Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry


# SUPPORTING INFORMATION

# Compensation for matrix effects on ICP-OES by on-line calibration methods using a new multi-nebulizer based on Flow Blurring® technology†

*Miguel Ángel Aguirre[a], Nikolay Kovachev[a], Beatriz Almagro[b], Montserrat Hidalgo[a] and Antonio Canals[a]*

*[a]Departamento de Química Analítica, Nutrición y Bromatología, Universidad de Alicante, Apdo. 99, Alicante E-03080, Spain. E-mail: a.canals@ua.es*

*[b]OneNeb (division of Ingeniatrics Tecnologías S.L.), P.I. Parque Plata. Camino Mozárabe, 41, 41900 Camas, Sevilla, Spain.*

*†Flow Blurring® and Flow Focusing® are technologies patented by Ingeniatrics Tecnologías S.L.*

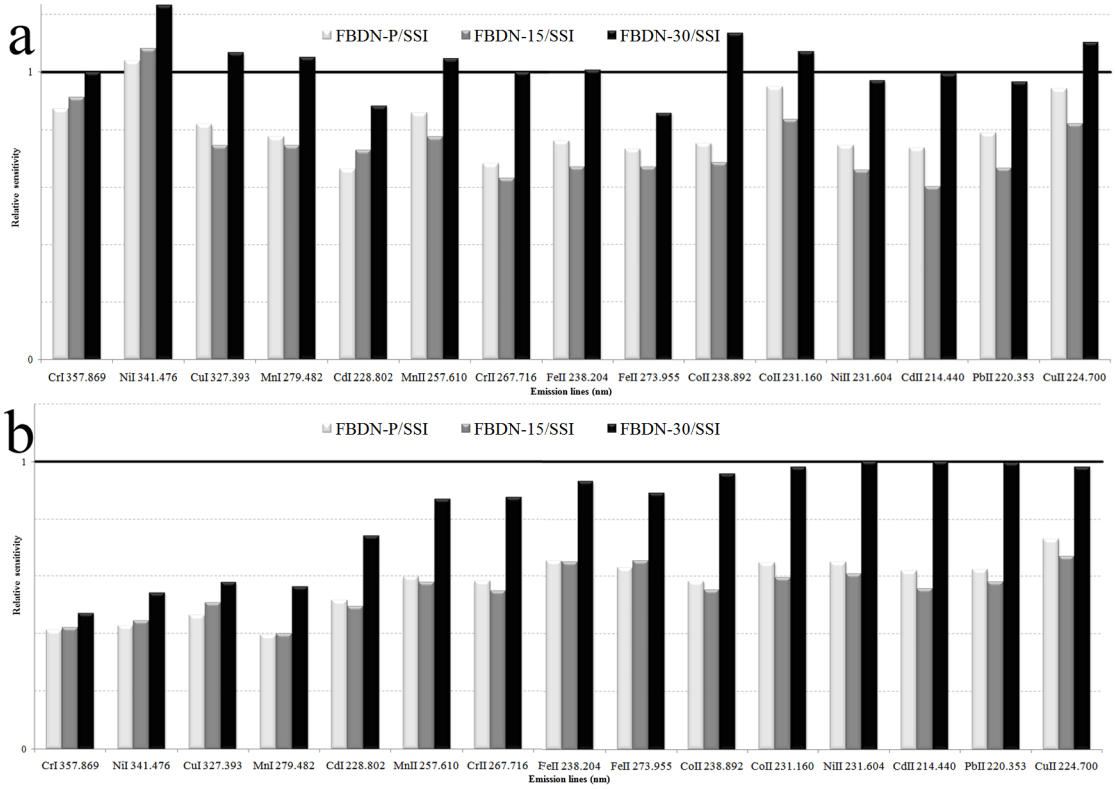


***Fig. S1*** Relative sensitivity obtained with external calibration (a) and internal standard calibration (b) methodologies for the different multinebulization systems. (See text for relative sensitivity definition).

**Table S1** ICP-OES operating conditions

| **Plasma parameters:** | **Value** |
|---|---|
| Outer gas flow (L $min^{-1}$) | 15 |
| Intermediate gas flow (L $min^{-1}$) | 0.2 |
| RF power (W) | 1300 |
| Nominal frequency (MHz) | 40 |
| Integration time (s) | Variable |
| Read time (s) | Variable |
| Number of replicates | 4 |
| Viewing mode | Axial |
| **Conikal nebulizer:** | |
| Gas flow rate (L $min^{-1}$) | 0.7 |
| Liquid uptake rate (µL $min^{-1}$) | 1000 |
| **FBDN-based systems:** | |
| Gas flow rate (L $min^{-1}$) | 0.7 |
| Liquid uptake rate (µL $min^{-1}$) | 400 |
| **Internal standard:** | |
| ZnI (213.857 nm) [a] | |
| ZnII (206.200 nm) [b] | |
| ZnII (202.548 nm) [c] | |

[a] Internal standard for all atomic emission lines.
[b] Internal standard for NiII (231.604 nm), PbII (220.353 nm).
[c] Internal standard for the other emission lines.

**Table S2** Emission lines and energy values.

| **Emission line (nm)** | **$E_{ion}$ (eV)** | **$E_{exc}$ (eV)** | **$E_{sum}$ (eV)** |
|---|---|---|---|
| CrI (357.869) | (6.77) | 3.46 | 3.46 |
| NiI (341.476) | (7.64) | 3.65 | 3.65 |
| CuI (327.393) | (7.73) | 3.79 | 3.79 |
| MnI (279.482) | (7.44) | 4.43 | 4.43 |
| CdI (228.802) | (8.99) | 5.42 | 5.42 |
| MnII (257.610) | 7.44 | 4.81 | 12.25 |
| CrII (267.716) | 6.77 | 6.16 | 12.93 |
| FeII (238.204) | 7.87 | 5.24 | 13.11 |
| FeII (273.955) | 7.87 | 5.51 | 13.38 |
| CoII (238.892) | 7.88 | 5.60 | 13.48 |
| CoII (231.160) | 7.88 | 5.93 | 13.81 |
| NiII (231.604) | 7.64 | 6.39 | 14.03 |
| CdII (214.434) | 8.99 | 5.78 | 14.77 |
| PbII (220.353) | 7.42 | 7.37 | 14.79 |
| CuII (224.700) | 7.73 | 8.23 | 15.96 |

**Table S3** Precision of the FBDN-based and SSI systems at three different concentration levels obtained using external calibration and internal standard calibration.[a]

| | ***RSD (%)*** | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ***SSI*** | | | | | | ***FBDN-P*** | | | | | | ***FBDN-15*** | | | | | | ***FBDN-30*** | | | | | |
| | ***External*** | | | ***Internal*** | | | ***External*** | | | ***Internal*** | | | ***External*** | | | ***Internal*** | | | ***External*** | | | ***Internal*** | | |
| ***Emission line (nm)*** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** | **0.2[b]** | **0.6[b]** | **1.0[b]** |
| CrI (357.869) | 1.1 | 0.8 | 1.1 | 1.3 | 1.2 | 2 | 0.8 | 0.3 | 0.9 | 0.5 | 0.3 | 0.3 | 0.9 | 0.8 | 0.7 | 0.7 | 0.7 | 0.6 | 0.8 | 0.8 | 0.9 | 0.4 | 0.4 | 0.5 |
| NiI (341.476) | 1.2 | 1.2 | 1.4 | 0.4 | 1.2 | 0.9 | 0.5 | 0.8 | 1.1 | 0.4 | 0.7 | 0.7 | 0.4 | 0.4 | 0.6 | 0.5 | 0.9 | 0.4 | 0.4 | 0.6 | 0.8 | 0.3 | 0.6 | 0.5 |
| CuI (327.393) | 0.3 | 1.2 | 1.5 | 1.3 | 1.3 | 2 | 0.4 | 0.2 | 0.7 | 0.6 | 0.9 | 0.9 | 0.6 | 1.0 | 0.7 | 0.6 | 0.4 | 0.12 | 0.8 | 0.7 | 0.8 | 0.4 | 0.4 | 0.5 |
| MnI (279.482) | 0.6 | 0.6 | 1.1 | 0.2 | 1.2 | 2 | 1.0 | 0.5 | 0.6 | 0.2 | 0.9 | 0.5 | 0.8 | 0.9 | 0.7 | 0.2 | 0.3 | 0.2 | 0.8 | 0.9 | 0.4 | 0.6 | 0.5 | 0.5 |
| CdI (228.802) | 1.2 | 0.8 | 0.9 | 0.5 | 1.0 | 1.0 | 0.9 | 0.4 | 0.9 | 0.7 | 0.6 | 0.4 | 0.7 | 0.3 | 0.4 | 0.7 | 0.7 | 0.5 | 0.4 | 0.9 | 0.8 | 0.5 | 0.4 | 0.7 |
| MnII (257.610) | 1.2 | 0.7 | 1.1 | 1.0 | 3 | 2 | 0.7 | 0.5 | 1.0 | 0.8 | 0.13 | 0.7 | 0.9 | 0.9 | 0.5 | 0.4 | 0.3 | 0.7 | 0.6 | 0.8 | 0.7 | 0.4 | 0.6 | 0.3 |
| CrII (267.716) | 0.9 | 1.0 | 1.2 | 0.3 | 3 | 2 | 0.9 | 0.5 | 0.8 | 0.6 | 0.8 | 0.7 | 0.7 | 0.9 | 0.5 | 0.3 | 0.2 | 0.7 | 0.6 | 0.8 | 0.6 | 0.5 | 0.3 | 0.4 |
| FeII (238.204) | 1.1 | 1.0 | 1.1 | 1.1 | 3 | 2 | 0.7 | 0.6 | 0.6 | 0.7 | 0.3 | 0.8 | 0.9 | 0.8 | 0.6 | 1.0 | 0.2 | 0.7 | 0.4 | 0.7 | 0.8 | 0.3 | 0.5 | 0.3 |
| FeII (273.955) | 1.0 | 2 | 1.0 | 1.2 | 0.7 | 0.6 | 0.7 | 0.5 | 0.3 | 0.4 | 0.7 | 0.4 | 0.5 | 0.4 | 0.4 | 0.8 | 0.5 | 0.6 | 0.3 | 0.9 | 0.5 | 0.2 | 0.5 | 0.5 |
| CoII (238.892) | 1.5 | 1.3 | 1.4 | 0.4 | 1.4 | 2 | 0.8 | 0.4 | 0.8 | 0.9 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.3 | 0.3 | 0.4 | 0.5 | 0.4 | 0.7 | 0.8 | 0.4 |
| CoII (231.160) | 1.4 | 2 | 2 | 0.3 | 0.9 | 0.4 | 0.4 | 0.6 | 0.3 | 0.1 | 0.7 | 0.4 | 0.4 | 0.5 | 0.5 | 0.7 | 0.3 | 0.5 | 0.5 | 0.6 | 0.5 | 0.3 | 0.7 | 0.3 |
| NiII (231.604) | 1.4 | 2 | 1.1 | 0.4 | 1.0 | 2 | 0.5 | 0.6 | 0.8 | 0.4 | 0.9 | 0.4 | 0.9 | 0.4 | 0.6 | 1.0 | 0.9 | 0.4 | 0.6 | 0.4 | 0.6 | 0.5 | 0.3 | 0.3 |
| CdII (214.434) | 1.1 | 0.8 | 1.2 | 0.3 | 3 | 2 | 0.3 | 0.8 | 0.7 | 0.4 | 0.5 | 0.5 | 0.7 | 0.7 | 0.6 | 0.3 | 0.5 | 0.2 | 0.9 | 0.2 | 0.6 | 0.6 | 0.4 | 0.3 |
| PbII (220.353) | 2 | 2 | 1.5 | 1.0 | 1.5 | 2 | 0.9 | 0.3 | 0.2 | 0.9 | 0.2 | 0.5 | 0.7 | 0.4 | 0.4 | 1.0 | 1.0 | 0.6 | 0.7 | 0.2 | 0.9 | 0.3 | 0.6 | 0.6 |
| CuII (224.700) | 2 | 2 | 2 | 0.2 | 0.7 | 0.3 | 0.7 | 0.4 | 0.3 | 0.6 | 0.6 | 0.5 | 1.0 | 0.6 | 0.5 | 0.7 | 1.0 | 0.9 | 0.3 | 0.3 | 0.6 | 0.4 | 0.6 | 0.6 |

[a]Underlined numbers represent RSD (%) values higher than the reference (results obtained with SSI at the same concentration level).

[b]mg $L^{-1}$.

**Table S4** Limits of detection (LOD) obtained using external calibration and internal standard calibration.[a,b]

| Emission line (nm) | LOD (µg $L^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SSI | | FBDN-P | | FBDN-15 | | FBDN-30 | |
| | External | Internal | External | Internal | External | Internal | External | Internal |
| CrI (357.869) | 0.3 | 0.4 | 0.04 | 0.5 | 0.4 | 1.1 | 0.7 | 0.4 |
| NiI (341.476) | 3 | 5 | 0.4 | 6 | 2 | 4 | 2 | 5 |
| CuI (327.393) | 0.4 | 1.3 | 1.0 | 1.1 | 0.6 | 1.0 | 0.3 | 0.9 |
| MnI (279.482) | 0.06 | 0.3 | 0.2 | 0.4 | 0.7 | 1.0 | 0.5 | 0.2 |
| CdI (228.802) | 0.06 | 0.2 | 0.4 | 0.13 | 0.09 | 0.3 | 0.11 | 0.2 |
| MnII (257.610) | 0.10 | 0.02 | 0.02 | 0.08 | 0.02 | 0.02 | 0.011 | 0.02 |
| CrII (267.716) | 0.05 | 0.5 | 0.04 | 0.05 | 0.03 | 0.08 | 0.06 | 0.13 |
| FeII (238.204) | 0.3 | 3 | 0.09 | 0.10 | 0.10 | 0.2 | 0.11 | 0.13 |
| FeII (273.955) | 0.11 | 6 | 0.08 | 0.3 | 0.3 | 0.5 | 0.4 | 0.7 |
| CoII (238.892) | 0.10 | 0.4 | 0.3 | 0.10 | 0.09 | 0.3 | 0.2 | 0.3 |
| CoII (231.160) | 0.2 | 0.9 | 0.08 | 0.2 | 0.10 | 0.3 | 0.2 | 0.3 |
| NiII (231.604) | 0.08 | 2 | 0.10 | 0.12 | 0.2 | 0.2 | 0.3 | 0.3 |
| CdII (214.434) | 0.2 | 0.4 | 0.3 | 0.4 | 0.6 | 0.5 | 0.2 | 0.6 |
| PbII (220.353) | 0.3 | 0.5 | 2 | 3 | 3 | 2 | 3 | 3 |
| CuII (224.700) | 0.3 | 0.4 | 1.1 | 1.2 | 1.1 | 2 | 1.3 | 2 |

[a] Liquid and gas flows used with FBDN-based systems as on Table S1.

[b] Underlined numbers represent LOD values higher than the reference (results obtained with SSI at the same concentration level).