thermoscientific

# High throughput and robust analysis of fertilizers using ICP-OES

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## ABSTRACT

Analytical testing laboratories frequently deal with heavy sample loads and a large suite of analytes but have limited time for delivering accurate results. In order to accomplish the desired productivity, short sample run times, robust methods, and minimum instrument downtime are fundamental requirements in such laboratories. This can be achieved with a technology such as inductively coupled plasma optical emission spectroscopy (ICP-OES) because it is traditionally highly matrix tolerant and modern ICP-OES instruments can additionally offer high sensitivity and speed.

## INTRODUCTION

The developed method measures major and trace elements in the radial mode that covers the full spectrum in a single exposure, from UV to visible range, simultaneously for all selected wavelengths without any additional data acquisition time. The small exposure times, when coupled with the Step Ahead feature of the autosampler, help realize a run time of only 36 s per sample (inlcuding uptake, analysis, and rinse) without the use of a discrete sampling valve. The method has been validated using standard reference materials, spike tests and a >5 hours long robustness test including >500 samples and regular QC checks. The results demonstrate high robustness and reliability, making the method an ideal choice for many different sectors where high productivity is required for anaylsing samples like water, waste water, soil, fertilizer, animal feed quality control, battery components and more.

## MATERIALS AND METHODS

In this study a Thermo Scientific™ iCAP™ PRO XP ICP-OES was used in combination with the Thermo™ Scientific™ iSC-65 autosampler (Figure 1) to offer a unique solution that combines accuracy and robustness with speed and simplicity, using fertilizer analysis as a case study to demonstrate the applicability of this configuration in high throughput laboratories.

Two commercially available fertilizers – one solid and one liquid – were used as samples in this study after microwave assisted digestion. Aliquots of 0.5 ± 0.05 g (for siolids) and , 2 g (for liquids) of homogenized sample were weighed directly into PTFE vessels 3 mL $HNO_3$, 1 mL HCl (both Trace Metal™ grade, Fisher Scientific) and 3 mL $H_2O$ (18 MΩ·cm) were added. For the liquid sample, 2 mL $HNO_3$, 0.5 mL HCl and 2 mL H2O was used. Before closing the vessels and placing them in the microwave for the digestion the samples were allowed to react with the reagents until all visible reaction was complete and no gases were being liberated anymore. 200 µg·L$^{-1}$ of Au was spiked into the samples as a Hg stabilizer. The samples were digested at 180° C for 10 minutes (ramp up time 20 mins) and allowed to cool down. The sample digests were particle free, they were recovered and made up to a final volume of 50 mL.

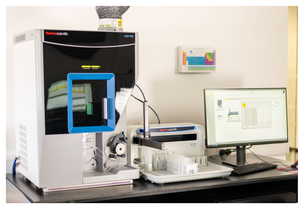

**Figure 1. iCAP PRO XP ICP-OES and iSC 65 autosampler**

**Table 1. Instrument configuration and typical operating parameters**

| Instrument parameter | Setting |
|---|---|
| Spray chamber | Glass cyclonic |
| Nebulizer | Glass concentric nebulizer |
| Center tube | 2.0 mm, quartz |
| Torch | EMT glass torch |
| Pump tubing | Sample: Tygon™ orange/white; Internal Standard: Tygon™ orange/blue; Drain: Tygon™ white/white |
| Pump speed | 45 rpm for data acquisition<br>125 rpm for Fast Uptake |
| Nebulizer gas flow | 0.65 L·min$^{-1}$ |
| Auxiliary gas flow | 0.5 L·min$^{-1}$ |
| Coolant gas flow | 12.5 L·min$^{-1}$ |
| RF Power | 1150 W |
| Exposure time | 5 s Radial iFR |
| Repeats | 3 |
| Autosampler | iSC-65 autosampler |
| Time per sample | 36 s |

All analytes were measured in radial viewing mode using the intelligent Full Range (iFR) mode available for the iCAP PRO XP Duo ICP-OES instrument. Whilst radial observation of the plasma provides the method´s robustness, the iFR mode enables the analysis of all analytes within a single exposure, covering the full spectrum range between 167 – 852 nm, irrespective of number of analytes and wavelengths selected.
The process of sample delivery offers an additional potential for time savings. The Step Ahead feature of the iSC-65 autosampler was used to start rinsing of the probe in parallel to data acquisition. The overall method finally yielded a sample runtime of only 36s seconds per sample, even without the use of a segmented flow sample introduction system.

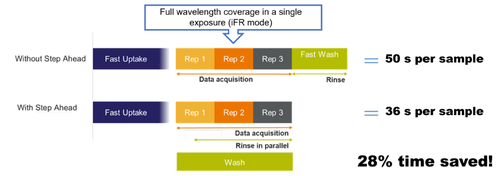


**Figure 2. Comparison of methods without and with the Step Ahead. All steps, i.e., sample uptake and stabilization, data acquisition with three repeats in Radial iFR mode (Rep 1, Rep 2, Rep 3 – 5 s each), and wash are realized in only 36 s.**

## RESULTS

A calibration blank and a set of calibration standards were prepared in 2% (v/v) $HNO_3$ and 0.5% HCl. 10 mg·kg$^{-1}$ each of Sc was used as internal standard to track and correct for matrix effects, if any. The internal standard solution was prepared in the same diluent (2% $HNO_3$ and 0.5% HCl) and added online via a T-piece to all samples and calibration solutions.

A 5 seconds exposure time per repeat was used for all analytes. Under these conditions, required sensitivity and linear dynamic range was easily achieved for all analytes, i.e. adhering to the recently updated EU regulation 2019/1009[1]. The results are displayed in table 2.

The accuracy of the method was tested using an SRM sample and a spiked simulated sample. The NIST SRM 695 (Trace Elements in Multi-Nutrient Fertilizer), run in triplicate, showed excellent recoveries between 86.7 – 101.4% for all analytes (Table 3).

**Table 2. Instrument detection limit (IDL or LOD = 3 x Stdev of repeat blank concentrations), $R^2$ and Method Limits of Quantification (LOQ = DF x 3 x LOD, where DF = Dilution Factor)**

| Element | Wavelength (nm) | Internal standard (nm) | $R^2$ | LOD (µg·kg$^{-1}$) | MLOQ with DF of 100 (mg·kg$^{-1}$) |
|---|---|---|---|---|---|
| Al | 396.152 | Sc 424.683 | 0.9997 | 7.69 | 2.31 |
| As | 189.042 | Sc 227.318 | 0.9999 | 13.40 | 4.02 |
| B | 249.678 | Sc 227.318 | 0.9998 | 4.50 | 1.59 |
| Ca | 422.673 | Sc 424.863 | 0.9998 | 3.11 | 0.93 |
| Cd | 214.438 | Sc 227.318 | 0.9995 | 0.50 | 0.15 |
| Co | 238.892 | Sc 227.318 | 0.9994 | 0.21 | 0.06 |
| Cr | 267.716 | Sc 227.318 | 0.9998 | 0.40 | 0.12 |
| Cu | 224.700 | Sc 227.318 | 0.9995 | 1.10 | 0.33 |
| Fe | 274.932 | Sc 227.318 | 0.9994 | 9.60 | 2.88 |
| Hg | 184.950 | Sc 227.318 | 0.9997 | 2.30 | 0.69 |
| K | 769.896 | Sc 424.863 | 0.9998 | 28.81 | 8.64 |
| Mg | 292.863 | Sc 227.318 | 0.9998 | 5.23 | 1.57 |
| Mn | 293.930 | Sc 227.318 | 0.9987 | 0.94 | 0.28 |
| Mo | 202.030 | Sc 227.318 | 0.9997 | 0.48 | 0.14 |
| Na | 588.995 | Sc 424.863 | 0.9994 | 3.50 | 1.05 |
| Ni | 221.647 | Sc 227.318 | 0.9999 | 0.89 | 0.27 |
| P | 213.618 | Sc 227.318 | 0.9999 | 8.50 | 2.55 |
| Pb | 220.353 | Sc 227.318 | 0.9999 | 7.28 | 2.18 |
| S | 180.731 | Sc 227.318 | >0.9999 | 3.50 | 1.05 |
| Zn | 213.856 | Sc 227.318 | 0.9995 | 1.10 | 0.33 |

**Table 3. Certified concentrations and recoveries in the NIST SRM-695, where dilution factor (DF) was 100, as well as Spiked concentrations, according to lowest limits in Regulation (EU) 2019/1009 and their recoveries in a simulated sample containing 1000 mg·kg$^{-1}$ K and 500 mg·kg$^{-1}$ P**

| Elements | Certified values | Recovery (%) | Spike concentration (µg·L$^{-1}$) | Recovery (%), n=3 |
|---|---|---|---|---|
| | in % | | | |
| Al | 0.61 ± 0.03 | 87.0 ± 4.1 | | |
| B | 0.111 ± 0.002 | 96.2 ± 5.5 | | |
| Ca | 2.26 ± 0.04 | 97.5 ±6.0 | | |
| Fe | 3.99 ± 0.08 | 101.4 ± 3.7 | | |
| K | 11.65 ± 0.13 | 92.3 ± 5.7 | | |
| Mg | 1.79 ± 0.05 | 97.7 ± 5.5 | | |
| Mn | 0.305 ± 0.005 | 90.2 ±5.5 | | |
| P | 7.2 ± 0.1 | 100.6 ±6.5 | | |
| Na | 0.405 ± 0.007 | 86.0 ±6.3 | | |
| Zn | 0.325 ± 0.005 | 90.1 ±4.9 | 5000 | 95.6 ± 2.1 |
| | in mg·kg$^{-1}$ | | | |
| As | 200 ± 5 | 88.0 ± 3.6 | 400 | 90.4 ± 5.5 |
| Cd | 16.9 ± 0.2 | 92.8 ± 4.6 | 15 | 106.7 ± 1.0 |
| Co | 65.3 ± 2.4 | 90.7 ± 5.0 | | |
| Cr | 244 ± 6 | 93.7 ± 6.2 | 20 | 105.0 ± 1.7 |
| Cu | 1225 ± 9 | 98.3 ± 6.2 | 2000 | 94.3 ± 3.2 |
| Hg | 1.955 ± 0.036 | 86.7 ± 2.9 | 10 | 96.1 ± 8.5 |
| Mo | 20 ± 0.3 | 89.8 ± 6.3 | | |
| Ni | 135 ± 2 | 95.9 ± 6.9 | | 95.4 ± 4.7 |
| Pb | 273 ± 17 | 93.8 ± 5.5 | 500 | 91.4 ± 5.0 |

The robustness of the method was tested for >5 hours with a single calibration block at the beginning, followed by a series of >500 unknown samples, including SRM solutions. The internal standard was monitored throughout to correct for matrix suppression/enhancement and/or drift. The results are shown in Figure 3. Quality control checks to verify the ongoing validity of the calibration curve (Continuing Calibration Verification (CCV)) were performed after every 25 unknown samples throughout the sequence.

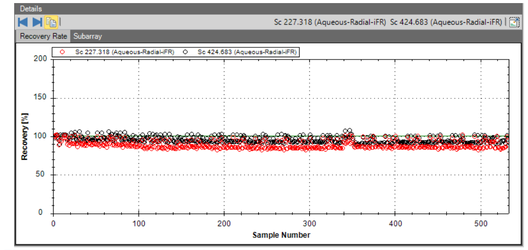


**Figure 3. High sample throughput and excellent internal standard recovery – more than 500 samples in 5.6 hours**

## CONCLUSIONS

- A quick and simple method with a run time of 36 s per sample (including uptake and wash) for a full analysis of elements present in fertilizers has been developed
- The use of the Step Ahead feature available on the iSC-65 autosampler compliments the speed of the iCAP PRO XP ICP-OES DUO. The combination of both provides the opportunity to reduce sample turnover times further by almost 30%.
- The method allows to achieve the typically required limits of quantifications for commonly regulated elemental contaminants in fertilizers and at the same time it can cover a large linear dynamic range between 0.01 – 20 mg·kg$^{-1}$ for trace elements and 1 – 1500 mg·kg$^{-1}$ for elements present in higher concentrations.
- The concept of the application can be easily extended to other sample types, such as soil or wastewater analysis. ICP-MS instruments can also benefit from single mode measurement and the high-speed capabilities of the iSC-65 autosampler

## REFERENCES

1. Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilizing products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003. https://eur-lex.europa.eu/eli/reg/2019/1009/oj

## TRADEMARKS/LICENSING



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