



Determination of nutritional elements in plant leaves using the Thermo Scientific iCAP 7400 ICP-OES Duo

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Keywords

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Goal

To demonstrate the advantages of a dual view Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) for the determination of nutritional elements in plant leaves.

Introduction

The commercial value of a plant as a food stuff or as a raw material for preparing medicines depends on the quality of the plant product. One measure of quality is the balance of different chemical and elemental constituents in the plant material. Typically the major elements (macronutrients, including calcium, potassium, phosphorus, nitrogen, magnesium, sulfur) as well as the trace elements (micronutrients, including boron, manganese, iron, nickel, copper, and zinc) are assessed to determine quality.

This allows the identification of nutrient deficiency, which can lead to a reduction in the quality of flowers, fruits or vegetables, produced by the plant. In addition, the elemental composition of the plant may explain the plant's medicinal or toxic properties.

With the development of ionomics (which involves the quantitative and simultaneous measurement of plant elemental composition and changes in this composition in response to physiological effects and genetic modifications [1-3]) new techniques for the quantitation of plant ions or their parts became of high importance.

In this study the advantages of Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES for the determination of nutritional elements in plant matrices are discussed, using plant leaf analysis as an example.

Instrumentation

For sample analysis, the Thermo Scientific iCAP 7400 ICP-OES Duo was used together with an aqueous sample introduction kit (Table 1) and an internal standard kit for online addition of the internal standard.

Table 1. Method parameters.

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Tygon™ orange/white Drain Tygon™ white/white
Pump Speed	50 rpm
Spray Chamber	Glass cyclonic
Nebulizer	Glass concentric
Center Tube	2 mm
Nebulizer Gas Flow	0.5 L·min ⁻¹
Auxiliary Gas Flow	0.5 L·min ⁻¹
Coolant Gas Flow	12 L·min ⁻¹
RF Power	1150 W
Number of Replicates	3
Exposure Time	UV 10 s and Vis 5 s for both Axial and Radial view

The duo configuration was chosen for its low detection capability in order to quantify not only the macro- but also the microelements in leaves. A Teledyne CETAC ASX-560 Autosampler was used to transfer the sample to the introduction system of the ICP-OES. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software simplifies method development by the intuitive creation of an analytical LabBook. The software allows for the flexible choice of sample introduction and method parameters for enhanced performance, and also provides easy options for post-analysis data manipulation.

Standard preparation

All standard solutions were prepared from single element solutions (1000 mg·L⁻¹, Fisher Scientific, Loughborough, UK). The individual solutions were made up with ultra-pure water (18 mΩ) and nitric acid (TraceMetal™ grade, Fisher Scientific, to a final concentration of 7.8% nitric acid). An internal standard solution of indium (2 mg·L⁻¹) was prepared in the same way. Standard solutions were prepared by dilution to cover the expected concentration range of analytes (Table 2).

Table 2. Concentrations of elements in calibration standards.

Element	Units	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6	Standard 7	Standard 8
Al, P	mg·L ⁻¹	75	50	25	5.0	2.5	0.5	0.05	0.005
B	mg·L ⁻¹	1.125	0.75	0.375	0.075	0.0375	7.5×10 ⁻³	7.5×10 ⁻⁴	7.5×10 ⁻⁵
Ba	mg·L ⁻¹	2.25	1.5	0.75	0.15	0.075	1.5×10 ⁻²	1.5×10 ⁻³	1.5×10 ⁻⁴
Be	μg·L ⁻¹	2.3	1.5	0.75	0.15	0.075	0.015	0.0015	0.00015
Ca	mg·L ⁻¹	1500	1000	500	100	50	10	1.0	0.10
Cu, Ni	μg·L ⁻¹	300	200	100	20	10	2.0	0.20	0.02
Fe	mg·L ⁻¹	45	30	15	3.0	1.5	0.30	0.03	0.003
K	mg·L ⁻¹	750	500	250	50	25	5.0	0.50	0.05
Li	μg·L ⁻¹	675	450	225	45	22.5	4.5	0.45	0.045
Mg	mg·L ⁻¹	300	200	100	20	10	2.0	0.20	0.02
Mn	μg·L ⁻¹	5630	3750	1880	375	188	37.5	3.75	0.375
Na	mg·L ⁻¹	15	10	5.0	1.0	0.50	0.10	0.01	0.001
S	mg·L ⁻¹	150	100	50	10	5.0	1.0	0.10	0.01
Zn	mg·L ⁻¹	1.5	1.0	0.50	0.10	0.05	0.01	0.001	0.0001

Sample preparation

Certified Reference Materials (CRMs) of dried apple leaves (SRM 1515, NIST, USA) and dried tobacco (Institute of Nuclear Chemistry and Technology, Poland) were used during this analysis.

Both materials were analyzed for moisture before each analysis using the loss on drying method. The result of the moisture analysis was then used to correct the results of analysis for moisture content. Prior to digestion each sample was weighed (0.5 to 0.8 g) into a PTFE high pressure vessel, nitric acid (6 mL, concentrated) and hydrogen peroxide (2 ml, concentrated, Fisher Scientific) were added. If material adhered to the walls of the vessel, it was washed down carefully with the acid. The hydrogen peroxide was added to aid the digestion of the organic matrix.

A Milestone Ethos EZ microwave oven equipped with an SK-10 segmented rotor and a temperature sensor was used for the digestion. The samples were digested according to the protocol in Figure 1. After digestion each sample was transferred to a volumetric flask (50 mL). The digestion vessel was washed with ultra-pure water (18 mΩ) and the wash solution was transferred to those flasks. The flask was then made up to volume with ultra-pure water. For each digestion cycle a duplicate of a digestion blank was run. This contained only acid and hydrogen peroxide and after digestion was treated the same way as samples.

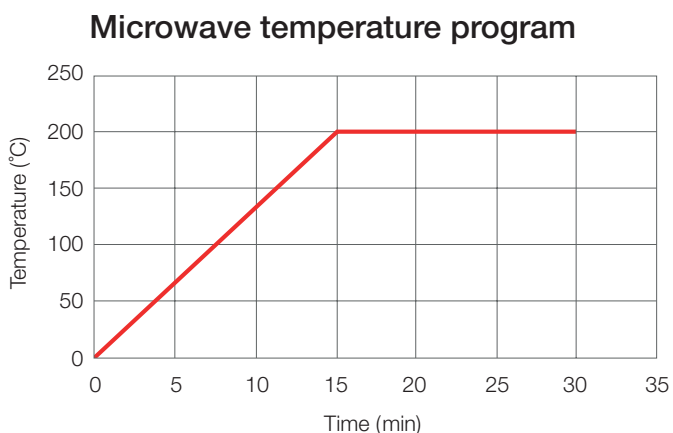


Figure 1. Temperature program of the microwave digestion.

The digested samples were introduced into the ICP-OES directly. For quantifying the elements present in leaf samples at levels above 1000 mg·kg⁻¹ (Al, Ca, K, Mg) the samples were further diluted in either 10 or 100 times with nitric acid (7.8%) prior to analysis.

Method development and analysis

A LabBook was created using the Qtegra ISDS Software. The parameters used for the analysis can be found in Table 1. The wavelengths (Table 3) used for the analysis were selected as they were free from matrix effects and provided the sensitivity to quantify the elements of interest in the expected concentration range.

The plasma was ignited and the instrument was allowed to warm up for a period of 15 minutes. A spectrometer optimization was performed directly before analysis.

Following method development the instrument was calibrated and the samples were analyzed. A method detection limit (MDL) study was carried out by analyzing the digestion blank with ten replicates and multiplying the standard deviation of this analysis by three. This was repeated three times and the average values for detection limits were calculated.



Results

Using the iCAP 7400 ICP-OES Duo allowed the determination of the elements of interest in the wavelength range from 166 to 847 nm in one analytical run using both radial and axial views. This allowed the most beneficial wavelengths and plasma view for each analyte to be used, minimizing matrix effects over the expected concentration range (Figure 2).

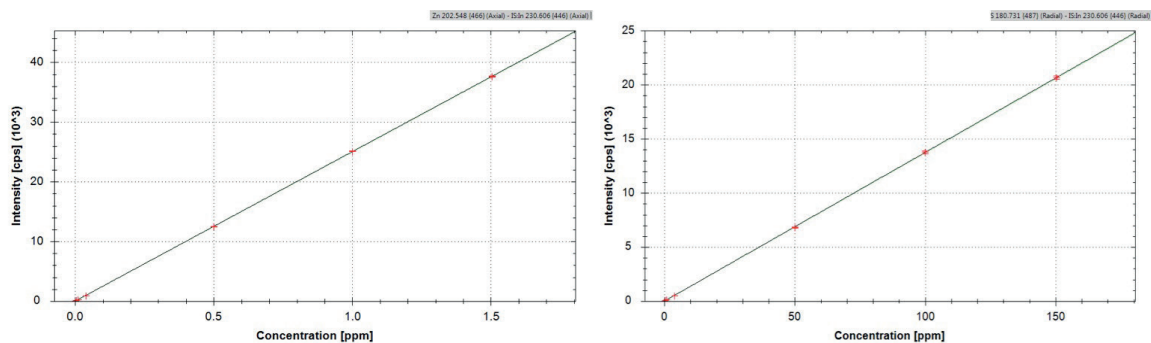


Figure 2. Calibration curves obtained for signals of zinc (micronutrient) and sulfur (macronutrient).

The determined concentrations of elements in apple and tobacco leaves were in good agreement with the specified values for the used CRMs (Table 3).

Table 3. MDLs and concentrations of elements in leaves.

Element and wavelength (nm)	MDL ($\mu\text{g}\cdot\text{L}^{-1}$)	Apple		Tobacco	
		Found ($\text{mg}\cdot\text{kg}^{-1}$)	Reference value ($\text{mg}\cdot\text{kg}^{-1}$)	Found ($\text{mg}\cdot\text{kg}^{-1}$)	Reference value ($\text{mg}\cdot\text{kg}^{-1}$)
Elements viewed radially					
Al 167.079	20	300	286	1800	1980
B 249.773	7	29	27	36	33.6
Ba 455.403	0.6	52	49	69	67.4
Ca 317.933	7	15000	15260	41000	39960
Cu 324.754	8	6.2	5.64	11	10.1
Fe 259.940	7	84	83	1610	1490*
K 766.490	300	16000	16100	21000	22710
Li 670.784	4	-	-	25	19.3*
Mg 279.553	0.3	2700	2710	8400	8530
Mn 257.610	0.8	58	54	193	180
Na 589.592	20	24	24.4	196	435*
P 177.495	9	1560	1590	1800	1700
S 180.731	10	1800	1800*	4300	4550
Elements viewed axially					
Be 313.042	0.03	-	-	0.071	0.0812*
Ni 221.647	0.4	1.0	0.91	8.9	8.50
Zn 213.856	0.2	12.7	12.5	56	52.4

*non certified values, information values only

The detection limits (DL) for the majority of the elements were much lower than $1 \mu\text{g}\cdot\text{L}^{-1}$ [5]. The deviations from the certified values were less than 10% in all cases. Higher deviations were observed only for lithium (30%) and sodium (55%) in the tobacco sample, but the concentrations of those elements in tobacco samples were information values only, therefore it is assumed that the deviations of concentrations for these elements would show less than 10% deviation, if those values were certified.

Conclusion

The iCAP 7000 Plus Series ICP-OES with duo view provides an unprecedented flexibility of analysis for determining macro- and microelements in plant matrices at the necessary levels of accuracy and sensitivity. The closed vessel microwave digestion procedure provides a complete digestion of a complex sample matrix into a form suitable to ICP-OES analysis without the loss of target elements. Qtegra ISDS Software allows to easily optimize method parameters depending on the sample matrix and delivers the highest simplicity, productivity, efficiency and quality in the analysis workflow.

References

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