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Kinetic study of continuous liquid-liquid extraction of wine with real-time detection

Hui-Hsien Yang^{a, b}, Ewelina P. Dutkiewicz^a, Pawel L. Urban^{b, c, *}

^a Department of Applied Chemistry, National Chiao Tung University, 1001 University Rd., Hsinchu, 300, Taiwan

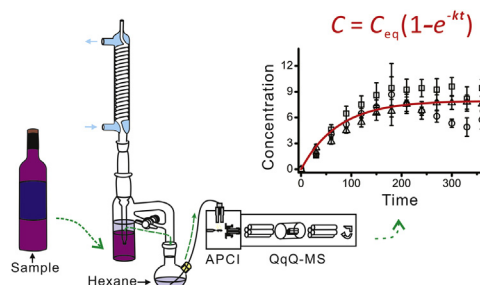
^b Department of Chemistry, National Tsing Hua University, 101, Sec 2, Kuang-Fu Rd., Hsinchu, 30013, Taiwan

^c Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, 101, Sec 2, Kuang-Fu Rd, Hsinchu, 30013, Taiwan

HIGHLIGHTS

- Continuous liquid-liquid extraction is hyphenated on-line with mass spectrometry.
- The analysis process is automated using an Arduino-based control module.
- The recorded real-time datasets are used to characterize the extraction kinetics.
- The on-line method is applicable to analysis of volatile species in wine.
- It enables monitoring changes in wine composition after opening bottle.

GRAPHICAL ABSTRACT



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ABSTRACT

Kinetic optimization of continuous liquid-liquid extraction (CLLE) can shorten sample preparation times and reduce losses of labile or volatile analytes. Here, we coupled a downscaled CLLE apparatus with atmospheric pressure chemical ionization interface of triple quadrupole mass spectrometer. Real-time sampling was guided by an Arduino-based programmable logic controller. The recorded datasets were processed to compute the extraction rate constants for the target analytes. The extraction time in subsequent on-line experiments was set to 180 min as a compromise between the reduction of the analysis time and maximizing its yield. Interestingly, off-line analysis of the extract produced different results than on-line analysis pointing to the immanent degradation of the collected extract aliquots. Next, we implemented this hyphenated system in the analysis of red wine samples, which were stored during different periods of time after opening the bottle. The results reveal differences in the depletion of the volatile wine components during storage.

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1. Introduction

Among the sample preparation techniques employed by chemists, liquid-liquid extraction (LLE) occupies a prominent position. Despite its long history, it cannot be completely replaced by more modern extraction schemes. It is versatile because it can be used to extract analytes with diverse properties: volatile and non-

* Corresponding author. Department of Chemistry, National Tsing Hua University, 101, Sec 2, Kuang-Fu Rd., Hsinchu, 30013, Taiwan.

E-mail addresses: ivy5566290@gmail.com (H.-H. Yang), edutkiewicz123@gmail.com (E.P. Dutkiewicz), urban@mx.nthu.edu.tw (P.L. Urban).

volatile, polar and non-polar, ionic and non-ionic [1–3]. Selectivity of LLE can readily be adjusted by using different extracting solvents or additives. In many laboratory-scale implementations, LLE is conducted manually. Attempts were made to automate liquid-phase extractions (e.g. Refs. [4,5]) However, highly mechanized LLE systems are costly and have limited flexibility. Continuous liquid-liquid extraction (CLLE) enables self-sustained extraction of samples with immiscible solvents in the presence of a heat source [6]. Though it circumvents mechanization, it facilitates unsupervised extraction of dilute samples over extended periods of time, what is necessary when analyzing low-abundance organic compounds.

While extractions are mostly conducted off-line (e.g. Ref. [7]), it is appealing to combine this sample preparation step with on-line detection systems. Detecting the extracted analytes in real time (or with little delay) eliminates one of the steps in the analysis workflow – minimizing the risk of extract degradation and reducing the manual operation burden [5,8–12]. Moreover, as shown for Soxhlet extraction [10], coupling extractions with on-line detection systems provides the data necessary for kinetic characterization of the extraction process. Obtaining kinetic information on the extraction of the target analytes from any sample of interest is useful because it enables rapid optimization of the sample preparation procedure. Extraction rates and yields may be affected by the type of sample matrix, extracting solvent, their volumes, as well as the geometry of the extraction chamber, and the temperature. Monitoring the extraction of a test sample in real time can provide sufficient number of data points to compute kinetic parameters based on one of the available extraction models. These values can later be used to select the optimum extraction times for further analyses. That advantage is important because too short extraction times lead to low extraction yields while too long extractions cause analyte losses (e.g. due to evaporation, adsorption, or degradation).

The self-sustained CLLE combines extraction with distillation. Thus, unlike in the conventional LLE methods, the same sample aliquot is constantly exposed to a flux of pure solvent that extracts the residual analytes even after an equilibrium condition is established in the previous step. However, CLLE requires the supply of thermal energy. We hypothesized that heating the extracting solvent during CLLE may contribute to analyte losses. Therefore, it is important to transfer the extract to the detector as quickly as possible to prevent extract degradation. The ultimate reduction in the time gap between the extraction and detection steps would be seen if the extraction and detection steps were combined. This goal can be achieved by hyphenating the extraction apparatus with the detector. Moreover, the extraction time should be carefully optimized by taking into account the temporal concentration profile of the extract. This kind of optimization would be straightforward if the analyte concentrations in the extract could be monitored over time. Mass spectrometry (MS) has broadly been utilized to perform temporal characterization of dynamic processes (e.g. Ref. [13]; for reviews, see [14,15]), and—due to its high selectivity—it is also the first choice for real-time monitoring of CLLE.

In order to verify the above hypothesis, we assembled a simple sampling and sample transfer system for real-time monitoring of liquid extracts and temporal characterization of the CLLE process. This system integrates an Arduino-based programmable logic controller (PLC). The liquid extracts are automatically fed to the atmospheric pressure chemical ionization (APCI) inlet of a triple quadrupole (Q/Q) mass spectrometer. The entire analysis process occurs without the intervention of the analyst. The recorded temporal datasets are subsequently treated to obtain the extraction rate constants for the target analytes.

2. Materials and methods

2.1. Materials

Ethanol (GC grade), water (LC grade), ethyl acetate, ethyl hexanoate, ethyl 3-hydroxyhexanoate, ethyl octanoate, ethyl butyrate, and ethyl 2-methylbutyrate were all purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethyl propionate, ethyl phenylacetate, and diethyl succinate were purchased from Alfa Aesar (Heysam, UK). Ethyl 3-phenylpropionate and ethyl lactate were purchased from TCI Chemicals (Chennai, India). Hexane (LC or GC grade; extraction liquid) was purchased from Merck (Darmstadt, Germany). Isotopically labeled diethyl succinate (1,2,3,4- $^{13}\text{C}_4$; isotopic enrichment: 99%; chemical purity: $\geq 98\%$) was purchased from Cambridge Isotope Laboratories (Andover, USA), and used as internal standard. In this study, the extraction techniques were tested on samples of a selected (undisclosed) brand of Spanish red wine (Syrah/Garnacha grapes) from 2011, with the alcohol content of 13.5% (vol.), purchased in a local supermarket (Hsinchu, Taiwan). The samples were normally collected within one week from opening the bottles, which were refrigerated (4 °C), except for the study of storage time, in which case the previously opened bottles were stored for ~7 months.

2.2. Miniature continuous liquid-liquid extraction system

In this study, we downscaled the CLLE apparatus and coupled it on-line with MS to enable analysis of the extracted compounds in real time (Fig. 1A). The miniature CLLE system with distillation stage was fabricated by the glass blowing workshop in the National Tsing Hua University (Hsinchu, Taiwan). The system was designed for extracting solvents lighter than the sample matrix (condenser output tube was dipped in the sample). The nominal volume of the extracting solvent spherical flask was 100 mL. It was filled with 30 mL of hexane. The typical volume of the aqueous sample was 47 mL (~10 × smaller than in a typical commercial CLLE apparatus). The extracting solvent flask was dipped in silicone oil bath placed on a hot plate (temperature setting: 90 °C; MR Hei-Tec; Heidolph, Schwabach, Germany). When hexane was boiling, it condensed and dripped into the sample reservoir through a coaxial glass tube. Hexane layer accumulated in the upper part of the sample reservoir. The excess of hexane extract drained to the solvent flask in the course of the extraction process through a side channel of the sample reservoir. To enable the flow of the extract to the solvent flask, the valve on that channel was open during the entire extraction process.

2.3. Real-time mass spectrometry

The extraction apparatus was coupled with the DUIS ion source of a triple quadrupole mass spectrometer (LCMS-8030; Shimadzu, Tokyo, Japan) via tubing: 70-cm fused silica capillary (I.D. 0.05 mm, O.D. 0.375 mm); 18-cm Fluran tubing (I.D. 0.51 mm, O.D. 0.91 mm); 80-cm fused silica capillary (I.D. 0.05 mm, O.D. 0.375 mm); and 3-cm polytetrafluoroethylene (PTFE) tubing (I.D. 0.3 mm, O.D. 1.58 mm). The DUIS ion source was set to APCI mode. The voltage applied to the APCI needle was 4.5 kV. The temperature of the heated block was set to 400 °C, while the temperature of the desolvation line was set to 250 °C. The drying gas (nitrogen) flow and the nebulizing gas (nitrogen) flow rates were set to 10 L min⁻¹ and 1.5 L min⁻¹, respectively. In most experiments, the mass spectrometer was operated in the positive-ion Q3 scan and multiple reaction monitoring (MRM) modes. The collision gas was argon. Its pressure was set to 230 kPa. The dwell time of each MRM transition was 25 ms. The collision voltages were optimized individually for every compound (from -30 to -10 V). The total loop time for Q3

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