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Rapid, one-pot derivatization and distillation of chlorophenols from solid samples with their on-line enrichment

R. Ganeshjeevan *, Raghavan Chandrasekar, Parasuraman Kadigachalam, Ganga Radhakrishnan

Eco Analytical Laboratory, Central Leather Research Institute, Chennai, India

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Abstract

A microwave-assisted steam distillation (MASD) sample preparation technique for extracting chlorophenols from solid samples was studied. This open vessel microwave system based study developed as an integrated method since it has incorporated extractive distillation, derivatization and on-line enrichment. Gas chromatography (GC) with electron-capture detection was used for the analysis. The study involved optimization of MASD parameters and on-line enrichments using spiked solid samples. MASD achieved recoveries for spiked soil samples in the range of 94–101% within 20 min with a collection of only 20 ml distillate facilitating on-line enrichment. Some real samples were analyzed that included soil, wood, leather, textiles, dyes and certified reference materials of soil and wood samples. Limit of detection values of 12 ng/g for pentachlorophenol and 194 ng/g for monochlorophenol were found. Recoveries of 96.6% in the case of soil certified reference material (CRM) with RSD 2.7% and 80.6% in the case of wood CRM with RSD 3.3% were observed in this study. MASD studied found to produce very clean extracts in comparison to reference techniques.

Keywords: Microwave-assisted steam distillation; Integrated microwave sample preparation; Chlorophenols; SPE; On-line enrichment

1. Introduction

The demand for very clean matrices of the samples is rising in particular for the growing sophisticated instrumental techniques targeted mainly for high resolution and sensitivity. The cleaner samples facilitate this by producing simplified instrumental output. Distillation techniques normally offer reasonably pure sample extracts [1]. There were many methods reported in recent times based on microwave-assisted steam distillation (MASD) for example Conte et al. [2] has developed a quick and effective detection of off-flavor compounds like geosmin, methyl isoborneol from fish samples; Grimm et al. [3], Lloyd and Grimm [4] and Zhu et al. [5] for the analysis of the same compounds from fish samples. Interestingly all these studies included on-line enrichments through solid-phase microextraction (SPME) except that of Conte et al. [6] who followed a solid-phase extraction (SPE) absorbent for trapping the analytes. For detecting the same analytes Grimm et al. [7] used an open vessel MASD followed by an off-line SPME enrichment. A recent publication for the extraction of PCBs and other organochloro pesticides from soil samples by MASD was reported by Numata et al. [8] who claimed that MASD achieved very clean matrices, and this study was also done by pressurized (sample) vessel. Similarly MASD was reported for inorganic volatile analytes [9–11]. MASD can be done by both open and closed sample vessels. Open vessel MASD is generally preferred from safety consideration. In the present study, focused (open vessel) microwave system has been employed for extractive distillation of chlorophenols mainly for pentachlorophenol (PCP) as is a well reported carcinogenic compound [12–14] from some solid samples that included the environmental matrices like soil and the consumer products like leather, textile, etc. Earlier, MASD with simultaneous liquid–liquid extraction (LLE) of PCP in organic waste and soils was reported by During et al. [15] that involved a pressurized vessel and also the derivatization was done off-line. In that work, the distillate was not separated during the distillation rather it was allowed to mix with a floating solvent in the original vessel. When chromatographic analysis of chlorophenols are done especially by gas chromatography (GC), they are derivatized that is widely by an acetyl derivatization, which also improves their non-polar character and hence better distillability. The acetate derivati-

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* Corresponding author. Tel.: +91 44 24430268; fax: +91 44 24430267.
E-mail address: clriexcel@yahoo.com (R. Ganeshjeevan).

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zation incorporated microwave-assisted extraction (MAE) for chlorophenols from fly ash samples was reported earlier by Criado et al. [16]. But that work involved pressurized microwave vessel and also did not include any on-line enrichment.

In conventional steam distillation (SD), for most of the analytes the distillation volumes are too high for exhaustive recoveries, which complicate the subsequent concentration steps like SPE as some analytes especially polar analytes have low break-through volumes. In general, a sample preparation involves extraction, purification, and in some cases also derivatization and these steps take place at multiple stages consuming time. When an integrated sample preparation approach becomes available all these steps can be effected in a single or fewer that would save time and also minimize transfer loss of analytes. The proposed MASD technique offered cleaner extract as many non-volatiles are cut off and minimized distillate that facilitated on-line enrichment and hence served as a one-step approach. The inclusion of even derivatization with distillation of chlorophenols before their on-line SPE enrichment made this approach an integrated sample preparation by this study. The MASD reported were all very quick with 1–15 min claims [2–7] in comparison to SD that took 60–150 min to achieve comparable recoveries and this MASD study also ensured the time advantage. With regard to PCP distillation, SD generated large distillate volume of over 300 ml while MASD did only a few milliliters (10–20 ml) for exhaustive recoveries. SD and SPE are two different modes of clean up that are made available for samples. Solvent minimized sample preparations are of growing importance and MASD could support for the same by evolving as an eco-friendly technique.

2. Experimental

2.1. Reagents

Chemicals like potassium carbonate, acetone, acetic anhydride, anhydrous sodium sulphate and triethylamine, used in this study were of analytical grade and HPLC-grade solvents of acetone and hexane were procured from Merck (India), Mumbai, India. Certified reference compounds of individual chlorophenols comprising 2-MCP, 3-MCP, 4-MCP (MCP = monochlorophenol); 3,5-DCP, 2,4-DCP, 2,6-DCP, 3,4-DCP, 2,5-DCP (DCP = dichlorophenol); 2,4,6-TCP, 2,3,5-TCP, 2,4,5-TCP, 2,3,6-TCP, 3,4,5-TCP, 2,3,4-TCP (TCP = trichlorophenol); 2,3,4,6-TeCP, 2,3,5,6-TeCP, 2,3,4,5-TeCP (TeCP = tetrachlorophenol); and pentachlorophenol (PCP), Supelco ENVI-18 and Supelclean LC-18 SPE materials were procured from Supelco (Bellefonte, PA, USA). Water of HPLC-grade purity was prepared using Milli-Q, model of Millipore (Bedford, MA, USA). Certified reference materials of soil (ERM-CC009) sample was arranged from Bundesanstalt für Materialforschung (BAM), Berlin, Germany and Beech wood (BCR-683) was arranged from Institute of Reference Materials and Measurements (IRMM), Retieseweg, Geel, Belgium.

A stock solution of a mixture of chlorophenols at 1000 mg/l of individual concentration was prepared using acetone and from this, working standard solutions were prepared freshly whenever required. The working standards were prepared for GC in the range 0.01–1.00 μg/ml using *n*-hexane, HPLC grade.

2.2. Equipment

The microwave system used for this study is an open vessel microwave system also known as focused microwave (FMW) system; model Soxwave 100 along with a programmer for operation procured from Prolabo, Fontenay-sous-Bois, France. The programmer is useful to rotate and fix the experimental conditions of microwave (MW) power in percentage (adjustable in steps of 5 upto a maximum of 50 corresponding to 60–300 W) and time duration in minutes (in steps of 10). This model works at atmospheric pressure. The frequency of MW radiation was 2450 MHz. Borosilicate glass extraction open vessel was fitted with a solvent collector and an overhead Graham's water condenser. A Julabo cooling water circulator of model FE1800, from Seelbach, Germany was used to support water condenser.

For GC, an Autosystem XL equipped with an electron-capture detection (ECD) system and operated with a Turbo Chrome Navigator workstation was procured from Perkin–Elmer (Norwalk, CT, USA). DB-17, a mid-polar capillary column of 30 m × 0.32 mm I.D., and 0.25 μm film thickness, procured from J&W Scientific (Folsom, CA, USA) was used for GC separation.

2.3. Methods

2.3.1. Preparation of spiked samples

The soil free from all the analytes under investigation, was air-dried, pulverized and sieved to a grain size of 2 mm. A total of 25 g of soil was mixed with acetone until the sample was completely soaked to form slurry. The whole 25 g slurried soil was spiked with an appropriate volume of standard solution (chlorophenols at 1 μg individual concentrations) to achieve 1 μg/g level of analyte. The contents were mixed well for over 3 h. The bulk of the solvent was evaporated at room temperature by thorough manual shaking. The sample was left for 48 h in a fume-hood to dry out completely and aged for 1 week at room temperature. The prepared soil sample was stored in a refrigerator at 4 °C until used for analysis.

Leather sample was prepared as powder of 100–200 mesh sizes while textile and paper samples were done as finely cut (ca. 1–2 mm^2) pieces. The dye samples preparation involved just breaking down any lumps if present. Spiking of leather, textile samples was done by using 1 ml of standard solution of the analytes (at 1 μg/ml), by adding the standards directly to the 1 g weighed sample and allowed to dry in air overnight. Similar spiking preparations of chlorophenols to the other samples were done.

2.3.2. Volume of water added to the samples

It was observed that for samples of swelling nature like leather and textiles, water volume of 15 ml was necessary for sample weights up to 2 g and 25–30 ml was found necessary for weights up to 5 g. Hence, an optimal volume of 25 ml of water was chosen for studies.