

Determination of toxic and nutritional elements in cereal and other plant seeds using the Thermo Scientific iCAP 7400 ICP-OES Duo

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Introduction

Plant seeds such as, sesame, millet, sunflower and cereal grains, have nutritive value and are grown in huge quantities and provide more food energy worldwide than any other type of crop. Different countries have different cereals as their staple food. This distinction derives from early agricultural civilizations who valued not only the staple food's nutrition but also their storability. For example, wheat is the most significant cereal in the diets of most European countries. On the other hand, rice is the primary grain used in China, Japan, South East Asia, Bangladesh, India, Pakistan, Brazil, Myanmar and Vietnam. The staple food cereal in Northern America, Central America and Africa is maize or corn, while millets and sorghum are widely consumed in India and Africa. Cereals are a good source of carbohydrates, vitamins, proteins and minerals including calcium, iron, sodium, potassium, copper, zinc etc., which serve as a source of energy for day to day life.

Goal

To demonstrate rapid and accurate determination of toxic and nutritional elements in food samples using the Thermo Scientific iCAP 7400 ICP-OES Duo.

Apart from being consumed within the country of production, cereals and other plant seeds are also exported to other countries. Exports require strict export compliance particularly in relation to toxic elements like arsenic, cadmium, lead, and mercury. National and international regulations are diverse and mainly based on the type of plant seed (Table 1). This application note demonstrates simple, fast and accurate determination of these elements along with nutritional elements present in a variety of cereals and other plant seeds using the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo. Various food samples were collected from exporters and local markets for the analysis.

Table 1. Concentration limits for toxic elements in plant seeds in India and other countries.

Element	Rice (mg·kg ⁻¹)			Sesame seeds (mg·kg ⁻¹)			Wheat (mg·kg ⁻¹)	
	Russia	EU ¹	FSSAI ²	Russia	EU ¹	FSSAI ²	EU ¹	FSSAI ²
Arsenic	0.2	-	1.1	0.3	-	1.1	-	1.1
Cadmium	0.1	0.2	1.5	0.1	0.1	1.5	0.1	1.5
Lead	0.5	0.2	2.5	1.0	0.2	2.5	0.2	2.5
Mercury	0.03	-	1	0.05	-	1	-	1

EU: European Union

FSSAI: Food Safety and Standards Authority of India

Instrumentation

For the sample analysis, the Thermo Scientific iCAP 7400 ICP-OES Duo was used together with an aqueous sample introduction kit, consisting of a concentric glass nebulizer and a cyclonic glass spray chamber as well as a 2 mm injector tube and aqueous pump tubing. The duo configuration was chosen for its low detection capability in axial view that is necessary when determining trace elements and the possibility to determine major components in matrix-rich samples in the radial view. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software simplifies method development and provides easy options for post-analysis data manipulation.

Sample and standard preparation

The sample preparation and analysis was performed according to the official method AOAC 984.27-1986³ (Microwave digestion of food samples followed by analysis with ICP-OES) and the FSSAI manual⁴ for the analysis of metals in food. Following samples were collected for analysis:

Rice 1: Pusa Basmati 1 parboiled, Lehragaga - PB
Rice 2: Pusa Basmati 1121 parboiled, Lehragaga - PB
Rice 3: Pusa Basmati 1509 parboiled, Sunam - PB

Wheat 1: WH 147, Jabalpur - MP

Wheat 2: Lok 1, Bhopal - MP

Wheat 3: Raj 3077, Indore - MP

Sesame Seed: Black Sesame Seed (*Sesamum indicum*), Guntur - AP

Corn (*Zea mays*), Gram (*Cicer aietenum*), Bajra (*Pennisetum glaucum*) and Jowar (*Sorghum vulgare*), procured from local market

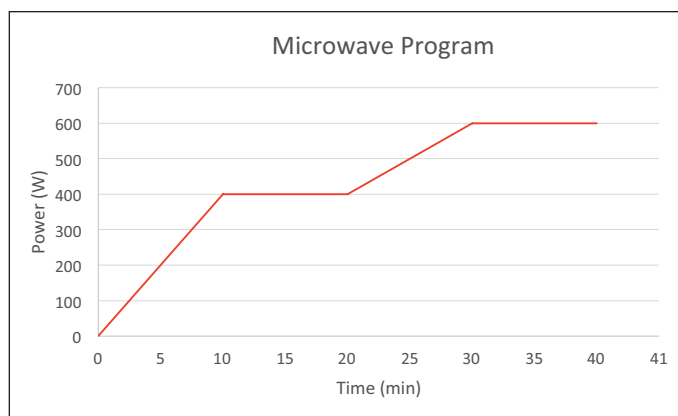


Figure 1. Power based microwave digestion program.

The samples (500 mg) were digested with an acid and peroxide mixture (4 mL TraceMetal™ grade HNO₃, 1 mL TraceMetal grade HCl and 1 mL Primar™ grade H₂O₂, Fisher Chemical) using a microwave digestion system (Multiwave Pro, Anton Paar). A power based microwave program was applied (Figure 1). After the digests had cooled down, they were transferred to sample vials and made to volume (18 MΩ ultra-pure water to a final volume of 25 mL).

Calibration standards were prepared by diluting a multi element solution (1000 mg·kg⁻¹ ICP multi-element standard solution IV, Merck, Germany) and single element solutions (1000 mg·kg⁻¹ arsenic and mercury, Sigma-Aldrich, Germany) with 18 MΩ ultra-pure water and nitric acid to a final concentration of 2% HNO₃ to achieve the concentrations listed in Table 2.

To validate the method and analysis results, replicates of the samples were spiked before digestion at different concentration levels. The internal standard yttrium was added manually at a concentration of 0.5 mg·kg⁻¹ to each solution.

Table 2. Concentrations of calibration standards and spiked sample solution in mg·kg⁻¹.

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Std 7	Std 8	Spiked sample
As	0.001	0.005	0.01	0.05	-	-	-	-	0.01
Ca	-	-	-	0.05	0.1	0.5	2.5	10	1
Cd	0.001	0.005	0.01	0.05	-	-	-	-	0.01
Co	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01
Cr	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01
Cu	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01
Fe	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01
Hg	0.001	0.005	0.01	0.05	-	-	-	-	0.01
K	-	-	-	0.05	0.1	0.5	2.5	10	1
Mg	-	-	-	0.05	0.1	0.5	2.5	10	1
Mn	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01
Na	-	-	-	0.05	0.1	0.5	2.5	10	1
Ni	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01
Pb	0.001	0.005	0.01	0.05	-	-	-	-	0.01
Zn	-	0.005	0.01	0.05	0.1	0.5	-	-	0.01

Method development and analysis

A method was created using the method parameters listed in Table 3. The wavelengths used for the analysis (Table 4) were selected as they were free from interferences and provided the sensitivity to quantify the elements of interest in the expected concentration range. The plasma was ignited and the instrument allowed to warm up for a period of 15 minutes. A spectrometer optimization was performed directly before analysis.

Table 3. Method parameters.

Parameter	Setting		
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white		
Flush Pump Speed	100 rpm		
Pump Stabilization Time	10 s		
Analysis Pump Speed	50 rpm		
Spray Chamber	Glass cyclonic		
Nebulizer	Glass concentric		
Nebulizer Gas Flow	0.5 L·min ⁻¹		
Coolant Gas Flow	12 L·min ⁻¹		
Auxiliary Gas Flow	0.5 L·min ⁻¹		
Center Tube	2 mm		
RF Power	1150 W		
Plasma View	Axial	Radial	
Exposure Time	UV 10 s, Vis 5 s	Vis 5 s	

Following method development, the instrument was calibrated and the samples analyzed. A method detection limit 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 of the detection limits were calculated.

Results

After digestion, all solutions were transparent with no visible particulate matter in the sample vial. The spike recoveries for all samples were within 80 – 120%, indicating good accuracy of the analytical method. Only the recovery of sodium in Rice (Table 4) was slightly higher with 137%.

Table 4. Wavelength, view and detection limits for each analyte. Calculated spike recoveries in percentage for the analyzed plant seed types.

Element	Wavelength (nm)	View	Instrument detection limit (µg·kg ⁻¹)	Method detection limit (µg·kg ⁻¹)	Spike recovery Rice (%)	Spike recovery Wheat (%)	Spike recovery Jowar (%)
As	189.042	Axial	1.7	85	102.2	90.6	90.4
Pb	220.353	Axial	2.0	100	80.6	95.9	100.3
Cd	214.438	Axial	0.1	4	104.7	97.5	100.7
Hg	184.950	Axial	0.6	31	107.2	81.3	105.1
Cr	267.716	Axial	0.7	35	108.2	101.0	105.4
Mn	257.610	Axial	0.1	5	110.0	86.9	118.0
Co	228.616	Axial	0.4	18	107.1	100.0	100.8
Ni	231.604	Axial	0.7	35	115.7	92.0	104.8
Cu	324.754	Axial	1.0	49	96.9	118.4	113.7
Zn	206.200	Axial	0.2	9	94.5	115.3	117.9
Fe	259.940	Axial	6.0	302	97.9	89.2	104.3
Na	589.592	Radial	52	2605	137.1	89.4	117.8
Mg	280.270	Radial	0.6	30	89.6	107.0	86.3
Ca	422.673	Radial	27	1365	106.7	119.6	119.9
K	766.490	Radial	520	26005	88.6	94.19	117.5

Table 5. Analyte concentrations in mg·kg⁻¹ for each sample. Where sample concentrations were below the method detection limit, this is indicated as <MDL.

Element	Rice 1	Rice 2	Rice 3	Wheat 1	Wheat 2	Wheat 3	Sesame seed	Corn	Gram	Bajra	Jowar
As	<MDL	<MDL	0.14	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Pb	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Cd	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.07	<MDL	<MDL	0.06	<MDL
Hg	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Cr	0.04	0.08	<MDL	0.06	0.06	0.08	0.19	0.07	0.10	0.12	0.06
Mn	2.47	2.42	3.04	38.2	37.3	34.2	16.0	9.57	25.3	12.3	9.99
Co	<MDL	0.02	0.02	<MDL	0.03	0.02	0.13	<MDL	0.16	0.10	0.03
Ni	0.07	0.29	0.17	0.41	0.29	0.11	1.07	0.24	0.41	1.04	0.40
Cu	1.94	1.56	2.30	3.80	4.12	4.22	14.80	1.69	7.26	3.50	1.85
Zn	6.03	5.13	6.66	25.3	20.9	20.9	53.7	23.4	31.1	23.7	19.8
Fe	3.35	3.45	2.83	34.0	33.1	33.2	70.5	12.2	47.8	41.4	32.8
Na	62.4	63.3	39.6	17.3	17.1	25.9	21.5	91.4	149	48.6	41.3
Mg	227	266	220	1049	912	938	3262	1254	1329	1016	1427
Ca	16.3	17.4	21.2	357	316	446	12671	71.1	1824	207	153
K	1258	1368	1139	3907	3813	3927	5245	2549	8731	4336	3829

Method detection limits (MDL) were calculated by applying a dilution factor of 50 to the instrument detection limits in Table 4. For arsenic, cadmium and lead the MDL is below the specification limits for toxic elements (see Table 1). However, the MDL for mercury is 0.03 mg·kg⁻¹ which is the concentration limit in the Russian regulation. Hence, under Russian regulation, another method such as hydride generation coupled to ICP-OES has to be applied for the accurate determination of mercury in food samples.

For the majority of the samples analyzed, all toxic analyte concentrations are below the MDL and therefore below the regulated concentration limit. Rice 1 has a slightly elevated level of arsenic (0.14 mg·kg⁻¹) and Sesame Seed as well as Bajra show increased concentrations of cadmium (0.06 and 0.07 mg·kg⁻¹, respectively). These values are still below the regulated concentration limits (Table 1) and the samples would be considered to be safe for human consumption.

Conclusion

The data clearly indicates that the Thermo Scientific iCAP 7400 ICP-OES Duo is a very powerful instrumental technique for cereal and seed analysis, both for toxic and nutritional elements in a single analytical method. The digestion technique as well as the developed analytical method have the capability of determining regulated toxic elements accurately, saving precious time and valuable laboratory resources with excellent overall productivity.

References

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