**Electronic supplementary information (ESI)**

# A NOVEL STRATEGY FOR DIRECT ELEMENTAL DETERMINATION USING LASER-INDUCED BREAKDOWN SPECTROSCOPY: FLUENCE CALIBRATION

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This supplementary material contains 2 Tables

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**Table S1. Trueness (%) and RSD (%) values obtained for Al and Pb determination by LIBS in PCB sample and for Al, K, Mg, Na and P determination by LIBS using different fluence combinations.**

| Elements (normalization) | PCB samples | | | | | |
|---|---|---|---|---|---|---|
| | **F1 x F2** | **F1 x F3** | **F1 x F4** | **F2 x F3** | **F2 x F4** | **F3 x F4** |
| Al (norm 7) | ns | ns | ns | 104 (17) | 80 (116) | ns |
| Pb (norm 1) | 105 (72) | 92 (27) | ns | 100 (36) | ns | ns |
| **Elements (normalization)** | **Fertilizer samples** | | | | | |
| | **F1 x F2** | **F1 x F3** | **F1 x F4** | **F2 x F3** | **F2 x F4** | **F3 x F4** |
| Al (norm 4) | ns | ns | ns | ns | 100 (1) | ns |
| K (norm 5) | ns | ns | ns | 113 (4) | 108 (6) | ns |
| Mg (norm 12) | ns | ns | ns | ns | 114 (63) | ns |
| Na (norm) | 88 (40) | 80 (29) | 106 (9) | ns | 117 (7) | ns |
| P (norm 1) | ns | 81 (17) | ns | ns | 104 (13) | ns |

**ns – not satisfactory trueness: out of range 80 to 120%.**

Signal type – Height for all elements and pulse laser fluence combinations.

**Table S2. Concentrations (mean ± standard deviation, n=3) of Al and Pb in PCB samples and Al, K, Mg, Na and P in fertilizers samples determined by ICP OES and used as reference concentration.**

| Fertilizers samples | Al | K | Mg | Na | P | PCB samples | Al | Pb |
|---|---|---|---|---|---|---|---|---|
| | g kg$^{-1}$ | | | | | | g kg$^{-1}$ | |
| Fert 1* | 2.8 ± 0.14 | 0.57 ± 0.052 | 2.69 ± 0.13 | 5.35 ± 0.27 | 142.7 ± 39.4 | PCB 1* | 48 ± 10.8 | 11.9 ± 2 |
| Fert 2* | 6.1 ± 0.3 | 116.5 ± 1.3 | 17.9 ± 0.5 | 4.05 ± 0.07 | 72 ± 1 | PCB 2 | 21.4 ± 0.6 | 0.72 ± 0.09 |
| Fert 3 | 8.6 ± 0.14 | 3.3 ±0.09 | 4.5 ± 0.14 | 6.1 ± 0.06 | 18.3 ± 0.17 | PCB 3 | 13.4 ± 0.7 | 4.7 ± 0.9 |
| Fert 4 | 1.7 ± 0.13 | 67.9 ± 0.19 | 4.4 ± 0.31 | 5.1 ± 0.19 | 46.3 ± 0.22 | PCB 4 | 10.2 ± 1 | 10.7 ± 0.6 |
| Fert 5 | 1.9 ± 0.04 | 65.2 ± 0.38 | 1.4 ± 0.02 | 4 ± 0.15 | 57.2 ± 0.31 | PCB 5 | 15.2 ± 0.9 | 6.9 ±1.6 |

* Certified concentration values from CRM or MR.