Simultaneous determination of hydride and non-hydride elements in fish samples using the Agilent 5110 SVDV ICP-OES with MSIS accessory

Application note

Food safety

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Introduction

Testing of food products for a wide range of elements including nutrients, micronutrients and toxic elements is a widely performed analysis to ensure the quality control of these products.

ICP-OES, with a vapor generation accessory, is often used for the determination of hydride forming elements in foods, resulting in higher performance and lower detection limits than with conventional nebulization. However, analysis of a combination of hydride and non-hydride elements can be time consuming and complex. Elements such as Cd, Cr, Cu, Ni, Fe, Pb and Zn are measured in one analysis using a conventional sample introduction system. Then, hydride forming elements such as As, Se, Hg and Sn are measured in a separate analysis with a

vapor generation accessory installed. For laboratories that routinely analyze both hydride and non-hydride forming elements in samples there is a significant time penalty in switching between the two sample introduction systems.

Agilent's Multimode Sample Introduction System (MSIS) is a flexible sample introduction system for the determination of hydride and non-hydride elements by ICP-OES. It can be operated in three modes: conventional nebulization mode, vapor generation mode or dual mode. In dual mode both hydride and non-hydride elements can be measured at the same time, eliminating complicated, time consuming sample introduction changeovers without sacrificing sensitivity to reduce instrument downtime.

The Agilent 5110 Synchronous Vertical Dual View (SVDV) ICP-OES is ideal for food testing laboratories, providing accurate results, speed and reduced operating costs. The robust vertically oriented torch, increases matrix handling capabilities, compared to most dual view ICP-OES systems that use a horizontal torch. This means uncompromised measurements with less cleaning, maintenance as well as an extended torch lifetime. The 5110 SVDV ICP-OES features Dichroic Spectral Combiner (DSC) technology that captures the axial and radial views of the plasma in a single read to aid in method development, shorten analysis time and reduce argon gas consumption. This makes the 5110 SVDV ICP-OES an ideal choice for food testing labs that require high throughput and excellent analytical performance without compromise.

To demonstrate the capabilities of the Agilent 5110 SVDV ICP-OES instrument, combined with the MSIS accessory, a range of hydride and non-hydride elements in a fish tissue certified reference material (CRM) were quantified in a single analytical run.

Experimental

Instrumentation

All measurements were performed on an Agilent 5110 Synchronous Vertical Dual View (SVDV) ICP-OES equipped with the Multi-Mode Sample Introduction System (MSIS) accessory and an SPS 4 autosampler. The MSIS was operated in dual mode, with the sample introduction system consisting of a SeaSpray nebulizer and 1.8 mm i.d. injector torch.

Experimental conditions were optimized for the determination of As, Se, Hg, Sn and standard nebulized elements. Instrument and method parameters used are listed in Table 1.

Table 1. Agilent 5110 SVDV ICP-OES instrument operating conditions

Parameter	Setting
Read time (s)	20
Replicates	3
Sample uptake delay (s)	30
Stabilization time (s)	25
Rinse time (s)	50
Pump speed (rpm)	25 (5 channel pump)
Fast pump	Off
RF power (kW)	1.4
Plasma flow (L/min)	12
Nebulizer flow (L/min)	0.65
Auxiliary Flow (L/min)	1
Nebulized sample tubing	White-white
Hydride sample tubing	Black-black
Hydride reductant tubing	Black-black
Background Correction	Fitted

Sample preparation

The DORM-4 Fish Tissue Certified Reference Material (CRM), from the National Research Council Canada, Ottawa, Ontario, Canada, was used to validate the accuracy and precision of the method. Approximately 0.2 g of the CRM was weighed into a microwave vessel followed by the addition of 2.5 mL HNO_3 (69%) and 1 mL H_2O_2 (>30% w/v). The CRM was digested using a Milestone UltraWAVE Single Reaction Chamber (SRC) microwave digestion system according to the heating conditions given in Table 2. The system serves as both a microwave cavity and reaction vessel, that delivers high temperature capabilities. Sealing of the vials was not required as the Single Reaction Chamber was pressurized using a nitrogen gas pressure of 45 bar, ensuring complete digestion.

After microwave digestion, the digested solution was transferred into a 50 mL flask, acidified with 1.25 mL HCl (32%) and diluted to 50 mL with 18.2 MΩ deionized water. This solution was left to sit for at least 30 minutes before analysis. The final acid concentration was 5% HNO_3 and 2.5% HCl. In all cases, a corresponding reagent blank was also prepared according to the specified microwave digestion procedure.

Table 2. Parameters for Milestone UltraWAVE microwave digestion system

Parameter	Setting
Ramp up time (min)	10
Temperature (°C)	200
Hold time (min)	10
Ramp down time (min)	10
Total time (min)	30

The sample was spiked to validate the method for Sn and Pb, as those elements were present in concentrations close to the MDL. Samples were spiked at concentrations of 1 µg/L for Sn and 20 µg/L for Pb using a 1000 µg/L standard solution.

Calibration standards and reagents

A series of multi-element working standards at 5, 20, 50 and 100 µg/L were prepared from 1000 mg/L single element stock solutions (Merck, UK). Standards were treated in the same manner as the samples, with the addition of the pre-reduction solution (described below). Working standards were prepared in 5% HNO_3 and 2.5% HCl.

A mixture of 2% L-Cysteine and 4% Tartaric was used as a pre-reduction solution, added in-line, as shown in Figure 1. To prepare the pre-reduction solution 20 mL of a 10% L-Cysteine solution (in 2% HCl) was added to 4 g Tartaric acid and made up to 100 mL with deionized water.

Sodium borohydride ($NaBH_4$) was used as the reducing agent to generate the gaseous metal hydride. The reductant solution contained 1.5% $NaBH_4$ (w/v) in 0.5% NaOH (w/v), where $NaBH_4$ acted as the reductant and NaOH was used as a stabilizer.

Hydride generation process

In this study the hydride generation process was carried out in two steps: acidification and hydride generation.

The efficiency of the hydride generation reaction depends on the oxidation state of the analyte, where lower oxidation states give more efficient hydride generation. HCl was used to acidify samples and reduce the oxidation state of hydride-forming analytes (as outlined in the sample preparation procedure).

The acidification step was followed by the mixing of the sample with the reductant solution (the $NaBH_4$ and NaOH solution described above). The reaction of $NaBH_4$ with acid produces hydrogen, which forms hydrates with the low oxidation state analytes (for example arsine AsH_3 and selenite SeH_3).

The hydride generation step was completed with an in-line mixing of a pre-reduction solution containing L-Cysteine and Tartaric acid with the sample. This increased the efficiency of the hydride generation process, increased sensitivity for hydride elements and improved the linearity for conventional nebulized elements, in particular Cu.

The setup of the MSIS used in this application is shown in Figure 1. Dual mode operation required a five channel peristaltic pump for the pre-reduction solution, sample (via conventional nebulization and hydride generation), reductant and waste. All tubing was left unblocked so both the nebulized sample and gaseous hydride were carried by argon gas into the plasma.

An additional solution line was added to the MSIS setup for the pre-reduction solution. Mixing of this solution and the sample occurred through a long piece of FEP sample capillary tubing made into a coil to aid with mixing, shown in red in Figure 1, prior to the MSIS spray chamber.

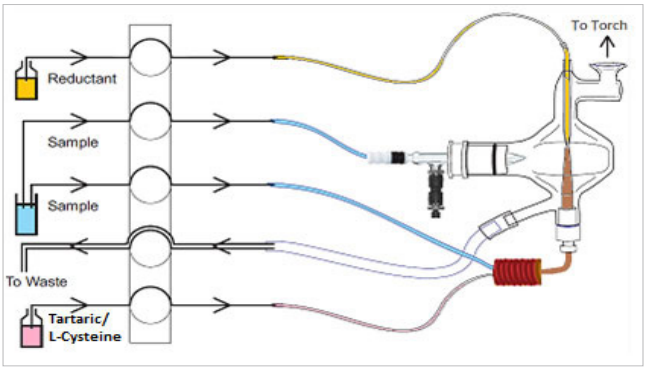

Figure 1. MSIS setup for dual mode, with an in-line pre-reduction mixing solution.

Results and discussion

CRM Recoveries

All hydride and non-hydride elements in the fish tissue CRM were measured in a single measurement using the MSIS in dual mode. The CRM was measured three times during the analytical sequence and the mean concentration, standard deviation and recovery were calculated for each analyte. Values shown in Table 3 reflect a 250 times dilution of the sample.

The recovery results for hydride forming elements such As, Se and Hg and standard nebulized elements in the fish CRM were within ±10% of the certified value.

Sn and Pb were present in concentrations close to the MDL, so the CRM sample was spiked for those elements to give concentrations of 1 µg/L and 20 µg/L respectively. Table 4 shows the spike recoveries for Sn and Pb in the fish tissue CRM with all measured recoveries within ±10% of the expected values.

The outstanding recovery results demonstrate the ability of the MSIS accessory to measure challenging elements such as As, Se, Hg and Sn by vapor generation in the presence of elements measured using standard nebulization, and achieve excellent recoveries across a wide concentration range. This eliminates the need to swap between different sample introduction systems for the analysis of hydride and non-hydride forming elements, making multi-elemental analysis of food samples quick and simple.

Table 3. Recoveries for hydride and non-hydride forming elements in DORM-4 Fish Tissue CRM

Element and wavelength (nm)	Certified value (mg/kg)	Measured result (mg/kg)	Average recovery (%)
As 188.980	6.87±0.44	6.88±0.38	100
As 193.696	6.87±0.44	6.84±0.38	100
Hg 184.887	0.41±0.036	0.392±0.012	95
Hg 194.164	0.41±0.04	0.380±0.007	92
Se 196.026	3.45±0.40	3.31±0.22	96
Sn 189.925	0.06±0.02	<LOQ	-
Cd 214.439	0.30±0.02	0.286±0.01	96
Cr 267.716	1.87±0.16	1.98±0.08	106
Cu 327.395	15.7±0.46	15.0±0.37	96
Fe 238.204	343±20	333±17	97
Mn 257.610	3.17±0.26	3.07±0.15	97
Pb 220.353	0.40±0.062	<LOQ	-
Ni 231.604	1.34±0.14	1.40±0.08	104
Zn 213.857	52.2±3.2	48.9±1.1	94

Table 4. Spike recovery results for Sn and Pb in the DORM-4 Fish Tissue CRM.

Element and wavelength (nm)	Spike conc. (µg/L)	Sample conc. (µg/L)	Measured spike conc. (µg/L)	SD (µg/L)	Spike recovery (%)
Sn 189.925	1.0	0.50	1.48	0.021	98
Pb 220.353	20	0.40	21.6	0.068	106

Method Detection Limits (MDL)

Three sigma Method Detection Limits (MDL) were calculated from ten replicate readings of the blank solution using a 20 second read time. The MDLs achieved for this method were more than sufficient for the simultaneous determination of hydride and non-hydride elements, and could be further improved by adjusting the chemistry for each individual element.

The MDL was measured three times over 3 non-consecutive days with results shown in Table 5. Excellent MDLs were obtained for all wavelengths.

The results demonstrate the high sensitivity of the 5110 ICP-OES with MSIS accessory for measuring hydride forming elements such as As, Se, Hg and Sn at low levels when measuring non-hydride forming elements at the same time.

Table 5. Agilent 5110 ICP-OES SVDV ICP-OES Method Detection Limits for hydride and non-hydride elements using the MSIS in dual mode

Element and wavelength (nm)	MDL (µg/L)
As 193.696	0.17
As 188.980	0.14
Hg 194.164	0.01
Hg 184.887	0.08
Se 196.026	0.42
Sn 189.925	0.10
Cd 214.439	0.09
Cr 267.716	0.29
Cu 327.395	0.34
Fe 238.204	0.24
Mn 257.610	0.03
Ni 231.604	0.97
Pb 220.834	0.98
Zn 213.857	0.26

Linear dynamic range

Calibration curves for all elements were linear with a correlation coefficient greater than 0.999 and less than 10% calibration error on each calibration point. Table 6 summarizes the calibration standard concentration range for all elements, and the achieved correlation coefficients. Figure 2 displays the calibration curves for As, Hg, Se and Sn. These demonstrate the ability of the 5110 ICP-OES, with MSIS accessory, to achieve excellent linearity across a wide calibration range for both hydride and non-hydride elements.

Table 6. Calibration range and correlation coefficient achieved for hydride and non-hydride elements using the MSIS in dual mode.

Element and wavelength (nm)	Standard conc. range (µg/L)	Linear correlation coefficient (r)
As 188.980	0-100	0.99978
As 193.696	0-100	1.00000
Hg 184.887	0-100	1.00000
Hg 194.164	0-100	0.99994
Se 196.026	0-100	0.99946
Sn 189.925	0-100	0.99998
Cd 214.439	0-100	0.99994
Cr 267.716	0-100	0.99987
Cu 327.395	0-100	0.99969
Fe 238.204	0-100	0.99988
Mn 257.610	0-100	0.99984

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Pb 220.353	0-100	0.99962
Ni 231.604	0-100	0.99980
Zn 213.857	0-100	0.99986

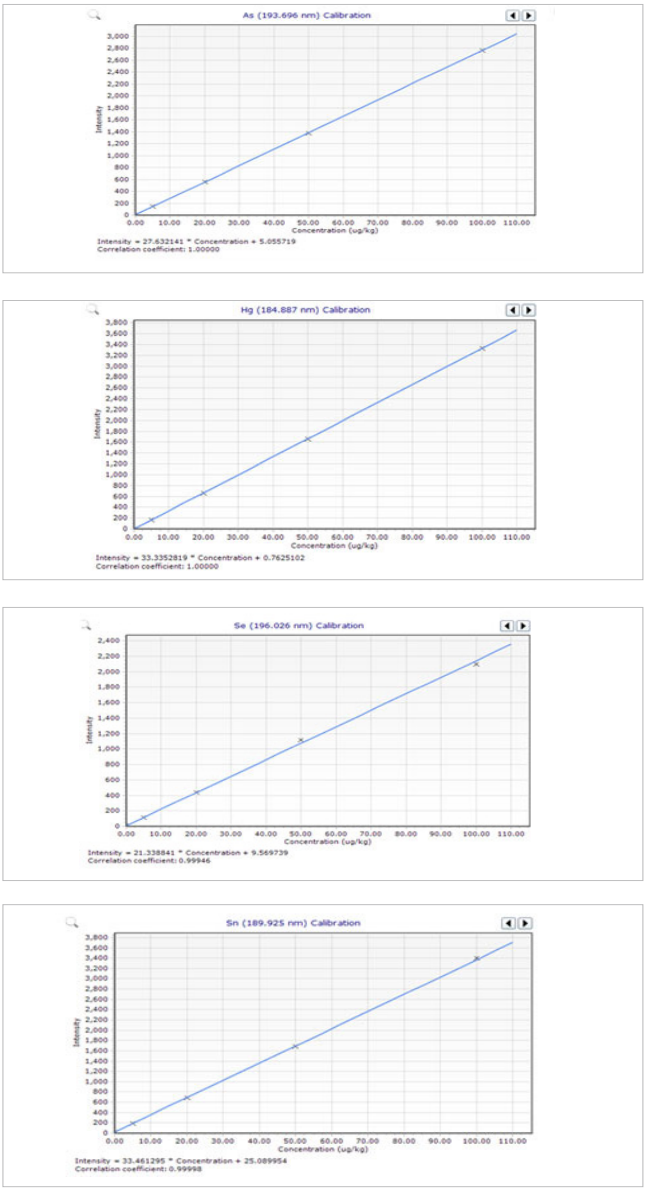

Figure 2. Linear calibration curves for As 193.696 nm, Hg 184.887 nm, Se 196.026 nm and Sn 189.925 nm.

Conclusions

A wide range of hydride and non-hydride forming elements in a fish tissue CRM were quantified in a single analytical run using the Agilent 5110 SVDV ICP-OES with the MSIS accessory. The MSIS method offers fast analysis time, high performance and simple, reliable operation. The setup is ideal for screening large numbers of food samples to meet the increasing demand for the routine determination of elements by vapor generation and standard nebulization at the same time.

The key findings of the study were:

- Excellent accuracy and precision was achieved for all elements using the dual mode MSIS setup
- Recovery results were all within ±10% of certified and spike values for elements determined by both vapor generation and conventional nebulization across a wide concentration range
- High sensitivity, excellent linearity and low detection limits were achieved, demonstrating the high analytical performance of the MSIS accessory even when operated in dual mode

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