

# Analysis of Food Stuff by ICP-OES Using Automated Sample Preparation

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## Overview

**Purpose:** This study focuses on the automation of the analytical instrumentation post sample digestion, especially preparation of standards and sample dilutions. Although the use of an auto diluter for ICP-OES is not a new concept, recent developments in integration of the hardware and software allow for great automation of the analytical process. This covers standard preparation, dilution of samples and automated decisions related to data quality such as internal standard suppression caused by sample matrix.

**Methods:** A food reference material (NIST 1568b Rice Flour) was digested according to a microwave assisted acid digestion protocol. The digested samples were analyzed against automatically prepared calibration solutions. Spikes were carried out to demonstrate the functions of the intelligent dilution features of the auto dilution unit.

**Results:** The serial dilution unit provided very good calibration curves with  $R^2 > 0.999$  for all elements. The accuracy of the calibration was within 10 % for all elements except some critical ones that may have got lost during preparation (Hg, Se) or those that were close to the detection limit (As, Sn). The intelligent dilution function brings samples into the calibration range or within the internal standard limits.

## Introduction

The safe production and monitoring of food and related products such as herbal medicines and dietary 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 Organization (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. Due to the critical nature of this type of analysis, automation to remove human error is seen as a key approach to ensuring consumer safety.

In this study maximum levels for food contaminants from different legislations (Table 1) were compared and added to a list of elements that were certified for a given standard reference material (SRM). Where reference data was not available or expected concentrations were very low, the sample got spiked at the concentrations in Table 1 (only Sn got spiked at 5 mg·kg<sup>-1</sup>).

**TABLE 1. Maximum levels of contaminants for foodstuff**

Element	Maximum level of contaminant (mg·kg <sup>-1</sup> )
As	0.1 <sup>a</sup>
Cd, Pb	0.2 <sup>a,b</sup>
Hg	0.02 <sup>b</sup>
Sn	50 <sup>c</sup>
Ni	1 <sup>b</sup>
Cr	1 <sup>b</sup>

a: Europe (EC No 1881/2006), b: China (GB 2762-2012), c: WHO (CF/5 INF/1)

## Methods

### Instrumentation

For the sample analysis, the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo (Figure 1) was used together with an aqueous sample introduction kit. A Teledyne CETAC™ ASX-560 autosampler with an SDX serial dilution unit was used to prepare standards and samples and to transfer the sample to the introduction system of the ICP-OES.

**FIGURE 1. iCAP 7400 ICP-OES**



## Sample Preparation

The standard reference material NIST SRM 1568b Rice Flour was digested in five replicates of which two were spiked with the concentration of test analytes at the maximum allowed concentration (Table 1). For the digestion, the rice flour was weighed (~1 g) into a PTFE high pressure vessels and 5 mL of concentrated nitric acid as well as 5 mL of water were added. For better oxidation of the organic matrix, 1 mL of concentrated hydrogen peroxide (Fisher Chemical™) was also added. The digestion was conducted in a Milestone Ethos EZ microwave equipped with an SK-10 segmented rotor and a temperature sensor. The temperature program comprised a gradient heating of ten minutes, going from ambient temperature to 180° C, which was then held for 15 minutes. After digestion the digest was transferred to a 50 mL volumetric flask and filled up with ultra-pure water to the measured mark. Additionally, for each digestion cycle a duplicate of a digestion blanks was run. This contained only acid, water and hydrogen peroxide and after digestion was treated the same way as the samples.

## Data Analysis

A method was created in Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) software. The plasma view was selected according to the expected concentrations. The wavelengths used for the analysis are shown in Table 3, these were selected as they were free from interferences and provided the sensitivity to quantify the elements of interest in the expected concentration range. The parameters used for the method can be found in Table 2. 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.

Following method development, the instrument was calibrated and the samples analyzed. A method detection limit study was carried out by analyzing three digestion blanks with ten replicates and multiplying the standard deviation of this analysis by three. For detection limits the average values were calculated.

## Results

### Reference Material and Spikes

The autodilution system produced very good calibration curves with correlation coefficients greater than 0.9990 for all elements (see Table 3). Almost all elements in the SRM have recoveries within 10 % of the expected value, many of them being within a 5 % range, which shows very good accuracy of the automatic calibration. Exceptions are Hg and Se with very low recoveries. Their concentration in the digest was below the detection limit (DL). However, a spike of mercury at a concentration of 50 \* DL showed a bad recovery of 38 % as well. A possible explanation is the volatility of the element and the consequent loss of it during digestion. For the elements As, Cd, Cr, Ni, and Pb, the spikes at the maximum level of contaminants for foodstuff had recoveries within 10 % of the expected value, proving the suitability of the method of analysis for these elements. Tin is usually dissolved in hydrochloric acid and may be lost due to precipitation during sample preparation in a nitric acid matrix.

**FIGURE 2. Samples being intelligently added with a new dilution factor to the sample list due to over range or internal standard errors.**

	Label	Status	Autodilution Factor
1	Blank	●	1
2	Std	●	2.5
3	Overrange	●	1
4	Overrange	●+	3.641
5	Salt Matrix	●	1
6	Salt Matrix	●+	10

### Intelligent Dilution

One sample was spiked with a high concentration of one of the analyzed elements to be over the range of the calibration curve and another one was spiked with a salt matrix to suppress the internal standard. The software recognized these samples to be outside the defined limits and added them with an adjusted dilution factor (see Figure 2).

**TABLE 2. Analysis settings.**

Parameter	Setting	
Pump Tubing	Sample Tygon™ White/White Drain Tygon™ Yellow/Blue	
Pump Speed	50 rpm	
Spray Chamber	Glass Cyclonic	
Nebulizer	Glass Concentric	
Center Tube	2 mm	
Nebulizer Gas Flow	0.5 L·min <sup>-1</sup>	
Auxiliary Gas Flow	0.5 L·min <sup>-1</sup>	
Coolant Gas Flow	12 L·min <sup>-1</sup>	
RF Power	1150 W	
Number of Replicates	3	
Exposure Time	Axial	Radial
UV	15	15
Vis	5	5

**TABLE 3. Analysis results.**

Element and Wavelength (nm)	Plasma View	R <sup>2</sup>	DL (µg·kg <sup>-1</sup> )	SRM Recovery (%)	Spike Recovery (%)
<b>Al 167.079</b>	Axial	0.9999	0.42	102.4	
<b>As 193.759</b>	Axial	1.0000	3.9	94.0	105.3
<b>Ca 396.847</b>	Radial	0.9999	0.34	100.9	
<b>Cd 214.438</b>	Axial	0.9999	0.15	98.2	105.8
<b>Cr 283.563</b>	Axial	0.9999	1.0	ND	106.6
<b>Cu 224.700</b>	Axial	0.9991	1.4	98.5	
<b>Fe 238.204</b>	Axial	0.9999	1.2	98.3	
<b>Hg 184.950</b>	Axial	0.9990	0.40	< DL	38.0
<b>K 766.490</b>	Radial	0.9996	111	97.3	
<b>Mg 280.270</b>	Radial	0.9999	0.67	92.6	
<b>Mn 259.373</b>	Axial	0.9999	0.27	102.0	
<b>Mo 202.030</b>	Axial	0.9999	0.51	101.7	
<b>Ni 221.647</b>	Axial	0.9998	0.69	ND	106.4
<b>P 213.618</b>	Radial	0.9999	26	104.2	
<b>Pb 220.353</b>	Axial	0.9996	2.1	ND	110.0
<b>S 180.731</b>	Axial	0.9999	4.0	97.0	
<b>Se 203.985</b>	Axial	0.9995	0.40	< DL	
<b>Sn 189.989</b>	Axial	0.9996	1.7	ND	26.8
<b>Zn 202.548</b>	Axial	0.9994	0.22	91.9	

ND = Not determined in the certified reference material; < DL = Analysis result in the digest solution was below the detection limit

## Conclusion

Contaminant elements in food can easily be determined by the demonstrated method of analysis conducted on the Thermo Scientific iCAP 7400 ICP-OES. This is especially true for direct analysis of the samples, e.g. fruit juices. However, with the dilution, due to digestion some contaminant elements are at or below the method detection limits (As, Hg and Pb) and will therefore need a more sensitive method of analysis such as ICP-MS which can be provided by the Thermo Scientific™ iCAP™ Q ICP-MS.

The auto dilution system under test may be of future interest for laboratory automation. It ensures easy and accurate preparation of the calibration curve and further helps to intelligently decide on re-measurement of samples when they are outside a certain specification. In this way valuable preparation time is saved through the automation and makes the user available for other important tasks.

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