

## Compensation of inorganic acid interferences in ICP-OES and ICP-MS using a Flow Blurring® multinebulizer†

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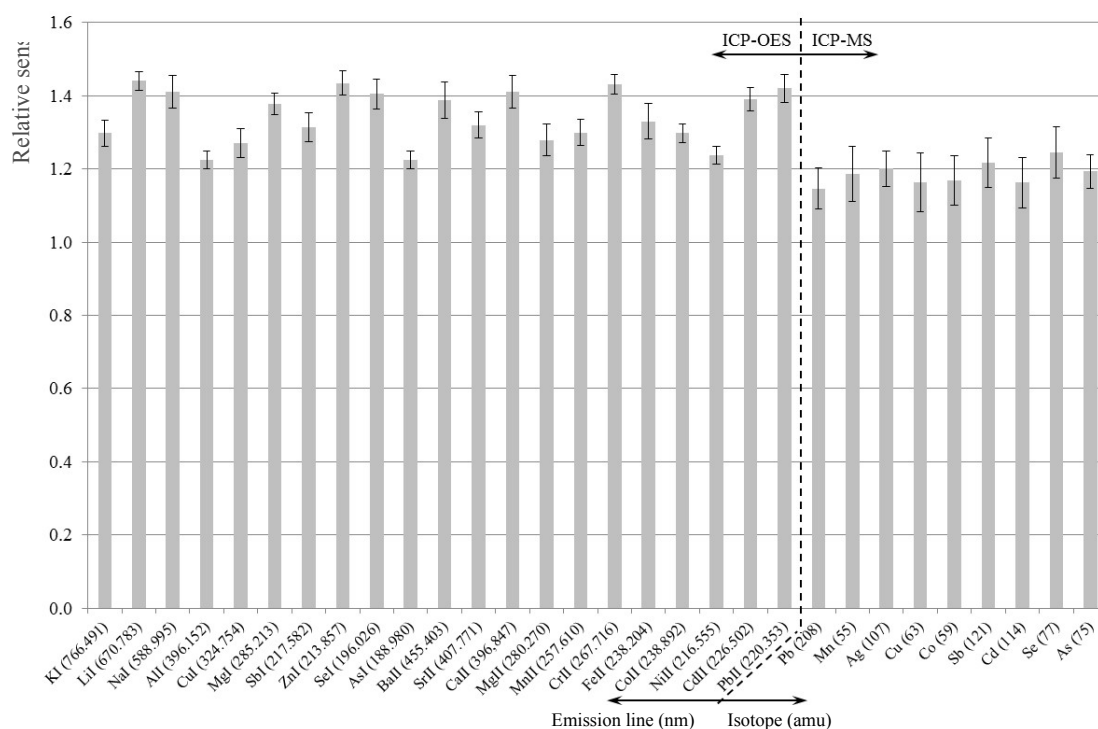
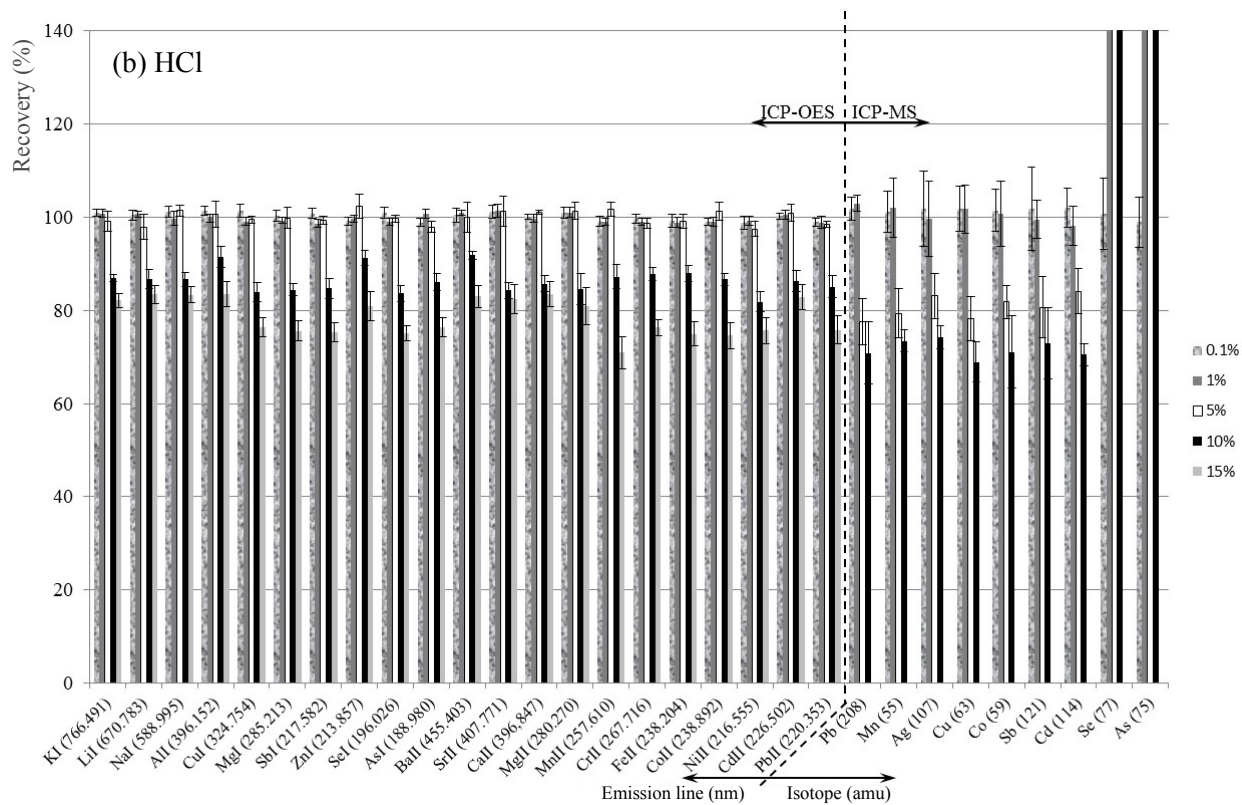
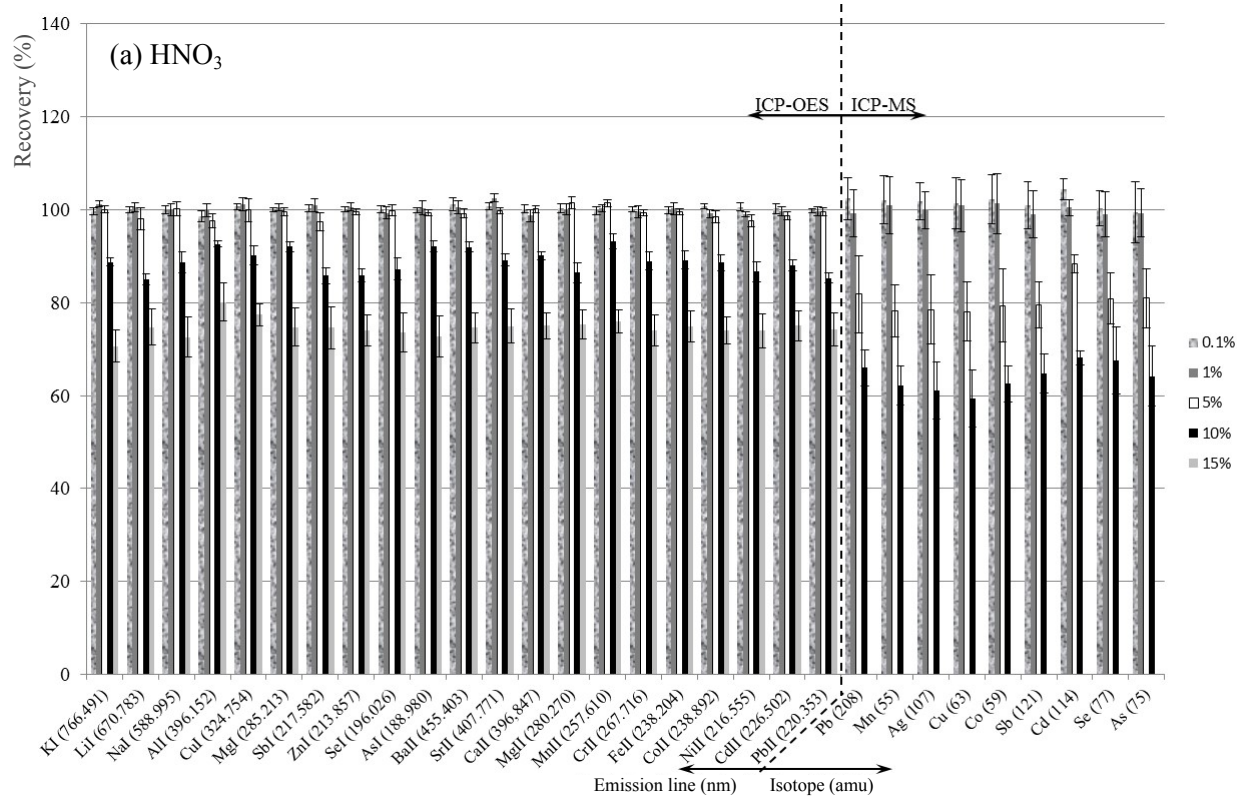


Figure S1. Relative sensitivity of FBMN-based and SSI systems for all emission lines and isotopes evaluated (*i.e.*, ratio between the sensitivity values obtained using the FBMN-based system and that obtained using the SSI system). The error bars represent the uncertainty of the relative sensitivity, calculated by applying the law of propagation of uncertainty.



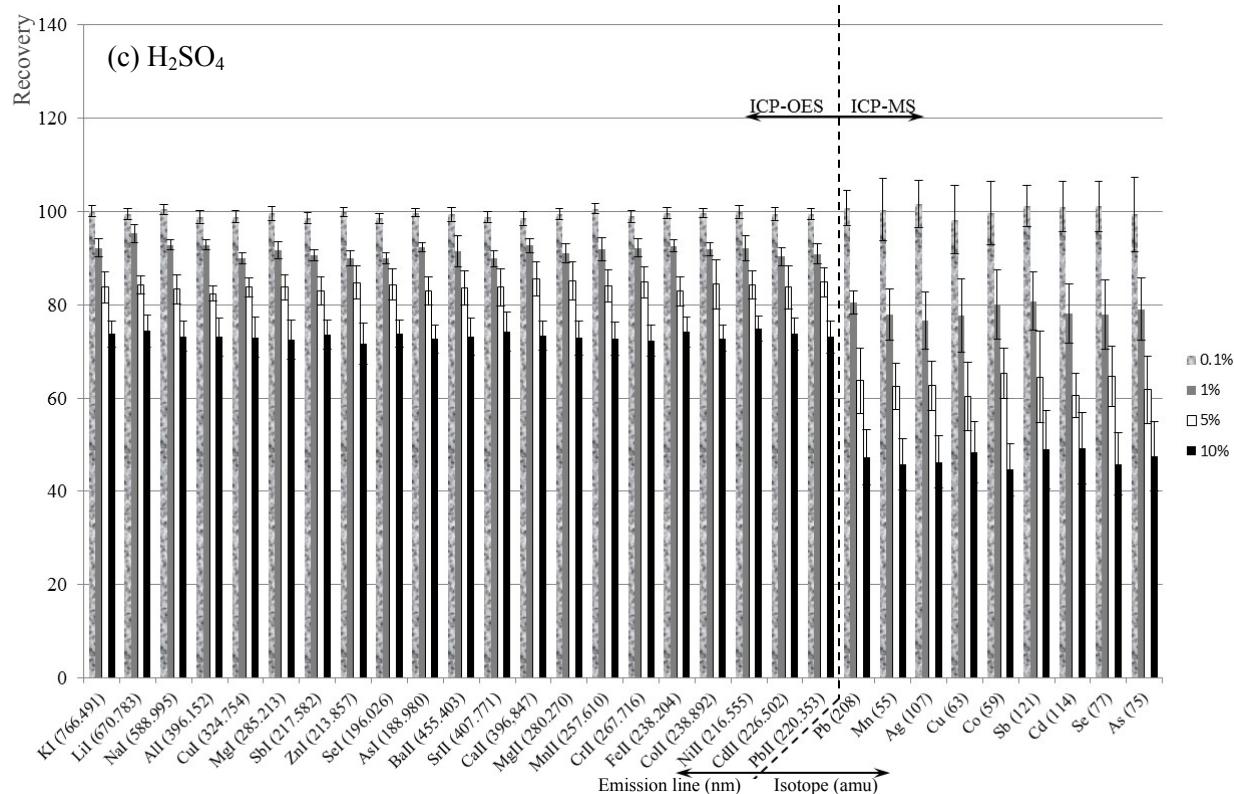
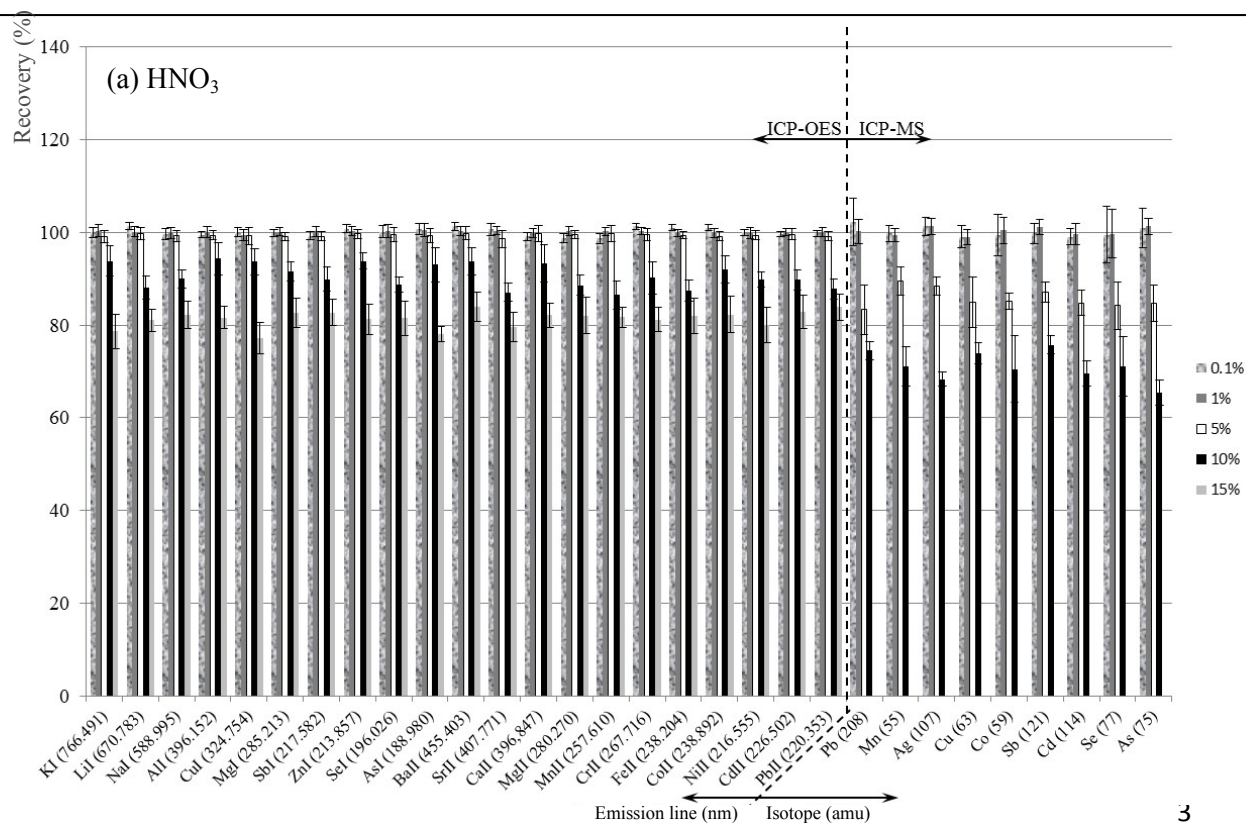


Figure S2. Percent recovery values obtained with the FBMN-based system and external calibration for three inorganic acids at different concentrations: (a)  $\text{HNO}_3$ , (b)  $\text{HCl}$  and (c)  $\text{H}_2\text{SO}_4$ . Dashed bars 0.1% ( $\text{w w}^{-1}$ ) acid concentration; dark grey bars 1% ( $\text{w w}^{-1}$ ) acid concentration; white bars 5% ( $\text{w w}^{-1}$ ) acid concentration; black bars 10% ( $\text{w w}^{-1}$ ) acid concentration; light grey bars 15% ( $\text{w w}^{-1}$ ) acid concentration.



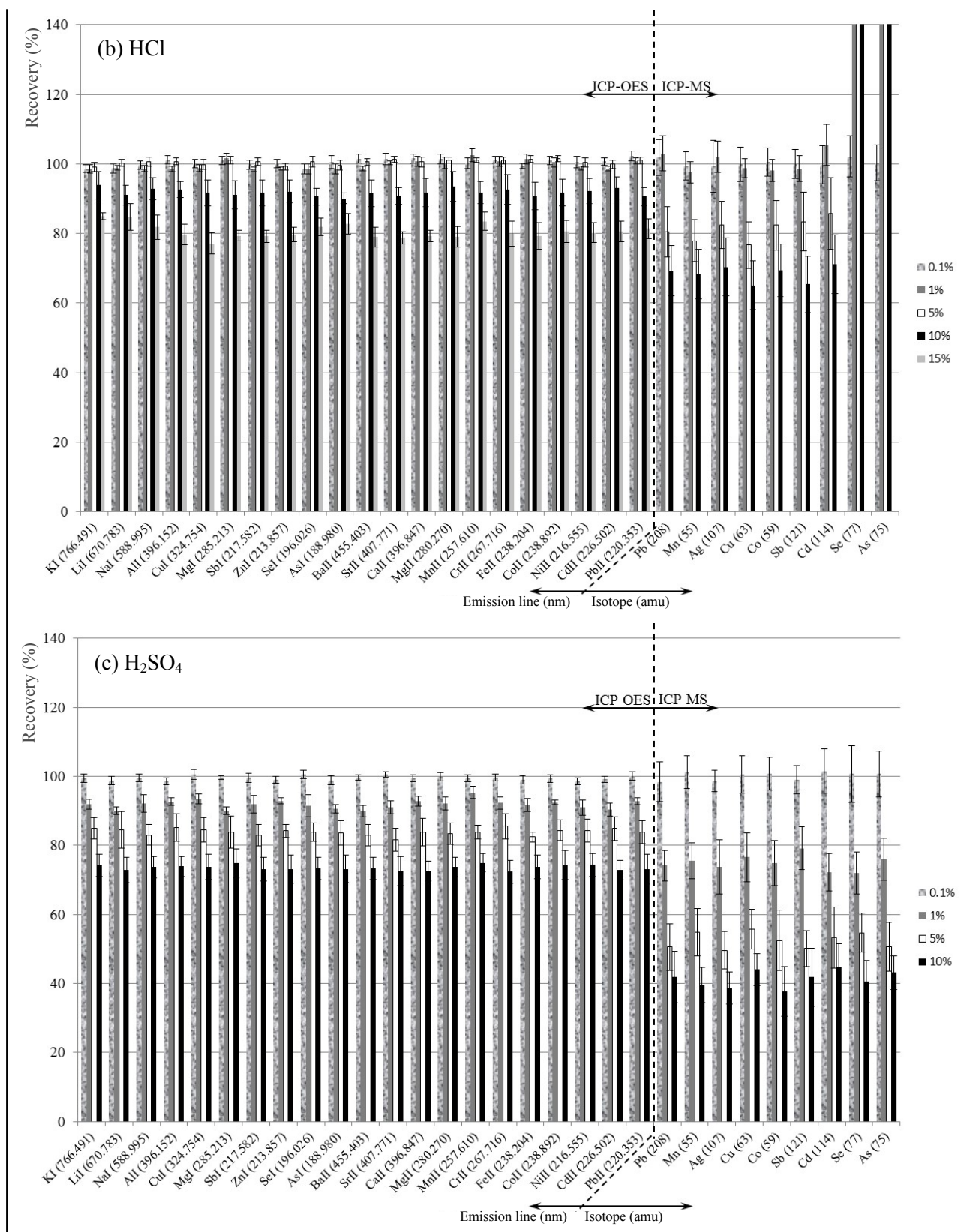
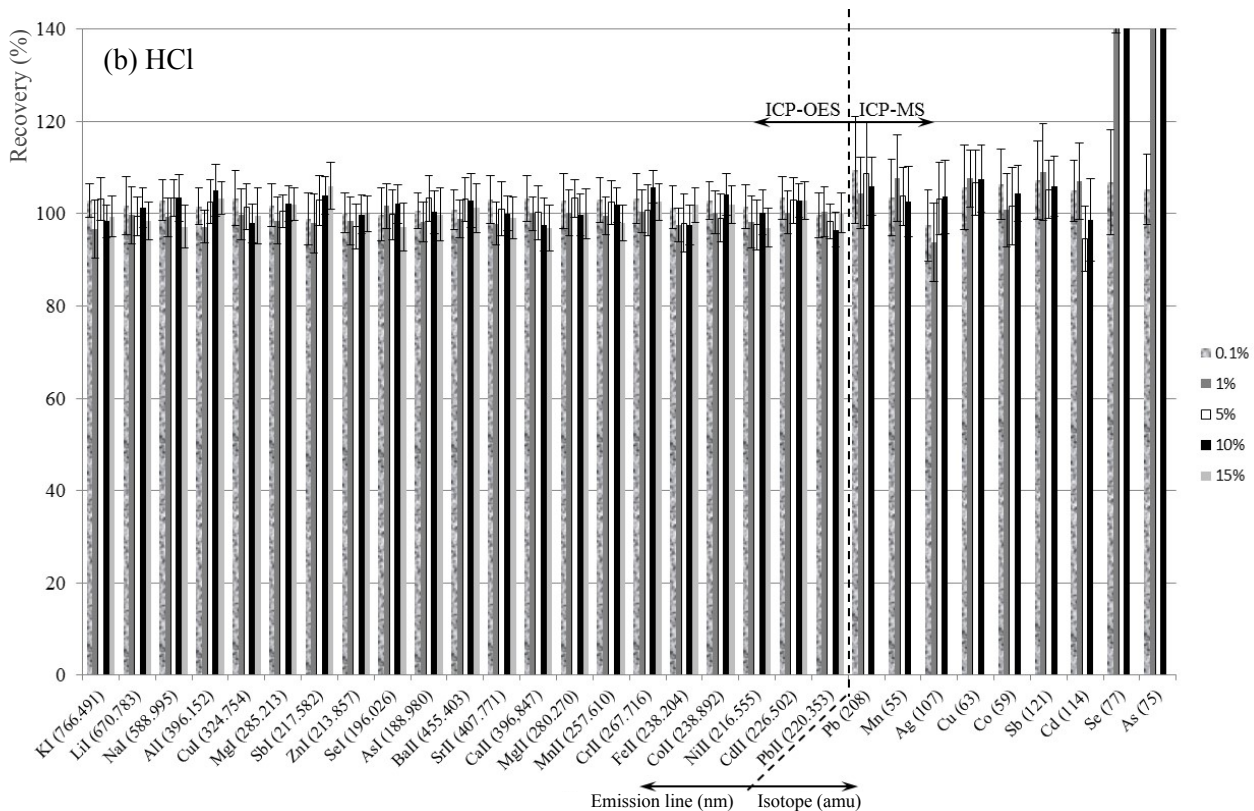
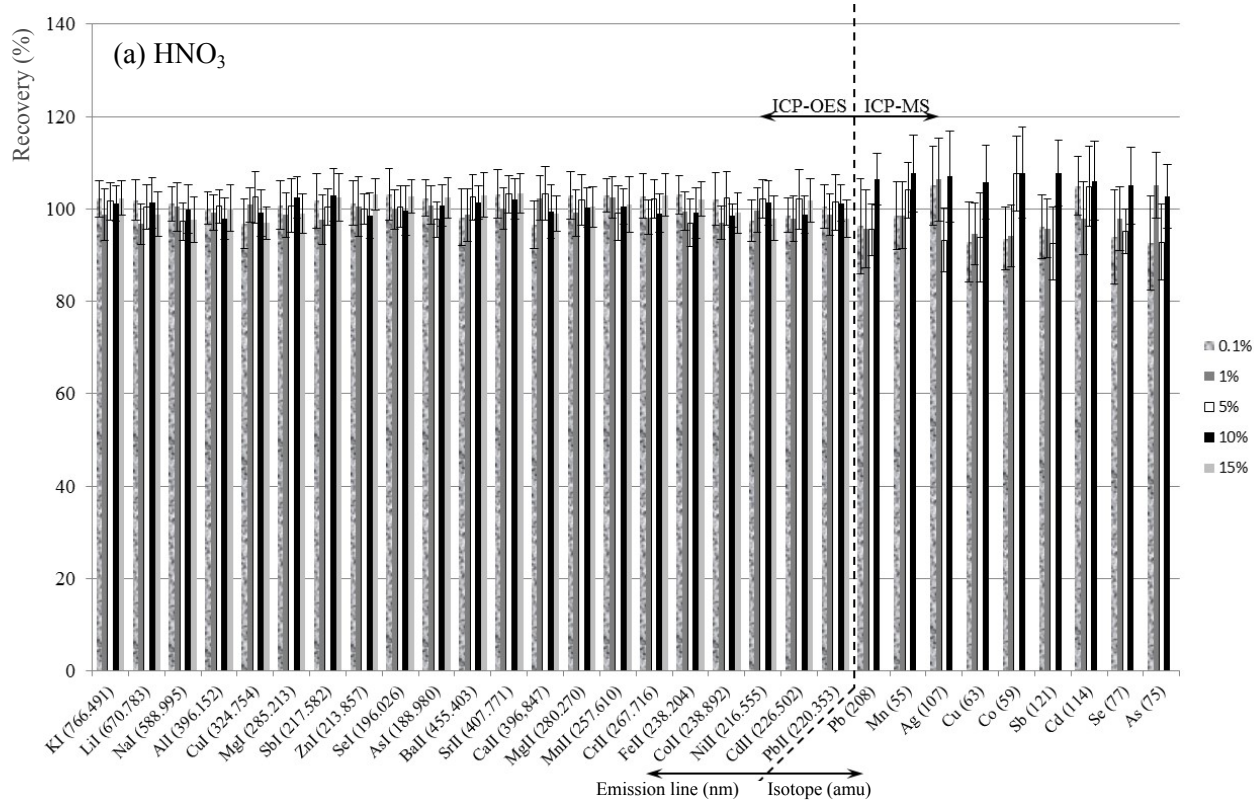


Figure S3. Percent recovery values obtained with the SSI system and external calibration for three inorganic acids at different concentrations: (a) HNO<sub>3</sub>, (b) HCl and (c) H<sub>2</sub>SO<sub>4</sub>. Dashed bars 0.1% (w w<sup>-1</sup>) acid concentration; dark grey bars 1% (w w<sup>-1</sup>) acid concentration; white bars 5% (w w<sup>-1</sup>) acid concentration; black bars 10% (w w<sup>-1</sup>) acid concentration; light grey bars 15% (w w<sup>-1</sup>) acid concentration.



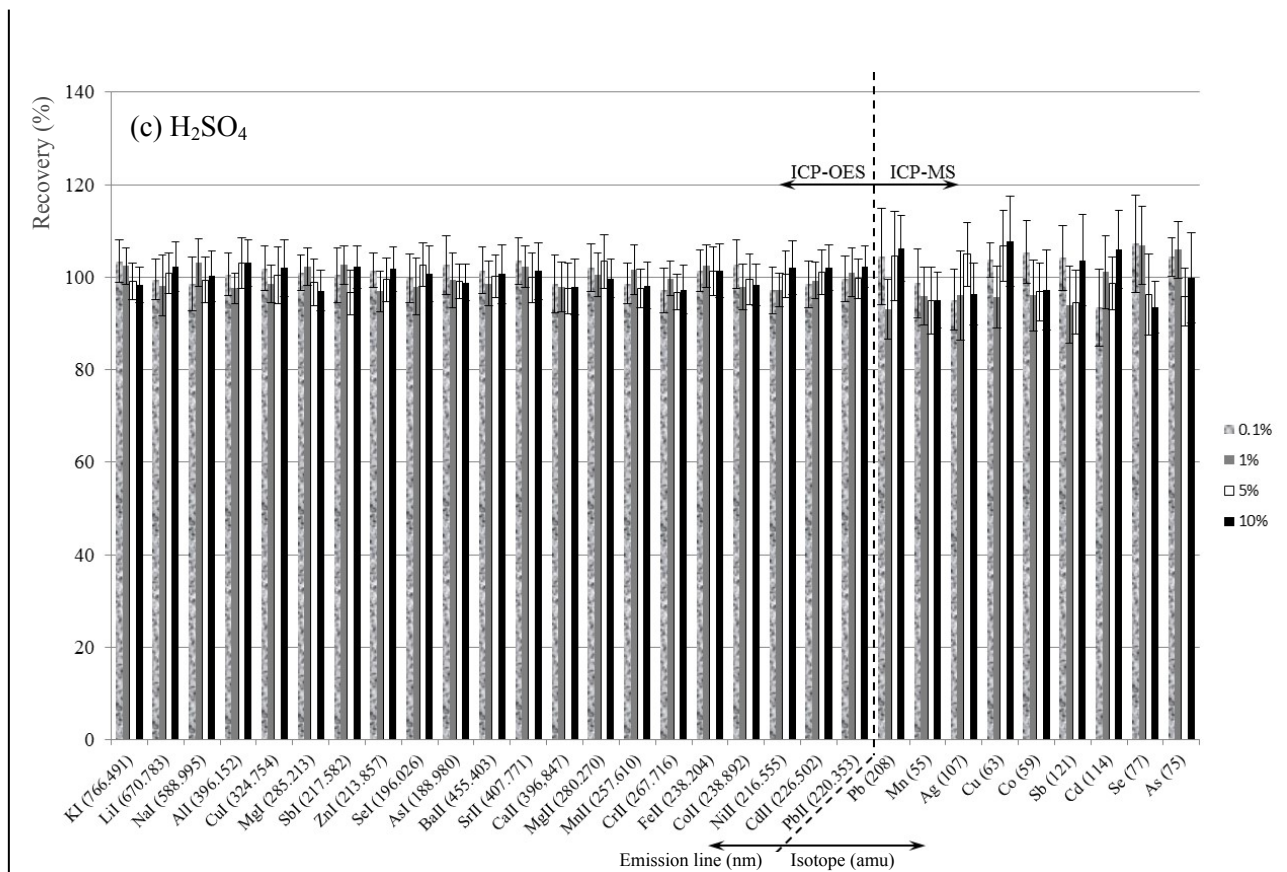
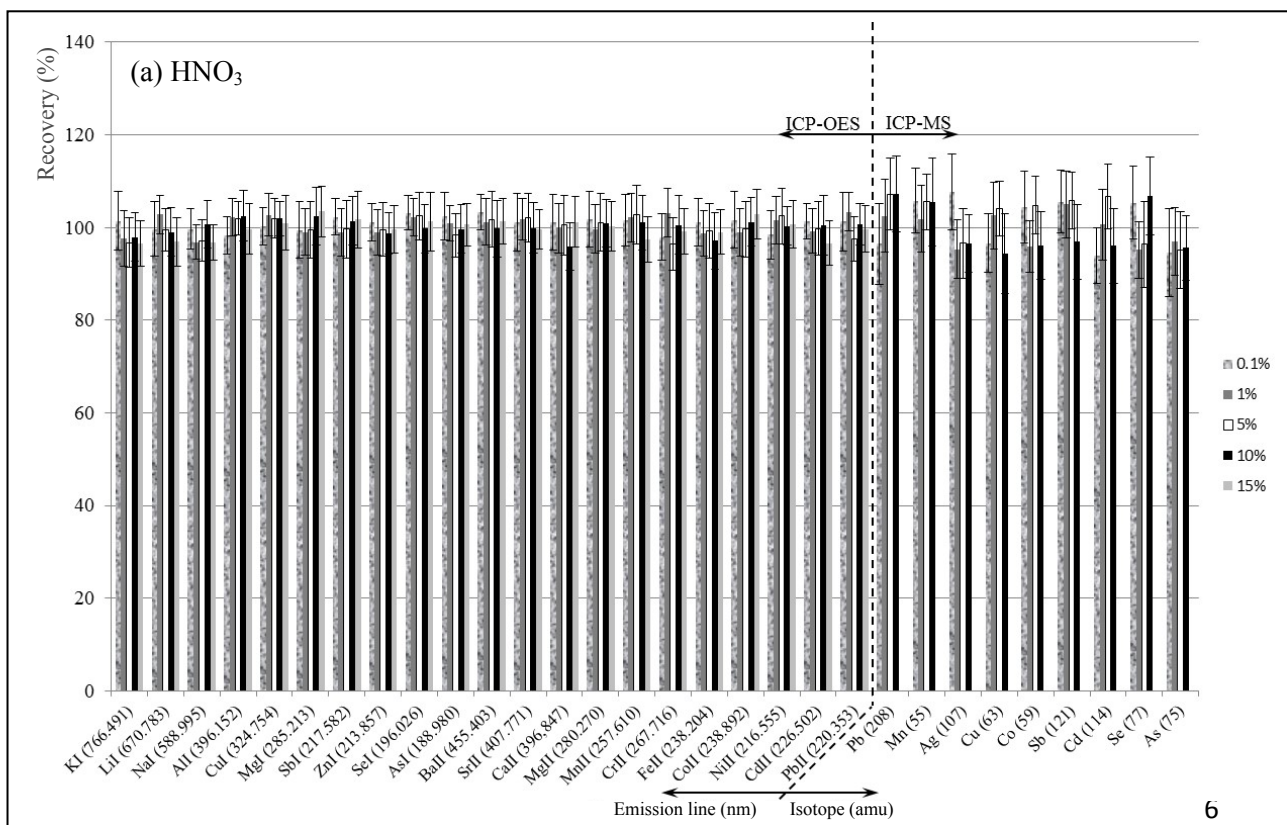


Figure S4. Percent recovery values obtained with the FBMN-based system and on-line standard addition calibration for three inorganic acids at different concentrations: (a)  $\text{HNO}_3$ , (b)  $\text{HCl}$  and (c)  $\text{H}_2\text{SO}_4$ . Dashed bars 0.1% (w w<sup>-1</sup>) acid concentration; dark grey bars 1% (w w<sup>-1</sup>) acid concentration; white bars 5% (w w<sup>-1</sup>) acid concentration; black bars 10% (w w<sup>-1</sup>) acid concentration; light grey bars 15% (w w<sup>-1</sup>) acid concentration.



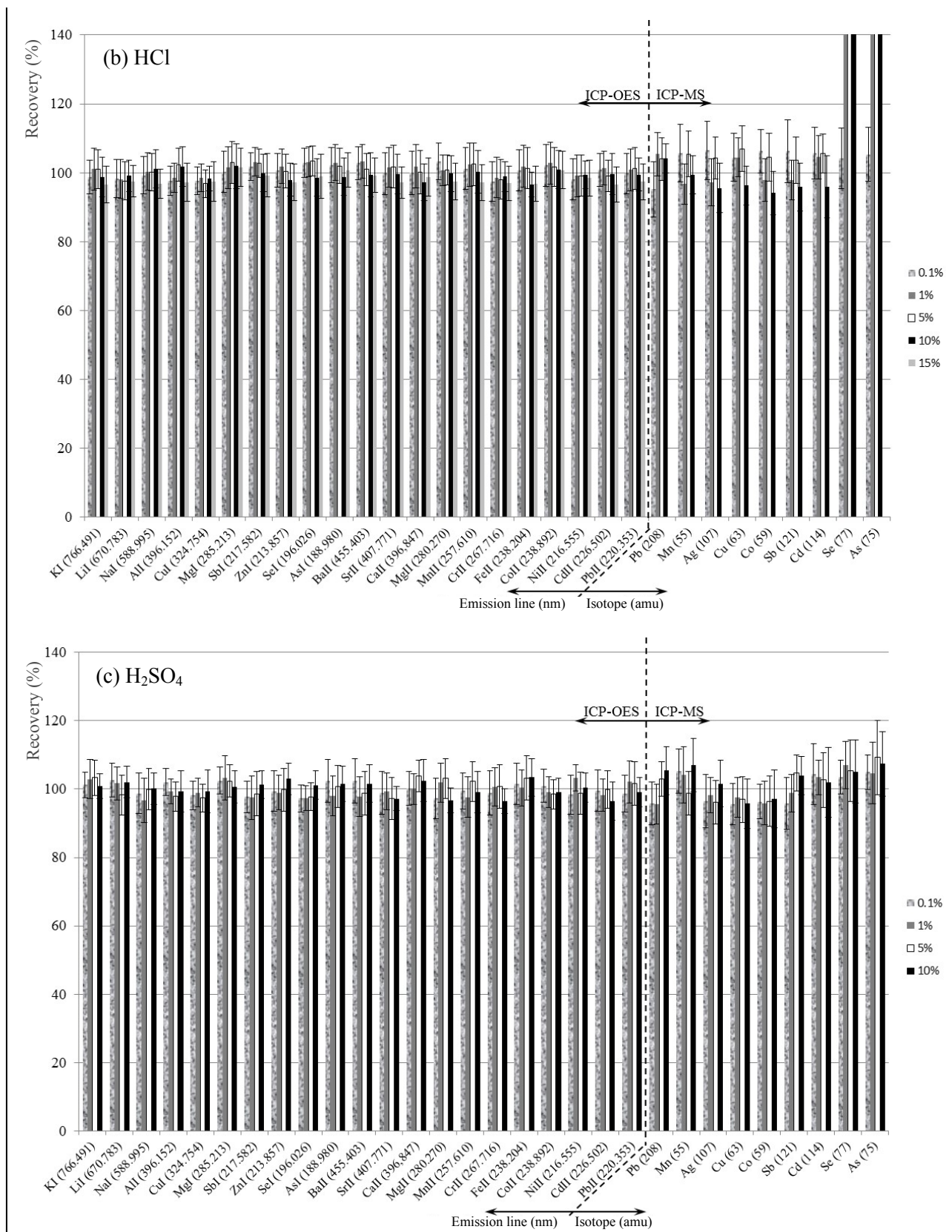


Figure S5. Percent recovery values obtained with the SSI system and conventional standard addition calibration for three inorganic acids at different concentrations: (a) HNO<sub>3</sub>, (b) HCl and (c) H<sub>2</sub>SO<sub>4</sub>. Dashed bars 0.1% (w w<sup>-1</sup>) acid concentration; dark grey bars 1% (w w<sup>-1</sup>) acid concentration; white bars 5% (w w<sup>-1</sup>) acid concentration; black bars 10% (w w<sup>-1</sup>) acid concentration; light grey bars 15% (w w<sup>-1</sup>) acid concentration.

Table S1. Emission lines and isotopes evaluated in ICP-OES and ICP-MS, respectively.

| Emission line (nm) | Excitation Energy (eV) | Ionization Potential (eV) | Energy sum (eV) |
|--------------------|------------------------|---------------------------|-----------------|
| KI (766.491)       | 1.62                   | -                         | 1.62            |
| LiI (670.783)      | 1.80                   | -                         | 1.80            |
| NaI (588.995)      | 2.10                   | -                         | 2.10            |
| AlI (396.152)      | 3.14                   | -                         | 3.14            |
| CuI (324.754)      | 3.82                   | -                         | 3.82            |
| MgI (285.213)      | 4.35                   | -                         | 4.35            |
| SbI (217.582)      | 5.70                   | -                         | 5.70            |
| ZnI (213.857)      | 5.80                   | -                         | 5.80            |
| SeI (196.026)      | 6.32                   | -                         | 6.32            |
| AsI (188.980)      | 6.57                   | -                         | 6.57            |
| BaII (455.403)     | 2.72                   | 5.21                      | 7.93            |
| SrII (407.771)     | 3.04                   | 5.69                      | 8.73            |
| CaII (396.847)     | 6.31                   | 2.93                      | 9.24            |
| MgII (280.270)     | 4.42                   | 7.65                      | 12.07           |
| MnII (257.610)     | 4.81                   | 7.44                      | 12.25           |
| CrII (267.716)     | 6.15                   | 6.77                      | 12.92           |
| FeII (238.204)     | 5.20                   | 7.87                      | 13.07           |
| CoII (238.892)     | 5.60                   | 7.86                      | 13.46           |
| NiII (216.555)     | 6.76                   | 7.64                      | 14.40           |
| CdII (226.502)     | 5.48                   | 8.99                      | 14.47           |
| PbII (220.353)     | 7.37                   | 7.42                      | 14.79           |
| Element (amu)      | Natural abundance      | Ionization Potential (eV) | Energy sum (eV) |
| Pb (208)           | 52                     | 7.42                      | 7.42            |
| Mn (55)            | 100                    | 7.44                      | 7.44            |
| Ag (107)           | 52                     | 7.58                      | 7.58            |
| Cu (63)            | 69                     | 7.72                      | 7.72            |
| Co (59)            | 100                    | 7.88                      | 7.88            |
| Sb (121)           | 57                     | 8.61                      | 8.61            |
| Cd (114)           | 29                     | 8.99                      | 8.99            |
| Se (77)            | 8                      | 9.75                      | 9.75            |
| As (75)            | 100                    | 9.79                      | 9.79            |

Table S2: Microwave-assisted acid digestion heating program.

| Step | Applied power (W) | Time (min) | Maximum internal temperature (°C) |
|------|-------------------|------------|-----------------------------------|
| 1    | 250               | 2          | 80                                |
| 2    | 0                 | 1          | -                                 |
| 3    | 250               | 5          | 120                               |
| 4    | 400               | 8          | 150                               |
| 5    | 450               | 8          | 170                               |
| 6    | 500               | 2          | 200                               |
| 7    | ventilation       | 10         | -                                 |

Table S3. RSD (%) values for SSI and FBMN-based systems at three different concentration levels.

| Emission line (nm) | RSD (%)           |                  |                  |                  |                  |                  |
|--------------------|-------------------|------------------|------------------|------------------|------------------|------------------|
|                    | FBMN-based system |                  |                  | SSI system       |                  |                  |
|                    | 0.4 <sup>a</sup>  | 1.2 <sup>a</sup> | 2.0 <sup>a</sup> | 0.4 <sup>a</sup> | 1.2 <sup>a</sup> | 2.0 <sup>a</sup> |
| KI (766.491)       | 0.6               | 1.8              | 1.0              | 1.4              | 2                | 2                |
| LiI (670.783)      | 1.1               | 2                | 1.5              | 1.1              | 3                | 2                |
| NaI (588.995)      | 3                 | 2                | 1.7              | 3                | 3                | 2                |
| AlI (396.152)      | 2                 | 3                | 2                | 1.1              | 3                | 2                |
| CuI (324.754)      | 2                 | 2                | 1.0              | 1.4              | 3                | 3                |
| MgI (285.213)      | 1.4               | 1.1              | 0.8              | 1.1              | 2                | 2                |
| SbI (217.582)      | 1.3               | 1.4              | 1.1              | 2                | 3                | 3                |
| ZnI (213.857)      | 2                 | 2                | 1.1              | 0.8              | 1.1              | 2                |
| SeI (196.026)      | 2                 | 3                | 2                | 3                | 2                | 2                |
| AsI (188.980)      | 2                 | 2                | 0.9              | 2                | 2                | 2                |
| BaII (455.403)     | 0.7               | 2                | 0.7              | 1.3              | 2                | 2                |
| SrII (407.771)     | 2                 | 3                | 1.0              | 2                | 1.0              | 1.4              |
| CaII (396.847)     | 0.6               | 2                | 0.4              | 2                | 3                | 2                |
| MgII (280.270)     | 2                 | 2                | 0.6              | 2                | 2                | 2                |
| MnII (257.610)     | 2                 | 3                | 1.4              | 2                | 2                | 2                |
| CrII (267.716)     | 1.0               | 2                | 1.0              | 2                | 2                | 3                |
| FeII (238.204)     | 1.0               | 3                | 1.1              | 2                | 2                | 2                |
| CoII (238.892)     | 2                 | 2                | 1.0              | 0.5              | 2                | 2                |
| NiII (216.555)     | 2                 | 2                | 0.8              | 2                | 2                | 2                |
| CdII (226.502)     | 1.0               | 2                | 1.0              | 2                | 2                | 3                |
| PbII (220.353)     | 1.1               | 2                | 0.6              | 0.5              | 3                | 3                |
| Isotopes (amu)     | FBMN-based system |                  |                  | SSI system       |                  |                  |
|                    | 1 <sup>b</sup>    | 6 <sup>b</sup>   | 12 <sup>b</sup>  | 1 <sup>b</sup>   | 6 <sup>b</sup>   | 12 <sup>b</sup>  |
| Pb (208)           | 4                 | 3                | 5                | 4                | 6                | 3                |
| Mn (55)            | 4                 | 2                | 3                | 5                | 5                | 5                |
| Ag (107)           | 6                 | 3                | 5                | 4                | 4                | 3                |
| Cu (63)            | 5                 | 4                | 4                | 5                | 4                | 4                |
| Co (59)            | 4                 | 2                | 3                | 3                | 4                | 4                |
| Sb (121)           | 4                 | 3                | 5                | 4                | 5                | 3                |
| Cd (114)           | 5                 | 3                | 4                | 5                | 5                | 4                |
| Se (77)            | 4                 | 5                | 5                | 5                | 5                | 6                |
| As (75)            | 6                 | 5                | 3                | 4                | 5                | 3                |

<sup>a</sup>In mg kg<sup>-1</sup>. <sup>b</sup>In µg kg<sup>-1</sup>

Table S4. Limits of detection (LOD) obtained in ICP-OES and ICP-MS using external calibration with the SSI and FBMN-based system.

| Emission line (nm) | LOD ( $\mu\text{g kg}^{-1}$ ) |            |
|--------------------|-------------------------------|------------|
|                    | FBMN-based system             | SSI system |
| KI (766.491)       | 2                             | 3          |
| LiI (670.783)      | 0.05                          | 0.08       |
| NaI (588.995)      | 5                             | 8          |
| AlI (396.152)      | 2                             | 3          |
| CuI (324.754)      | 1.2                           | 2          |
| MgI (285.213)      | 2                             | 3          |
| SbI (217.582)      | 31                            | 43         |
| ZnI (213.857)      | 0.9                           | 1.4        |
| SeI (196.026)      | 33                            | 48         |
| AsI (188.980)      | 20                            | 36         |
| BaII (455.403)     | 0.04                          | 0.06       |
| SrII (407.771)     | 0.03                          | 0.05       |
| CaII (396.847)     | 2                             | 3          |
| MgII (280.270)     | 0.4                           | 0.8        |
| MnII (257.610)     | 0.15                          | 0.3        |
| CrII (267.716)     | 1.2                           | 2          |
| FeII (238.204)     | 1.0                           | 2          |
| CoII (238.892)     | 3                             | 4          |
| NiII (216.555)     | 8                             | 10         |
| CdII (226.502)     | 0.7                           | 1.2        |
| PbII (220.353)     | 26                            | 38         |
| Isotopes (amu)     | LOD ( $\text{ng kg}^{-1}$ )   |            |
|                    | FBMN-based system             | SSI system |
| Pb (208)           | 13                            | 16         |
| Mn (55)            | 2                             | 3          |
| Ag (107)           | 19                            | 28         |
| Cu (63)            | 10                            | 13         |
| Co (59)            | 3                             | 4          |
| Sb (121)           | 15                            | 20         |
| Cd (114)           | 3                             | 4          |
| Se (77)            | 45                            | 61         |
| As (75)            | 20                            | 24         |

Table S5. Nitric acid concentration before and after acid digestion of whole milk powder samples obtained by titration.

| Solution    | Commercial whole milk powder<br>(Real sample) |                                       |                                     | Whole milk powder<br>(Certified reference material) |                                       |                                     |
|-------------|-----------------------------------------------|---------------------------------------|-------------------------------------|-----------------------------------------------------|---------------------------------------|-------------------------------------|
|             | Mass<br>(g)                                   | Initial<br>[HNO <sub>3</sub> ]<br>(%) | Final<br>[HNO <sub>3</sub> ]<br>(%) | Mass<br>(g)                                         | Initial<br>[HNO <sub>3</sub> ]<br>(%) | Final<br>[HNO <sub>3</sub> ]<br>(%) |
| Blank       | -                                             | 14                                    | 14                                  | -                                                   | 16                                    | 15                                  |
| Replicate 1 | 0.3000                                        | 14                                    | 8                                   | 0.2858                                              | 16                                    | 11                                  |
| Replicate 2 | 0.2945                                        | 14                                    | 8                                   | 0.2910                                              | 15                                    | 10                                  |
| Replicate 3 | 0.3051                                        | 14                                    | 8                                   | 0.2927                                              | 16                                    | 11                                  |