A platform integrating gas-diffusion separation and Ni(OH)\textsubscript{2}-based electrode for point-of-use determination of ethanol in fermentation broths.

Gabriela F. Giordano\textsuperscript{1,2} (PG), Luis Carlos S. Vieira\textsuperscript{1} (TM), Angelo L. Gobbi\textsuperscript{1} (PQ), Renato S. Lima\textsuperscript{1,2} (PQ), Lauro T. Kubota\textsuperscript{2} (PQ)

\textsuperscript{1}Microfabrication Laboratory, Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM); \textsuperscript{2}Department of Analytical Chemistry, Institute of Chemistry – UNICAMP.

Key words: Rapid test; point-of-use; nickel electrode; ethanol; X-ray photoelectron spectroscopy.

\section*{Introduction}
Ethanol is the most produced biofuel in the world. Various methods were proposed to determine ethanol in fermentation broths. However, the development of point-of-use platforms to perform \textit{in situ} assays is still needed in this field. Herein, electrochemical detectors are promising outputs such as those incorporating Ni(OH)\textsubscript{2}/NiOOH. These species have high catalytic activity for oxidation of ethanol.\textsuperscript{1} For selectivity of the analysis, one simple way is gas diffusion separation. It relies on the separation of volatiles from sample to receptor through gas permeable membrane.\textsuperscript{2} Thus, we specifically focuses on deployment of a rapid test tool integrating such detection and separation methods to determine ethanol in sugar cane fermentation broths.

\section*{Results and Discussion}
Electrochemical deposition of Ni(OH)\textsubscript{2} on Ni surface (working electrode) was performed by applying -1.27 mA cm\textsuperscript{-2} in nickel nitrate solution. The stabilization of Ni(OH)\textsubscript{2} structure was provided by adding Co\textsuperscript{2+} and Cd\textsuperscript{2+}.\textsuperscript{1} The insertion of these ions was confirmed by XPS high resolution spectra and mapping image. This electrode was applied to analyze ethanol standards (2.0 to 30.0 mmol L\textsuperscript{-1}) by cyclic voltammetry.

The electrode did not provide selective direct analyses of ethanol in the real samples of fermentation broths. Thereby, the electrochemical platform was coupled to gas diffusion separation in order to ensure accurate measurements (see \textbf{Fig. 1 (B)}). It was achieved by direct interpolation in saline medium-based analytical curve (Na\textsubscript{2}SO\textsubscript{4} with 1.2 mS cm\textsuperscript{-1} conductivity). This curve and the obtained voltammograms are shown in \textbf{Fig. 1 (A)}. The resulting concentrations of analyte are in \textbf{Table 1}. These data were in agreement with those recorded by FTIR based on Student’s t-tests at 95% confidence level (\(\alpha = 0.05\) and \(n = 5\)).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Samples} & \textbf{FTIR} & \textbf{Electrochemical platform} \\
& (\(n = 3\)) & (\(n = 5\)) \\
\hline
S1 & 15.7 ± 0.1 & 15.9 ± 1.5 \\
S2 & 15.1 ± 0.1 & 14.9 ± 1.1 \\
S3 & 15.5 ± 0.2 & 16.7 ± 1.0 \\
\hline
\end{tabular}
\end{table}

\section*{Conclusions}
An integrated platform was developed for point-of-use determination of ethanol in fermentation broth. Despite the high complexity of samples, the platform ensured direct determinations by employing saline medium for construction of the analytical curve. XPS analyses showed the modification of the working electrodes by Ni(OH)\textsubscript{2} and additives (Co\textsuperscript{2+} and Cd\textsuperscript{2+}). In addition, the mapping image results were in accordance with our hypothesis about stabilization of Ni(OH)\textsubscript{2} structure.

\section*{Acknowledgements}
CTBE for supplying the samples.

\begin{thebibliography}{9}
\end{thebibliography}