Ensuring Regulatory Compliance of Foodstuffs using the Thermo Scientific iCAP 6000 Series ICP-OES

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Application Note 40858

Key Words
ICP, iCAP 6000 Duo, Trace Elements, GMP Compliance, Internal Standard

Benefits in Brief

- International protocol compliance of toxic metals in multiple matrices
- Plug and play sample introduction for quick and easy maintenance
- Robust RF generator for reliable sample handling, regardless of the matrix
- Online internal standard addition with full analyst flexibility to turn on/off pre or post analyses

Introduction

The safe production and monitoring of food and related products such as herbal medicines and dietry supplements is ever more prevalent with the increase in homeopathic and organic traditional remedies and diets re-emerging into world culture. The industry standards are largely based upon ISO FDIS 22000 whereas HACCP (Hazard Analysis and Critical Control Point) is a more popular control system used by food and drug organizations. The World Health Organisation (WHO) has adopted many HACCP systems into its own Codex regulations. Each region regulates the process from the ground up, with normative documents for soils analysis, harvesting and storage and then onto more stringent controls when it comes to the manufacturing and labelling of foodstuffs.

In the US, food and pharmaceutical manufacturers must pass GMP (Good Manufacturing Practice) certification, in line with the FDA's 21 CFR Parts 111 & 112 which affect the dietary supplements industry and deals with the manufacturing, processing and holding of these substances. 21 CFR Parts 210 & 211 regulations affect the pharmaceutical industry, with Part 210 dealing with the manufacturing, processing and holding of drugs and Part 211 with finished pharmaceuticals. In addition to this, product labelling requirements set by the U.S. Congress under the Nutritional Labelling and Education Act of 1990 require the full nutritional labelling of 14 mandatory nutrients for Food and Drug Administration regulated packaged foods. As China exports a large proportion of their traditional medicines to the US, they must conform with FDA and

ISO standards in addition to their own specific 2005 version Chinese Codex which specifies the maximum permissible limits of Pb, Cd, Hg, As and Cu in Chinese medicine. In India, a growing market for traditional herbal medicines, the Government of India, Ministry of Health & Welfare, Department of Ayurveda, Yoga & Naturopathy, Unani, Siddha and Homoeopathy (AYUSH) has produced a notification confirming that testing of heavy metals, namely As, Pb, Hg, & Cd, is mandatory for export purposes.

Instrumentation

The award winning Thermo Scientific iCAP 6000 Series ICP was chosen for the analysis. This range features bespoke plug and play sample introduction for quick and easy maintenance, coupled with a solid state RF generator for ultimate robust and repeatable sample handling, regardless of the matrix. The standard sample introduction kit was used for this application and the parameters below employed during analysis.

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Table 1: Instrument Parameters.

Parameter	Setting
Sample pump tubing	Orange/white tygon
Pump rate	50 rpm
Nebulizer	Standard concentric
Nebulizer argon pressure	0.6 L/min or 0.22 MPa
Spray chamber	Standard cyclonic
Centre tube	2.0 mm
Torch orientation	Duo
RF forward power	1150 W
Auxiliary flow	0.5 L/min

A microwave Lab station with high-pressure rotor, temperature and pressure monitoring was used for sample digestion.

Method

Reagents

- Nitric Acid, sg 1.42, AnalaR grade.
- 1000 ppm single element standards for Cu, Fe, Mn, Pb, Sn, Sr and Zn.
- 1000 ppm Y single element standard was used to prepare the Internal Standard.

Certified Reference Materials

- Skim Milk Powder, ARC/CL
- Japanese Diet, NIES CRM no.27
- Poultry Feed, LGC7173
- Tomato Paste, ERM – BC084a

Sample Preparation

Samples were weighed out and allowed to dry (final weight ~ 0.5 g), 5 ml of Nitric Acid was then added before they were microwave digested using a standard food program in a high pressure microwave system. The samples were allowed to cool before being made up to 25 ml with deionized water.

Standard Preparation

High purity standards were used to prepare the calibration standards for this method. They were then acid matched to the samples (20% HNO_3). Table 2 below indicates the concentration of each of the standards which was selected to cover the linear range of the samples.

All samples and standards were analyzed with an internal standard of 5 ppm yttrium solution. This was added automatically using the Internal Standard Mixing Kit, p/n 8423 120 51551. By connecting an additional pump tube and adding the internal standard on-line continuous accurate dilution of the sample is assured.

Table 2: Standard Concentrations.

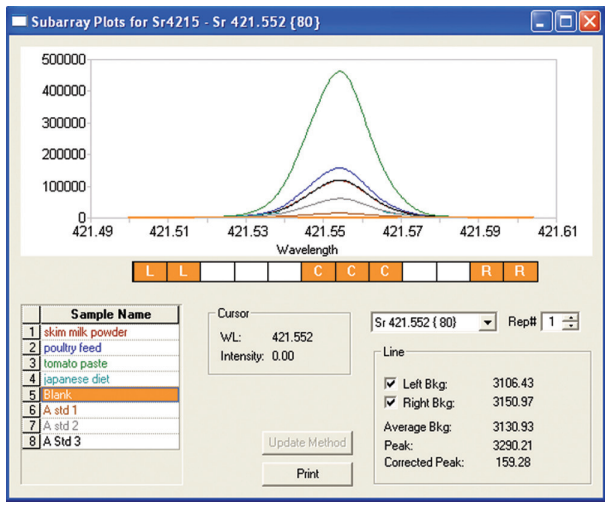
Element	Concentration in ppb
Cu, Fe, Mn, Sr	0, 10, 50, 100
Fe	0, 50, 250, 500
Pb, Sn	0, 10, 50, 500
Zn	0, 250, 500, 1000

Method Development

As the samples comprised different matrices, an internal standard was employed which acts as a dynamic correction for suppression/enhancement of signals due to viscosity, matrix or sample transport differences. iTEVA was set up to automatically correct all signals by referencing appropriate yttrium lines to method wavelengths. All low (UV) method wavelengths were referenced to yttrium 224.306 nm and all high (Vis) method wavelengths were referenced to yttrium 324.228 nm. iTEVA uniquely allows the analyst to turn the internal standard on/off pre or post analysis (and per element/wavelength), saving valuable method development time as only one analysis needs to be performed to determine if an internal standard is required for the method.

The method was then calibrated and all samples analyzed in a single run. The calibration blank was analyzed using 10 replicates and standard method settings (15 second integration for low wavelengths, and 5 second integration for high wavelengths) to determine the method detection limit by multiplying the standard deviation of the analysis by 3 (MDLs are listed in the Results table below). The subarray peaks for each element was examined to ensure that they were interference free and the correct background points were employed (see example Sr 421.552 nm below). By overlaying all the subarrays it is possible to determine if there are any overlaps/interferences, and identify any differences between samples and calibration standards, as demonstrated below in Figure 1.

Figure 1: Strontium 421.552 nm subarrays for all samples



Results

Table 3: Results of Certified Reference Materials and recoveries. % recovery is calcluated on the stated value and does not make correction for stastical bias allowed. Values in parenthesis () are not certified values. Method Detection Limits (MDLs) are derived from liquid acid matched blank.

Element and Wavelength	M.D.L.	Skim milk powder			Japanese diet			Poultry feed			Tomato paste		
		Found	Certified	%	Found	Certified	%	Found	Certified	%	Found	Certified	%
Units	ppb	ppm	mg/kg	Recovery	ppm	mg/kg	Recovery	ppm	mg/kg	Recovery	ppm	mg/kg	Recovery
Cu 327.396 nm	0.219	0.596	0.59±0.148	101.02	2.74	2.8±0.1	97.86	15.67	(16)	97.94	---	---	---
Fe 259.940 nm	1.3574	5.078	4.54±0.855	111.85	18.2	(18)	101.11	132.3	139±29	95.18	---	---	---
Mn 257.610 nm	0.3693	0.3566	0.44±0.104	81.05	8.71	8.9±0.2	97.87	87.92	(88)	99.91	---	---	---
Pb 220.353 nm	0.722	digested<d.l.	0.016±0.003	N/A	---	---	---	---	---	---	0.329	0.316±0.021	104.11
Sn 283.999 nm	1.7873	---	---	---	---	---	---	---	---	---	228	225±11	101.33
Sr 421.552 nm	0.1815	---	---	---	5.058	4.9±0.2	103.22	---	---	---	---	---	---
Zn 213.856 nm	0.2794	41.75	41.68±1.056	100.17	20.96	20.9±0.9	100.29	82.82	77±8	107.56	---	---	---

A Fullframe was performed on the Poultry Feed sample which displays a graphical presentation of the spectrum recorded by the Charge Injection Device (CID) detector, and can identify all the elements present in the sample. The bright spots on the image are indicative of the presence of an element, the position of spot shows the wavelength of the element while the brighter the spot, the more intense the concentration. Fullframe is very useful for true unknown analysis as it can be used for qualitative analysis, or also for semi-quantitative analysis (with results typically within 15% of the full-quantitative result). On the Fullframe shown below (see Figure 2), the method elements are identified with the colored boxes that relate to the legend on the right hand side of the image. Any other elements can be identified using the Wavelength Finder function, which is available with a single click. From the poultry feed Fullframe, the presence of Ca at % levels was obvious (circled in red) in addition to the method elements.

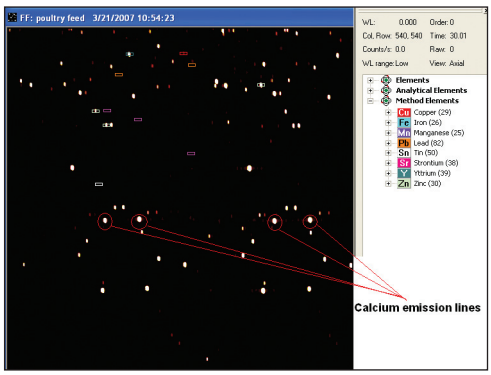


Figure 2: Fullframe of Poultry Feed sample

Conclusions

The method detection limits determined show that the iCAP 6000 Series is ideal for food and medicine testing requirements, as an example, the Indian Standards set by AYUSH for Pb is 10 ppm, which is well above the detection limit of 0.722 ppb gained here. The table below states the regulatory requirements for different countries and the method detection limit gained from this analyses, proving the suitability of the iCAP for this application.

The use of microwave digestion allowed for easy sample preparation with a common technique applicable to many different sample types. Method development was made easy with the use of an automatic Internal Standard correction to overcome the effects of different matrices. This enabled a wide variety of samples to be processed accurately, using the same method.

Table 4: Method Detection Limits and International standards.

Element	MDL	AYUSH	Chinese CODEX	
			Traditional Chinese Medicine	Chemical Drug
Units	ppb (mmol/ml)	ppm	ppm	mmol/ml
Cu	0.219 (0.0139)	N/A	≤20	1.8 - 2.2
Fe	1.3574 (0.0758)	N/A	N/A	1.8 - 2.2
Mn	0.3693 (0.0202)	N/A	N/A	0.45 - 0.55
Pb	0.722 (0.1495)	10	≤5	N/A
Sn	1.7873 (0.2121)	N/A	N/A	N/A
Sr	0.1815 (0.0159)	N/A	N/A	N/A
Zn	0.2794 (0.0182)	N/A	N/A	9.0 - 11.0

Related Articles:
Determination of major and trace elements in foodstuffs using microwave digestion and ICP. Ask your local representative for Application note no. 40755.

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