

Environmental

# Combining full spectrum read-out and innovative automation capabilities for the robust and fast analysis of major and trace elements in fertilizers using ICP-OES

## Authors

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## Keywords

ICP-OES, robustness, method validation, sensitivity, Step Ahead, limits of quantitation, analytical testing, toxic elements

## Goal

To demonstrate the capabilities of the Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument, in conjunction with the Thermo Scientific™ iSC-65 Autosampler, for the fast and robust elemental analysis of fertilizers

## Introduction

Fertile soils are essential for optimum plant growth. Therefore, fertilizers play a quintessential role in ensuring timely and proper food supplies at a global level. Characterizing the composition of fertilizing products is important as elements and compounds present within them supply plants and crops with essential nutrients but can also be a source of harmful components. These contaminants can be detrimental to human health as they migrate up the food chain. Regulations exist worldwide providing strict requirements for the composition of fertilizers, covering both essential macro- and micronutrients as well as potentially harmful compounds and elements. Agricultural fertilizers distributed in the European Union must comply to the latest requirements set out in the Regulation (EU) 2019/1009,<sup>1</sup> repealing the older requirements from

July 2022 onwards. The regulation describes different fertilizer types and sets limits for the total inorganic contents of the different element contaminants (except for Cr (VI)) within fertilizers. The ranges of those limits are listed in Table 1.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is the technique of choice for the analysis of fertilizers, as it provides the ability to measure up to %-levels for certain analytes, in combination with analysis at trace levels for critical contaminants. Such analysis is typically carried out in testing laboratories that often face a seasonal variation of the sample load, causing an extreme demand on sample throughput and response time. In such situations, shortening the sample analysis time helps to maximize laboratory throughput and conduct sample analysis within the committed timelines. This requires a fast and reliable ICP-OES instrument and also an efficient autosampler to handle hundreds of samples daily. Laboratories further resort to discrete sampling valve systems for reducing time spent on sample delivery and successive washing steps. However, such accessories introduce additional complexity to the entire analytical setup and also require a significant additional financial investment.

This study describes how the iCAP PRO XP ICP-OES Duo instrument and the iSC-65 Autosampler can be used to simultaneously measure the total concentrations of different major and trace elements (including the total concentration of Cr) within fertilizers with high speed and accuracy. This combination of instruments offers unique features that help testing laboratories to increase productivity without compromising robustness, by enabling the use of a simple analysis method that is capable of sample turnover times of less than 40 seconds per sample, without the need to use a discrete sampling valve.

**Table 1. The ranges of limits defined for different impurity elements within different fertilizer products in the Regulation (EU) 2019/1009**

Elements	Limits (mg·kg <sup>-1</sup> )	Target concentrations with DF = 100 (µg·kg <sup>-1</sup> )
As	40	400
Cd	1.5–10	15–100
Cr (VI)	2	20
Cu	200–600	2,000–6,000
Hg	1–120	10–1,200
Ni	1–100	10–1,000
Pb	50–120	500–1,200
Zn	500–1,500	5,000–15,000

## Experimental

### Instrument parameters

An iCAP PRO XP ICP-OES Duo instrument, along with an iSC-65 Autosampler, was used in this study for major and trace element analysis of fertilizer samples and a standard reference material (SRM). The sample introduction system for aqueous matrices was used for the analysis (instrument parameters listed in Table 2).

**Table 2. Instrument configuration and typical operating parameters**

Instrument parameter	Setting
<b>Spray chamber</b>	Glass cyclonic
<b>Nebulizer</b>	Glass concentric nebulizer
<b>Center tube</b>	2.0 mm, quartz
<b>Torch</b>	EMT glass torch
<b>Pump tubing</b>	<ul style="list-style-type: none"> <li>• Sample: Tygon™ orange/white</li> <li>• Internal standard: Tygon™ orange/blue</li> <li>• Drain: Tygon™ white/white</li> </ul>
<b>Pump speed</b>	<ul style="list-style-type: none"> <li>• 45 rpm for data acquisition</li> <li>• 125 rpm for Fast Uptake</li> </ul>
<b>Nebulizer gas flow</b>	0.65 L·min <sup>-1</sup>
<b>Auxiliary gas flow</b>	0.5 L·min <sup>-1</sup>
<b>Coolant gas flow</b>	12.5 L·min <sup>-1</sup>
<b>RF power</b>	1,150 W
<b>Exposure time</b>	5 s Radial iFR
<b>Repeats</b>	3
<b>Autosampler</b>	iSC-65 Autosampler
<b>Time per sample, using Step Ahead, including uptake, acquisition, and wash</b>	36 s

All analytes were measured in radial viewing mode using the intelligent Full Range (iFR) mode. While radial observation of the plasma provides method robustness, the iFR mode enables the analysis of all analytes within a single exposure, covering the full spectrum range between 167 nm and 852 nm, irrespective of number of analytes and wavelengths selected. This means the full list of target analytes, with multiple wavelengths in different regions of the spectrum, can be measured without increasing the measurement time. The Radial iFR mode also provides excellent sensitivity for all elements along with a broad linear dynamic range so that an additional mode switching to axial observation can be omitted. Thus, both high and low concentration elements can be confidently quantified in samples of interest in a single mode to significantly improve the speed of analysis. Using a single mode, as opposed to two modes (i.e., covering the visible and UV range of the optical spectrum), reduces analysis time by at least 50%, considering the same exposure times in both modes.

Due to the superior sensitivity of the iCAP PRO XP ICP-OES instrument used in this study, an exposure time as low as 5 s could be applied to satisfy the sensitivity requirements of different methods and regulations applicable for the analysis of fertilizers. For applications where higher sensitivity may be required, for example, food analysis, longer exposure times can be chosen using the same setup.

### Autosampler settings

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 autosampler probe in parallel to data acquisition of the sample, thereby saving valuable time.

The Step Ahead parameters were optimized such that the probe was able to move to rinse shortly after finishing sample uptake, so that the proposed method yielded a sample analysis time of only 36 s per sample, including uptake, acquisition (with three repeats), and wash (Figure 1). Without this feature, the same analysis would have taken 50 s per sample instead. Thus, using Step Ahead creates a 28% time savings in this case and provides significant gains in productivity.

### Sample preparation

Two commercially available fertilizers—one solid and one liquid—were used as samples in this study. The samples and the SRM were weighed directly into PTFE vessels for closed vessel microwave digestion. The sample and reagent amounts used were  $0.5 \pm 0.05$  g of homogenized sample powders, 3 mL  $\text{HNO}_3$ , 1 mL HCl (both Trace Metal™ Grade, Fisher Scientific) and 3 mL  $\text{H}_2\text{O}$  (18 M $\Omega$ -cm). For the liquid sample, 2 g of sample, 2 mL  $\text{HNO}_3$ , 0.5 mL HCl, and 2 mL  $\text{H}_2\text{O}$  were 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  $\mu\text{g}\cdot\text{L}^{-1}$  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 min) and allowed to cool down. The sample digests were particle free. They were recovered and made up to a final volume of 50 mL.

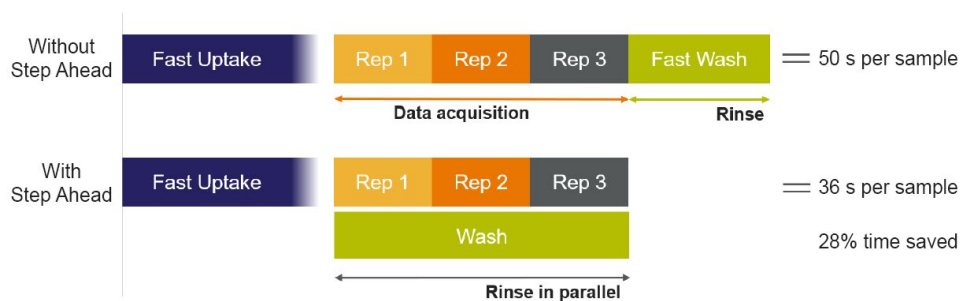
### Standards and reference materials

A calibration blank and a set of calibration standards were prepared in 2% (v/v)  $\text{HNO}_3$  and 0.5% HCl using single element standards (1,000  $\text{mg}\cdot\text{L}^{-1}$ , SPEX™ CertiPrep™ Group, Metuchen, NJ, US) of individual analytes. The individual standard concentrations and sample groups were chosen according to regulatory limits and expected concentrations of the different elements in typical fertilizer samples (Table 3).

10  $\text{mg}\cdot\text{kg}^{-1}$  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%  $\text{HNO}_3$  and 0.5% HCl) and added online via a T-piece to all samples and calibration solutions. NIST™ SRM™ 695 (Trace Elements in Multi-Nutrient Fertilizer) was included in the study to demonstrate accuracy. To mimic a fertilizer matrix, a solution of 1,000  $\text{mg}\cdot\text{kg}^{-1}$  K and 500  $\text{mg}\cdot\text{kg}^{-1}$  P was spiked with the lowest permitted amounts of trace impurity elements to serve as an additional accuracy check. 200  $\mu\text{g}\cdot\text{L}^{-1}$  of Au was added to all solutions.

### Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for data acquisition, processing, and reporting.



**Figure 1. Comparison of methods without and with the Step Ahead feature of the iSC-65 Autosampler.** All steps of the analysis—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, resulting in a 28% time savings per sample.

## Results and discussion

### Linearity and sensitivity

The concentrations of different analytes in the calibration standards are presented in Table 3. The linearity ranges start from 0.01 mg·L<sup>-1</sup> for the regulated trace elements, whereas for the major elements, which are expected in higher concentrations in fertilizer samples, the calibrated range was extended to

1,500 mg·L<sup>-1</sup>. Linear calibration curves with values of R<sup>2</sup> exceeding 0.9994 were obtained for all analytes (Tables 3 and 4).

The Radial iFR viewing mode with 5 s exposure time per repeat was used for all analytes. This helps easily achieve the required linear dynamic range as well as the required sensitivity for the different analytes for adhering to the Regulation (EU) 2019/1009 (Table 4).

**Table 3. Concentrations of stock solutions and calibration standards**

Element group	Concentrations (mg·L <sup>-1</sup> )					
	Std 1	Std 1	Std 2	Std 3	Std 4	Std 5
As, Cd, Co, Hg, Mo, Ni, Pb, V, Cr	0.01	0.1	1	2	5	-
B, Cu	-	0.2	2	4	10	20
Mn, Zn, Al	-	1	10	20	50	100
Ca, Mg, Fe, S, Na	-	5	50	100	250	500
P	-	10	100	200	500	1,000
K	-	15	150	300	750	1,500

**Table 4. The sensitivity achieved for the target elements, expressed in terms of instrument detection limit (IDL or LOD = 3 × Stdev of repeat blank concentrations) and method limits of quantification (MLOQ = DF × 3 × LOD, where DF = dilution factor)**

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

## Accuracy

The accuracy of the method was tested using an SRM sample and a spiked simulated sample. The SRM 695, run in triplicate, showed excellent recoveries between 86.7% and 101.4% for all analytes (Table 5).

The spike recovery test, performed at the lowest permissible limits according to Regulation (EU) 2019/1009 (Table 1), also showed excellent recoveries varying from 90.4% to 106.7% (Table 6).

## Robustness

The method yielded a sample turnover time of 36 s for a full analysis per sample, without the use of an additional sample valve. This translates to a high sample turnover on a daily basis, provided the method is also capable of running uninterrupted sample analysis over several hours without a drop in data quality or need for maintenance. This was tested in a robustness experiment that was set up for >5 hours with a single calibration block at the beginning, followed by a series of >500 unknown samples, including SRM solutions. Quality control checks were run after every 25 unknown samples throughout the sequence, to verify the ongoing validity of the calibration curve (Continuing Calibration Verification - CCV). The Std 2 was used as the QC solution. The internal standard was monitored throughout to correct for matrix suppression/enhancement and/or drift.

The internal standard showed no matrix effect and negligible drift over the entire duration of the sequence. The internal standard recoveries in the Radial iFR mode were between 86% and 110% (Figure 2). The QC recoveries over the entire measurement block were within 80–120% (Figure 3).

## Real sample analysis

The solid and liquid fertilizer samples measured in this study were characterized for their elemental concentrations using the developed method. The results are presented in Table 7. The major constituent in both samples was K, found in 31% and 5% of the solid and liquid samples, respectively. Other major elements detected in high concentrations in the samples were Ca, Na, and S in the range of 0.1–3% in both samples. None of the regulated contaminants listed in Table 1 were found above the permitted concentrations. However, low amounts of Cr (0.3–2.8 mg·kg<sup>-1</sup>) and Cd (0.01–0.03 mg·kg<sup>-1</sup>) were measured (Table 7).

**Table 5. Certified concentrations and recoveries in the NIST SRM 695, where dilution factor (DF) was 100**

Elements	Certified values	Expected concentrations in solution, with DF = 100	Recovery (%)	Err (1σ, n = 3)
	in %	in mg·kg <sup>-1</sup>		
Al	0.61 ± 0.03	61	87.0	4.1
B	0.111 ± 0.002	11.1	96.2	5.5
Ca	2.26 ± 0.04	226	97.5	6.0
Fe	3.99 ± 0.08	399	101.4	3.7
K	11.65 ± 0.13	1165	92.3	5.7
Mg	1.79 ± 0.05	179	97.7	5.5
Mn	0.305 ± 0.005	30.5	90.2	5.5
P	7.2 ± 0.1	720	100.6	6.5
Na	0.405 ± 0.007	40.5	86.0	6.3
Zn	0.325 ± 0.005	32.5	90.1	4.9
	in mg·kg <sup>-1</sup>	in mg·kg <sup>-1</sup>		
As	200 ± 5	2	88.0	3.6
Cd	16.9 ± 0.2	0.169	92.8	4.6
Co	65.3 ± 2.4	0.653	90.7	5.0
Cr	244 ± 6	2.44	93.7	6.2
Cu	1225 ± 9	12.25	98.3	6.2
Hg	1.955 ± 0.036	0.01955	86.7	2.9
Mo	20 ± 0.3	0.2	89.8	6.3
Ni	135 ± 2	1.35	95.9	6.9
Pb	273 ± 17	2.73	93.8	5.5

**Table 6. Spiked concentrations, according to lowest limits in Regulation (EU) 2019/1009, and their recoveries in a simulated sample containing 1,000 mg·kg<sup>-1</sup> K and 500 mg·kg<sup>-1</sup> P**

Element	Spike concentration (μg·L <sup>-1</sup> )	Recovery (%), n=3
As	400	90.4 ± 5.5
Cd	15	106.7 ± 1.0
Cr	20	105.0 ± 1.7
Cu	2,000	94.3 ± 3.2
Hg	10	96.1 ± 8.5
Ni	10	95.4 ± 4.7
Pb	500	91.4 ± 5.0
Zn	5,000	95.6 ± 2.1

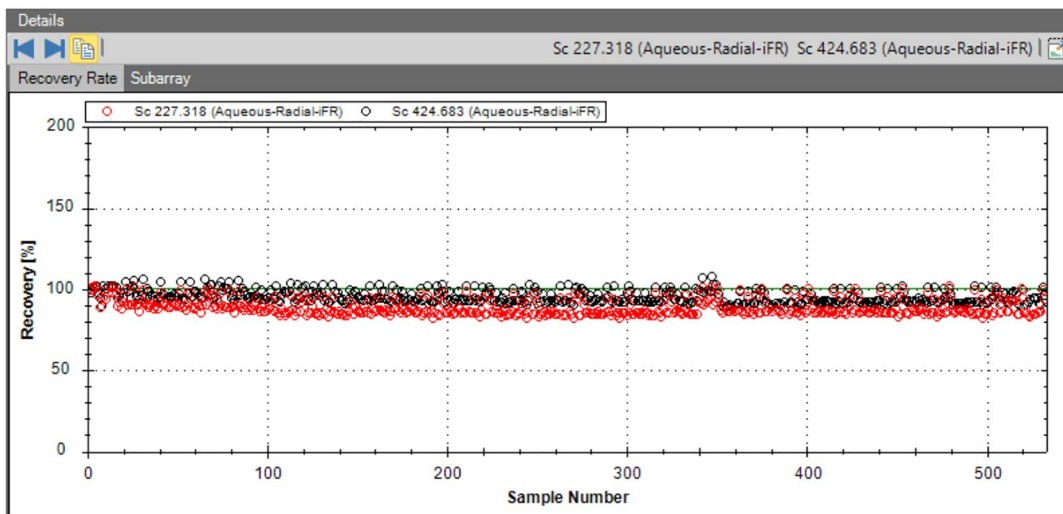


Figure 2. High sample throughput and excellent internal standard recovery—more than 500 samples in 5.6 hours

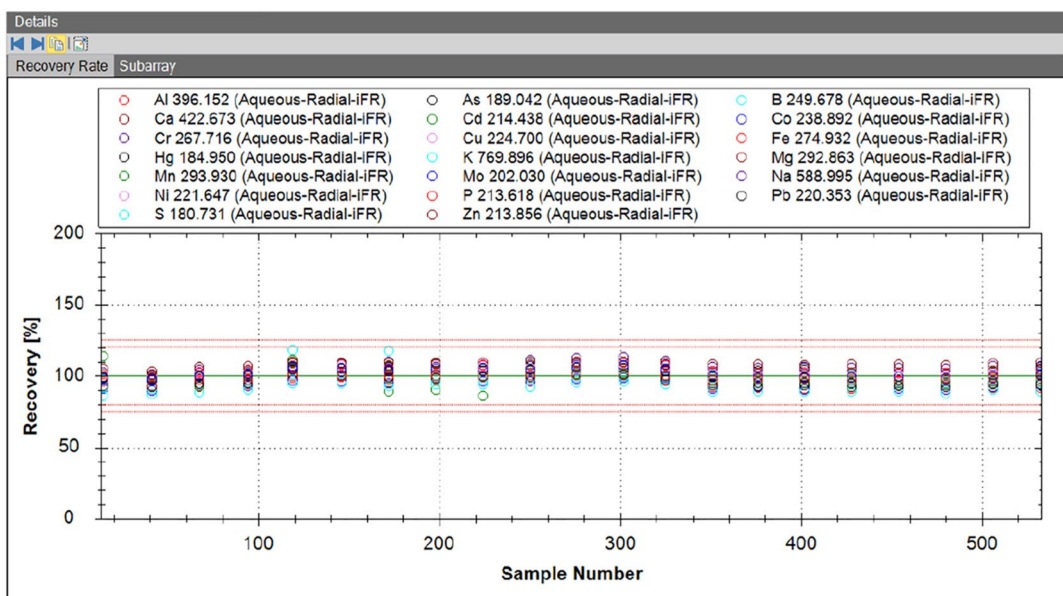


Figure 3. QC recoveries over approximately 6 hours of continuous measurements

Table 7. Multielement concentration of solid and liquid fertilizer samples measured in this study

Element	Concentration in solid sample (mg·kg <sup>-1</sup> or %)	Concentration in liquid sample (mg·L <sup>-1</sup> or %)	Element	Concentration in solid sample (mg·kg <sup>-1</sup> or %)	Concentration in liquid sample (mg·L <sup>-1</sup> or %)
Al	12.61 ± 0.4	17.53 ± 0.26	<i>K in %</i>	30.9 ± 0.25	5.43 ± 0.30
As	0.15 ± 0.1	<DL	Mg	36.5 ± 3.3	263.9 ± 1.85
B	6.05 ± 0.6	4.24 ± 0.77	Mn	5.19 ± 0.6	43.31 ± 0.34
<i>Ca in %</i>	1.41 ± 0.06	0.65 ± 0.01	Mo	0.14 ± 0.001	0.22 ± 0.005
Cd	0.01 ± <0.001	0.03 ± <0.001	<i>Na in %</i>	1.15 ± 0.01	0.33 ± 0.03
Co	0.07 ± 0.1	0.96 ± 0.02	Ni	<DL	<DL
Cr	2.83 ± 1.3	0.34 ± 0.05	P	1569.77 ± 41.2	409.67 ± 12.0
Cu	0.54 ± 0.2	0.29 ± 0.04	Pb	<DL	<DL
Fe	17.42 ± 6.8	170.74 ± 1.22	<i>S in %</i>	3.01 ± 0.01	0.05 ± <0.01
Hg	<DL	<DL	Zn	1.30 ± 0.7	55.60 ± 0.02

## Conclusions

This application note presents a fast and optimized method for the quick, accurate, and robust analysis of major and trace elements in fertilizers using the iCAP PRO XP ICP-OES Duo instrument and the iSC-65 Autosampler. The highlights of the study are listed below:

- A quick and simple method with a run time of 36 s per sample for all target elements in fertilizers has been developed. This has been achieved using the excellent sensitivity in radial mode and the fast data acquisition capabilities of the iCAP PRO XP ICP-OES Duo instrument using the iFR mode. Due to the fully simultaneous acquisition across the full optical spectrum, an additional exposure can be eliminated, offering a 50% reduction of the time required for data acquisition.
- The use of the Step Ahead feature available on the iSC-65 Autosampler compliments the speed of the iCAP PRO XP ICP-OES Duo instrument and the chosen settings in this method by enabling rinsing parallel to data acquisition. The combination of both provides the opportunity to reduce sample turnover times further by almost 30% compared to a standard setup.
- The method allows achievement of the typically required limits of quantification for commonly regulated elemental contaminants in fertilizers—such as As, Cd, Cr, Hg, Ni, and Pb—with respect to the criteria prescribed in the Regulation (EU) 2019/1009. At the same time, it is capable of covering a large linear dynamic range of 0.01–20 mg·kg<sup>-1</sup> for trace elements and 1–1,500 mg·kg<sup>-1</sup> for elements present in higher concentrations. If the total concentration of Cr is found to be higher than the specified limit, then a speciation technique may be used to determine the amount of Cr (VI) present in the samples. 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.<sup>2</sup>
- Continuous, uninterrupted measurements of >5 hours covering more than 500 unknown samples proves the accuracy and unmatched robustness of the developed method, which makes the iCAP PRO XP ICP-OES Duo instrument an ideal choice for high productivity analytical testing laboratories.

## 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>
2. Blog post in Analyte Guru. <https://www.thermofisher.com/blog/analyteguru/how-to-increase-your-elemental-analysis-labs-productivity-fast/>

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