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Journal of Chromatography A, 806 (1998) 317–324

JOURNAL OF CHROMATOGRAPHY A

Solid-phase microextraction and gas chromatography–mass spectrometry for determining chlorophenols from landfill leaches and soil

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Received 29 September 1997; received in revised form 19 January 1998; accepted 20 January 1998

Abstract

This work evaluates solid-phase microextraction coupled with GC–MS (electron impact ionization and negative chemical ionization) to determine chlorophenols in landfill leaches and soil. A polyacrylate coated fiber is used to investigate the optimal experimental procedures, which include adsorption time, pH, salt effect, desorption time, temperature and the depth of the fiber in the injector. Detection limits are determined to be in low ng/l range and better than those obtained by US Environmental Protection Agency methods using a conventional extraction technique for chlorophenols in water. According to the analytical validations, the linearity of the absorption ranges from 0.1–100 μg/l with R.S.D.s below 9%. In addition, the feasibility of applying the proposed method to determine chlorophenols in real samples is examined by analyzing landfill leachate samples and soil samples contaminated with pentachlorophenol. All the studied chlorophenols are determined in the soil contaminated samples. Moreover, the pentachlorophenol detected in the landfill leachate is estimated in the level of 21.6 μg/l with an internal standard method. The quantities of the other studied chlorophenols are at the level of 0.1 μg/l. The effects of humic acids and a surfactant on the extraction of chlorophenols in the landfill leachate have been studied. © 1998 Elsevier Science B.V.

Keywords: Soil; Sample preparation; Environmental analysis; Chlorophenols; Pentachlorophenol

1. Introduction

The aquatic environment is increasingly affected by organic chemicals which are inevitably introduced into the environment in large quantities according to their specific applications. Chlorophenols have been widely used as preservative agents, pesticides, antiseptics and disinfectants [1]. They are also used as intermediates in many industries, particularly in producing dyes, plastics and pharmaceuticals. Chlorophenols can also be obtained as a result of hydrolysis, oxidation and microbial degradation of chlorinated pesticides. Chlorine treatment of drinking water also produces chlorophenols [2]. These substances are carcinogenic and quite persistent [3]. Of those, pentachlorophenol (PCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,4-dichlorophenol (2,4-DCP) and 2-chlorophenol (2-CP) have been cited among 11 priority pollutants in the US Environmental Protection Agency (EPA) list [4]. Therefore, a rapid, accurate and sensitive analytical method is acquired to identify and determine these compounds in different sample matrices.

Although many methods have been developed to

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0021-9673/98/$19.00
PII S0021-9673(98)00075-2

determine chlorophenols, they are based primarily on chromatographic techniques including liquid chromatography [5,6], gas chromatography [7,8], supercritical fluid chromatography [9,10] and capillary electrophoresis [11,12]. The chromatographic and electromigration methods offer a successful separation and detection of chlorophenols in a single run. However, the validity of an analytical sample for trace chlorophenols analysis depends on proper sampling and preconcentration. Previous investigations have set forth various types of extraction methods for chlorophenols in water, including liquid–liquid extraction [13,14] and solid-phase extraction [15,16]. The conventional extraction methods, although efficient and precise, are relatively time consuming, hazardous to human health as they use organic solvents and extremely expensive with respect to the disposal of solvents. Therefore, a relatively simple, fast and solvent free extraction method must be developed. Solid-phase microextraction (SPME) can resolve many of the above problems. Zhang et al. [17] have detailed the underlying principles and merits of trace organic analysis and applying SPME technique to extract trace organic compounds in a complex matrix. Buchholz and Pawliszyn [18] initially applied SPME to analyze chlorophenols in water. Those investigators also obtained a detection limit at the nanogram per liter level for GC–flame ionization detection (FID) and GC–MS using a saturated sodium chloride solution at pH 4. In addition, they analyzed a sewage sample, indicating that the matrix significantly influenced the extraction of heavier chlorinated phenols [19]. Möder et al. [20] later employed this technique to examine the influences of humic acids and of a surfactant on the recoveries of phenols. According to their results, the effect of low recoveries could be compensated by extending the extraction time. In a related investigation, Dean et al. [21] used SPME coupled with GC–FID to estimate the octanol–water partition coefficients of chlorophenols. Their results have demonstrated that the partition coefficients of chlorophenols increases with the substituted chlorine number in the chlorophenols.

This work applies SPME coupled with GC–MS to determine the five priority pollutant chlorophenols in landfill leachates and soil real samples. The soil samples obtained from the southern area of Taiwan had been contaminated with PCP that was generated from a chemical manufacturing plant. Herein, the optimum conditions for determining chlorophenols in water are systematically studied. To demonstrate the proposed methods applicability, the SPME behavior, detection limits, linear dynamic detection ranges and reproducibility are studied by determining the amount of chlorophenols. The influences of humic acids and a surfactant on the determination of chlorophenols in landfill leachates have also been studied.

2. Experimental

2.1. Reagents and materials

The standard solutions of 2-CP, 2,4-DCP and 2,4,6-TCP (purity≥99%) at a concentration 5000 μg/ml in methanol were all obtained from NSI Environmental Solutions (Research Triangle Park, NC, USA) and used as received. PCP was purchased from Supelco (Bellefonte, PA, USA). The standard 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) from TCI (Tokyo, Japan) was purified by recrystallization from diethyl ether. The final purity is over 99%. The internal standard 2,4,6-tribromophenol was also obtained from TCI without further purification. The stock mixed standards spiked with internal standard were then diluted to the required concentration using methanol to produce standard solutions and maintained at 4°C in a refrigerator. The buffers for various pH values were prepared by mixing potassium chloride with hydrochloric acid, or citric acid with hydrochloric acid, or citric acid and sodium hydroxide, or potassium dihydrogenphosphate and disodium hydrogenphosphate. All chemicals and reagents used in this study were analytical or research grade. All silanization of glassware was performed by soaking the glassware overnight in toluene solution at a concentration of 10% dichlorodimethylsilane. The glassware was rinsed with toluene and methanol and oven-dried for 4 h. Next, the landfill leachate samples were collected from a sewage farm at Taichung (Taiwan). Soil samples were then obtained from the PCP contaminated soil location on the campus of an abandoned chemical manufacturing site in the southern Taiwan. The soil

was screened of rocks and debris using two soil screens with mesh sizes of 1.981 mm and 2.000 mm. Finally, the soil was shaken through the mesh screen, collected and stored at 4°C in a refrigerator. The samples were prepared by dissolving 40 mg of soil in 12.5 ml of 20 μg/l internal standard solution and, then, the solution was diluted to 50 ml with pH 1 buffer solution and 5 *M* KCl added. In Soxhlet extraction, a 2-g soil sample was extracted with 150 ml of *n*-hexane–acetone (1:1) for 8 h. The procedure adopted for deriving standardized humic acid solution was proposed by Johnson et al. [22]. The detergent (Snoop liquid leak detector, Nupro, OH, USA) was used as a surfactant.

2.2. Apparatus

SPME was performed with a commercially available polyacrylate fiber having a film thickness of 85 μm and housed in its manual holder (Supelco,). The fiber was conditioned in the hot injection port of the gas chromatograph at 300°C for 2 h. During extraction, the aqueous samples were continuously agitated with a magnetic stir bar on a stir plate resolving about 1000 rpm.

Analysis by GC–MS was performed with a Hewlett-Packard MS Engine mass spectrometer (Palo Alto, CA, USA) with HP 5890 Series II gas chromatograph and a split/splitless injection port. The column was a 30 m×0.25 mm I.D. fused-silica capillary column DB-5.625 and a stationary phase thickness of 0.5 μm (J&W Scientific, Folsom, CA, USA). The gas chromatograph was operated in a splitless mode and the injector port temperature at 290°C. The splitless time was 1 min. The GC–MS transfer line temperature was maintained at 310°C. The oven was initially set at 60°C, programmed to 190°C at a rate of 30°C/min and from 190°C to 310°C at a rate of 10°C/min. The total analysis time of a single run is 16 min. Various ionization modes of mass spectrometer, including electron ionization mode with electron energy of 70 eV, positive and negative chemical ionization with methane as reagent gas, were operated. In quantitative analysis the selected ion monitoring (SIM) mode was chosen to enhance the sensitivity. For this purpose, characteristic ions were monitored in five groups of two ions, with a dwell time of 40 ms for different groups of ions. The full scan of mass number range from 45–350 u was used to determine appropriate masses for selected ion monitoring. The scan time is 1 s. The total organic compounds (TOCs) analysis in landfill leachate was performed with a TOC Analyser (OI Analytical, College Station, TX, USA).

3. Results and discussion

3.1. GC–MS determination

The highest sensitivity is desired to monitor chlorophenols at trace levels in the water, thereby, quantitative analyses were performed by MS in the SIM mode. In general, the most abundant ion was used for the ion of monitoring and the quantification; the specific ion was used as the confirmed ion. The electron impact ionization (EI) and chemical ionization (CI) mass spectra for standard chlorophenols were obtained. The molecular ion or pseudo-molecular ion of all chlorophenols is the most abundant ion, regardless of the ionization mode used. Therefore, the molecular ion of all chlorophenols was chosen as the quantitative ion and the ion $[M+2]^+$ generated from the isotope of chlorine atom was used as confirmed ion. Table 1 lists the analytical SIM conditions for the studied chlorophenols for various ionization methods.

By using a standard solution of chlorophenols, various ionization modes of MS were compared with respect to the response obtained to evaluate the

Table 1
Analytical conditions of chlorophenols, as determined by GC–MS (SIM) with various ionization modes

Compound	t_R (min)	Selected ion/confirmed ion: EI, PCI[a], NCI		M_r
2-CP	3.35	128/130 (3:1)		128
2,4-DCP	4.34	162/164 (3:2)		162
2,4,6-TCP	5.34	196/198 (1:1)		
			(3:1)[b]	196
2,3,4,6-TeCP	6.64	232/230 (4:3)		230
PCP	8.17	266/264, 268 (15:9:10)		
		267/269	(3:2)[b]	
		230/232	(3:2)[c]	264

[a] Protonated molecular ion was chosen in PCI.
[b] The ions were chosen in PCI.
[c] The ions were chosen in NCI.

optimum ionization technique for trace analysis of chlorophenols in water. According to those results, the sensitivities of EI and negative chemical ionization (NCI) are more than ten-times higher than those in positive chemical ionization (PCI). The NCI technique yields better results for those chlorophenols in which the number of chlorine molecules is higher than three. However, using this mode is limited primarily by the problem of peak tailing. In this study, EI is therefore, chosen to investigate the optimum conditions of SPME.

3.2. Development of SPME

Analyte extraction during SPME experiments can widely vary due to matrix effects, choice of absorbent, absorption time, desorption temperature as well as many other factors. After the samples have been trapped on the fiber with the sorbent, the desorption temperature for the analytes absorbed onto the fiber influences the amount of analytes to be analyzed. Generally, the desorption temperature is set to the thermal desorption. The desorption temperatures monitored ranged from 210 to 310°C. According to our results, the peak areas of all chlorophenols increase with an increasing desorption temperature. For 2-CP, 2,4-DCP and 2,4,6-TCP, the peak areas gradually decrease when the desorption temperature exceeds 290°C. The decreased desorption can be attributed to the high temperature that causes the thermal degradation of chlorophenols. Carryover or memory effect is a problem frequently encountered when using the SPME method to analyze an organic compound. A second desorption performed at 310°C after the initial desorption run was used to determine whether the analytes remain on the fiber. Carryover was calculated as the ratio of peak area estimated at 310°C to that obtained at the investigated desorption temperature. The carryover is less than 1% for all chlorophenols at a temperature exceeding 290°C. According to those results, desorption temperature was chosen at 290°C to extract the studied chlorophenols in water.

The desorption time, desorption temperature and depth of the fiber in the injector determine the amount of analytes desorbed from the fiber coating. Desorption time was investigated within a range of 0.1 to 5 min, by leaving the fiber in the injector for a progressively longer period of time and maintaining the injector temperature at 290°C. The analytes desorbed increase with desorption time and reach a maximum after 2 min. The fiber's depth in the injector was measured with a syringe carriage piercing the septum and stopping at the depth controlled by the holder from 1.5 to 4.5 mm. According to those results, the analytes desorbed increase with an increasing depth of the fiber in the injector port. Such an increase is probably attributed to a temperature gradient with the injector port. For all subsequent experiments, the fiber was desorbed at the maximum length (4.5 cm) of the syringe carriage in an injector for 2 min.

The mechanism of SPME is based on an equilibrium between the analytes concentration in the sample and that in the solid-phase fiber coating. The extraction time determines the amount of analyte trapped on the fiber which reaches the maximum under equilibrium conditions. For test equilibrium time, the samples mixed using a stirring bar and ultrasonic vibration were investigated. The equilibrium was reached after 40 min and 20 min for using stirring bar and ultrasonic vibration, respectively. However, the ultrasonic vibration technique is limited in that chlorophenols will degrade and ultimately decrease the extraction. Therefore, using SPME, chlorophenols in water were extracted with a stirring bar for 40 min.

Herein, we also added strong acid and different salts into the matrix (individually or in combination) to examine the effects of ion strength and pH on the extraction of chlorophenols with the SPME fiber. The salt effect was investigated by simply using 5 *M* NaCl and 5 *M* KCl. Table 2 indicates that at pH 1, the amount of chlorophenols extracted increased depending on the pK_a of the different chlorophenols[1]. The lower pK_a of chlorophenols, implied a larger effect on the extraction. At a low pH, the acid–base equilibrium of chlorophenols shifted toward the neutral form, which has a higher affinity for the fiber, thereby increasing the extraction efficiency. The ''salting out'' effect by adding salt into the matrix increases the amount extracted, depending on the solubility of the chlorophenols.

[1] pH values of 1–7 were studied; based on the results (not shown), pH 1 was chosen for our experiments.

Table 2
Matrix effect enhancement of the extraction of chlorophenols with SPME

Compound	pK_a[a]	Factor increase					
		With pH 1	With NaCl	With KCl	With pH 1 and NaCl	With pH 1 and KCl	With pH 1 and KCl+NaCl
2-CP	8.48	1.1	4.2	2.4	2.4	2.1	3.8
2,4-DCP	7.25	1.1	1.9	1.8	1.8	1.6	1.9
2,4,6-TCP	7.42	1.2	1.2	1.3	1.3	1.9	1.6
2,3,4,6-TeCP	–	1.4	1.1	1.4	1.2	1.4	1.2
PCP	4.74	1.4	1.1	1.2	1.2	1.6	1.3

[a] From Refs. [23,24].

The magnitude of enhancement in extraction, as attributed to the addition of salt, ranged from 1.1 to 4.2. The effect of combining acid and salt was performed by combining pH 1 and adding salt, or a mixture of salts. Under these conditions, the extraction is enhanced with all chlorophenols which are in their neutral form and are salted out of solution and into the fiber coating. The ion conductivities of the KCl solution (0.1632 S/cm) and KCl combined with NaCl solution (0.1642 S/cm) were a little better than that obtained in NaCl solution (0.1614 S/cm). For high-molecular-mass chlorophenols, the enhancement with adding KCl offers a better of extraction than that with adding NaCl. Pentachlorophenol is the most toxic compound of chlorophenols. Herein, the solution was adjusted at pH 1 and added KCl for all studies.

3.3. Precision and detection limit

The method's precision was determined by performing eight consecutive fiber extractions with the same concentration under the optimal conditions having been studied. For this test, a solution containing 25 μg/l of each compound was investigated. At room temperature, the reproducibility expressed as relative standard deviation (R.S.D.) of the fiber ranged between 4 and 9%, and the precision of the SPME method was deemed acceptable.

The linearity was studied at a concentration ranging from 0.01 to 100 μg/l for each compound with 2,4,6-tribromophenol used as the internal standard. The correlation coefficients are 0.999 except for 2-CP where it was 0.998. The linear range experiments provided the necessary information to estimate the detection limits, based on a signal-to-noise ratio of 3. Table 3 compares the limits of detection (LODs) obtained using SPME–GC–MS with both conventional liquid–liquid extraction in EPA methods 604 (GC–FID) and 625 (GC–MS with full scan). As this Table indicates, the obtained LODs for chlorophenols in SPME are better than those achieved using standard EPA methods. The LODs for the determination of all chlorophenols can be down to the ng/l level in water (PCP and 2,4,6-TCP 1 ng/l, 2,4-DCP 2 ng/l). This result is better than that reported in literature [18]. The results of chlorophenols detected would not be significantly different in the deionized or tap water.

3.4. SPME of landfill leachate

The proposed method's effectiveness in determining chlorophenols in real samples was tested by analyzing landfill leachate samples. The SPME was operated at the optimum conditions that have been

Table 3
Estimated limits of detection for SPME coupled with GC–MS compared to limits of detection of standard EPA methods for chlorophenols

Compound	SPME (μg/l) EI		EPA method (μg/l) (liquid–liquid extraction)	
	A[a]	B[b]	Method 604 (FID)	Method 625[c] (GC–MS)
2-CP	0.03	0.04	0.31	3.3
2,4-DCP	0.002	0.002	0.39	2.7
2,4,6-TCP	0.001	0.002	0.64	2.7
2,3,4,6-TeCP	0.0005	0.001	–	–
PCP	0.001	0.002	7.4	3.6

[a] Deionized water.
[b] Tap water.
[c] Method 625 analysis with full scan mode of MS.

determined. The pentachlorophenol was found, i.e., about 21.6 μg/l, in the landfill leachate sample by quantification with the addition of internal standard, about 28.5 μg/l by quantification with standard addition method. The quantities of the other studied chlorophenols are in the range of 0.11 μg/l to 0.16 μg/l. In this technique, 12.5 ml of landfill leachate samples were added 12.5 ml of pH 1 buffer solution and saturated with KCl and spiked with 20 μg/l of the internal standard. The samples were also studied by spiking with 25 μg/l of standard chlorophenols in a standard addition method. In liquid–liquid extraction, 50 ml of landfill leachate samples were spiked 20 μg/l of internal standard and extracted with 100 ml *n*-hexane–acetone (1:1) mixed solvent. Only 14.7 μg/l of PCP was detected in landfill leachate samples extract. Those results further confirm that the SPME–GC–MS system is highly effective in analyzing trace pentachlorophenol.

3.5. Matrix influence

The humic acids and surfactant matrix in water frequently inhibit the extraction of organic compounds in an aqueous solution. The effect varies according to the amount and kinds of humic acids or surfactant. For check the matrix effect, the water spiked with the standard chlorophenol mixture at 25 μg/l level and landfill leachate samples were loaded with defined amounts of the humic acids as well as surfactant. The TOCs in landfill leachate sample were detected at a concentration of 376.8 mg/l. The results listed in Table 4 show clear reduction of the chlorophenols recoveries if surfactant or humic acids were added. The decrease of extraction efficiency of chlorophenols in water were observed, regardless of the concentration of humic acids or surfactant spiked. The significant reduction in extraction efficiency was observed in landfill leachate sample with addition of the humic acids or surfactant. The extraction of chlorophenols in matrix could be improved by a longer extraction time. The extraction after 70 min sampling time were improvable the extraction efficiency. The means that the humic acids and surfactant in aqueous solution not only obstruct the diffusion of the chlorophenols to the coating, but also inhibit the absorption of chlorophenols onto the fiber.

3.6. Analysis of soil samples by SPME–GC–MS method

The soil having been contaminated with PCP was generated as a result of chemical processing activities at a demolished chemical manufacturing plant. Spiked addition method and internal addition method were used to quantify chlorophenols in soil samples with SPME. The studied chlorophenols except 2-CP were detected in soil samples (Fig. 1). Table 5 compares soil extraction methods by using Soxhlet extraction and SPME using internal standard and a standard addition techniques. According to the results, the most abundant pollutant in the contaminated soil sample detected is PCP. The amount of chlorophenols extracted in the Soxhlet extraction is slightly higher than that obtained in the SPME

Table 4
Comparison of the chlorophenols extraction in spiked solution (recoveries in %) and landfill leachate (in μg/l) with adding defined matrix by SPME

Compound	25 μg/l, pH 1, KCl saturated solution (%)							Landfill leachate (μg/l)				
	Extraction times							Extraction times				
	Without matrix addition	Humic acids (2.375 mg/l)		(100 μg/l)		Surfactant (100 mg/l)		Without matrix addition	Humic acids (100 μg/l)		Surfactant (100 mg/l)	
	40 min	40 min	70 min	40 min	70 min	40 min	70 min	40 min	40 min	70 min	40 min	70 min
2-CP	1.2	0.8	1.4	1.0	1.7	0.8	1.4	0.11	0.06	0.19	0.05	0.13
2,4-DCP	1.1	0.7	1.4	0.8	1.6	0.7	1.4	0.16	0.11	0.13	0.09	0.18
2,4,6-TCP	3.2	2.4	3.4	2.4	3.4	2.3	4.5	0.13	0.05	0.18	0.02	0.19
2,3,4,6-TeCP	5.9	4.9	7.3	4.8	7.2	4.9	9.4	0.13	0.02	0.20	0.01	0.18
PCP	14.3	13.2	14.6	12.9	14.3	13.6	15.1	21.61	7.86	23.97	2.82	24.52

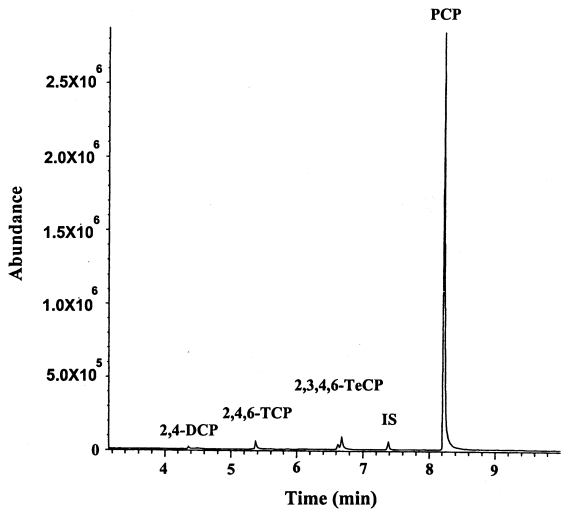

Fig. 1. Mass ion chromatogram (TIC) of a real soil sample.

method. This may possibly contribute to the chlorophenols absorbed in the soil particle. However, the extraction time for SPME (40 min) is less than that for Soxhlet extraction (8 h). Moreover, the method's precision is investigated by performing eight extractions from soil samples which contaminated with chlorophenols. The R.S.D.s ranged from 5 to 9% for all target compounds are obtained. The results demonstrate suitability of the SPME–GC–MS approach to the analysis of trace chlorophenols in soil samples.

4. Conclusion

This study evaluated SPME combined with GC–MS for determining the chlorophenols in landfill leachate and soil samples. The method is precise and can be used over a wide linear range. Detection limits ng/l level of chlorophenols in water are achieved and are better than those reported by the EPA using conventional methods. Matrix conditions affect the sensitivity of detection. The humic acids and a surfactant affect the extraction efficiency. The matrix not only hamper the diffusion of the chlorophenols to the coating, but also inhibit the absorption of chlorophenols onto the fiber. These effects could be compensated by the extension of the extraction time. This technique is also used to determine chlorophenols in real samples including a landfill leachate sample and soil samples. The studied chlorophenols except PCP (21.6 μg/l) are in the level of 0.1 μg/l in the landfill leachate sample. PCP, 2,4-DCP, 2,4,6-TCP and 2,3,4,6-TeCP are determined in contaminated soil. The technique offers a low level sensitivity to trace determination of chlorophenols in landfill leachate and soil samples containing high amounts of interferences.

Acknowledgements

The authors would like to thank the National Science Council of Taiwan for financially supporting this work under Contract No. NSC 85-2113-M-005-013. The authors express their appreciation to Professor Chin-Jen Lu and Mr. Chang-Yu Chen in Department of Environmental Engineering for TOC analysis.

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Table 5
Comparison of SPME and Soxhlet extraction methods for detection of chlorophenols in soil samples

Compound	SPME method (μg/g)		Soxhlet extraction method (μg/g)
	Internal standard	Standard addition	
2-CP	ND[a]	ND	ND
2,4-DCP	0.9	1.9	2.0
2,4,6-TCP	2.4	3.7	4.4
2,3,4,6-TeCP	7.6	8.4	12.8
PCP	533.8	562.2	642.4

[a] ND: Not detected.

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