Accurate Analysis of Foodstuffs using Vapor Generation Atomic Absorption Spectroscopy and ICP-OES

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Abstract

Consumers these days are much more aware of food safety and also more interested in the contents of the food they consume. Legislation is changing to meet the consumer demand in light of many 'incidents' involving food safety. With this complex legislation and pressure, there are several options available to the analyst when it comes to the analysis of such samples.

Growing concerns about the possible presence of the toxic chemical, mercury, in the food supply chain have led to tighter restrictions on its presence in the food we eat which has led to the enforcement of regulations that state a maximum concentration of mercury in fish of approximately 0.5 mg/kg wet weight. Coupled with the VP100 vapour generation accessory, the iCE 3000 Series AA spectrometers are capable of reaching detection limits of 0.01 mg/kg in solid. The advantages of multi element analyses cannot be denied for high throughput laboratories, where AAS and ICP-OES are often used in conjunction with each other in order to cover the linear dynamic range required for the analysis of foodstuffs. Using the iCAP 6000 Series ICP-OES, two multi element methods are presented which demonstrate the analysis of majors, minors and trace element contaminants in a variety of foodstuffs.

This paper will discuss some of the many world wide legislations and how AAS and ICP-OES can be used for compliance.

Legislation

- Concentrations of nutritional and toxic elements in food stuffs closely monitored by organizations worldwide such as the US FDA and WHO
- Prominent issue concerns mercury in fish, a major source of human mercury poisoning
- General enforcement is 0.5 - 1.0 mg/kg mercury in fish (wet weight)[1,2]
- Many other foodstuffs governed by guidelines and legislations worldwide

AA Instrumentation

The Thermo Scientific iCE 3500 AA was used with the VP100 Vapor Generation Accessory for the analysis of Hg in fish. The iCE 3500 combines high-precision optics, state-of-the-art design and user friendly, wizard driven software to provide unrivalled analytical performance.

The VP100 uses a continuous flow 4-channel system. A gas-liquid separator directs vapor only to the spectrometer. A specially designed mercury cell with an extended path length was used in this analysis to provide enhanced sensitivity.

The Thermo Scientific iCE 3500 AA Spectrometer and the VP100 Continuous Flow Vapor Generation Accessory

AA Methods

A method was developed to analyze low levels of Hg in fish by VGAAS. Sample preparation workflow is shown in Figure 1, AA and VP100 parameters are shown in Table 1.

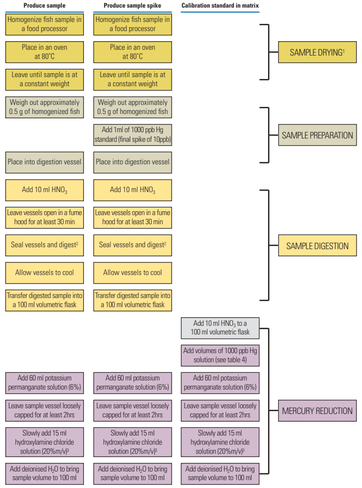


Figure 1: Sample preparation workflow for the analysis of Hg in fish by VGAAS

Spectrometer Parameters	
Wavelength	253.7 nm
Lamp Current	75 %
Bandpass	0.5 nm
Background Correction	D2 Quadline
Resamples	5
Measurement Time	4.0s

VP100 Parameters	
Pump Speed	40 rpm
Gas Flow	200 ml/min
Acid Reagent	50 % HCl
Reductant	7.5 % stannous chloride in 10 % HCl
Measurement Delay	70

1 Sample drying phase is not necessary if the final concentration of mercury is needed for a wet-weight sample

2 Refer to the manufacturers guidelines when designing a digestion program. An example of a program is given in Table 3

3 CARE: The reaction is exothermic and the flask may become hot. Also, make sure to add the hydroxylamine chloride slowly, otherwise the solution may foam and eject some sample from the flask.

Table 1: AA and VP100 parameters for the analysis of Hg in fish by VGAAS

AA Results

Excellent linearity over the range 0-100 ppb was obtained with $R^2 = 0.9989$, as shown in Figure 2.This equates to up to 20 mg/kg in initial fish sample. Method detection limit (MDL) and characteristic concentration (CC) were calculated using the "Instrument Performance" Wizard in the SOLAAR software. MDL was 0.068 ppb, equivalent to 0.014 mg/kg in initial fish sample, with a CC of 0.724 ppb. CRMs and spiked recoveries were used to test the method, results are shown in Table 2.

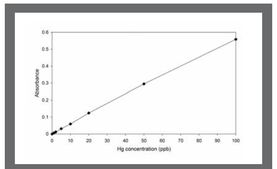


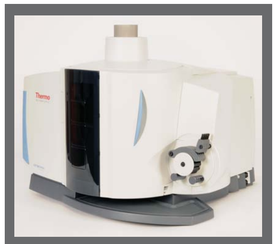
Figure 2: Calibration curve for the analysis of Hg in fish by VGAAS

Sample	Expected Concentration (mg/kg)	Meaasured Concentration (mg/kg)	Percentage Recovery (%)
Salmon 1	2	1.89	94
Salmon 2	2	1.94	97
Salmon 3	2	1.99	99
Sardine 1	2	1.93	97
Sardine 2	2	2.08	104
Sardine 3	2	1.91	95
DORM-2 1	4.64 ± 0.26	4.59	99
DORM-2 2	4.64 ± 0.26	4.53	98
DORM-2 3	4.64 ± 0.26	4.57	98

Table 2: CRMs and spiked recoveries for the analysis of Hg in fish by VGAAS

ICP Instrumentation

The Thermo Scientific iCAP 6500 Duo model was used for the analysis of major and minor elements in a variety of foodstuffs. The iCAP 6000 Series features bespoke sample introduction kits with a solid state RF generator for ultimate robustness and repeatability. The Duo model was chosen to allow maximum sensitivity using the axial view, whilst maintaining excellent matrix tolerance and interference-free analysis in the radial view.



The Thermo Scientific iCAP 6000 Series ICP

Parameter	Setting
Pump tubing	Orange/white tygon sample White/white tygon drain
Pump rate	50 rpm or 0.22 MPa
Nebulizer	Standard concentric
Nebulizer argon flow rate	0.6 L/min
Spray chamber	Standard cyclonic
Centre tube	2.0 mm
Torch orientation	Duo
RF forward power	1150 W
Auxiliary flow	0.5 L/min
Integration times	
High wavelengths	5 seconds
Low wavelengths	15 seconds

Table 3: ICP-OES parameters for the analysis of multiple elements in foodstuffs

ICP Methods

A single multi element method for the determination of major and trace elements in foodstuffs using ICP-OES was created. The following CRMs were microwave digested as per recommendations in Nitric and or Hydrochloric acid : 0.5 g of Total Diet, bovine liver and wheat flour. All samples were made up to a final volume of 50 mL in deionized water. Analytical elements of interest, analytical working range and viewing orientation are shown in Tables 4&5 below.

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

Table 4: Measured elements and standard concentrations

Element Viewing	
As, Cd, Cu, Mn, Ni, Pb, Zn	Axial
Ca, Fe, Mg	Radial

Table 5: Viewing orientation (radial or axial)

An additional method was developed to demonstrate trace level determination of toxic elements to ensure regulatory compliance of foodstuffs. 0.5 g portions of skim milk powder, Japanese Diet, poultry feed and tomato paste CRMs were digested in a microwave using 5 mL Nitric acid, an diluted to a final volume of 25 mL in deionized water. Analytical elements of interest and standard concentrations are shown in Table 6 below.

Element	Concentration in ppm
As	0.01, 0.05
Cu, Mn	0.1
As, Ni	0.5
As, Cu, Fe, Mn, Ni, P, Zn, Ca, Mg	1
Zn	5
Cu, Fe, Ca, Mg, P	10
Ca, P	50

Table 6: Measured elements and analytical working range

An internal standard was used to compensate for differences in viscosity, matrix and sample transport efficiency. 5 ppm yttrium was added using the Internal Standards Mixing Kit to provide online continuous, accurate sample dilution. UV method wavelengths were referenced to yttrium 224.306 nm and visible method wavelengths were referenced to yttrium 324.228 nm.

ICP Results

Results for the analyzed foodstuff CRMs are shown in Tables 7&8 with % recoveries.

Element & Wavelength Units	NBS1577a Found ppm	NBS1577a Cert. mg/kg	NBS1577a % recovery	NBS1567 Found ppm	NBS1567 Cert. mg/kg	NBS1567 % recovery	ARC182 Found ppm	ARC182 Cert. mg/kg	ARC182 % recovery	MDL ppm
As 189.042 nm	0.0503	0.047	107.02	---	---	---	---	---	---	0.004
Ca 317.933 nm	133.6	120	111.33	195	190	102.63	2670	2860	93.36	0.0099
Cu 327.396 nm	153.3	158	97.03	2.105	2	105.25	---	---	---	0.0016
Fe 274.932 nm	192.9	194	99.43	18.86	18.3	103.06	---	---	---	0.0433
Mg 285.213 nm	576.5	600	96.08	---	---	---	719.2	785	91.62	0.0046
Mn 257.610 nm	10.14	9.9	102.42	8.634	8.5	101.58	12.98	12.9	100.62	0.0001
Ni 231.604 nm	---	---	---	0.1719	0.18	95.50	0.2863	0.271	105.65	0.0003
P 178.284 nm	11490	11100	103.51	---	---	---	---	---	---	0.0024
Zn 206.200 nm	122.2	123	99.35	10.96	10.6	103.40	29.16	28.9	100.90	0.0003

Element and Wavelength Units	M.D.L. ppb	Skim milk powder Found ppm	Skim milk powder Certified mg/kg	Skim milk powder % Recovery	Japanese diet Found ppm	Japanese diet Certified mg/kg	Japanese diet % Recovery	Poultry feed Found ppm	Poultry feed Certified mg/kg	Poultry feed % Recovery	Tomato paste Found ppm	Tomato paste Certified mg/kg	Tomato paste % 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	---	---	---.

Table 7 (top): ICP-OES results from Method 1, Table 8 (bottom): ICP-OES results from Method 2

Conclusions

- Mercury in Fish was analysed by VGAAS using the iCE 3000 Series AA and VP100 vapor generation accessory.
- Excellent linearity, stability and accuracy was obtained and meets current globally accepted legislation
- Precise and accurate results were obtained for the analysis of foodstuffs at major, minor and trace levels using the iCAP 6000 Series ICP
- Method development was made easy with the flexible wavelength choice offered by the unique CID detector, axial and radial viewing orientations and an internal standard mixing kit.

References

1. Commission Regulation (EC) No 1881/2006 of 19 December 2006: Setting Maximum Levels for Certain Contaminants in Foodstuffs
2. Codex General Standard for Contaminants and Toxins in Foods CODEX STAN 193-1995 Rev.3-2007

Full experimental conditions, methods and results can be found in our application notes:

- AN40755: Robust single method determination of major and trace elements in foodstuffs using the Thermo Scientific iCAP 6000 Series ICP
- AN40858: Ensuring regulatory compliance of foodstuffs using the thermo Scientific iCAP 6000 Series ICP
- AN40992: Accurate analysis of low levels of mercury in fish by vapor generation AA

For more information visit www.thermo.com/trace

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