



On-line monitoring of Soxhlet extraction by chromatography and mass spectrometry to reveal temporal extract profiles



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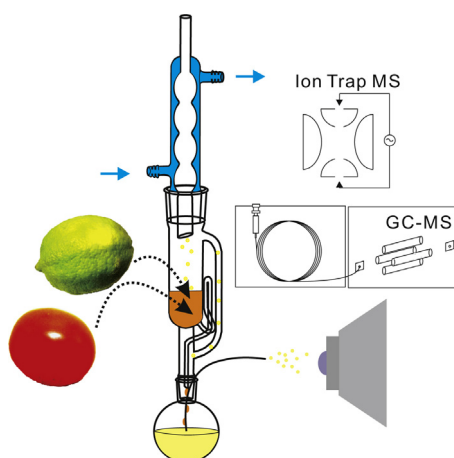
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HIGHLIGHTS

- Soxhlet extraction is coupled on-line with chromatography and mass spectrometry.
- Dynamic extract profiles are recorded in real time.
- Soxhlet extraction of selected metabolites from real samples is characterized.
- Mathematical models are applied to the real-time extraction data.

GRAPHICAL ABSTRACT



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ABSTRACT

Soxhlet extraction is a popular sample preparation technique used in chemical analysis. It enables liberation of molecules embedded in complex matrices (for example, plant tissues, foodstuffs). In most protocols, samples are analyzed after the extraction process is complete. However, in order to optimize extraction conditions and enable comparisons between different types of extraction, it would be desirable to monitor it in real time. The main development of this work is the design and construction of the interface between Soxhlet extractor and GC–MS as well as ESI–MS system. The temporal extract profiles, obtained in the course of real-time GC–MS monitoring, have been fitted with mathematical functions to analyze extraction kinetics of different analytes. For example, the mass transfer coefficients of pinene, limonene and terpinene in lemon sample, estimated using the first-order kinetic model, are 0.540 h^{-1} , 0.507 h^{-1} and 0.722 h^{-1} , respectively. On the other hand, the Peleg model provides the following extraction rates of pinene, limonene and terpinene: 0.370 nM h^{-1} , 0.216 nM h^{-1} and 0.596 nM h^{-1} , respectively. The results suggest that both first-order kinetic and Peleg equations can be used to describe the progress of Soxhlet extraction. On-line monitoring of Soxhlet extraction reveals extractability of various analytes present in natural samples (plant tissue), and can potentially facilitate optimization of the extraction process.

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1. Introduction

Extraction is a sample preparation step commonly used in analytical chemistry. It enables the release of analyte molecules which are trapped within structures of complex samples [1]. It can also improve analytical selectivity. The available extraction methods can be classified according to the nature of the sample and extractant phases. The most common extraction modes include solid–liquid extraction [2–4] and liquid–liquid extraction [5,6]. Soxhlet extraction is one of the well-established and widely used extraction methods [7,8]. The Soxhlet extractor was invented by Franz Ritter von Soxhlet in 1879 [9]. It provides an efficient route for liberating analytes trapped in complex samples without excessive mechanization and manual effort. Its first application targeted lipids present in milk [10]. The range of its current applications is extensive. Unlike other methods, Soxhlet extraction enables thorough leaching of compounds embedded in complex matrices with freshly distilled aliquots of solvent. In general, the Soxhlet extraction process encompasses the following steps (cf. [8]):

- (i) vaporization of the extraction solvent,
- (ii) condensation of solvent vapors,
- (iii) leaching analyte molecules from the sample by the condensed solvent,
- (iv) accumulation of extract in the siphon (side channel of the extractor manifold),
- (v) movement of the extract plug downwards to the solvent flasks,
- (vi) repetition of steps (i)–(v).

When a non-polar extraction solvent is used, following several extraction steps, less polar components are released from the sample and mixed with the extraction solvent. Apart from the conventional Soxhlet extraction, other variants of this classical method are available, including: high-pressure Soxhlet extraction, automated Soxhlet extraction [11], ultrasound-assisted Soxhlet extraction [12] and microwave-assisted Soxhlet extraction [13–15].

While Soxhlet extraction has a long history and is widely used, most studies utilizing this technique involve collection of final extracts for further processing [16–20], or comparison with other sample preparation techniques, for example, microwave-assisted extraction [21,22], super fluidic extraction [23–26], and accelerated extraction [27,28]. Although Soxhlet extraction is commonly used to investigate complex materials [29–31], it is a time-consuming step. For example, Soxhlet extraction of acrylamide from potato chips was accomplished within several days [32] while extraction of phenolic compounds from plant tissue (*Potentilla atrosanguinea*) samples took several hours [33]. If one could estimate the time required for liberation of target analytes from a given sample, in a semi-automated manner, it might be possible to shorten the total time of the extraction procedure, increasing the efficacy of the whole analytical process.

The initial samples loaded to the extractor are not completely homogeneous. Thus, one may expect that different compounds, embedded in the sample, may be liberated with different yields, and that their “extractability” could change in the course of the extraction process. Only few reports discuss the processes occurring inside the Soxhlet apparatus during extraction. The Soxhlet extraction of linear alkylbenzene sulfonates from sediment samples was monitored using an on-line flow-injection preconcentration/derivatization/detection manifold [34]. The release of polycyclic aromatic hydrocarbons from solid samples was monitored on-line by fluorescence detection [35]. In other work, physical effects of the Soxhlet extraction of microalgae were verified by means of microscopy [36]. Following concentrations of

the extracted molecules in real time can certainly facilitate characterization of the extraction process. Previously, we used on-line chromatographic and mass spectrometric techniques to monitor the progress of solid–liquid extractions [37,38]. In this study, we aimed to develop and test methods for on-line monitoring of Soxhlet extraction, which could enable kinetic characterization of the extraction process. To achieve this goal, we implemented two different experimental approaches: (i) real-time sampling gas chromatography (GC) hyphenated with mass spectrometry (MS), and (ii) real-time sampling electrospray ionization (ESI)-MS. Real-time analysis is advantageous because it can provide immediate information on the progress of extraction, mitigating the inconvenience of sample collection, sample storage, and reducing the risk of sample decomposition or contamination. GC–MS analysis targets volatile compounds. It enables identification and quantification of non-polar analytes. On the other hand, ESI-MS can readily detect ionisable polar compounds. It is particularly suitable for analysis of liquid samples delivered at atmospheric pressure. Thus, it is occasionally coupled with liquid-phase sample preparation devices. While GC–MS can enable on-line quantitative analysis of dynamic samples obtained from the Soxhlet extraction, the ESI-MS approach, implemented here, does not include a separation stage, which makes it less suitable for quantitative analyses. Using these two platforms, we intended to unravel the temporal characteristics of Soxhlet extraction, which could further be described by mathematical models, thus enabling future comparisons of different modes of extraction.

2. Materials and methods

2.1. Chemicals and samples

Isopropanol (analysis grade), methanol (LC grade), water (LC grade), caffeine, thymol, *D*-limonene, β -pinene and γ -terpinene were all purchased from Sigma–Aldrich (St. Louis, Missouri, USA). The model samples used in this study were sections of lemon (*Citrus limon*; $\emptyset \approx 5$ cm) fruit (175, 215 and 240 mg, in the case of on-line GC–MS; 43, 53 and 67 mg, in the case of on-line ESI-MS) and cherry tomato (*Solanum lycopersicum*; $\emptyset \approx 2$ cm) fruit (72, 78 mg, in the case of on-line ESI-MS). The raw material was purchased in a local supermarket (“Welcome Market”, Hsinchu, Taiwan). The samples used in the extraction experiments were stored in the freezer (4 °C) and sectioned by scissors right before the extraction. They contained both peel and flesh of the fruit.

2.2. On-line gas chromatography coupled with mass spectrometry

A standard Soxhlet extractor (125 mL, 20-cm; YSC, Hsinchu, Taiwan) was fitted with a 30-cm bubble condenser, and a 250-mL spherical flask dipped into silicone oil bath positioned on a hot plate (C-MAG HS 7 Digital; IKA, Königswinter, Germany) set to 120 °C. An aliquot of 100 mL of isopropanol was filled into the spherical flask. The Soxhlet extractor manifold was filled with glass wool. The sample was placed in the middle of the glass wool plug.

In order to monitor changes in the composition of sample extract during the Soxhlet extraction of lemon samples, first we implemented an on-line GC–MS method. It takes advantage of the on-line sampling system assembled previously in our laboratory [38]. Briefly, the sample is aspirated from the sample chamber with aid of peristaltic pump, and directed toward the inlet port of the GC apparatus. Two pinch valves (12 V DC, P/N 075P2NO12-01S and P/N 075P2NC12-01S; Bio-Chem Fluidics, Boonton, NJ, USA) enable metering small volumes of the sample aliquots. In the current (modified) setup (Fig. 1), we inserted a 14-cm section of fused silica

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