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Application Note

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Claristep® Filtration Assembly – A Novel Sample Preparation Method suitable for the Analytics of Phthalates in Solid Environmental Samples

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Abstract

The filtration clean-up of particle laden environmental samples for phthalates analytics is a common step in sample preparation prior to GC-MS. Here, we demonstrate that Claristep® syringeless filtration units 0.45 µm and 0.2 µm are suitable for the filtration clean-up of phthalate samples. A mix of eight phthalates and one adipate was filtered at a concentration of 10 µg/mL with neither detectable adsorption nor releasing of these compounds from the filter unit. Furthermore, it was shown by GC-MS screening that no detectable compounds were extracted.

Introduction

Phthalates are used as softeners by the plastic industry on a large scale, especially for the production of plasticized PVC materials. Due to their toxic nature and their loose binding to the plastic polymer, phthalates are a hazard to both human health and the environment if released into ecosystems through waste water and garbage.

In order to analyze phthalates as well as organic contaminants in solid environmental samples like sewage sludge, sediments, waste, and soil an extraction step with an organic solvent is necessary. For analytical accessibility of mostly dark colored and strong opaque extracts a clean-up step and | or a filtration step is usually performed. Usually filtration of organic extracts is carried out with glass filter units equipped with a cellulose nitrate filter to avoid organic contaminations which would interfere with the analytical measurement data. In this study, the suitability of Claristep® Filtration assemblies as an alternative to the glass filtration units was tested for phthalates analytics.

The Claristep® Filtration unit is composed of the polyolefin plastic material polypropylene with the filter membrane material regenerated cellulose. To investigate the interaction of these materials with organic contaminants phthalates where chosen as a model class for organic contaminants found e.g. in sludge. For this purpose, the recovery rates of selected phthalates in ethyl acetate extracts (filtrated versus non-filtrated) were determined and compared. The analysis was performed according to DIN 19742:2014-08: "Soil quality - Determination of selected phthalates in sludge, sediment, solid waste and soil after extraction and determination using gas chromatography mass spectrometry (GC-MS)" and the respective results can be used as representatives for applications also utilizing other organic analytical methods. Furthermore, a GC-MS screening of potential interferences originating from Claristep® Filtration assemblies was obtained.

Figure 1: The Claristep® filtration system comprises a filter station and filter units. The station consist of a base, a lid and an exchangeable tray. The filter units are made of polypropylene and a regenerated cellulose membrane.

Materials and Methods

Solvent ethyl acetate (p. A.) as well as the internal standard (ISTD) 2-fluorobiphenyl (analytical standard) were purchased from Sigma-Aldrich. Phthalates were obtained from Neochema as a mix and single substances. Two different Sartorius Claristep® Filter types differentiated in their pore sizes were used. These were: Claristep® 0.45 µm (17C06FT---96), Lot: 60292103 and Claristep® 0.20 µm (17C07FT---96), Lot: 60208103. The GC MS measurements were carried out with a PerkinElmer Clarus 600GC coupled to a PerkinElmer Clarus 600T MS Turbo. The GC oven was equipped with a PerkinElmer Elite 5MS in the dimension: 60 m × 0.25 mm × 0.25 µm with Helium as carrier gas. The injector program initiated with 75 °C for 0.1 min and heated up to 250 °C (200 °C/min) for 10 min. The injection was done splitless and 1 µL sample volume was injected. The following thermal program was performed: 35 °C (0.1 min) to 300 °C (15 °C/min) hold 30 min. Both the transfer line and the MS source were tempered of 250 °C. The mass spectrometer operated in full scan mode in the scan range of 35–600 m/z.

A stock solution in ethyl acetate containing eight phthalates and one adipate as analytes (shown in table 1) and the internal standard (ISTD) in the concentration of 10 µg/mL was prepared. Aliquots of approximately 0.5 mL of the stock solution were filtered through two different Claristep® Filtration assemblies with pore sizes of 0.2 and 0.45 µm.

The filtrates were collected directly in GC-MS vials placed in the Claristep® filtration assembly. Vials were closed with a PTFE | siloxane cap and, subsequently analyzed by gas chromatography and mass spectrometry (GC-MS). This preparation and measurement procedure will additionally provide an overview of potential compounds extracted from the Claristep® Filters. The chromatograms of the filtrated aliquots were compared with chromatograms of the non-filtrated stock solution directly injected into the GC-MS system. Two determinations were performed for every test. For full scan mode the limit of quantification (LOQ) is 1 µg/mL. The ISTD was used as injection standard.

Results and Discussion

The results are shown in Table 1. The standard uncertainty of measurements was determined according to EURACHEM | CITAC Guide CG 4 (Third Edition). The Recovery rates in percentage were calculated by the ratio of the response of the analytes in the non-filtrated samples to the filtrates.

The concentration of the filtrated stock solution of 10 µg/mL was recovered in ranges from 98 to 103 % which is within the standard uncertainty of measurement. These results indicate that neither of the added phthalates and adipate were retained nor released from the Claristep® Filters as a extractable compound.

RT	Compound Name	CAS	Relative Uncertainty of measurements in percent (k=2)	Recovery Rates of Claristep® 0.2 µm in percent	Recovery Rates of Claristep® 0.45 µm in percent
13.31	Dimethyl phthalate (DMP)	131-11-3	18.76	101.75	102.94
14.43	Diethyl phthalate (DEP)	84-66-2	11.79	99.20	100.79
15.76	Di-n-propyl phthalate (DPP)	131-16-8	14.03	100.13	100.40
17.04	Di-n-butylphthalat (DBP)	84-74-2	13.07	99.14	100.76
17.26	Bis (2-methoxyethyl) phthalate	117-82-8	12.16	102.21	100.72
19.62	Benzyl butyl phthalate (BBP)	85-68-7	25.54	98.25	99.73
19.66	Bis (2-ethylhexyl) adipate	103-23-1	23.45	99.28	100.34
20.78	Bis (2-ethylhexyl) phthalat (DEHP)	117-81-7	12.62	98.17	102.57
20.98	Dicyclohexyl phthalate	84-61-7	14.55	100.41	102.03

Table 1: Recovery rates of selected compounds filtered by Claristep® units with pore sizes of 0.2 µm and 0.45 µm. Compounds are assigned according to their retention time.

For GC-MS scanning analysis the concentration of 10 µg/mL is adequate, since the full scans of mass to charge ratios provide lower resolution and, therefore, higher LOQs (Limit Of Quantification) are obtained compared to the single ion mode (SIM) used in the DIN 19742:2014-08. The full scan mode used in this study additionally allows screening for potential phthalates as extractables from the Claristep® Filters. In Figure 1, the chromatograms of filtered and non-filtered samples are exemplarily shown for Claristep® 0.45 µm. Since the scans of 0.45 µm and 0.2 µm were identical, and a pore size of 0.45 µm is more relevant for environmental analytics, only data obtained with Claristep® 0.45 µm is shown.

The main objective of this part of the investigation was to screen if any interfering compounds could be extracted from the utilized Claristep® filter. In a first approximation and in accordance to the DIN 32645:2008-11 and ISO 11843-7 the signal to noise ratio of 3:1 approximates the limit of detection. In this regard, it could be shown that no compound above this limit was detectable in the chromatograms shown below. For example, the highest signals of unknown compounds (peaks at the retention time of 13.41 min and at 15.1 min) had a signal to noise ratio of 2.9:1. Taking that into account, it can be concluded that the observed peaks responses to noise and not to interfering compounds.

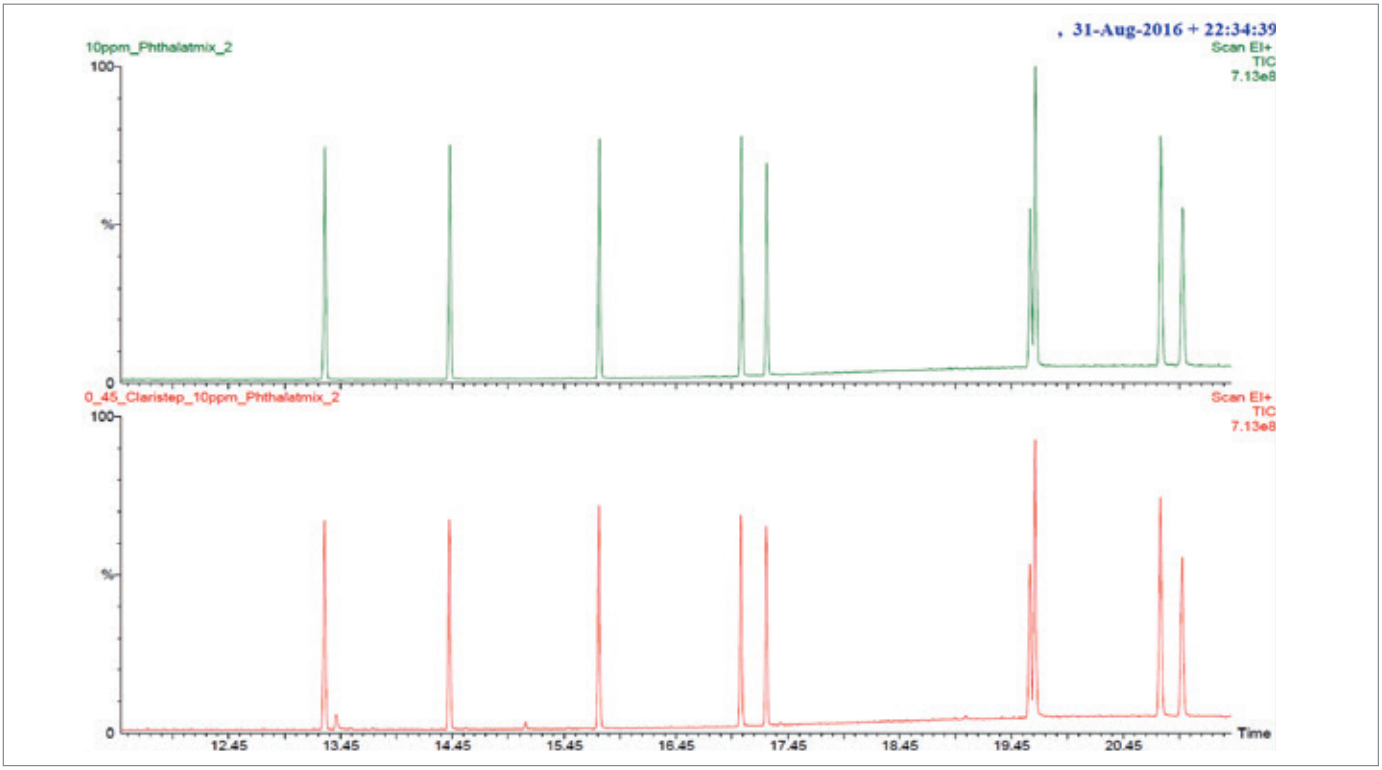

Figure 2: Full screen chromatograms for the selected phthalates and adipates of non-filtrated (green) and filtrated (red) samples with Claristep® Filter 0.45 µm. The assignment of the peaks according to their Retention time (RT) is shown in Table 1.

Conclusion

In the current study Claristep® Filters were tested in their adsorptive behavior of phthalates as analytes which should be an indication of their behavior towards other organic contaminants as well. GC-MS screening was used to identify potential extractables of the Filter assemblies. Phthalates and adipates, which have the high detectable interaction with the Filters compared to other organic compounds, are neither retained nor released during filtration of an ethyl acetate solution.

Moreover, the screening analysis indicates that no other detectable compound was extracted from the Claristep® Filters. Thus it can be concluded, that using ethyl acetate as solvent causes minimal until non-existent interferences with the filter (material).

This result concludes that Claristep® Filtration assemblies are suitable for preparation of samples for phthalate analysis according to DIN 19742:2014-08 and thus also for other organic analytes of similar solubility. The great advantage of the Claristep® Filtration assemblies compared to the classic glass filter unit is that eight samples can be prepared simultaneously. This method reduces the costs of analysis as minimal hands on time is required.

References

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