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Quick Simultaneous Determination of NMP and DMAc in Synthetic Fibers by Py-GC-MS using A Thermal Desorption Function

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Abstract- The simultaneous analyses of NMP and DMAc in synthetic fibers that have been regulated recently due to their human hazard properties were studied by both a conventional GC-MS method and a thermal desorption(TD)-GC-MS method that uses Py-GC-MS instrument using the thermal desorption function. Method validation characteristics such as linearity, precision of peak area and retention time. limit of quantification on their determination using a new TD-GC-MS method were found to be acceptable according to the well-recognized method validation guidelines and the current regulation limit. Recovery ratios of DMAc from the spiked synthetic fibers were estimated to be 95.2% to 97.1% with Soxhlet extraction using methanol as measured by GC-MS. Residual amounts of NMP and DMAc in commercial meta-aramid, polyester, and spandex fibers were measured by and GC-MS and TD-GC-MS, respectively and showed a good correlation between two methods with the ratio of 85.5% to 119%. Results of this study suggested that the TD-GC-MS analysis can provide both a good screening and a guick determination of NMP and DMAc in synthetic fibers without any solvent extraction of fiber samples that is a routine and time consuming pretreatment in the conventional GC-MS analysis.

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I. INTRODUCTION

MP(N-Methyl-2-pyrrolidinone) and DMAc(N,N-Dimethylacetamide) have enhanced its utility as a solvent or co-solvent in many synthetic reaction systems and polymeric solutions.¹⁻⁷ Due to its good solvency properties NMP has been used in many industrial applications including photoresist stripping; degreasing and coatings (polyamide, epoxy and polyurethane) in the electronics industry; agricultural formulations; consumer and industrial cleaners; an extraction solvent in lube oil processing in petrochemical industry; paint stripping; polymer solutions for fiberspinning.¹⁻⁴ DMAc has been also commonly used as a solvent for fibers (e.g., polyacrylonitrile, polyamide, spandex, meta-aramid) as well as for manufacture of agro chemicals, dyes, synthetic resins and pharmaceuticals.^{1,3-7}

However, their uses are now being regulated due to their human hazard.^{8,9} As classified as CMR (Carcinogenic, Mutagenic or toxic to Reproduction category) substances, the EU regulated NMP and DMAc as a candidate list of SVHC (Substances of Very High Concern) in 2011,¹⁰ while NMP was regulated as the CHCC list (reporting list of chemicals of high concern to children) in the CSPA (Children's Safe Products Act) of the U.S. state of Washington.¹¹ Especially, the limit value of 0.1% (w/w) was newly set from 2012 for synthetic fibers by Oeko-tex Standard 100 that has been a global leading textile ecolabel since the middle 1990s.¹²

The most common method the for determination of these solvent residues is based on an extraction of the sample with an organic solvent and subsequent analyses by GC-MS(Gas Chromatography-Mass Spectrometry).¹³ In this study, thermal desorption (TD)-GC-MS method was investigated to determine the amount of solvent residues like NMP and DMAc in synthetic fibers without the need of extraction from fibers. For this purpose, the instrument Py-GC-MS (Pyrolyzer Gas Chromatography-Mass Spectrometry) was tried only using a thermal desorption function without a usual pyrolysis.

II. EXPERIMENTAL

a) Instrumentation

Py-GC-MS(PY2020iD, Frontier Lab; HP 7890, MS(5975C), Agilent) and GC-MS(HP 6890, MS(5973N), 7683 Autosampler, Agilent) were used respectively, for comparison. Thermal desorption function of Py-GC-MS was used with temperature programmed from 200°C to 340°C for furnace avoiding the much higher temperature that are commonly used in case of pyrolysis of samples. Other detailed conditions are described in Table 2.

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Table 1 : Current	prohibitions on use	e of NMP and	DMAc in industria	l products

Substance	CAS No	Chemical structure	Hazard classification	Global prohibition on use		
	040 110.			CSPAª	REACH ^b	Oeko-Tex Standard 100°
NMP	872-50-4	N-CH3	CMR : Toxic to reproduction category 2	CHCC list	Candidate List of SVHC for	Limit value of 0.1%(w/w)
DMAc	127-19-5	N H ₃ C CH ₃	CMR : Toxic to reproduction category 2	-	Authorization (0.1%(w/w) in article)	Limit value of 0.1%(w/w)

a. CSPA(Children's Safe Product Act) in Washington State, U.S.; CHCC(Chemicals of High Concern to Children)

b. REACH(Registration, Evaluation, Authorization, and Restriction of Chemicals); SVHC(Substances of Very High Concern) c. Globally recognized textile ecolabel

Table 2 : Instrumental conditions for TD-GC-MS analyses of NMP and DMAc

	Thermal desorption mode	Double shot analysis		
	Thermal desorption time	14 min		
		-Initial : 200 °C (for 0 min)- 20 °C/min to 300°C		
Thermal desorption	Furnace temperature program	(for 0 min)- 5 °C/min to 340 °C (for 1 min)		
CONDITION ^a	Interface temp.	300 ℃		
	Sample amount loaded	Fiber : 1 mg Standard solutions mixed in a cup : 5 μL (NMP) + 5 μL (DMAc)		
	Column	HP- INNOWAX Column (30 m(L) X 0.25 mm(ID) X 0.25 m(T))		
	Carrier gas	Helium with flow rate of 1 mL/min		
GC condition ^b	Injection mode	Split ratio of 20 : 1		
	Temperatures	Injector 250 °C, Detector 280 °C		
		- Initial : 50 °C for 1 min		
	Oven temperature program	- 15 °C/min to 250 °C (for 5 min)		
	Scan mode	Range : 25 \sim 600 amu		
MS condition (Acquisition mode)	SIM mode	Selected ions(Reference ions), m/z : - NMP 99 (42, 44, 98) - DMAc 87 (43, 44, 72)		

(a) Loading of a fiber sample



Fig.1 : Schematic diagram of TD-GC-MS analysis of synthetic fibers

2016

b) Reagents

Methyl alcohol (HPLC grade, 99.5%, J.T.Baker) was used for preparation of standard solutions of DMAc and NMP as well as extraction of synthetic fibers. DMAc (HPLC grade, 99.0%, MACRON Chemicals) and NMP (Guaranteed reagent, 99.0%, JUNSEI) were purchased.

c) Samples

Three kinds of commercial synthetic fibers such as meta-aramid, polyester, and spandex were used as obtained in the form of yarns. Each sample was cut into short fibers (ca. $3\sim5$ mm) to achieve homogeneity.

d) Validation data for TD-GC-MS measurement

Standard solutions of 1.25, 2.5, 5.0, 10.0 ng/µL were prepared for NMP and DMAc, respectively, by diluting their stock solutions (1,000 ng/ μ L) with methanol. A 5 μ L portion of each standard solution with the same concentration was loaded by a micro-syringe into a cup to make a mixed standard solution of NMP and DMAc. According to the instrumental conditions described in Table 2, TD-GC-MS measurement of the mixed standard solution of each concentration was repeated 7 times. Then, relative standard deviations (RSD) of retention times and peak areas for each concentration of NMP and DMAc were calculated. Limit of detection (LOD) and limit of quantification (LOQ) of each substance were calculated using the linear equation of standard curve (Y = aX + b) according to "Eqs. (1) and (2)". 14,15

$$LOD = 3.3 \times \sigma/S \tag{1}$$

$$LOQ = 10 \times \sigma/S$$
 (2)

- σ : Standard deviation of intercept (b) of linear equation (Y = aX + b)
- S : Slope (a) of linear equation (Y = aX + b)

GC-MS measurement of DMAc standard solutions in the range of 0.3125 \sim 5 ng/µL were done in the same way for comparison according to the instrumental condition described in Table 2.

e) Calibration curves for GC-MS and TD-GC-MS analyses of fiber samples

For GC-MS analyses, five standard solutions of 0.3125, 0.625, 1.25, 2.5 and 5 ng/ μ L were prepared for NMP and DMAc, respectively, by diluting their stock solutions (1,000 ng/ μ L) with methanol and subjected to GC-MS analyses according to the condition mentioned. in Table 2. The calibration curve for each substance was built with the mean values (n=3). For TD-GC-MS analyses, standard solutions of NMP were prepared with concentrations of 2.5, 5.0, 10.0, 20.0 ng/ μ L and standard solutions of DMAc were prepared with concentrations of 12.5, 25.0, 50.0, 100 ng/ μ L. In four sample cups, 5 μ L of each of NMP and DMAc standard solutions was loaded by micro-syringes (Figure 1) in the order of their concentrations so that each analyte in four

cups ended up with 12.5, 25, 50, 100 ng for NMP and 62.5, 125, 250, 500 ng for DMAc. The calibration curve for each substance was built with the mean values (n=3).

f) GC-MS analyses of spiked fiber samples

To estimate the recovery efficiency of DMAc from synthetic fibers by methanol extraction, spiked fiber samples were prepared by pipetting 1 mL of DMAc standard solution of 1000 μ g/mL to the exactly weighed fiber in the thimble filter.¹⁴ The spiked sample were subjected to the Soxhlet extraction followed by GC-MS measurement mentioned in sections of pretreatment and instrumentation. Recovery ratio of DMAc was calculated by dividing the measured amount by the theoretical amount. The corresponding fiber sample was also analyzed in the same procedure to check the presence of DMAc in the sample before spiking. Three replicates were done for samples and their spiked samples.

g) GC-MS analyses of fiber samples

Each fiber sample (ca. 2 g) was weighed precisely into a thimble filter (ADVANTEC[®], ID 25 mm, OD 28 mm, L 100 mm) and extracted using a Soxhlet apparatus for 6 h with 100 mL methanol. After Soxhlet extraction, methanol was evaporated by a Turbovap concentrator and the sample solution was made up by adjusting the volume exactly to 10 mL with methanol. Three replicates were done for pretreatment of each sample. A portion of 1 μ L was subjected to GC-MS analysis described in Table 2.

h) TD-GC-MS analyses of fiber samples

One mg of each fiber sample was approximately loaded into the stainless steel cup (80 μ L Disposable eco cup, Frontier Lab) and the exact weight was recorded. Without any sample treatment the sample cup was placed in a furnace and subjected to TD-GC-MS analysis described in Figure 1(a) and Table 2. Three replicates were done for each sample.

III. Results and Discussion

a) Validation characteristics of TD-GC-MS analysis of NMP and DMAc using Py-GC-MS using a thermal desorption function

TD-GC/MS analysis was tried with Py-GC-MS in a way that outgases were emitted (thermally desorbed) from a fiber sample in a sample cup inside the furnace (250 °C), collected into the inlet part of GC and analyzed by GC-MS. The difference from the normal TD-GC-MS to identify the major VOCs emissions in industrial sites and to control organic compounds in a clean room or in wafer surfaces is that sorbent tube sampling and the subsequent TD-GC/MS analysis are used for these purposes.¹⁶⁻¹⁸ However, in this study, the chemical instrument Py-GC-MS was used with a lower temperature without using a pyrolysis condition. To obtain the precision of retention time and peak areas of TD-GC/MS analyses of NMP and DMAc, a portion of standard solutions of four concentrations in the range of 1.25 to 10 ng/ μ L was loaded in a cup. In our experimental condition, NMP and DMAc were fully separated with retention times of 11.1 min and 8.8 min, respectively. NMP with higher boiling point, 204.3 °C was eluted later than DMAc with b.p of 163 °C ~ 165 °C.^{8,9} When each standard solution was analyzed by TD-GC/MS seven times, precision of retention times and

peak areas were evaluated by calculating RSD of retention times and peak areas. RSD of retention times were estimated to lie in 0.02% ~ 0.05% (NMP) and 0.05% ~ 0.20% (DMAc) while RSD of peak areas were 3.96% ~ 6.71% (NMP) and 2.78% ~ 6.42% (DMAc) that are acceptable (Figure 2) .²⁰ These values are slightly bigger than RSD of 0% for retention times and 1.12% ~ 3.16% for peak areas that were obtained by GC-MS analyses of DMAc.



Fig. 2: Precision of retention times and peak areas (n=7) of NMP and DMAc using the TD-GC-MS system in this study **Concentration range(TD-GC-MS)*, *1.25 to 10 ng/μL; Volume loaded*, *5 μL; Split ratio 1:20*.

*Concentration range(GC-MS for comparison), 0.3125 to 5 ng/µL; Volume loaded, 1 µL; Splitless.

Linearity during TD-GC-MS measurements was also secured with R² of 0.9989 for NMP and R² of 0.9998 for DMAc from the regression line established with 5 concentrations in the range of 1.25 ng/ μ L \sim 10 ng/ μ L because R² of 0.99 is often used as criterion of linearity (Table 3).¹⁵

When a split ratio of 20:1 was used in TD-GC-MS analysis, LODs were estimated in Table 3; 0.023

 $ng/\mu L$ or 0.115 ng in solution for NMP; 0.266 $ng/\mu L$ and 1.33 ng in solution for DMAc. When 1 mg of fiber was subjected to the TD-GC-MS measurement, LODs in measurement of NMP and DMAc in fibers were found to be 0.115 ng/mg and 1.33 ng/mg, respectively. LOQ can be further calculated as 3.03 times LOD according to Eqs. (1) and (2).

Table 3. Limit of detection in TD-GC-MS analyses of NMP and DMAc in this si	tudy
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	Substance	Range measured		Y = aX + b		_	LOD°	LOD ^d
Measurement method		Conc. (ng/µL)	Conc. (ng) ª	Slope a	Standard deviation of b	R ²	in solution	in fiber (ng/mg)
							0.023 ng/µL	
TD-GC-MS	NMP	1.25~ 10	$6.25 \sim 50$	23,317	160	0.9989	0.115 ng ^a	0.115
			(0.3125~				(0.006 /	(0.006) ^b
			2.5) ^b				0.0180 ng) ^b	
	DMAc	1.25~ 10	6.25 ~ 50 (0.3125~	19,204	1,547	0.9998	0.266 ng/μL	1 33
							1.33 ng ^a	(0.067) ^b
			2.5) ^b				(0.067 ng) ^b	(0.007)
GC-MS for	DMAc	0.3125 ~ 5	0.3125 ~ 5	538,680	1.123	0.9999	0.007 ng/µL	0.035
comparison				,	, =-		0.007 ng ^a	0.000

a. Volume loaded in TD- GC-MS, 5 μ L, split ratio of 20:1; Volume loaded in GC-MS, 1 μ L, splitless

b. Absolute amounts after considering the split ratio; for example, 0.3125 ng = 6.25 ng / 20

c. $LOD_{solution} = 3.3 \times \sigma/S$; σ , standard deviation of intercept; S, slope of linear equation; $LOQ_{solution} = 10 \times \sigma/S$

d. For TD-GC-MS, one mg of fiber was analyzed in this study; for GC-MS, LOD_{fiber} = LOD_{solution} x 5 where dilution factor = 5 (2 g fiber in final volume 10 mL (methanol)) based on recovery ratio = 100 %

e. Y: peak area

GC-MS analyses of NMP and DMAc in synthetic fibers after Soxhlet extraction with methanol

The common method for the determination of solvent residues is based on an extraction of the sample with an organic solvent and subsequent analyses by gas chromatography with mass selective detection (MSD).¹³ Because NMP and DMAc are polar solvents and water-miscible,^{8,9} methanol was chosen to extract them from synthetic fibers.

Figure 3 showed that recovery ratios of DMAc from aramid, polyester and spandex fibers with spiking method^{14,19} were 97.1%, 95.2% and 96.8%, respectively. These recovery ratios correspond well to the acceptable recovery percentages of $95\% \sim 105\%$ given at the analyte concentration of 0.1%.^{20,21}



Fig. 3 : Recovery ratios of DMAc from the spiked synthetic fiber samples by Soxhlet extraction using methanol as measured by GC-MS (n=3)

*Spiked amounts of NMP and DMAc, each of 1,000 mg/kg.

When three kinds of commercial synthetic fibers were Soxhlet-extracted with methanol and analyzed by GC-MS, DMAc and NMP were detected in the level of several tens to hundreds ng per one mg of fiber (Table 4-a). Although these amounts are under the current regulation limit, 0.1% w/w (1,000 ng/mg) (Table 1)¹⁰⁻¹², it

seems that DMAc and NMP are still common solvents to produce synthetic fibers such as aramid, polyester and spandex fibers¹⁻⁹ and become possibly present in final products as residues. The amounts detected by GC-MS analyses were compared with those obtained by TD-GC-MS analyses.

Table 4 : Fiber Samples and Contents Of NMP and DMAc as measured by GC-MS and TD-GC-MS

Samples	Substance	Amounts mea	Ratio, b/a (%)	
	s analyzed by GC-MS (a)			by TD-GC-MS (b)
Aramid	NMP	62 ± 7^{a}	53 ± 14	85.5
fiber	DMAc	417 ± 12	381 ± 27	91.4
Polyester	NMP	Not detected ^b	Not detected ^b	-
fiber	DMAc	158 ± 8	137 ± 6	86.7
Spandex	NMP	18 ± 5	21 ± 6	116.7
fiber	DMAc	79 ± 6	94 ± 7	119.0

a. Standard deviation (n = 3)

b. Below detection limit (0.12 ng/mg as estimated from Table 3)

TD-GC-MS analyses of NMP and DMAc in synthetic fibers without sample pretreatment

In our TD-GC-MS analyses of NMP and DMAc in synthetic fibers, thermal desorption of residual organic solvents from a fiber can occur in a sample cup that was heated from 200 °C to 340 °C. Outgases from the fiber were collected in a furnace and analyzed by GC-MS as shown in the scheme of Figure 1-a. This process that occurred in a furnace part enabled to omit the Soxhlet extraction that was necessary in the GC-MS analysis discussed in the previous section. The amounts of NMP and DMAc in the same fiber samples detected by TD-GC-MS analyses lied in the level of several tens to hundreds ng per one mg of fiber (Table 4-b) and showed that there is a good correlation between two methods. NMP with boiling point, 204.3 °C and DMAc with b.p of 163 °C ~ 165 °C^{8,9} seemed to be almost completely desorbed thermally from fibers in the scheme of Figure 1-a. Total ion and selected ion monitoring (SIM) chromatograms of a aramid fiber sample were shown in Figure 5.



Fig. 4 : Calibration curves for simultaneous determination of NMP and DMAc by TD-GC-MS.



Fig. 5 : TD-GC-MS chromatograms of aramid fiber and mixed standard solution. (a) TIC chromatogram and (b) SIM chromatogram (m/z = 87, 99) of aramid fiber, (c) SIM chromatogram (m/z = 87, 99) of mixed standard solution. Fiber sample, 1 mg of aramid fiber; Mixed standard solution of 5 μ L NMP (10 ng/ μ L) and 5 μ L DMAc (10 ng/ μ L)

TD-GC-MS method using a Py-GC-MS instrument can be applied for a screening of residual organic solvents in a fiber as proved in our study or possibly in other plastic products. With corresponding calibration curves of mixed standard solutions (Figs 4

and 5-c), а quick simultaneous quantitative determination of NMP and DMAc was also possible resulting in significantly correlated measured values with those determined by the conventional GC-MS (Table 4). Another successful application of TD-GC-MS method for the product analysis was previously reported as analysis of phthalate esters in PVC.22-24 The TD-GC-MS method using a Py-GC-MS instrument developed in this study provides a convenient way without sample pretreatment to monitor residual organic solvents in fiber products with detection limit far below the current limit value of 0.1 %(w/w) (Tables 1 and 3).

IV. CONCLUSION

Development and validation of a fast TD-GC-MS method using a Py-GC-MS instrument for simultaneous determination of NMP and DMAc in fiber samples were carried out in this study. The acceptability of TD-GC-MS as a new convenient method to screen and determine residual organic solvents used during synthetic fiber processing was evaluated successfully by comparing data obtained by conventional GC-MS analyses. Validation characteristics of TD-GC-MS measurements including precision of retention times (RSD within 0.05 % for NMP, 0.2 % for DMAc) and peak areas (RSD within 6.71 % for NMP, 6.42 % for DMAc) and linearity (R^2 = 0.9989 for NMP, 0.9998 for DMAc in the concentration range of 1.25 \sim 10 ng/µL) were obtained. Limits of detection for NMP and DMAc were measured to be 23 ppb and 266 ppb in solution; 0.115 ppm and 1.33 ppm in fiber, respectively. With commercial aramid, polyester, and spandex fibers, residual amounts were measured by TD-GC-MS with the comparable ratio of 85.5% \sim 119% to those of GC-MS data.

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