rsd (%)
2-nitrophenol	0.730	1.17	0.615	0.75	–	–
4-nitrophenol	2.263	1.80	2.065	6.13	1.360	18.54
4-chloro-2-nitrophenol	1.236	1.78	1.092	4.38	–	–
2,4-dinitrophenol	1.871	2.26	1.375	8.79	0.663	6.52
2-methyl-4,6-dinitrophenol	1.987	1.38	1.569	11.54	0.807	10.70

AR: peak area ratios of 20 ng of each nitrophenol relative to 10 ng of internal standard.

In FHD technique, different reagents such as N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA), N,O-bis(trimethylsilyl)acetamide (BSA) and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were examined to find out the most effective silylation reagent. As shown in Table 1, the mixed reagents, BSTFA containing 10% trimethylchlorosilane (TMCS), did not react with 2-nitrophenol and 4-chloro-2-nitrophenol and gave poor derivatizing yields for other nitrophenols. Although MSTFA is somewhat less potent than BSA or BSTFA, it reacted readily with nitrophenols under the condition of FHD technique. MSTFA seemed to react more quantitatively than BSA with noticeably lower relative standard deviations (rsd), as shown in Table 1. When BSA was used for the actual samples extracted from waste water, quantitative analysis could not be achieved due to interfering peaks formed during FHD. Consequently, MSTFA was selected as the silylating agent in the FHD technique. Further-

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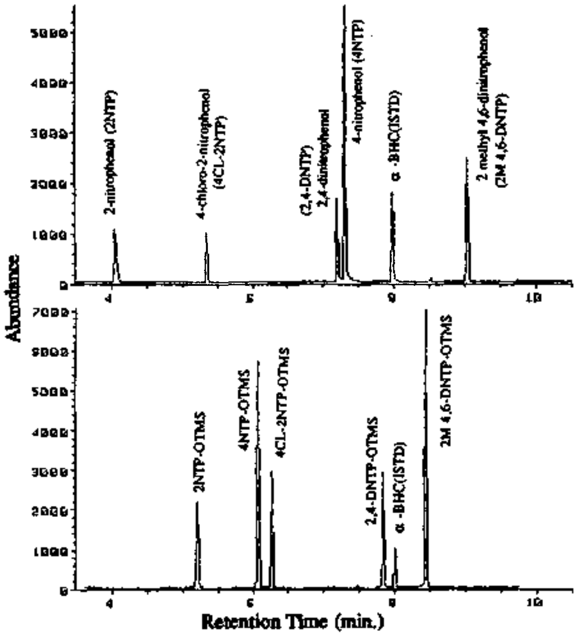

Figure 1. Typical total ion chromatograms of standard underivatized nitrophenols (upper trace) and their flash heater trimethylsilyl derivatives (lower trace). Chromatographic conditions as follows: injection temperature 280℃; split ratio 10 : 1; column SE-54 25 m×0.2 mm; oven temperature: initial 140℃ held for 2 min and then programmed 20℃/min to 280℃. α-BHC was used as an internal standard.

more, this reagent and its by-products are more volatile than other reagents and showed less interference with the early eluting compounds.

According to the study for the influence of the volume of MSTFA injected, two microliters of MSTFA led complete reaction and gave the best precision. The FHD yield was not enhanced as the volume of reagent injected was further increased.

The total ion chromatograms of standard solution containing 20 ng/μl of nitrophenols and 10 ng/μl of an internal standard, α-BHC before and after FHD, are compared in Figure 1. Although 2-nitrophenol and 4-nitrophenol are structural isomers, their retention times are greatly different, as shown in Figure 1. It can be explained that free 2-nitrophenol experiences considerably more intramolecular hydrogen bonding than free 4-nitrophenol, since the stronger intramolecular hydrogen bonding results in the increasing the volatility. But the retention time of 4-nitrophenol-OTMS derivative was shorter than the of free 4-nitrophenol because TMS group may also contribute to improve the volatility.

The structures of the flash heater trimethylsily derivatives were confirmed by GC/MS. The mass spectra of O-trimethylsilyl nitrophenols showed characteristic ions at molecular ion (M^+), $(M\text{-}15)^+$ and $(CH_3)_3Si^+$ which support the formation of O-trimethylsilyl nitrophenols. As underivatized nitrophenols were not detected, the reaction was assumed to be complete. In contrast, both underivatized nitrophenols and OTMS-nitrophenols could be detected in the case of silylating nitrophenols with a conventional silyl derivatizing method when reaction conditions are not optimized.

Table 2. Area Ratios and Relative Standard Deviation (rsd) of Underivatized Nitrophenols, TMS Derivatives Prepared by FHD and Conventional Method Measured in GC/MS-SIM Mode (n= 4)

Compound	Underivatized nitrophenols		TMS-nitrophenols by FHD		TMS-nitrophenols by conventional method	
	AR	rsd (%)	AR	rsd (%)	AR	rsd (%)
2-nitrophenol	0.843	1.11	2.789	7.01	1.873	7.20
4-nitrophenol	3.516	12.81	6.107	8.31	5.224	3.84
4-chloro-2-nitrophenol	0.625	1.97	3.097	7.38	2.087	9.23
2,4-dinitrophenol	0.976	10.69	2.957	6.95	1.948	10.48
2-methyl-4,6-dinitrophenol	1.384	2.86	7.116	9.25	2.128	12.43

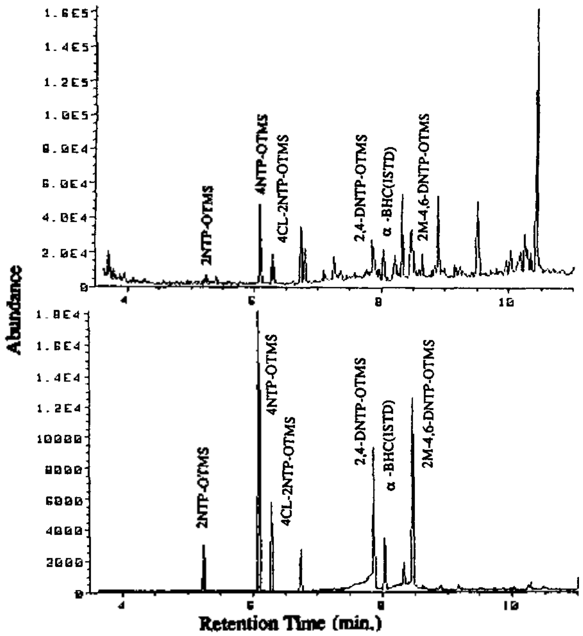

Figure 2. Comparison of total ion chromatogram in scan mode (upper trace) and SIM chromatogram (lower trace) obtained from spike waster water at 0.1 ppm of each nitrophenol after flash heater trimethylsilylation. Chromatographic conditions are the same as in Figure 1.

Table 2 compares the relative peak area ratios for underivatized nitrophenols, flash heater trimethylsilylated derivatives and conventionally prepared trimethylsilyl derivatives measured in GC/MS SIM mode. The peak area ratios are decreasing in the following order: FHD-nitrophenols>TMS-nitrophenols>underivatized nitrophenols. Especially, area ratios of 4-chloro-2-nitrophenol and 2-methyl-4,6-dinitrophenol are greatly increased by using FHD technique. The maximum yields of their trimethylsilyl derivatization were achieved when the reaction mixture containing nitrophenols and MSTFA was heated at 80℃ for 1 hour. As the derivatization efficiency of the conventional method depends on many factors such as reaction time, reaction temperature, silyl donor ability of reagents and catalyst, the optimum conditions differ for each nitrophenol. But in FHD technique, the nitrophenol-

Table 3. Standard Calibration Curves for Nitrophenols Measured in GC/MS-SIM Mode With Flash Heater Derivatization Technique

Compound	Equation of calibration	Correlation coefficient
2-nitrophenol	$Y=(3.33\times10^{-2})X-0.107$	0.9989
4-nitrophenol	$Y=(6.25\times10^{-2})X+0.106$	0.9987
4-chloro-2-nitrophenol	$Y=(5.74\times10^{-2})X-0.115$	0.9991
2,4-dinitrophenol	$Y=(2.85\times10^{-2})X-0.112$	0.9994
2-methyl-4,6-dinitrophenol	$Y=(7.02\times10^{-2})X-0.229$	0.9988

OTMS derivatization was not greatly affected by these factors.

In general, the base peak for all nitrophenol-OTMS derivatives was $(M-15)^+$ ion whereas the intensities of molecular ions were weak. Therefore, $(M-15)^+$ ions should be used in selected ion monitoring mode for quantitative or confirmative purposes. Typical total ion chromatograms are shown in Figure 2 where extracts by C_{18}-bonded phase cartridge from the wasted water sample spiked with nitrophenols at 0.1 ppm were analyzed by GC/MS- in scan and SIM modes. The advantage of SIM over scan mode in the signal to noise ratio is quite obvious, as shown in Figure 2.

In order to check the linearity of the derivatization method, calibration curves in the concentration range of 15-200 ng/μ*l* were constructed for each nitrophenol and calculated according to the method of least squares, relating y (the peak area ratio of the OTMS-derivative to the internal standard) to x (the concentration of the nitrophenol in ng/u*l*). Table 3 lists the data for the calibration curves which were linear over the concentration range for the five nitrophenols. The minimal detectable amount was about 0.5 ng for 4-nitrophenol and 2-methyl-4,6-dinitrophenol and about 1.5 ng for 2-nitrophenol, 4-chloro-2-nitrophenol and 2,4-dinitrophenol.

The flash heater derivatization technique can be successfully used for nitrophenolic compounds which are not easily derivatized with the conventional derivatization method. This method eliminates the hydrolysis and requires less time in forming TMS derivatives when the sample and derivatizing agent are injected directly into a gas chromatograph. The specificity and the sensitivity are improved by the use of a capillary column and selected ion monitoring mode. The use of SIM mode has provided a choice for the detection of several ions of interest in any analysis. The presence of one to two ions at specific retention time is presumptive evidence that specific nitrophenols are present. This makes the method suitable for identification of complex mixtures and for quantitative analysis in nanogram range.

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Nucleophilic Substitution Reaction and Elimination Reaction of 2-Phenylethyl Arenesulfonates

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The substitution reaction of 2-phenylethyl substituted (*X*)-benzenesulfonates with substituted (*Y*)-pyridines and elimination reaction of 2-substituted (*Z*)-phenylethyl (*X*)-substituted benzenesulfonate with *tert*-BuO⁻ are found to follow a concerted S_N2 and a concerted E2 mechanism, respectively, on the analysis of ρ_{ij} by applying multiple Hammett equation.

Menschutkin-type reaction of substituted benzyl arenesulfonates[1] and phenacyl arenesulfonates[2] with *tert*-amines have been studied in detail using cross interaction terms of three moieties of substrate, leaving group, and nucleophile.

Although the effect of substituent on the reaction of 2-phenylethyl arenesulfonates[3,4] with pyridines have been studied previously, cross interaction terms mentioned above have not been studied. In the present paper, we report the interaction of 2-phenylethyl arenesulfonates with pyridines and apply the method to the elimination reaction of a series of 2-(*Z*)-phenylethyl *p*-substituted (*X*)-arenesulfonates[5] with potassium *tert*-butoxide in *tert*-butanol at 40℃.