



Supplementary Materials 3D-Printed Graphene Electrodes Applied in an Impedimetric Electronic Tongue for Soil Analysis

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Received: 17 September 2019; Accepted: 22 October 2019; Published: 24 October 2019

1. Electrical impedance spectroscopy

1.1. Sandy soil

We present in this section three independent electrical measurements for 8 sandy soil samples analyzed (NPK = 000, 100, 010, 001, 200, 020, 002 and 222) with 4 sensing units of an e-tongue setup. The results are illustrated from Figure S1 to S4.





Figure S1. Capacitance versus frequency spectra measured with bare IDE sensing unit for sandy soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.



Figure S2. Capacitance versus frequency spectra measured with PDDA/CuTsPc sensing unit for sandy soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.





Figure S3. Capacitance versus frequency spectra measured with PDDA/MMt-K sensing unit for sandy soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.

10-7

10-8

10-9

10⁻¹⁰

10⁻¹¹

10-7

10⁰

sandy soil

10¹

PDDA/PEDOT:PSS

10²

10³

Frequency, f(Hz)

Capacitance, C (F)





.

10⁴

Figure S4. Capacitance versus frequency spectra measured with PDDA/PEDOT:PSS sensing unit for sandy soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg mL⁻¹.

1.2. Clayey soil

In this section we will present the three independent electrical measurements for the 8 clayey soil samples analyzed (NPK = 000, 100, 010, 001, 200, 020, 002 and 222) obtained by the 4 sensing units, from Figure S5 to S8.



Figure S5. Capacitance versus frequency spectra measured with bare IDE sensing unit for clayey soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.





Figure S6. Capacitance versus frequency spectra measured with PDDA/CuTsPc sensing unit for clayey soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.





Figure S7. Capacitance versus frequency spectra measured with PDDA/MMt-K sensing unit for clayey soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.





Figure S1. Capacitance versus frequency spectra measured with PDDA/PEDOT:PSS sensing unit for clayey soil samples enriched with different amounts of N, P and K in aqueous solution at 1 mg·mL⁻¹.

2. Principal Component Analysis



Figure S2. Principal component analysis (PCA) for the 1 kHz capacitance data of the e-tongue system applied to liquid aliquots of clayey soil samples enriched with different amounts of N, P and K. These data were obtained ~2 years before the results presented in the manuscript. Both experiments followed the same procedure, with new sensing units fabricated for the distinct tests.

3. Limit of detection



Figure S10. Capacitance data obtained for the bare IDE sensing unit at 1 kHz of sandy and clayey soil control samples and enriched with a higher amount of potassium (S-002).





Figure S11. Capacitance data obtained for the PDDA/PEDOT:PSS sensing unit at 1 kHz of sandy and clayey soil control samples and enriched with a higher amount of potassium (S-002).