

# Elemental Analysis in Food for Risk Assessment and Provenance Studies

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## OVERVIEW

**Purpose:** To present the capabilities and advantages of elemental analysis techniques for identifying, quantifying and profiling trace elements in food samples, for the purposes of ensuring food safety and authenticity.

**Methods:** To evaluate the performance and capabilities of ICP-OES and ICP-MS for food analysis, different certified reference materials were analysed. The selected reference materials contained elements which could lead to severe bias in the results, if interferences were not eliminated efficiently. The results showed excellent agreement with certified values and hence demonstrated complete interference removal.

**Results:** Precise and accurate results for digested food samples were achieved using the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo and the Thermo Scientific™ iCAP™ TQ triple quadrupole ICP-MS. The iCAP 7400 ICP-OES was shown to be effective for measuring high and medium level element concentrations, while being simple to operate. The iCAP TQ ICP-MS combined with an ESI prepFAST™ Autodilution System allowed rapid and accurate analysis of 24 elements in two different modes (SQ-KED and TQ-O2) to ensure elimination of all interferences, while reducing the amount of manual interaction during sample preparation.

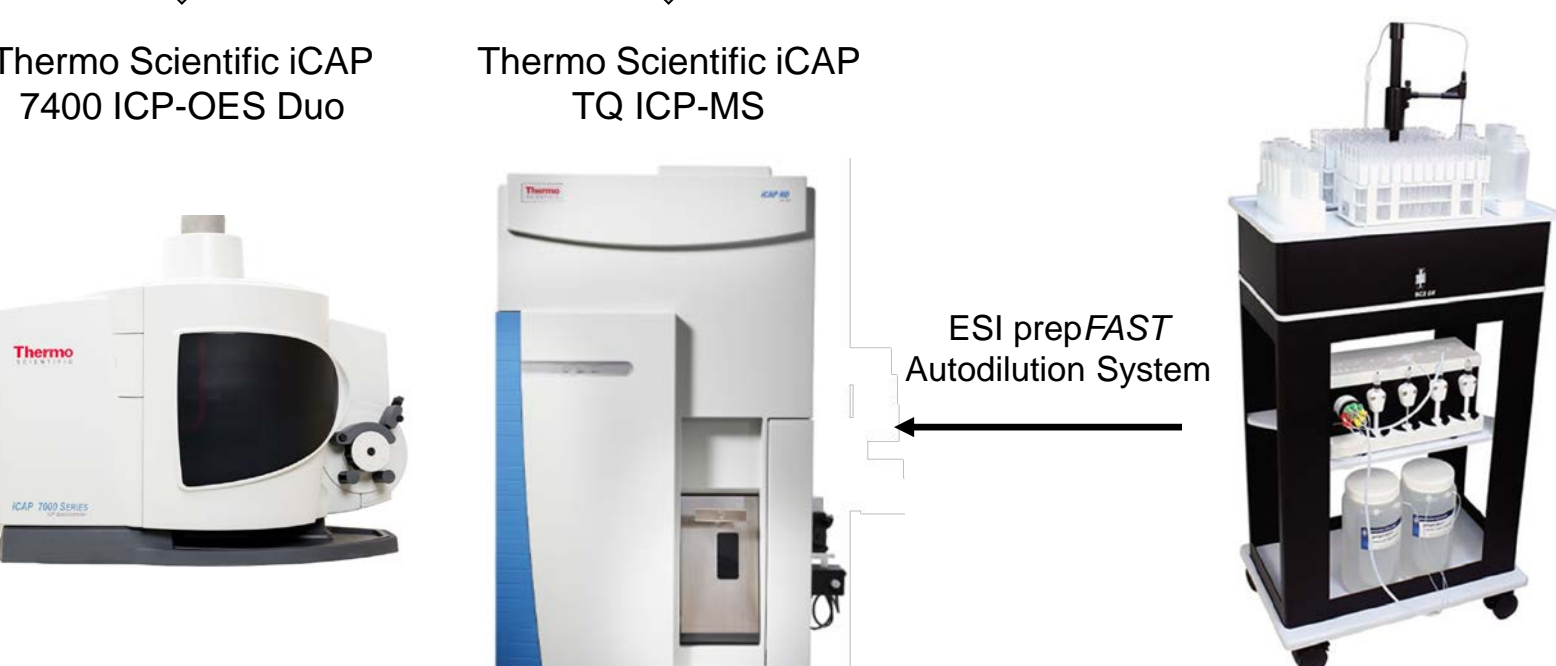
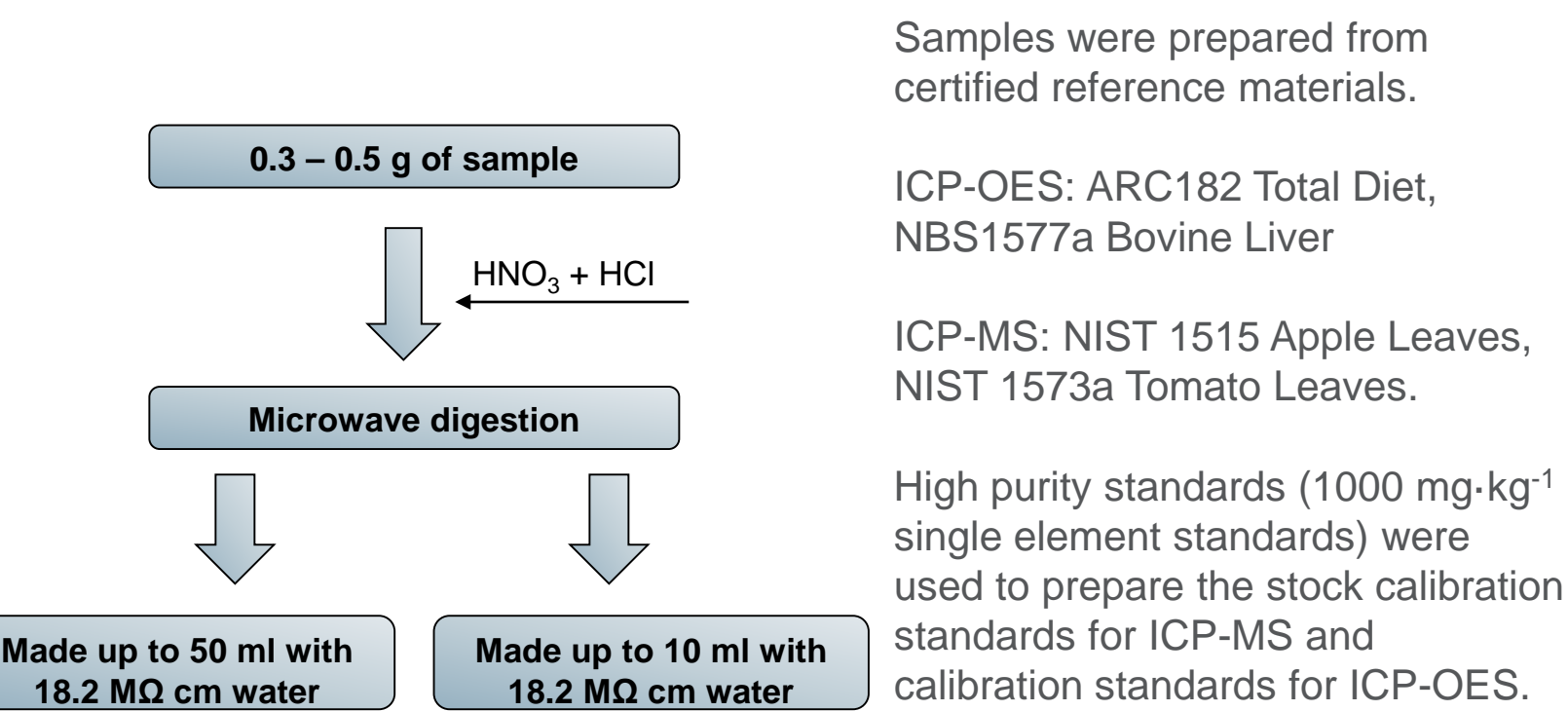
## INTRODUCTION

To ascertain the quality of food and food products, the analysis of toxic, essential and nutritional elements has become a routine task for food quality monitoring. Elements such as arsenic, cadmium, mercury or lead can enter the food chain via a series of pathways including, but not limited to, industrial pollution or environmental contamination. Recent public alerts on arsenic or lead contamination in food and water supplies have contributed to increased attention on this particular issue, but there is also a high demand for clear information on nutrients and contaminants from health-conscious consumers. For these reasons, it is essential to have simple, robust, multi-elemental analysis methods for accurately quantifying and profiling major and minor concentrations of elements in food. ICP-OES and ICP-MS are sensitive and rapid techniques with wide linear dynamic ranges and as such are ideal tools for the analysis of trace and major analytes in food. 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. For example, elements such as the rare earths (e.g. Nd, Gd) can cause significant false positive signals on critical analytes such as arsenic or selenium, as a result of the formation of doubly charged ions in the plasma. Elimination of these interferences is crucial to obtain correct results. In addition, the appearance and distribution of elements such as rare earths may give additional insight into the provenance of foodstuffs.

To keep up with the demands of the market, analytical laboratories need to be capable of analysing a high number of samples, containing both major and trace levels of a variety of elements, in the shortest possible time. While ICP-OES is suitable for many applications, as will be shown in this poster, this analysis is generally accomplished using single quadrupole ICP-MS instruments, with a single measurement mode applied for analysis of all the target elements in a suite. This single mode approach dramatically reduces the measurement time required per sample and reduces analysis cost. However, some interferences, such as the doubly charged ions of rare earth elements mentioned above, require triple quadrupole ICP-MS instruments to consistently remove them. At the same time as quantifying the target set of analytes, screening a sample set for other elements that don't require full quantification can be accomplished using a full mass scan, allowing unexpected elements in the sample to be identified, even months after the original analysis. This paper reviews the use of ICP-OES and triple quadrupole ICP-MS instrumentation technology for analysis of trace elements in different food samples.

## MATERIALS AND METHODS

### Sample preparation.



## Instrumentation

An iCAP 7400 ICP-OES Duo instrument was chosen for this analysis as 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-O2 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. Qtegra 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 skimmer, 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> , 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 Qtegra ISDS, allowing both user defined prescriptive and intelligent autodilution for samples falling outside of previously defined ranges (calibration range or internal standard recovery) to be used.

## RESULTS

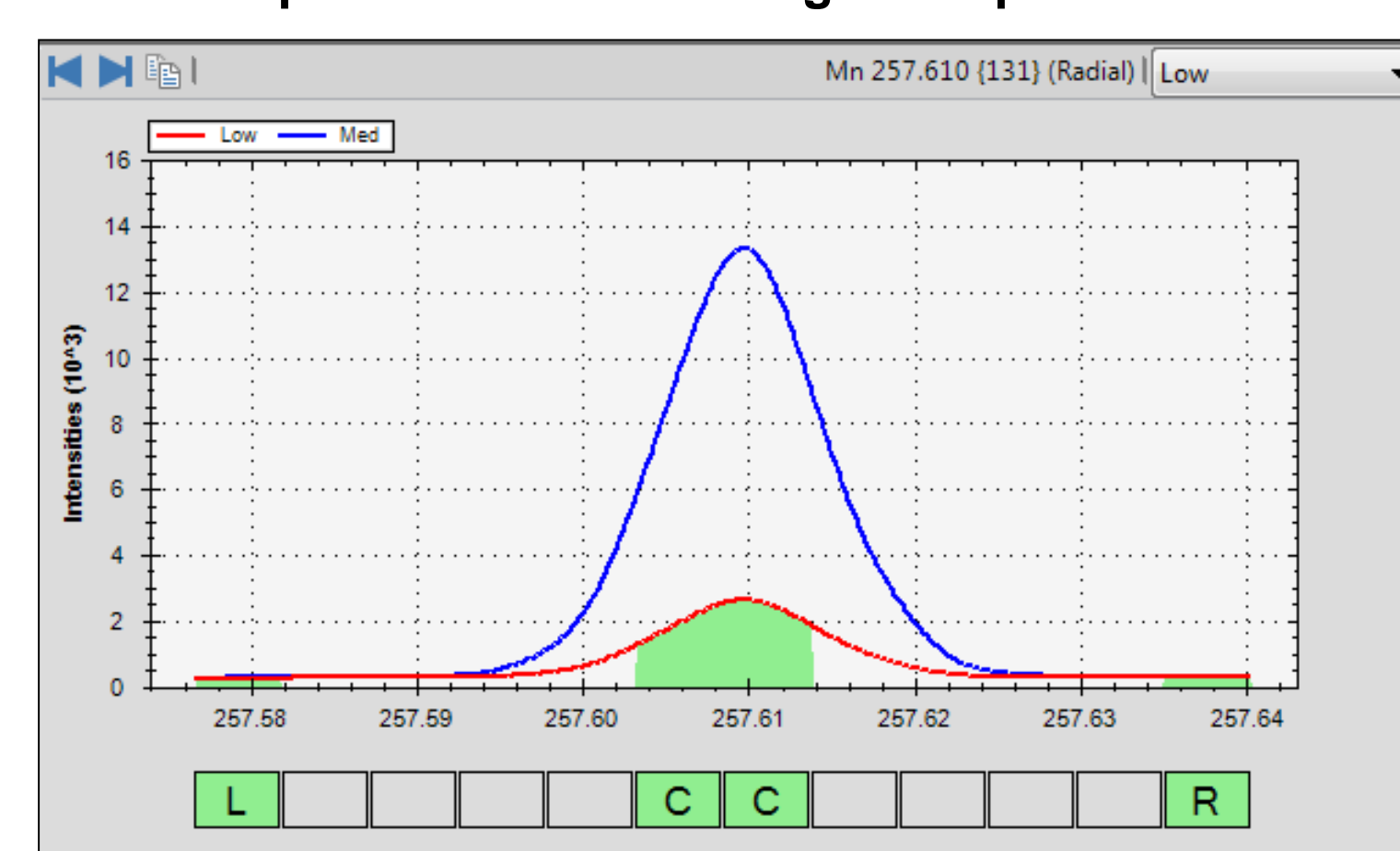
### ICP-OES analysis

ICP-OES is a well established technique for the routine analysis of trace elements, with detection limits sufficient to meet most regulatory requirements and the robustness required to tolerate a wide variety of sample matrices. For samples requiring the analysis of both major and trace elements, the ability to switch between radial and axial plasma observation with the iCAP 7400 Duo ICP-OES allows a large concentration range to be covered.

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 centre and background points.



Initially, more than one wavelength was selected for each element (using multiple views axial/radial). The subarrays (see Figure 1 for an example subarray) for each wavelength were then examined and the most appropriate wavelength for the application was chosen based on the presence of interferences, calibration curve performance, 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 analysed in a single sequence with a dilute acid rinse (0.5% HNO<sub>3</sub>) between samples. The analysis results are shown in Table 3. Suitable dilutions were made for over-range elements to ensure that they fell within the calibration range.

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

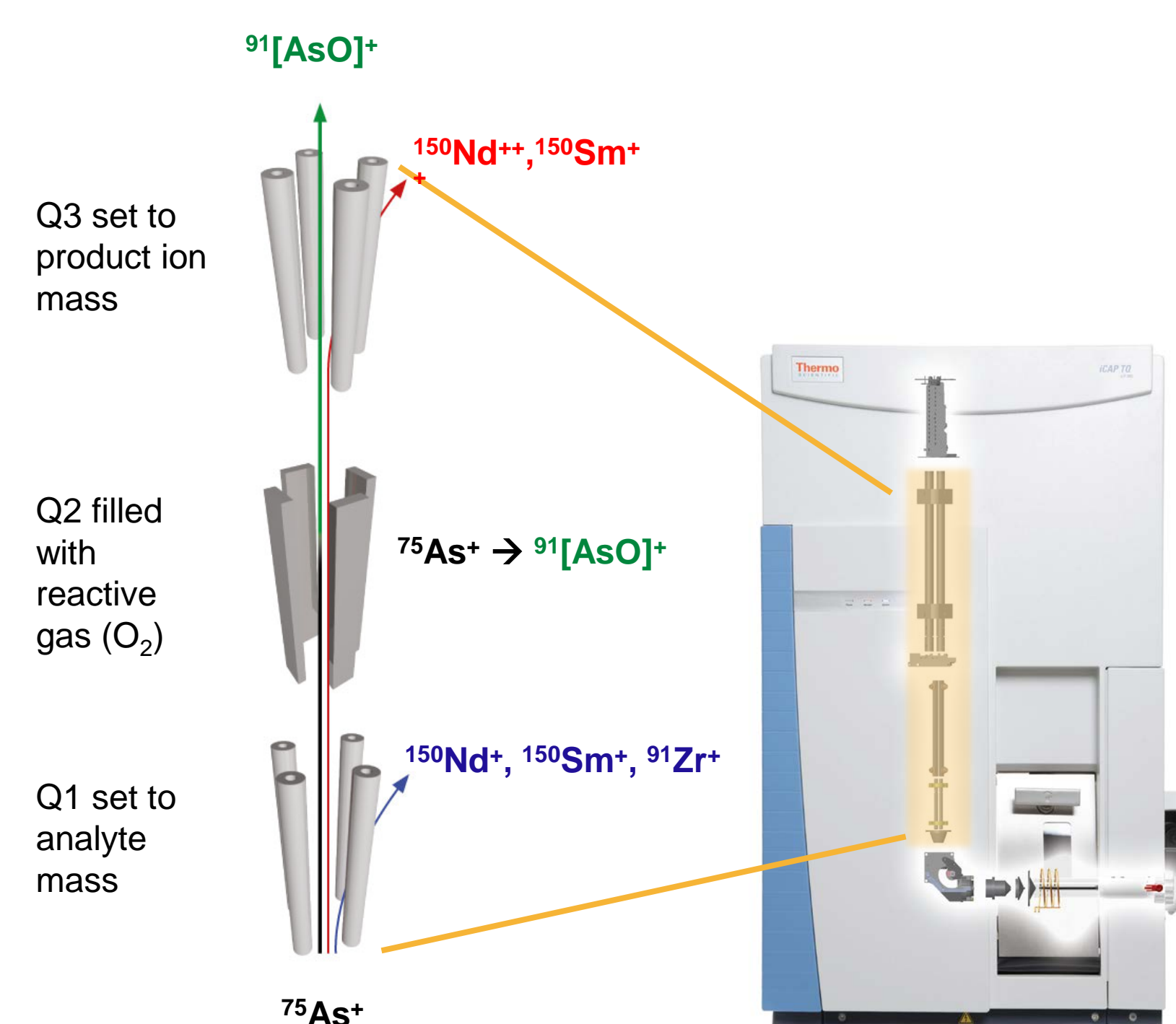
Element	NBS1577a			ARC182		
	Found in solid	CRM	Recovery (%)	Found in solid	CRM	Recovery (%)
Ca	133.6	120	111.33	2670	2860	93.36
Cu	153.3	158	97.03	N/A	N/A	N/A
Fe	192.9	194	99.43	N/A	N/A	N/A
Mg	576.5	600	96.08	719.2	785	91.62
Mn	10.14	9.9	102.42	12.98	12.9	100.62
Ni	N/A	N/A	N/A	0.2863	0.271	105.65
P	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 collision cell gas with 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 instruments, such as the iCAP TQ ICP-MS, is required.

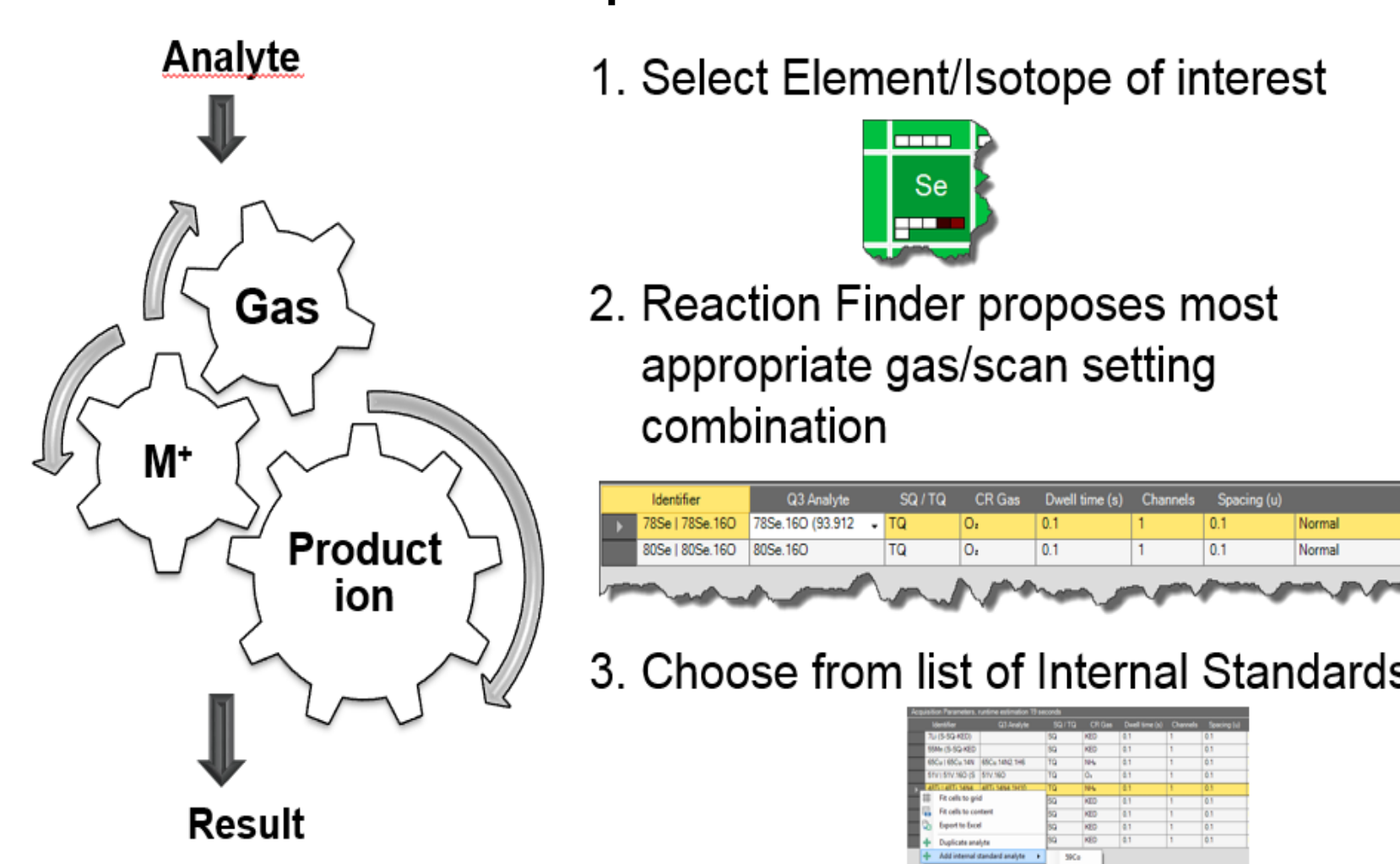
Figure 2 illustrates how triple quadrupole ICP-MS removes interference from doubly charged ions on As (other interferences, such as ArCl<sup>+</sup>, are also removed at the same time).

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, the measurement modes used on a single quadrupole based instrument will give satisfactory detection limits while largely eliminating potential interferences, but in various cases triple quadrupole technology is required. In order to facilitate method set up for the iCAP TQ ICP-MS and leverage the full potential of advanced interference removal using triple quadrupole technology, 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 below.

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. The results for arsenic and selenium show false positives when analyzed without triple quadrupole technology due to the formation of Nd<sup>2+</sup> and Gd<sup>2+</sup> ions. However, the Reaction Finder Method Development Assistant automatically selects a measurement mode based on triple quadrupole ICP-MS to effectively eliminate these interferences (in this case, TQ with O<sub>2</sub> cell gas mode).

Figure 4. Mass spectrum showing masses 125 to 175. The observed signals correspond to Ba, as well as the rare earth elements, such as Nd and Gd.

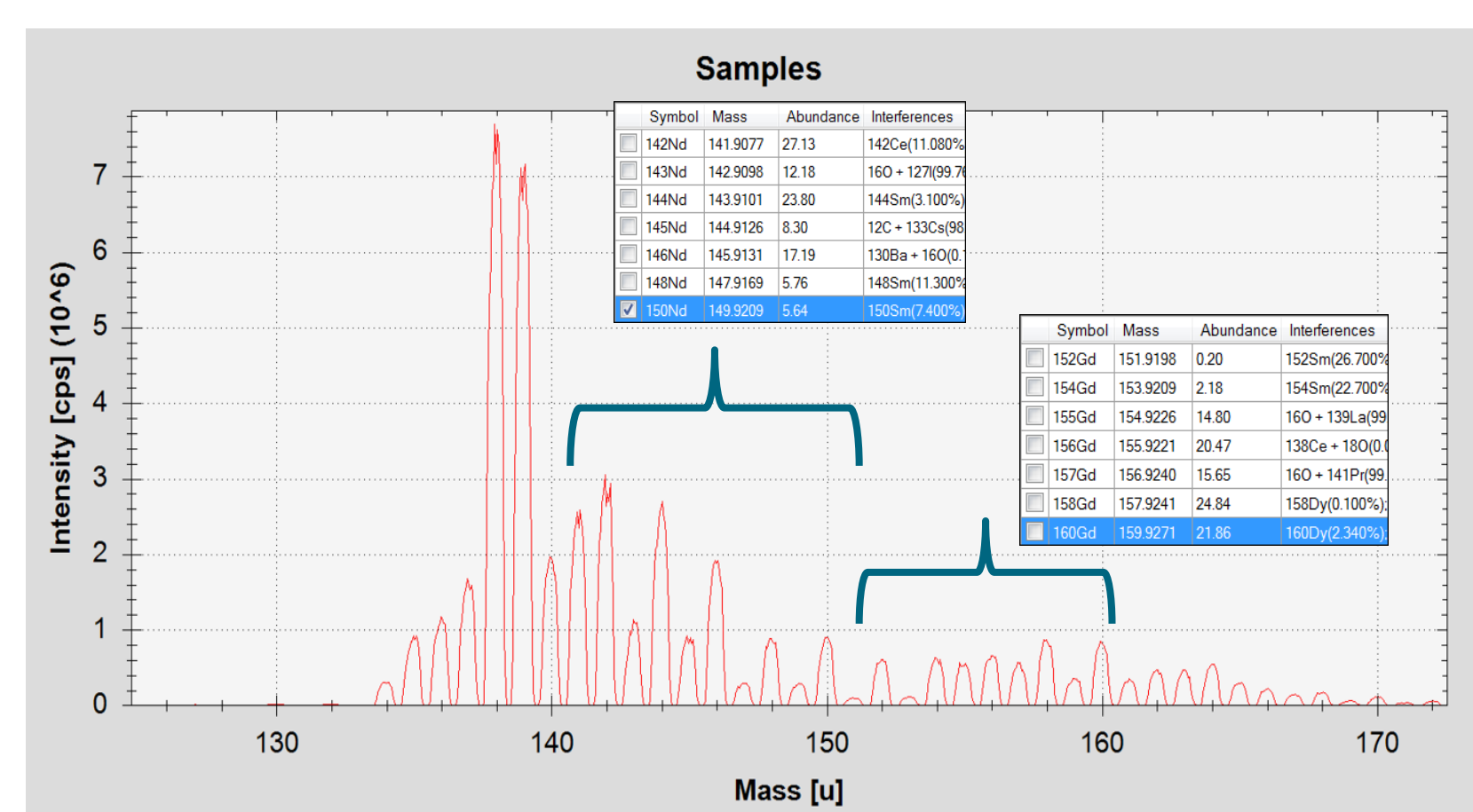


Figure 4 also illustrates how the rare earth element profile in a sample can be used to help identify the provenance of that sample. Small variations in the relative concentrations of the rare earths can in some cases link the sample to a particular geographical area, allowing the original food material to be confirmed as authentic or identified as falsely labelled.

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, including arsenic and selenium, are in good agreement with the certified values. At the same time, sulphur and phosphorous, which are heavily interfered in single quadrupole based ICP-MS and therefore typically measured using ICP-OES in an independent analysis, can be analyzed.

Table 4. Results for the NIST CRM 1515 Apple Leaves and NIST CRM 1673a Tomato Leaves using the 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>33</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±0.03	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	1.27±0.19	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 effectively measure major and minor elements precisely and accurately in digested foodstuffs.
- Using triple quadrupole ICP-MS, trace elements can be determined, interference free, in food samples, making it ideal for food safety and quality assurance measurements.
- Examining the relative concentrations of elements such as the rare earths in foodstuffs can assist with determining sample provenance and establishing if the foodstuff is authentic or not.

## REFERENCES

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

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