

# Total Elemental Analysis of Food Samples with ICP-OES and ICP-MS

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## ABSTRACT

**Purpose:** This poster demonstrates the use of both inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) to determine elements of interest in food samples.

**Methods:** Different certified reference materials were analyzed using both ICP-OES and ICP-MS. The selected reference materials contained elements which could lead to severe bias in the results, if interferences were not eliminated efficiently. The results however showed excellent agreement with certified values and hence demonstrate complete interference removal.

**Results:** Precise, accurate results for digested food samples are easily attained on the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo as well as on the Thermo Scientific™ iCAP™ TQ ICP-MS. Whereas analysis with the iCAP 7400 ICP-OES could be shown to be a powerful, yet simple to operate, the combination of the iCAP TQ ICP-MS and ESI *prepFAST*™ Autodilution System allowed rapid and accurate analysis of 24 elements in two different modes (SQ-KED and TQ-O<sub>2</sub> to eliminate all interferences), while reducing the amount of manual interaction during sample preparation.

## INTRODUCTION

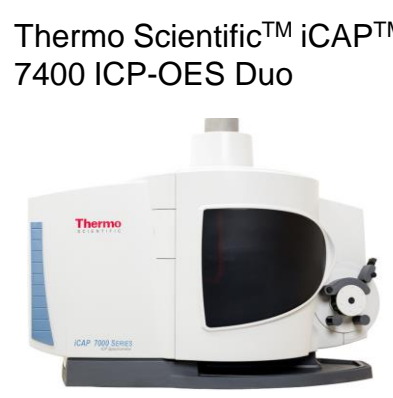
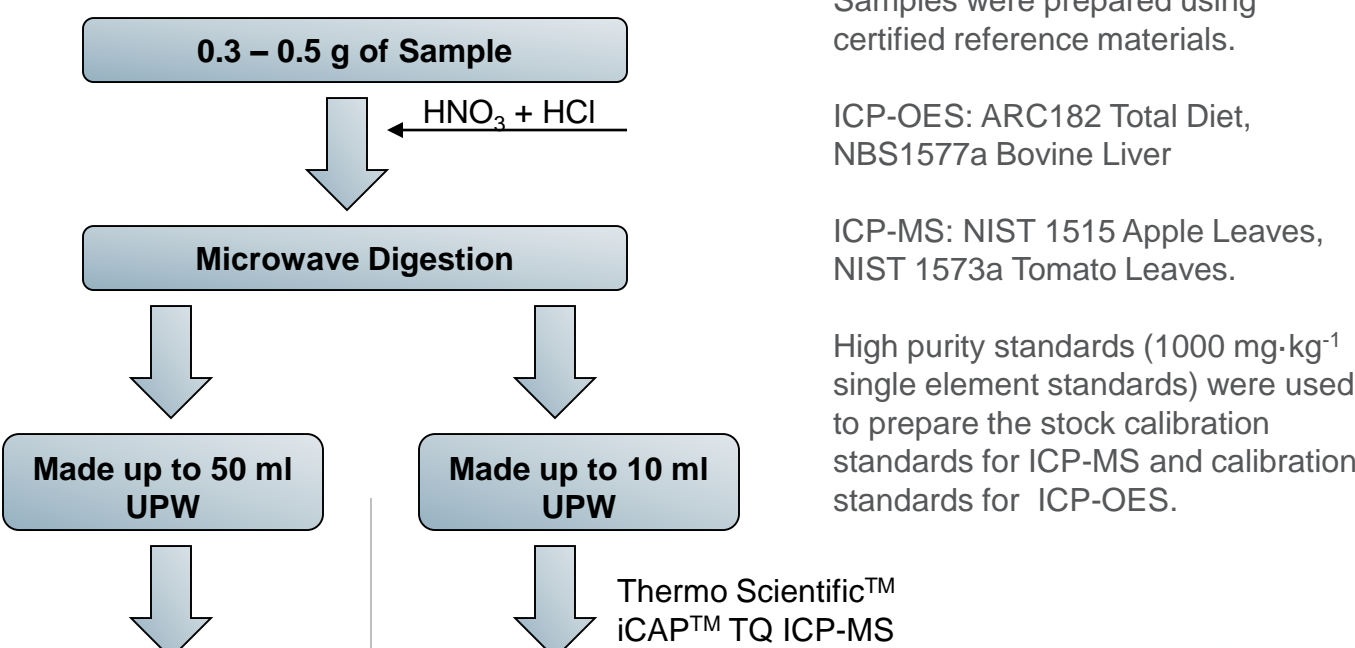
The measurement of toxic, essential and nutritional elements in food has, through regulatory drivers and today's health-conscious consumers become a routine part of food quality monitoring. Alongside regulatory compliance, it is necessary to monitor potentially toxic contaminants that could enter the food chain via a series of pathways including, but not limited to, industrial pollution or environmental contamination. For these reasons, it is essential to have a simple, robust, multi-elemental analysis method for major and minor concentrations of elements in food.

ICP-OES and ICP-MS are sensitive and rapid techniques with wide linear dynamic range and as such are ideal tools for the analysis of trace and major analytes in food in one analytical run. The accuracy of these techniques is demonstrated through the analysis of food based certified materials following microwave digestion.

The principal challenge for trace elemental ICP-based techniques are interferences that stem from the complex food matrix, the reagents used to prepare the sample and the plasma source. This paper reviews different strategies including collision/reaction cell (CRC) strategies in triple quadrupole ICP-MS for the accurate analysis of trace elements in more challenging matrices.

## MATERIALS AND METHODS

### Sample Preparation



## Method

### Instrumentation

An iCAP 7400 ICP-OES Duo instrument was chosen for this analysis it enables maximum sensitivity using axial view whilst maintaining excellent matrix tolerance in radial view. The instrument parameters used for the ICP-OES are listed in Table 1. The iCAP TQ ICP-MS was operated in SQ-KED mode and TQ-O<sub>2</sub> mode using the parameters presented in Table 1. All instruments were controlled using the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution (ISDS) Software. This instrument agnostic software platform uses dedicated plug-ins to include different types of analytical instrumentation, as well as peripheral devices such as autosamplers or automated dilution systems from industry leading manufacturers. It therefore dramatically simplifies training requirements for laboratories utilizing both techniques for the determination of trace elements.

Table 1. ICP-MS and ICP-OES operating parameters.

Parameter	iCAP 7400 ICP-OES Duo	iCAP TQ ICP-MS
Nebulizer	Glass concentric	PFA ST Nebulizer (Green) 100 µL·L <sup>-1</sup>
Spraychamber	Glass cyclonic	Quartz cyclonic spraychamber cooled @ 3 ° C
Injector	2.0mm Quartz	2.5 mm Quartz
Interface	N/A	Ni sampler and Ni skimmer with 3.5 mm insert
RF Power	1150 W	1550 W
Nebulizer Gas	0.6 L·min <sup>-1</sup>	1.0 mL·min <sup>-1</sup>
Auxiliary Gas Flow	0.5 L·min <sup>-1</sup>	N/A
Coolant Gas Flow	12 L·min <sup>-1</sup>	N/A
TQ-O <sub>2</sub>	N/A	100% O <sub>2</sub> gas @ 0.3 mL·min <sup>-1</sup>
SQ-KED	N/A	100 % He gas @ 4.3 mL·min <sup>-1</sup> with 3V KED
Dwell Time	N/A	0.1 second per analyte, 5 sweeps
Exposure Time	UV 15 s, Vis 5 s	N/A
Lens Setting	N/A	Optimized using autotune routines

### Autodilution System

Samples were presented for analysis with the iCAP TQ ICP-MS using an Elemental Scientific *prepFAST* Autodilution System. Using prescriptive dilution, all samples were automatically diluted directly before the analysis using ICP-MS. Again, the autodilution unit was controlled within the Qtegra ISDS Software, allowing to use both user defined prescriptive as well as intelligent autodilution for samples falling outside of previously defined ranges (calibration range or internal standard recovery).

## RESULTS

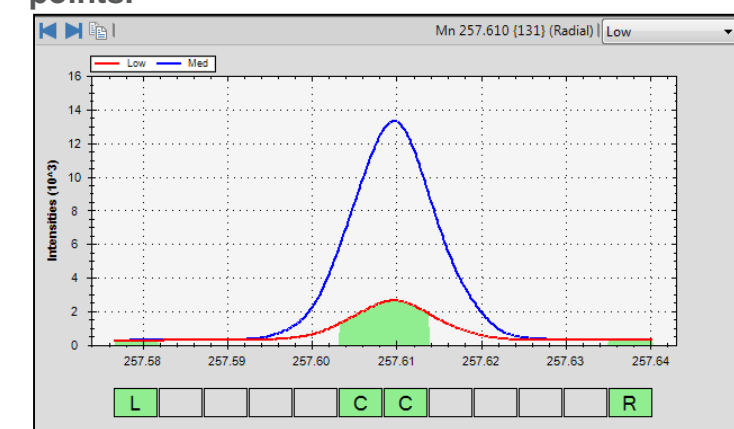
### ICP-OES Analysis

ICP-OES is a well established technique for the routine analysis of trace elements, allowing to achieve detection limits sufficient to meet most regulatory requirements and being robust to tolerate a wide variety of sample matrices. For samples requiring the analysis of both major as well as trace elements, the possibility to switch between radial and axial plasma observation allows to cover a large concentration range.

Table 2. Element, wavelength and plasma view used for ICP-OES measurement.

Element	Wavelength (nm)	View
Ca	317.933	Radial
Cu	327.396	Axial
Fe	274.932	Radial
Mg	285.213	Radial
Mn	257.610	Axial
Ni	231.604	Axial
P	178.284	Axial
Zn	206.2	Axial

Figure 1. Subarray plot for Mn 257.610 nm, indicating the peak center and background points.



Initially, more than one wavelength was selected for each element (using multiple views axial/radial). The subarrays for each wavelength were then examined and the most appropriate wavelength for the application was chosen based on the presence of interferences, calibration curve, recoveries of standards, QCs, and CRMs and the required linearity for the element (Table 2). The subarray plots for each element can be easily manipulated by the analyst, allowing the optimum peak integration and background correction points to be selected.

The calibration standards and samples were analyzed in a single sequence with a dilute acid rinse (0.5% HNO<sub>3</sub>) between samples. The sample data was measured by interpolation and results are shown in Table 4. Suitable dilutions were made to over-range elements to ensure they fell within the calibration range.

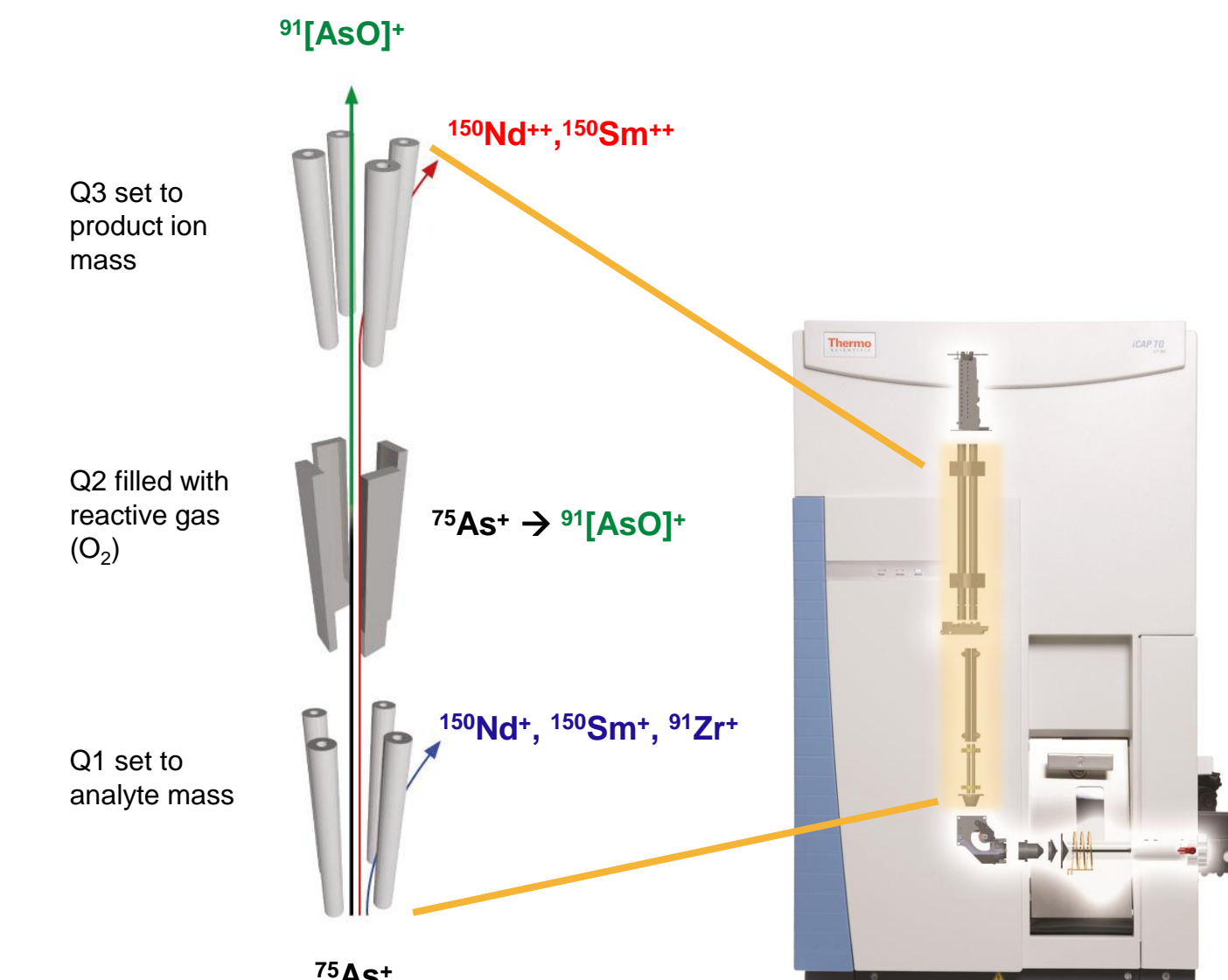
Table 3. ICP-OES results of measurement and CRM in mg·kg<sup>-1</sup> and calculated recoveries in %.

Element	NBS1577a			ARC182		
	Found in solid	CRM	Recovery (%)	Found in solid	CRM	Recovery (%)
Ca	133.6	120	111.33	2670	2860	93.36
Cu	153.3	158	97.03	N/A	N/A	N/A
Fe	192.9	194	99.43	N/A	N/A	N/A
Mg	576.5	600	96.08	719.2	785	91.62
Mn	10.14	9.9	102.42	12.98	12.9	100.62
Ni	N/A	N/A	N/A	0.2863	0.271	105.65
P	11490	11100	103.51	N/A	N/A	N/A
Zn	122.2	123	99.35	29.16	28.9	100.9

### ICP-MS Analysis

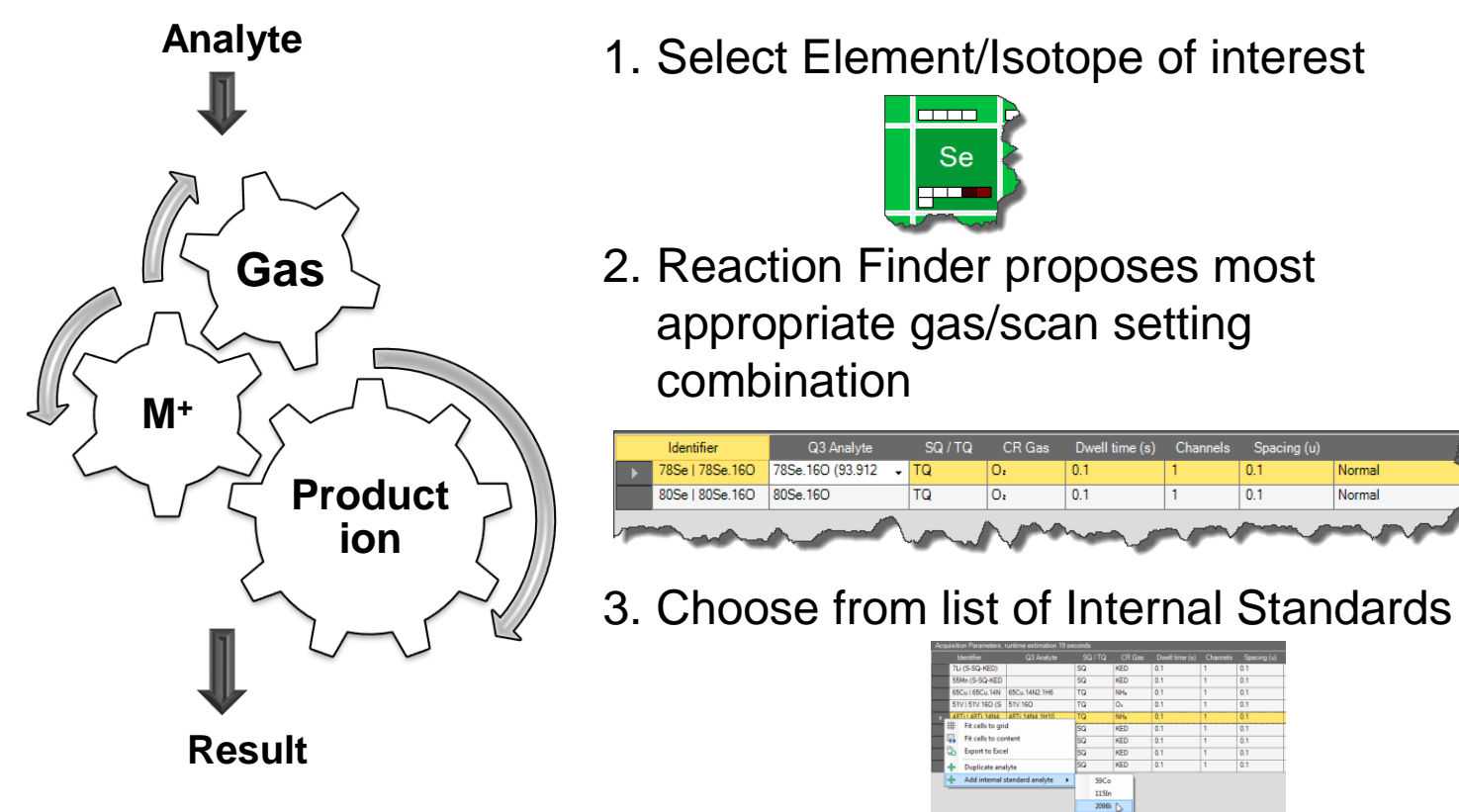
Whilst ICP-OES is an excellent and powerful tool for the analysis of trace elements in food samples, ICP-MS can offer even lower detection limits and higher dynamic range to analyze both trace and major elements in one run. However, ICP-MS is affected by different types of spectral interferences. Most interferences observed are polyatomic in nature (e.g. <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>) resulting in a false positive signal on <sup>75</sup>As) and can be removed using helium and kinetic energy discrimination on single quadrupole based systems. In some cases, other interferences may be observed, for example, doubly charged ions formed from rare earth elements, also resulting in false positive signals on elements such as arsenic or selenium. To overcome these interferences, the use of triple quadrupole ICP-MS instrumentation, like the iCAP TQ ICP-MS, is required.

Figure 2: Interference removal for <sup>75</sup>As using the iCAP TQ ICP-MS with O<sub>2</sub> as reactive gas



Selection of the most appropriate combination of reactive gas and scan settings however may be difficult for most users of ICP-MS instrumentation. For most elements, measurement modes as used on a single quadrupole based instrument will also give the lowest detection limits while fully eliminating potential interferences. In order to facilitate the process of setting up methods for the iCAP TQ ICP-MS leveraging the full potential of advanced interference removal using triple quadrupole technology, the Qtegra ISDS Software contains the Reaction Finder Method Development Assistant. The process of setting up a method using Reaction Finder is outlined in figure 3:

Figure 3. Overview of the Reaction Finder Method Development Assistant.



One example for a sample leading to potentially unresolved interferences is NIST 1515 apple leaves. A full spectrum reveals the presence of a variety of rare earth elements with considerable concentrations, as shown in figure 4. Therefore, the results for elements such as arsenic and selenium will be showing false positives when analyzed without triple quadrupole technology due to the formation of e.g. Nd<sup>+</sup> or Gd<sup>+</sup> ions. However, the Reaction Finder Method Development Assistant will automatically select a measurement mode based on triple quadrupole ICP-MS to effectively eliminate these interferences.

Figure 4. Mass spectrum showing mass range between 125-175. The observed signals correspond to Ba, as well as different rare earth elements, such as Nd or Gd, among others.

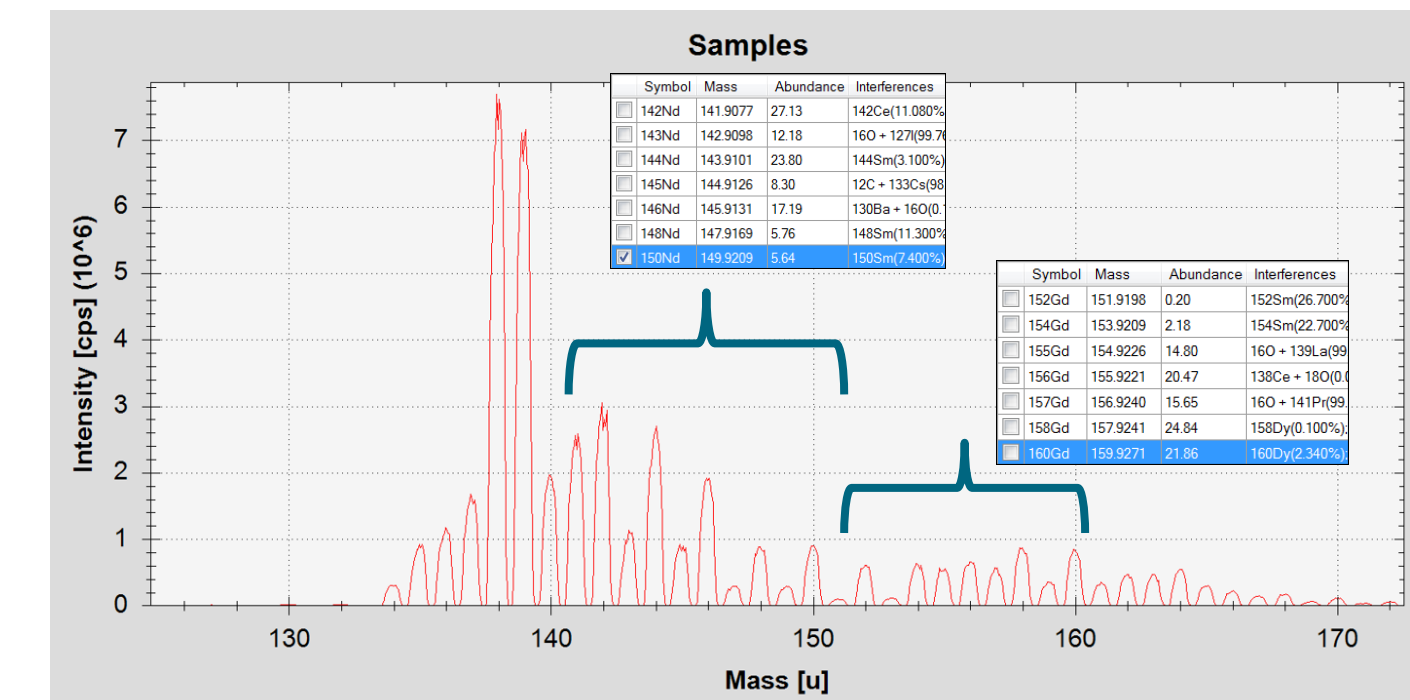


Table 4 shows the results obtained for the analysis of both reference materials under investigation, NIST 1515 (apple leaves) and 1573A (tomato leaves). As can be seen, all reported concentrations are in perfect agreement with certified values, including arsenic and selenium. At the same time, also sulfur and phosphorus can be analyzed, which are normally heavily interfered in single quadrupole based ICP-MS, and therefore typically measured using ICP-OES in an independent analysis.

Table 4. Results for the NIST CRM 1515 Apple leaves and NIST CRM 1673a Tomato leaves by iCAP TQ ICP-MS.

Analyte	IDL (µg·L <sup>-1</sup> )	MDL (µg·kg <sup>-1</sup> )	NIST 1515 apple leaves N=3		NIST 1573A tomato leaves N=3	
			Measured (mg·kg <sup>-1</sup> )	Certified (mg·kg <sup>-1</sup> )	Measured (mg·kg <sup>-1</sup> )	Certified (mg·kg <sup>-1</sup> )
<sup>11</sup> B	0.4	52.4	25.2±0.6	27±2	30.0±0.2	33.3±0.7
<sup>23</sup> Na	4	524	29.3±0.8	24.4±1.2	123±1.5	136±4
<sup>24</sup> Mg	1	131	2686±84	2710±80	10556±210	12000*
<sup>27</sup> Al	0.1	13.1	258±8.4	286±9	532±13	598±12
<sup>31</sup> P as <sup>31</sup> P <sup>16</sup> O	0.05	6	1530±10	1590*	2040±33	2160±40
<sup>32</sup> S as <sup>32</sup> S <sup>16</sup> O	0.02	2.6	1819±15	1800*	9779±0.2	9600*
<sup>39</sup> K	3	393	16106±75	16100±200	27299±198	27000±500
<sup>44</sup> Ca	1	131	15218±2300	15260±1500	49339±235	50500±900
<sup>51</sup> V	0.001	0.13	0.24±0.01	0.26±0.03	0.80±0.01	0.835±0.010
<sup>52</sup> Cr	0.005	0.66	0.29±0.01	0.3*	1.97±0.02	1.99±0.06
<sup>55</sup> Mn	0.003	0.39	52.6±0.6	54±3	242±1.9	246±8
<sup>57</sup> Fe	1	131	81.5±1.6	80*	366±4.8	368±7
<sup>59</sup> Co	0.011	1.44	0.08±0.003	0.09*	0.57±0.01	0.57±0.02
<sup>60</sup> Ni	0.023	3.01	0.85±0.13	0.91±0.12	1.57±0.02	1.59±0.07
<sup>63</sup> Cu	0.088	11	5.59±0.05	5.64±0.24	4.7±0.1	4.7±0.14
<sup>66</sup> Zn	0.026	3.41	11.3±0.16	12.5±0.3	28.2±0.37	30.9±0.7
<sup>75</sup> As as <sup>75</sup> As <sup>16</sup> O	0.006	0.79	0.036±0.003	0.038±0.007	0.117±0.003	0.112±0.004
<sup>75</sup> As	0.004	0.52	0.469±0.012	0.038±0.007	0.143±0.01	0.112±0.004
<sup>78</sup> Se as <sup>78</sup> Se <sup>16</sup> O	0.003	0.39	0.052±0.006	0.050±0.009	0.053±0.01	0.054±0.003
<sup>78</sup> Se	0.046	6.03	1272±187	0.050±0.009	0.11±0.01	0.054±0.003
<sup>85</sup> Rb	0.004	0.52	9.1±0.17	9*	13.97±0.03	14.89±0.27
<sup>88</sup> Sr	0.002	0.26	25.5±0.34	25±2	84.8±0.49	85*
<sup>98</sup> Mo	0.003	0.39	0.094±0.01	0.094±0.013	0.47±0.06	0.46*
<sup>111</sup> Cd	0.001	0.13	0.013±0.001	0.014*	1.45±0.03	1.52±0.04
<sup>121</sup> Sb	0.001	0.13	0.012±0.005	0.013*	0.057±0.003	0.063±0.006
<sup>138</sup> Ba	0.002	0.262	48.8±0.1	49±2	60.2±0.7	63*
<sup>208</sup> Pb	0.001	0.131	0.422±0.002	0.470±0.024	-	N.D.
<sup>232</sup> Th	0.001	0.131	0.03±0.002	0.03	0.107±0.002	0.12*
<sup>238</sup> U	0.001	0.131	0.008±0.002	0.006*	0.033±0.001	0.035*

## CONCLUSIONS

- ICP-OES can measure major and trace elements with equal success. Precise and accurate results for digested foodstuffs samples are easily obtained.
- Using triple quadrupole ICP-MS, excellent performance for the determination of trace element analysis in food samples can be achieved, making it ideal for food safety and quality assurance measurements.
- The Reaction Finder Method Development Assistant allows simple method development through automatic selection of the optimum analysis conditions for the analytes of interest.

## REFERENCES

- Total elemental analysis of food samples using the Thermo Scientific iCAP TQ ICP-MS with autodilution, Application Note 43446; Thermo Fisher Scientific
- Robust simple method determination of major and trace elements in foodstuffs using the Thermo Scientific iCAP 7400 ICP-OES Duo, Application Note 40755; Thermo Fisher Scientific

## TRADEMARKS/LICENSING

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