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Single-drop microextraction followed by in-drop derivatization for the analysis of organic compounds by gas chromatography

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Abstract

Microextraction has become a buzz word in the recent years in the scientific area of analytical chemistry. Over the last decade, newer miniaturised approaches to liquid extraction have emerged, resulting in solvent and sample savings and less time consuming analysis. Single-drop microextraction (SDME) has been developed as a viable and easy-to-use method based on the partitioning between sample matrix and organic droplet phase. However, there are numerous examples where analytical derivatizations are required to enhance sensitivity, selectivity, extraction efficiency and overall quality of the data. Improvements resulting from derivatization in instrumental methods are well known. The absence of data in chemical reaction accompanied by mass-transfer in liquid-liquid and gas-liquid microextraction, calls for a meticulous treatment of SDME in-drop derivatization for the purpose of analytical implementation. Leveraging the inherent characteristics of an organic microdrop as a tiny reactor, a threefold aim is set out in order: **I.** to develop a theoretical approximation to the in-drop derivatization SDME using phenolic compounds for liquid-liquid and two aldehydes for gas-liquid, as model compounds, **II.** to gauge the significance of mass-transfer and chemical reaction in an organic drop viewed as an analytical reactor and **III**. to underscore the importance of the *a priori* knowledge of the characteristics of such a system related to its analytical aspects.

Keywords**:** *single-drop microextraction, derivatization, gas chromatography*

Introduction

Microextraction has become one of the dominant trends in analytical chemistry. By definition, "microextraction" is an extraction technique where the volume of the extracting phase is very small in relation to the volume of the sample. In microextraction, extraction yields hinge on the partitioning (or more strictly on the partitioning coefficient) of analyte(s) between the sample bulk phase and the extraction deprived-phase. The higher the affinity the analyte has for the extraction phase relative to the sample matrix, the greater the amount of analyte extracted. One of the major features of microextraction is that extraction of analytes is not exhaustive; therefore, only a fraction of the initial analyte is extracted for analysis. Since partitioning is not dependent on analyte concentration, quantification of sample concentration may be done from the absolute amount extracted. Once sufficient extraction time has elapsed for the equilibrium to be established, further increases in extraction time do not affect the amount of analyte extracted. Therefore, extraction technique is simplified and precision is improved.

When used in combination with state-of-the-art analytical systems, microextraction can result in faster analysis, higher sample throughput, lower solvent consumption, less manpower per unit sample and improved sensitivity.

Single-drop microextraction (SDME) was introduced in 1996 and described a configuration in which a droplet of organic solvent hanging at the end of a PTFE rod or a microsyringe needle replaces the coated fiber of solid-phase microextraction [1-3].

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Two alternative microextraction modes have been described: 1. Static SDME, where the organic drop is exposed to an aqueous sample solution and the analytes are transferred to the organic drop by diffusion until thermodynamic equilibrium is attained or the extraction is stopped and 2. Dynamic SDME, which is performed between microliters of aqueous sample and microliters of extraction agent-solvent by repetitively pulling and pushing the plunger within the glass barrel of a microsyringe. Dynamic mode achieves higher enrichment factors within shorter extraction time but relatively poorer precision.

Major challenge in the utilization of SDME in chromatographic analysis is the proper selection of optimized extraction conditions. Therefore, researchers can opt for strategies between the classical and the more elaborated mathematically-supported ones. Method-development strategies usually discount analytical derivatization because of additional steps, excess of reagent and the concomitant potential for interferences. However, numerous examples require analytical derivatizations to enhance sensitivity, selectivity, extraction efficiency and overall quality of the data. The development of automated - miniaturized techniques in connection with the measuring analytical devices at hand, demonstrated that concerns (e.g. extra steps and time requirements) are not an issue.

Results and Discussion

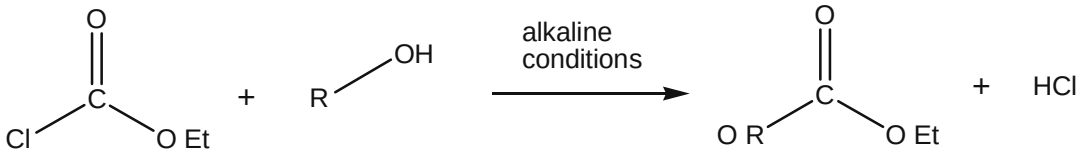
In-drop derivatization single-drop microextraction assisted by ion- pairing transfer

In microextraction between phases and derivatization, mass transfer and chemical reaction are to be contemplated. In a two-phase system (aqueous-organic), either of the phases can be dispersed into the other in droplet size, by agitation. Contact area of two phases can be increased with higher agitation rate. In SDME, the organic droplet macroscopically can be regarded as the dispersed phase. The single drop is viewed as a rigid analytical system. So, from the analytical and theoretical point of view, it is important to quantitatively describe the diffusion-reaction behaviour in a single dispersed drop which bears a reactive species, in order to assess the overall performance.

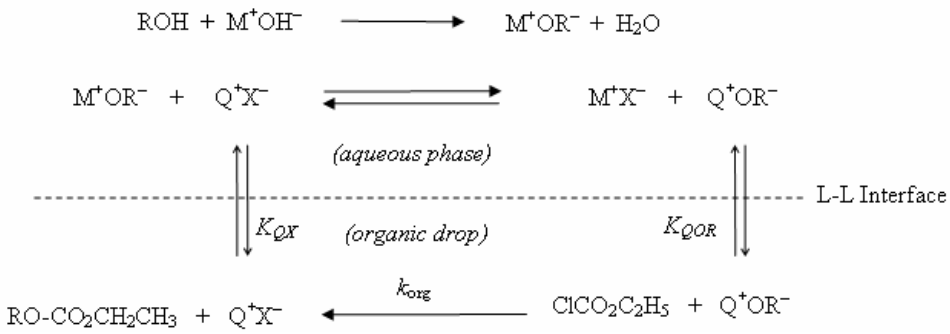
The theory of mass transfer accompanied by chemical reaction in multiphase systems has been described [4]. The two-film model classifies these reactions into four regimes on the basis of a:

1. very slow reaction in bulk organic phase,
2. slow reaction in bulk organic phase but no reaction in the organic phase film,
3. fast reaction in the organic phase film, and
4. instantaneous reaction of reactants diffusing at a reaction plane in organic phase film

The theory suggests that the mass-transfer is prominent in the regimes 2 and 4, and thus the rate of agitation plays a dominant role. To study the role of the mass transfer and chemical reaction in a single organic drop, the following derivatization reaction was implemented and the product formed was monitored by gas chromatography.



In addition, an ion-pairing agent was necessary for the liquid-liquid ion-pair transfer-substitution reaction to occur according to the schematic diagram bellow [5]:



Fast agitation can increase the rate of derivatization through increasing the mass-transfer rate of phenolates to the droplet. Therefore, a diffusion-limited reaction instead of a kinetically-controlled one is to be elaborated.

Initial rates of derivatization increase marginally with increasing temperature from 20 to 35 °C. That is, the process might not be free from mass-transfer effects.

In addition, the energy of activation (*E*a) values (1.2-3.1 kcal/mol) signifies that mass-transfer limitations are present. The pronounced effect of the rate of agitation, the trivial impact of temperature on the conversions and initial rates and the low activation energies advocate reactions involving a mass-transfer effect.

Therefore, the reactions are realised in the organic drop and might be in regime 2 (slow reaction) or regime 4 (instantaneous reaction) relying on the theory of mass transfer with chemical reaction. According to the theory, there should be a concentration gradient for the ion-pair in the film of the organic droplet and its concentration in the bulk reaction phase is zero.

Evaluation of headspace in-drop derivatization single-drop microextraction

Static and dynamic drops have been employed as gas sampling interfaces (tiny reactors) to collect various gases (efficient atmospheric reactors). The t*wo-film theory* assumes that on both sides next to the gas–liquid interface there are thin stagnant layers, termed *films*, through which the different components are transferred slowly by diffusion alone. The mass flux across interface is proportional to the difference between the interfacial and the bulk concentrations. The so-called 'fast reactions' are considered to be completed predominantly in the liquid film, whereas the 'slow reactions' is asserted to occur almost entirely in the bulk liquid phase. The experimental results with hexanal, formaldehyde and 1,3,5-trichlorophenylhydrazine showed that fast derivatization reactions which take place in the liquid film, can be amenable to higher variability of the results when the derivatizing agent and/or the organic drop solvent are volatile thus leading to partial loss from the drop. Experimental conditions like organic solvent and temperature may impact the applicability of a method.

Conclusion

Microextraction is an emerging and viable preparation-analytical technique. The in-drop derivatization could arguably qualify as a reasonable alternative to the well-known on-fibre derivatization solid-phase microextraction. Prediction can be made to confirm the role of mass transfer in organic drop located either in a solution or in the headspace. The examination of mathematical equations pertinent to basic theoretical framework is a useful point of departure in considering limitations to the overall in-drop microextraction-derivatization.

The *a priori* knowledge of such characteristics as the locale of reaction in the drop and mass transfer in relation to kinetic parameters can be useful for the selection of the experimental conditions and the viability of a microextraction-derivatization analytical method.

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