

USE OF SMARTPHONE FOR TURBIDIMETRIC DETECTION AND CONTROL OF TURBULENT MICROFLUIDIC PLATFORM TOWARD FULL AUTOMATION OF MICROEMULSIFICATION-BASED METHOD

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Abstract: *we address in this work a potential alternative for development of point-of-use technologies. Our method was based on smartphone for turbidimetric detection and control of turbulent microfluidic set-up aiming a total automation of microemulsification-based method (MEC). The method showed simplicity, autonomy, real-time result recording, and ability for remote data transmission. The device was fabricated by polymerization and scaffold removal (PSR) method to provide harsh flow rate-assisted turbulence. Such fully automatic microfluidic platform was applied in determination of ethanol in commercial alcoholic beverages. The accuracy ranged from 95.0 to 104.2%.*

Keywords: Smartphone; Microfluidic; Turbulence; Point-of-use; Automation.

Introduction: our research group has proposed in 2014 a potential alternative for the development of point-of-use technologies that ensures cheap, fast, portable, and instrument-free experiments bypassing the necessity for skilled users.¹⁻⁴ Called MEC (microemulsification-based method), this technique relies on thermodynamic stabilization of emulsions toward analytical determinations, precise or preliminary. More specifically, such technique relies on the effect of the analyte over the entropy of water-amphiphile-oil (W-AP-O) emulsions, changing the minimum volume of AP necessary for thermodynamically stabilizing these dispersions for a fixed W-O ratio. This process leads to the formation of microemulsions (ME) and the fraction of such minimum volume of AP is the analytical response of the MEC. The analyte can be present on W, O, or AP phase and the detection of this response is based on a binary chemical information: the cloudy-to-transparent conversion that acts like a turning point in titrations. Despite its advantages for in-situ analyses, the MEC shows poor analysis velocity. In this regard, we were intended to make an easy-to-use and 'all-in-one' (AIO) device by performing a smartphone-mediated full automation of the MEC in microfluidics. This platform takes advantages of the smartphone (user-friendly and widespread operation, low cost, portability, and computational capability) and microscale flow devices (low consumption of chemicals and high precision and analytical frequency) for in-situ and rapid analyses. The dispersion phases were mixed by turbulence at harsh flow rates into the microchips that were composed of a single piece of PDMS. All the analytical routines were realized by the smartphone through the development of applicative (App) in Android. More specifically, the smartphone controlled the pumps, performed the detection by turbidimetry, and treated the data in real time. This platform was applied in the determination of ethanol in standard samples and alcoholic beverages.

Experimental: the approach to fabricate the chip relied on sequential steps of polymerization and scaffold removal (PSR) using nylon as scaffold as detailed in the literature.⁵ The microfluidic device presented three inlet channels and consisted of a bulky piece of polydimethylsiloxane (PDMS), tolerating harsh flow rates needed to generate turbulence in microfluidics (**Fig. 1(a)**). The platform consisted of syringe-pumps, hoses, chip, and smartphone (**Fig. 1(b)**). For microemulsification, the dispersions were water (W), oleic acid (O), and ethanol (AP phase,). The analyte was ethanol, added in the W phase at different concentrations. The analyte concentration was expressed as volume fraction of ethanol to water (Φ_E). The water and oil phases were simultaneously pumped into the device at a flow rate each of 5.0 mL min⁻¹, producing a total flow of 10.0 mL min⁻¹. Conversely, the AP flow rate was gradually increased until the generation of ME. The total flow rates ranged from 14.0 up to 24 mL min⁻¹. One user-friendly Android App was deployed for conducting all the analytical operation. For this purpose, the software was responsible for setting experimental parameters of the syringe pumps, turn on and turn off the pumps, monitoring the cloudy-to-transparent transition by recording the RGB values at the outlet of the chip (detection zone), and real-time acquiring and processing the analytical signals showing the obtained spectrum (signal as a function of the AP flow rate, called mecogram) after the analysis. This analytical signal (S_a) was calculated by the App from a linear combination of R, G, and B. Importantly, the tests were divided into two steps: exploratory and precise analyses. In the first case, the AP flow rate was gradually increased in increments of 1.0 mL min⁻¹ after 3 s in order rapidly to localize the region of cloudy-to-transparent transition. In the precise analysis, the increments in this flow rate were reduced to 0.2 mL min⁻¹. This stage was intended to determine with best precision and accuracy the MEC

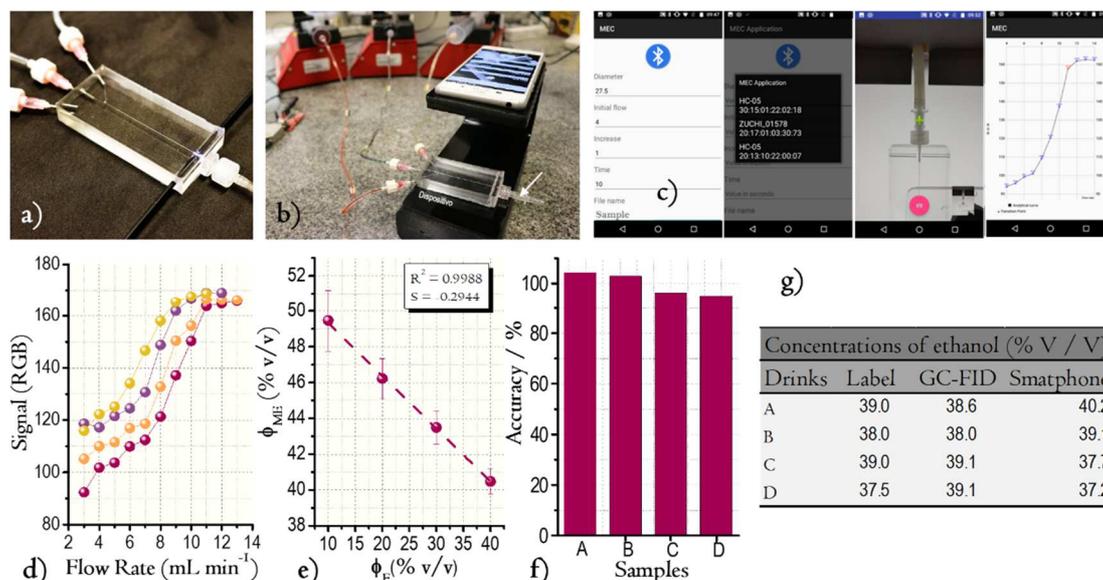


Fig. 1. Full automation of MEC using smartphone and microfluidic setup. Chip (a), platform (b), workflow of App including the configuration of experimental parameters, acquisition of photos by smartphone, and mecogram (c), results (mecograms) to standards of ethanol in water (d), analytical curve (e), accuracy for the alcoholic beverages (f), and concentrations of ethanol (% v/v) in these commercial samples ($n = 5$) (g). In (f,g), the samples are related to *cachaça* (A and C) and vodka (B and D). Photo (a) shows optical fibers integrated to the PSR chip, which were used to guide radiation of a LED/photodiode system with the intent to perform turbidimetry (data not shown).

analytical response, namely, the minimum AP flow rate necessary to generate ME (ϕ_{ME}). This value was attained from the cloudy-to-transparent transition that acted like a turning point in titration. Considering an analytical curve composed of ϕ_{ME} vs. ϕ_E , the amounts of ethanol found in the beverages was automatically shown in the smartphone display (Fig. 1(c)) when the method was applied to the real samples. These values of ϕ_E were compared with the concentrations of ethanol illustrated in the beverage labels and also determined by gas chromatography with flame ionizing detector (GC-FID).

Results and discussion: from the mecogram to ethanol standards (Fig. 1(d)), ϕ_{ME} was observed in total flow rates higher than 18 mL min^{-1} . Reynolds number was estimated to be 1107, indicating the presence of turbulence inside the PSR microchannels ($400\text{-}\mu\text{m}$ diameter).⁵ Vigorous mixings were necessary because the microemulsification needs a strong decrease in interfacial tension of W-O interfaces. The creation of high flow rate-assisted turbulence in microchannels was only recently addressed in literature.^{5,6} This flow solves a crucial bottleneck in microfluidics: the generation of high throughput homogeneous mixings. The analytical curve (Fig. 1(e)) presented a wide linear ($R^2 > 0.99$) with limit of linearity of $40.0\% \text{ v/v } \phi_E$ and analytical sensitivity equal to 0.3. The smartphone was successfully applied in determination of ethanol in commercial alcoholic beverages. Assuming ϕ_E determined by GC-FID as reference values, the levels of accuracy for four samples ranged from 95.0 to 104.2% (Fig. 1(f)). In addition, the data obtained by the smartphone were in agreement with both those concentrations shown in the sample labels and determined by GC-FID according to Student's t-test at 95% confidence level (Fig. 1(g)).

Conclusion: The automatic AIO platform herein shown greatly improves the precision and analytical frequency of MEC, a potential alternative toward point-of-use applications. Such feature contributes to the employment of this technology by non-specialist people, providing in-situ measurements and real time readout.

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