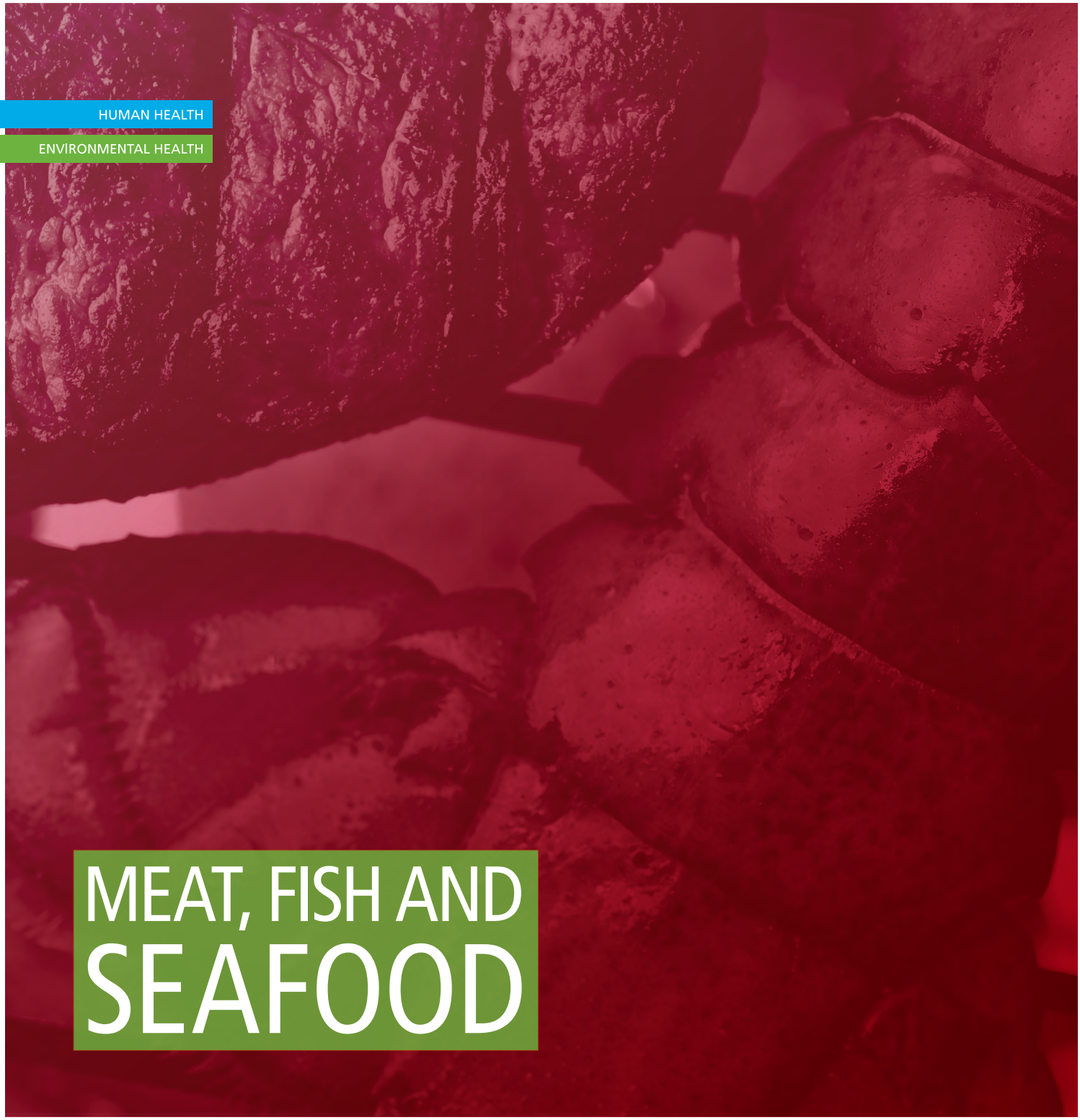
HUMAN HEALTH

ENVIRONMENTAL HEALTH



MEAT, FISH AND SEAFOOD

Meat, Fish and Seafood Compendium

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MEAT, FISH AND SEAFOOD

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APPLICATION BRIEF

ICP - Mass Spectrometry

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The Elemental Analysis of Meat and Seafood with the NexION 300/350 ICP-MS

Introduction

The elemental content of food products is very important, both in relation to nutritional and toxic elements. Nutritional elements can either be native to the food substance or can be added to enhance the health benefits. Toxic elements can enter food either through the environment or processing during production. Hopefully, toxic elements will be present at extremely low levels, while nutritional elements will be present at optimal levels: if too high, they may be toxic; if too low, the food will not provide the necessary nutrition. Therefore, the elemental analysis of food requires the ability to measure both trace and high levels.

The elemental capabilities and dynamic range of inductively coupled plasma mass spectrometry (ICP-MS) make it ideally suited for the analysis of food materials. The ultratrace detection limits of ICP-MS permit the determination of low-level contaminants, such as Pb, As, Se, and Hg, while the macro-level nutritional elements, such as Ca, Mg, K, and Na, can be quantified using the extended dynamic range capability of ICP-MS which provides the ability to measure concentrations over nine orders of magnitude. However, there are still a number of challenges to overcome, including complex sample matrices, high levels of dissolved solids, and interferences. With the proper ICP-MS instrumental conditions and design, all of these issues can be overcome, allowing for the successful analysis of food samples, as described elsewhere[1]. This work will focus on the analysis of meat and seafood; foods such as these are high in protein content which is important for body growth and repair.

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Experimental

Sample Preparation

NIST® 8414 Bovine Muscle and NIST® 2976 Mussel Tissue were used in this work. Approximately 0.5-0.6 g were digested in duplicate with 5 mL of nitric acid (Fisher Scientific™, Optima grade) and 2 mL of hydrogen peroxide (Fisher Scientific™, Optima grade) in pre-cleaned PTFE microwave sample vessels. The digestion program consisted of 30 min of heating and 15 min of cooling, as shown in Table 1. All samples were completely dissolved, resulting in clear solutions that were diluted to a final volume of 50 mL with deionized water. No further sample dilutions were necessary. Gold was added to all solutions at a final concentration of 200 µg/L to stabilize mercury. Preparation blanks, consisting of the acid mixture, were taken through the same microwave digestion program as the samples.

Table 1. Microwave Digestion Program.

Step	Power (W)	Ramp (min)	Hold (min)
1	500	1	4
2	1000	5	5
3	1400	5	10
4 (cooling)	0	—	15

Instrumental Conditions

All data in this study were generated under normal operating conditions on a PerkinElmer NexION® 300/350X ICP-MS using an autosampler. The instrumental operating conditions are shown in Table 2.

Table 2. ICP-MS Instrumental Operating Conditions for this Application.

Parameter	Value
Nebulizer	Glass concentric
Spray chamber	Glass cyclonic
Cones	Nickel
Plasma gas flow	18.0 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	0.98 L/min
Sample uptake rate	300 µL/min
RF power	1600 W
Total integration time	0.5 (1.5 seconds for As, Se, Hg)
Replicates per sample	3
Universal Cell Technology™*	Collision mode

*PerkinElmer, Inc.

Calibration

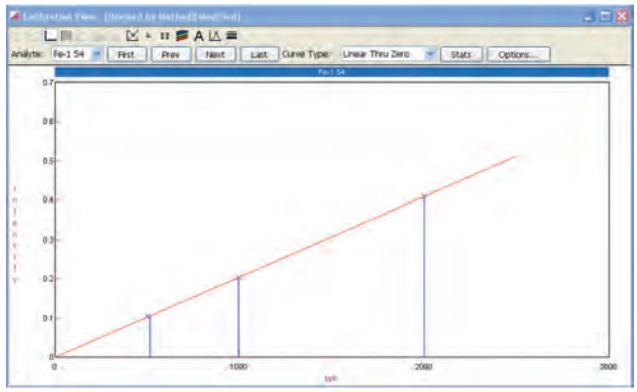
Multielement calibration standards, representing all the analytes in the SRMs, were made up from PerkinElmer Pure single and multielement standards and diluted into 10% HNO_3. Gold was added to all solutions at a final concentration of 200 µg/L to stabilize mercury. Calibration standard ranges were based on whether the analyte was expected to be a high-level nutritional element like potassium (K) or sodium (Na), low/medium-level essential element like manganese (Mn) or iron (Fe), or trace/ultratrace contaminant such as lead (Pb) or mercury (Hg).

Depending on the certified value of the analytes, five different calibration ranges were made up to cover the complete range of elements being determined:

- High-level nutritional analytes: 0-300 ppm
- Medium-level essential analytes: 0-20 ppm
- Low-level essential analytes: 0-2 ppm
- Trace-level contaminants: 0-200 ppb
- Ultratrace-level contaminants: 0-20 ppb

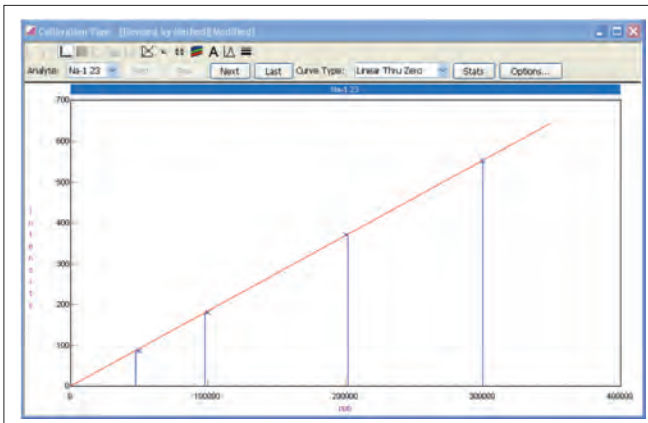
Figures 1 to 5 show representative calibration curves for each range.

In addition to the analyte elements used for the multielement calibration, the standards, blanks, and samples were also spiked on-line using a mixing tee with a solution of ^{6}Li, Sc, Ge, In, and Tb for internal standardization across the full mass range. Acetic acid was added to the internal standard solution to compensate for residual carbon left over from the sample digestion.



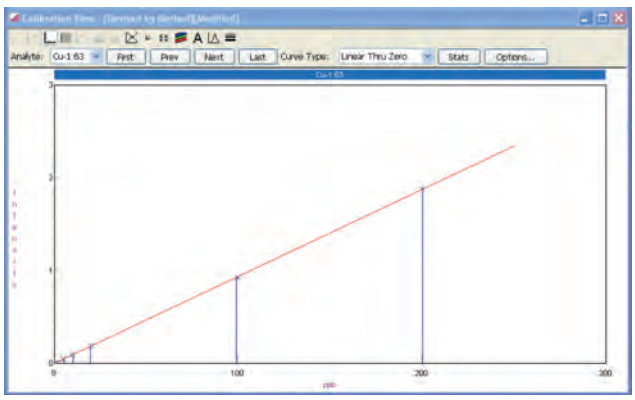
^{54}Fe Correlation Coefficient = 0.99997.

Figure 1. Calibration curves for ^{54}Fe (0-2 ppm).



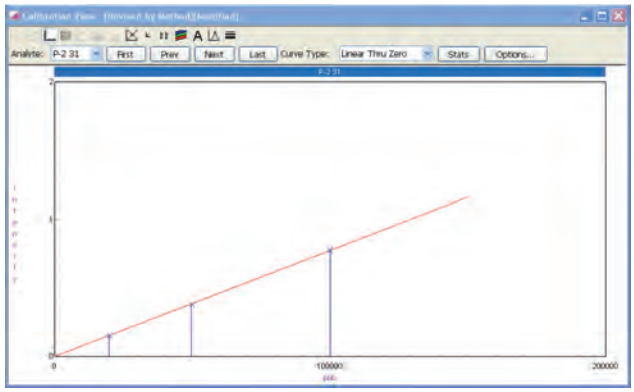
^{23}Na Correlation Coefficient = 0.99996.

Figure 2. Calibration curve for ^{23}Na (0-300 ppm).



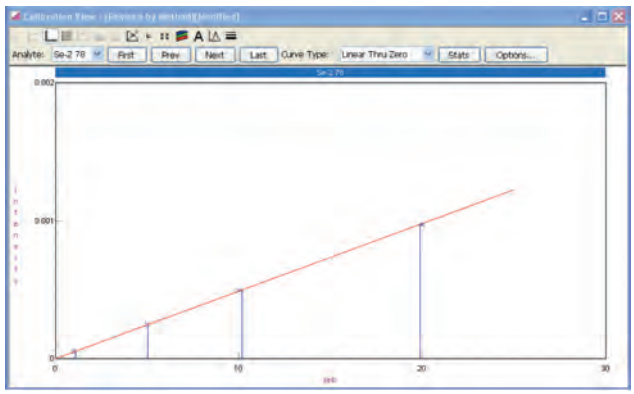
^{63}Cu Correlation Coefficient = 0.99999.

Figure 3. Calibration curve for ^{63}Cu (0-200 ppb).



^{31}P Correlation Coefficient = 0.99999.

Figure 4. Calibration curve for ^{31}P (0-100 ppm).



^{78}Se Correlation Coefficient = 0.99995.

Figure 5. Calibration curve for ^{78}Se (0-20 ppb).

Results

Quantitative results for two sample preparations of the NIST® 8414 Bovine Muscle and NIST® 2976 Mussel Tissue reference materials are shown in Tables 3 and 4. All elements in every sample were determined with Universal Cell operating in Collision mode using helium as the cell gas. Figures in parentheses ( ) in the Reference Value column are not certified values but are included for information purposes only. The data show very good agreement with the certified values, especially for the elements that suffer from known spectral interferences. The elements that are outside the specified limits are mostly the ones that are well recognized as environmental contaminants, which have most likely been impacted by the sample preparation procedure.

Table 3. Analysis of NIST® 8414 Bovine Muscle using the NexION 300/350 ICP-MS.

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	0.6 ±0.4	0.4
Na	23	2100 ±80	2000
Mg	26	960 ±95	960
Al	27	1.7 ±1.4	1.6
P	31	8360 ±450	7250
S	34	7950 ±410	6820
K	39	15170 ±370	14180
Ca	44	145 ±20	143
V	51	(0.005)	0.006
Cr	52	0.071 ±0.038	0.092
Fe	54	71.2 ±9.2	71.2
Mn	55	0.37 ±0.09	0.44
Co	59	0.007 ±0.003	0.014
Ni	60	0.05 ±0.04	0.05
Cu	63	2.84 ±0.45	2.81
Zn	66	142 ±14	140
As	75	0.009 ±0.003	0.011
Se	78	0.076 ±0.010	0.11
Sr	88	0.052 ±0.015	0.081
Mo	98	0.08 ±0.06	0.08
Cd	111	0.013 ±0.011	0.013
Sn	118	–	0.14
Sb	121	(0.01)	0.01
Ba	137	(0.05)	0.04
Hg	202	0.005 ±0.003	0.003
Pb	208	0.38 ±0.24	0.34
Tl	205	–	0.002
Th	232	–	<0.00008
U	238	–	<0.00002

Table 4. Analysis of NIST® 2976 Mussel Tissue using the NexION 300/350 ICP-MS.

Element	Mass (amu)	Reference Value (mg/kg)	Experimental Value (mg/kg)
B	11	–	27.5
Na	23	(35000 ±1000)	35000
Mg	26	(5300 ±500)	4800
Al	27	(134 ±34)	149
P	31	(8300)	6900
S	34	(19000)	16000
K	39	(9700 ±500)	9700
Ca	44	(7600 ±300)	7400
V	51	–	0.87
Cr	52	(0.50 ±0.16)	0.50
Fe	54	171.0 ±4.9	190
Mn	55	(33 ±2)	40
Co	59	(0.61 ±0.02)	0.67
Ni	60	(0.93 ±0.12)	0.87
Cu	63	4.02 ±0.33	3.91
Zn	66	137 ±13	145
As	75	13.3±1.8	16.4
Se	78	1.80 ±0.15	2.52
Sr	88	(93 ±2)	79
Mo	98	–	0.56
Cd	111	0.82 ±0.16	0.88
Sn	118	(0.096 ±0.039)	0.103
Sb	121	–	0.011
Ba	137	–	0.61
Hg	202	0.061 ±0.0036	0.058
Pb	208	1.19 ±0.18	1.06
Tl	205	(0.0013)	0.003
Th	232	(0.011 ±0.002)	0.012
U	238	–	0.22

Conclusion

This work has demonstrated the ability of PerkinElmer's NexION 300/350X ICP-MS to effectively measure macro-level nutritional elements in the same analysis run as lower-level elements, without having to dilute the samples. The agreement between experimental and certified results for NIST® 8414 Bovine Muscle and NIST® 2976 Mussel Tissue demonstrates the accuracy of the analysis. Instrument design characteristics eliminate deposition on the ion optics, leading to long-term stability in high-matrix samples, while permitting trace levels to be accurately measured.

References

1. "The Determination of Toxic, Essential, and Nutritional Elements in Food Matrices Using the NexION 300/350 ICP-MS", PerkinElmer Application Note.

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APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

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The Preparation and Analysis of Polycyclic Aromatic Hydrocarbons in Meat by GC/MS

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbon molecules containing two or more aromatic rings. Some PAHs, such as benzo[a]pyrene, are classified as carcinogens; PAHs are commonly found in the environment as a result of partially burned organic materials, such as petroleum, plastics, rubber, lubricants and wood. In addition to environmental concerns, there are concerns about PAHs in food, especially in grilled meats.

The European Union (EU) introduced legislation in early 2005 in response to food-contamination data collected by the Scientific Committee on Food (SCF). The SCF identified 15 PAHs that possess carcinogenic properties. Directive 2005/69/EC of the European Parliament and of the Council of 16 November 2005 identified an additional PAH as probably carcinogenic.[1] The joint set of PAHs was recognized as the 15 + 1 EU priority PAHs. It is necessary to accurately determine the level of 15 + 1 EU priority PAHs in food to respond to European legislation and ensure food safety.

This application note will present a method developed to measure 15 + 1 EU priority PAHs at low levels using gas chromatography mass spectrometry (GC/MS). It will also describe a reliable procedure for extraction and purification of PAHs from meat samples. The sample preparation will focus on benzo[a] pyrene. In addition to method optimization and calibration, a variety of meat samples are analyzed and the amount of PAHs determined.

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Experimental

Solvent Extraction

A solvent extractor (Dionex® ASE 300) was used to extract the meat samples analyzed in this application. A glass microfiber filter was put at the outlet end of the extraction cells. Then 1 g of diatomaceous earth was put on top of the glass fiber filter. 5 g of homogenized-meat sample were mixed with 5 g of Florisil®. The resulting material was poured into the extraction cells. 2 g of anhydrous sodium sulfate was put into the collection vials to remove all water in the meat samples. Table 1 shows the instrumental setup parameters for the accelerated solvent extractor.

Table 1. **Instrumental Parameters for the Solvent Extractor.**

Solvent	Cyclohexane
Pressure of Nitrogen	1400 psi
Extraction Temperature	100 °C
Heat Time	5 min
Static Time	5 min
Cycles	2
Flush Volume	60%
Purge Time	100 sec

Gel Permeation Chromatography (GPC)

The extract was concentrated to 2 mL using a rotary evaporator at 35 °C and diluted quantitatively to 5 mL with cyclohexane:ethylacetate (50:50 v/v). It was then filtered through a PTFE filter (5 µm) to remove any particulates.

The GPC system was an AccuPrep™ MPS and AccuVap™ Inline with an Express™ GPC cleanup column from J2 Scientific. 2 mL of each sample was injected into GPC. Samples were eluted at a flow rate of 4.7 mL/min by cyclohexane:ethylacetate (50:50 v/v) (dump time 0–15 min, collect time 15–20 min).

The focus of the sample analysis, as mentioned in the introduction, was on benzo[a]pyrene. As a result, the collection time of the GPC began just before the elution of benzo[a] pyrene to eliminate as much matrix as possible. The timing of the fraction collection sent most of the co-extracted matrix to waste; however, it also resulted in the dumping of the 5 highest-molecular-weight PAHs in the mix. If these PAHs were of interest the GPC, collect time would be adjusted to collect all of the PAHs. Following fraction collection, the final volume was adjusted to 1.5 mL with cyclohexane.

Standard Preparation

A stock solution at 20 µg/mL was prepared by diluting 0.2 mL of a 1000 µg/mL PAHs standard to 10 mL with cyclohexane.

1 µg/mL standard working solution was prepared by diluting 0.5 mL of a 20 µg/mL PAHs standard stock solution to 10 mL with cyclohexane.

An internal standard solution mixture of naphthalene-D8, phenanthrene-D10, chrysene-D12 and perylene-D12 at 20 ng/µL was prepared by diluting 0.2 mL of a 1000 µg/mL internal standard solution mixture to 10 mL with cyclohexane.

Working calibration standards at 5, 10, 20, 50, 100, 200, 500 ng/mL were prepared fresh each day. 5 µL of the 20 ng/µL internal standard solution was injected into each GC vial containing 1 mL of the working standard or sample.

GC/MS Conditions

In this application, the PerkinElmer® Clarus® 680 GC/MS system was used to identify and quantify PAHs. Table 2 shows the detailed instrumental setup parameters for the GC/MS system.

Table 2. **Instrumental Parameters.**

Gas Chromatograph	**PerkinElmer Clarus 680 GC**
Oven Program Initial Temperature	50 °C
Hold Time 1	2 min
Ramp 1	25 °C/min to 200 °C
Hold Time 2	0 min
Ramp 2	15 °C/min to 310 °C
Hold Time 3	19.67 min
Equilibration Time	0.2 min
Column	PerkinElmer – Elite™-5ms 30 m x 0.25 mm x 0.25 µm
Injector	Programmable Split/Splitless
Injection Mode	Splitless and Pressure Pulse
Injection Volume	1 µL
Inlet Temperature	280 °C
Liner	Deactivated Liner (P/N N6502002)
Carrier Gas	Helium
Carrier Gas Flow Rate	1 mL/min
Mass Spectrometer	**PerkinElmer Clarus 600 MS**
Mass Range	45-450 u
Solvent Delay Time	6 min
Scan Time	0.20 sec
InterScan Delay Time	0.05 sec
Transfer Line Temperature	280 °C
Source Temperature	240 °C
Mutiplier	500 V
InterChannel Delay Time	0.05 sec
SIM Mode	8 SIM groups
SIR Dwell Time	0.04 sec
Software	TurboMass™ 5.4.2

The regulatory limits for the analysis of benzo[a]pyrene require low-level analysis. In order to achieve this level of detection in sample matrix, it was necessary to use selected ion monitoring (SIM). The steps to create a SIM MS method follow:

- Each PAH had one quantifier ion and two qualifier ions (Table 3 – Page 4).
- The dwell time of each ion was 0.04 seconds.
- All isomers were in the same group. Other PAHs were in the separate groups.

Results

The precision of the method was evaluated with a 100 ng/mL standard – Table 3 shows % RSD from this experiment. Figure 1 is an example chromatogram of a 200 ng/mL standard injection.

Chrysene-D12 and perylene-D12 were used as internal standards. Peak-area ratio was used to calculate amounts of PAHs.

The peak-area ratio for the compound in the sample was calculated by dividing the peak area of the compound (target ion) by the peak area (target ion) of the internal standard (IS):

$$Peak-area\ ratio = \frac{Peak\ area\ of\ the\ component\ ion}{Peak\ area\ of\ the\ IS\ ion}$$

Amounts of PAHs were calculated by plotting the peak-area ratio in the following calibration functions:

$$conc\ (x) = \frac{y(peak-area\ ratio) - b^{\ y=ax+b}}{a}$$

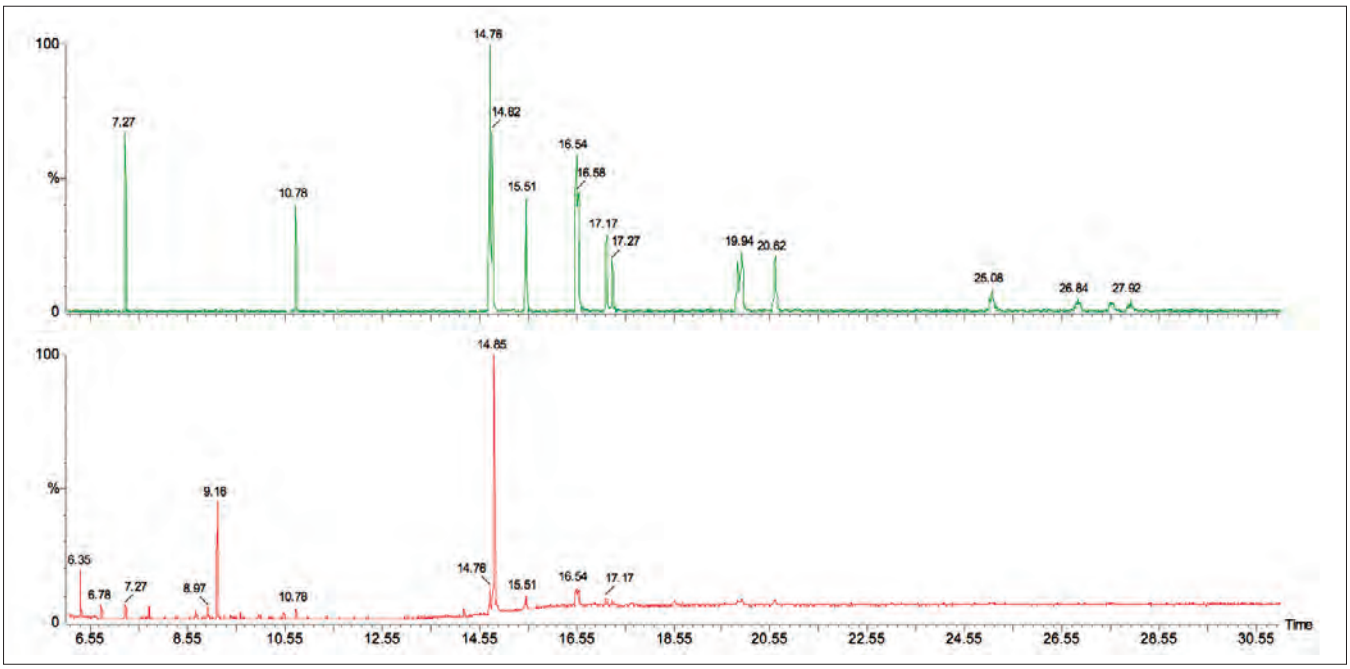

Figure 1. Total ion chromatogram (TIC) of 200 ppb PAHs standard solution (lower) and the sum of extracted quantifier ions of PAHs (upper).

Table 3. **Calibration Table for PAHs.**

Name	Retention Time	Quantifier Ion	Qualifier Ion 1	Qualifier Ion 2	%RSD of Peak Area (n=7) 100 ng/mL	r^2 (5 – 500 ppb)
Naphthalene-D8	7.28	136	137	108		
Phenanthrene-D10	10.79	188	189	80		
Cyclopenta[cd]pyrene	14.78	226	227	224	0.5	0.9999
Benz[a]anthracene	14.78	228	229	226	1.1	0.9996
Chrysene-D12	14.79	240	241	236		
Chrysene	14.83	228	229	226	3.0	0.9999
5-Methylchrysene	15.52	242	241	239	1.5	0.9997
Benzo[b]fluoranthene	16.56	252	253	250	0.3	0.9986
Benzo[j]fluoranthene	16.56	252	253	250	0.3	0.9986
Benzo[k]fluoranthene	16.56	252	253	250	0.3	0.9987
Benzo[a]pyrene	17.19	252	253	250	0.3	0.9981
Perylene-D12	17.29	264	265	260		
Indeno[1,2,3-cd]pyrene	19.89	276	277	138	0.4	0.9972
Dibenzo(a,h)anthracene	19.96	278	279	276	0.1	0.9965
Benzo[ghi]perylene	20.65	276	277	138	0.9	0.9997
Dibenzo[a,l]pyrene	25.09	302	151	150	0.3	0.9959
Dibenzo[a,e]pyrene	26.85	302	151	150	0.2	0.9942
Dibenzo[a,i]pyrene	27.56	302	151	150	0.2	0.9913
Dibenzo[a,h]pyrene	27.94	302	151	150	0.2	0.9926

Following the calibration of the system, 5 g of bacon, preserved ham and sausage were analyzed and the PAH concentrations quantified (Table 4 – Page 5). Table 4 also presents the recoveries of the matrix spike and matrix-spike duplicate, which were fortified with PAHs at 100 ng/mL. The resultant chromatogram for the analysis of the preserved ham sample is pictured in Figure 2.

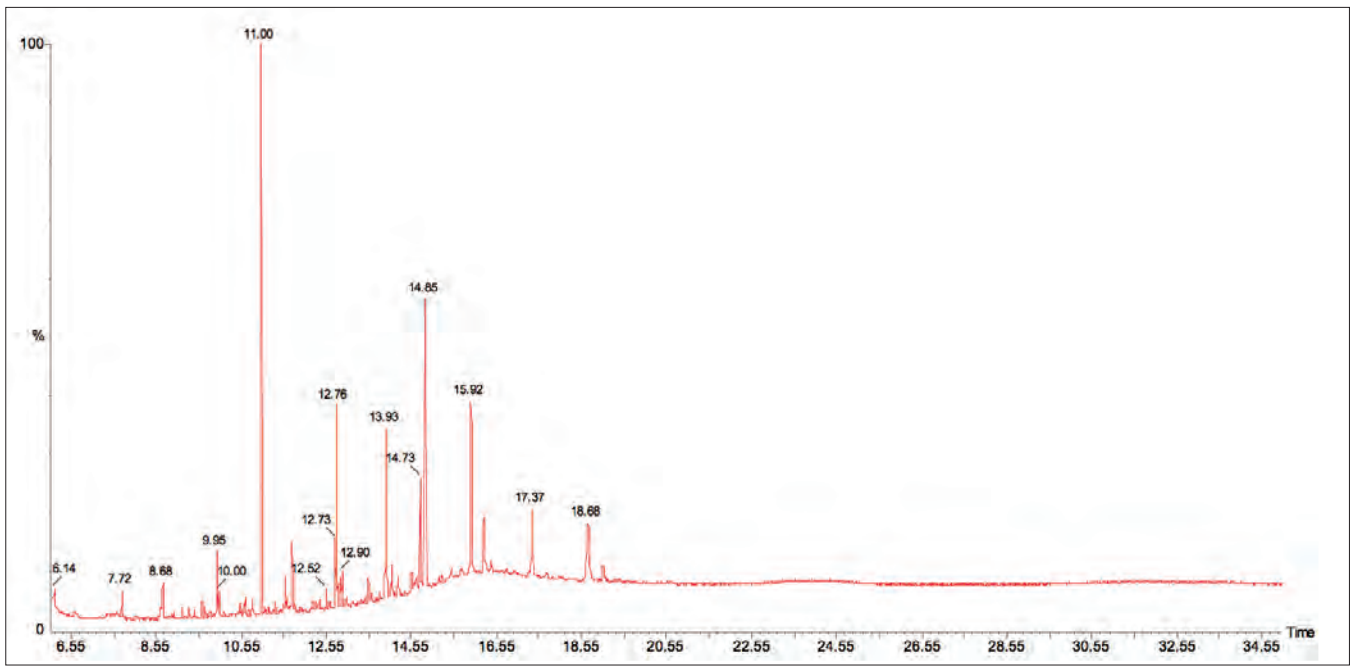

Figure 2. Total ion chromatogram (TIC) of the analysis of preserved ham sample.

Table 4. **Sample Analysis and Matrix-Spike Recovery.**

Sample	Compounds	Conc. (ng/mL)	MS Recovery (%)	MSD Recovery (%)
Bacon	Cyclopenta[cd]pyrene	9.3	14.6	11.6
	Benz[a]anthracene	22.1	78.0	76.5
	Chrysene	18.4	76.6	75.1
	5-Methylchrysene	9.5	73.9	64.0
	Benzo[b]fluoranthene	15.2	63.4	61.7
	Benzo[j]fluoranthene	15.2	63.4	61.7
	Benzo[k]fluoranthene	15.1	63.5	60.8
	Benzo[a]pyrene	14.2	61.3	50.9
	Indeno[1,2,3-cd]pyrene	11.7	47.4	36.4
	Dibenzo(a,h)anthracene	14.3	38.0	35.1
Preserved Ham	Cyclopenta[cd]pyrene	12.0	11.2	13.3
	Benz[a]anthracene	21.8	89.1	75.7
	Chrysene	15.6	90.0	76.8
	5-Methylchrysene	12.0	81.6	61.9
	Benzo[b]fluoranthene	17.0	73.7	63.1
	Benzo[j]fluoranthene	17.0	73.7	63.1
	Benzo[k]fluoranthene	16.9	73.8	63.3
	Benzo[a]pyrene	14.4	73.1	65.5
	Indeno[1,2,3-cd]pyrene	10.5	63.7	56.9
	Dibenzo(a,h)anthracene	12.0	40.1	44.7
Sausage	Cyclopenta[cd]pyrene	7.8	68.1	75.7
	Benz[a]anthracene	21.6	63.3	69.1
	Chrysene	11.3	66.3	74.4
	5-Methylchrysene	6.3	70.7	78.0
	Benzo[b]fluoranthene	12.8	51.3	56.3
	Benzo[j]fluoranthene	12.8	51.3	56.3
	Benzo[k]fluoranthene	12.7	51.5	53.2
	Benzo[a]pyrene	12.0	50.4	54.7
	Indeno[1,2,3-cd]pyrene	11.6	42.2	44.7
	Dibenzo(a,h)anthracene	14.4	37.3	39.8

Discussion

The matrix-spike recoveries for benzo[ghi]perylene, dibenzo[a,l]pyrene, dibenzo[a,e]pyrene, dibenzo[a,i]pyrene and dibenzo[a,h]pyrene of all the meat samples was 0%. As was mentioned in the experimental discussion, the focus of this experiment was benzo[a]pyrene, thus the timing of the fraction collection of the GPC was optimized for it. There were high levels of oleic acid in the meat samples. The molecular weight of oleic acid is 282, which is quite close to the molecular weight of benzo[ghi]perylene (MW 276) and dibenzo[a,l]pyrene, dibenzo[a,e]pyrene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene(MW 302). When collection time was set from 15 to 20 min, much less matrix interference was observed improving the method performace for benzo[a]pyrene, but eliminating the highest-molecular-weight PAHs.

If the PAHs listed above are of importance, the collection time of the GPC can be changed to 14 to 20 min. The matrix interference will increase, however the recoveries for benzo[ghi]perylene, dibenzo[a,l]pyrene, dibenzo[a,e]pyrene, dibenzo[a,i]pyrene and dibenzo[a,h]pyrene will improve.

Conclusion

This application note demonstrates that the Clarus 680 GC/MS system is effective in the analysis of PAHs in meat samples. An effective sample-preparation technique was developed to extract PAHs from meat. GPC was used to remove much of the matrix associated with meat samples. The GC/MS system was calibrated across the range of 5–500 ppb, with a linear response. Three meat samples were analyzed, including samples spiked with known amounts of PAHs, and recoveries reported.

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1. DIRECTIVE 2005/69/EC of the European Parliament and of the Council of 16 November 2005.

2. J.A. Gomez-Ruiz, et al., Talanta (2009), doi:10.1016/j.talanta. 2009.07.041.

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APPLICATION NOTE

Differential Scanning Calorimetry

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Glass Transition Measurement of Undried Fish Gelatin with Fast Scan DSC Technique

Background

Glass transition (Tg) measurement of undried bio-polymers is challenging using the conventional DSC technique. The glass transition (Tg) is frequently masked by the moisture vaporization event. This is particularly troublesome in biomaterial where transitions near 100 ˚C and 0 ˚C are common. HyperDSC® separates two overlapping events with different kinetic properties, therefore Fast Scan DSC techniques (HyperDSC) allow measurements beyond the range of conventional DSC. Double Furnace DSC has superior performance, such as extremely short equilibration time, high sensitivity and high resolution. These support the HyperDSC technique. HyperDSC expands the DSC capabilities beyond the limitations of the conventional slow scan DSC technique by allowing us to separate the overlapping events with different kinetics and to amplify weak thermal events. In this paper, we demonstrate the HyperDSC capability to measure the Tg event of the undried fish gelatin samples with a very short test cycle time.

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Analysis/Methodology

Instrument configurations: PerkinElmer® Double Furnace DSC 8000 with the Intercooler 2P cooling device

Samples

1) Pure fish gelatin

2) Blended fish gelatin (labeled as 25 Sorb-3, 25 Sorb-4 and 25 Sorb-5), each contains unknown amount of sorbitol, starch and some plasticizers as additives.

Sample Preparation Pure and blended gelatin were crushed or cut with a knife into similar, small sized pieces. All samples were crimped in a standard Al solid pan – samples not hermetically sealed (at approximate weight of 8 mg).

Test Method Parameters Scan from -50 ˚C to 200 ˚C, at 10 ˚C/min (slow scan).

Scan from -60 ˚C to 200 ˚C, at 100 ˚C/min (HyperDSC).

Results and Discussion

Running the samples in the conventional DSC slow scan at 10 ˚C/min gave a broad endothermic peak that is observed from approximately 40 ˚C up to 190 ˚C in all fish gelatin samples (Figure 1). This peak is predominately due to the volatile vaporization which masks the relatively weak Tg of the fish gelatin compounds. Due to the overlapping of these two events, it is difficult to determine the Tg with conventional DSC techniques. Other researchers have used conventional DSC with hermetically sealed volatile pans for a similar study.[1] In their work, the Tg was detected by suppressing the vaporization event. This has the disadvantage of exposing the fish gelatin to elevated pressure and may cause changes in the material. Other techniques such as Dynamic Mechanical Analysis can detect the Tg, but required a special sample preparation to allow successful handling of a delicate sample and often takes a long time to run the test.

Figure 2 shows the TGA weight change profile for undried fish gelatin. Note the temperature of the volatile loss step which coincides with the volatile vaporization endothermic peak in Figure 1. This suggests the endothermic event is vaporization.

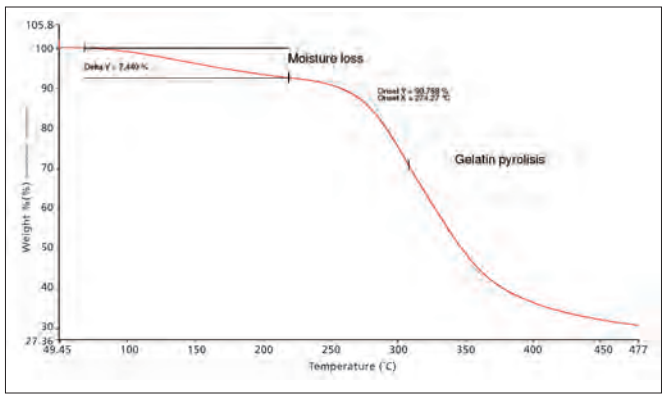

Figure 2. TGA thermogram of pure fish gelatin sample shows a weight loss step which is due to the volatile vaporization.

HyperDSC is capable of separating the overlapping Tg and volatile vaporization events as the latter is a time-dependent kinetic event by pushing the latter to higher temperature. The fish gelatin samples were scanned at 100 ˚C/min and the gelatin Tg is now clearly observed in all samples as shown in Figure 3. Similar work with HyperDSC has been used to separate the Tg and moisture vaporization in other systems. It has been reported in the study of wheat gluten, heparin, proteins, and polyamides[2,3] to name a few. This ability to measure concealed events is important for the study of biopolymers since the Tg is highly dependent on the moisture content[4,5] and water volatilization often masks the transitions.

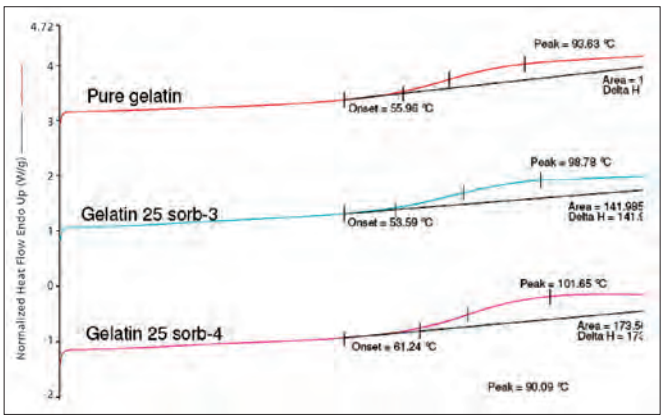

Figure 1. DSC thermograms of pure and blended fish gelatin samples at conventional 10 ˚C/min. Volatile vaporization produces a broad endothermic peak which masks the Tg event. Beside the endothermic peak, there is no evidence of other thermal events.

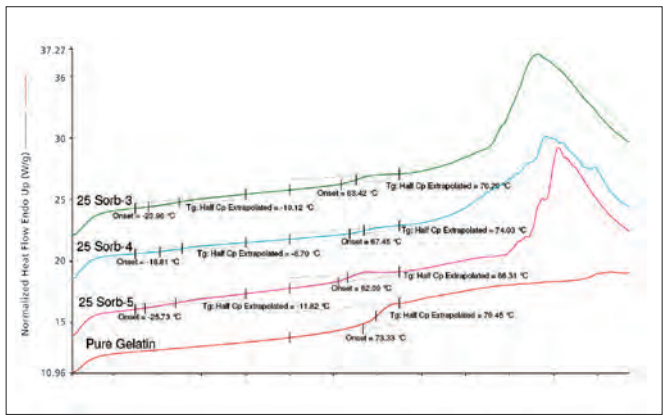

Figure 3. DSC theromgrams of the same fish gelatin sample using HyperDSC at 100 ˚C/min. HyperDSC exposes the Tg event after the moisture vaporization is pushed to a higher temperature.

In addition to the gelatin Tg, HyperDSC reveals a weak sub-ambient Tg, between -30 ˚C and -10 ˚C in all blended samples at 100 ˚C/min. This sub-ambient Tg, shown in Figure 3, is not visible with the conventional 10 ˚C/min slow scan. HyperDSC amplifies the weak signal. Similar works relating to the amplification of weak thermal events by the HyperDSC technique have been reported in graphite composite, sucrose and lactose studies.[6,7,8] In this case, the weak sub-ambient Tg is believed to be related to either the sorbitol or plasticizer used in these blended samples.

Conclusions

This case study shows that Fast Scan DSC (HyperDSC) is capable of detecting the water masked Tg in the undried fish gelatin biopolymer. In addition, it reveals a previously undetected weak Tg. The measurements using HyperDSC were carried out in a few minutes, making HyperDSC an ideal approach for faster analysis and screening.

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APPLICATION NOTE

Atomic Absorption

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Analysis of Fish and Seafoods with AAnalyst 800 Atomic Absorption Spectrophotometer for Trace Metal Contamination, in Accordance with AOAC Methods 999.10 and 999.11

Introduction

Increased knowledge about the nutrient content of biological organisms is essential for a thorough understanding of ecological stoichiometry and nutrient transport in and among ecosystems. As a result of water pollution in coastal area, many problems in food safety like heavy metal accumulation have been recognized in farmed fish, which is one of the important fishery food resources. The heavy metals accumulated in fish not only have a bad influence on fish but they also affect the health of human beings through the food chain. It is pointed out that remarkable heavy metals were contained in fish meals that are used as major raw materials for aquaculture feeds. The Itai-itai disease of the Toyama Jintsu River area in Japan was the documented case of mass cadmium poisoning. Itai-itai disease is known as one of the Four Big Pollution Diseases of Japan.

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In the present work, we demonstrate the ability of AAnalyst™ 800 atomic absorption spectrophotometer in analyzing a variety of fish samples. Sample preparation has been done in two different ways i.e. by AOAC Method 999.10, which is the official method for the sample preparation of fish samples with microwave digestion and AOAC Method 999.11, which is the preparation of fish samples with conventional dry ashing using a muffle furnace.

Experimental

The measurements were performed using the PerkinElmer® AAnalyst 800 atomic absorption spectrophotometer (PerkinElmer, Inc. Shelton, CT, USA) (See Figure1) equipped with WinLab32™ for AA Version 6.5 software, which features all the tools needed to analyze samples, report and archive data and ensure regulatory compliance. PerkinElmer high efficiency double beam optical system and solid-state detector provide outstanding signal-to-noise ratios and Deuterium background correction eliminates most interferences. A PerkinElmer corrosion-resistant nebulizer, which can be used for solutions containing hydrofluoric acid, was used for all the flame absorption measurements. A single slot air-acetylene 10 cm burner head was used for all air-acetylene experiments.

The AAnalyst 800 features longitudinal Zeeman-effect background correction and a solid-state detector which is highly efficient at low wavelengths. The AAnalyst 800 uses a transversely heated graphite atomizer (THGA) which provides uniform temperature distribution across the entire length of the graphite tube. The THGA features an integrated L'vov platform which is useful in overcoming potential chemical interference effects common in the GFAAS technique.

Figure 1. PerkinElmer AAnalyst 800 Atomic Absorption Spectrophotometer.

A PerkinElmer/Anton-Paar Multiwave™ 3000 Microwave Oven was used for the microwave-assisted digestion of fish and seafood samples. This is an industrial-type oven which can be equipped with various accessories to optimize the sample digestion. In this case, the samples were digested in the Rotor 8XF100 comprising eight 100 mL high pressure vessels made of PTFE-TFM in their respective protective ceramic jackets. TFM is chemically modified PTFE that has enhanced mechanical properties at high temperatures compared to conventional PTFE. This vessel has a "working" pressure of 60 bar (870 psi) and can operate at temperatures up to 260 °C. A Pressure/Temperature (P/T) Sensor Accessory was also used for this work. The P/T sensor simultaneously measures temperature and pressure for one vessel. All vessels' temperatures were monitored with the IR Temperature Sensor Accessory. This device gives thermal (over-temperature) protection to the reactions in all of the vessels by measuring the temperature remotely at the bottom surface of each vessel during the digestion process.

Figure 2. PerkinElmer/Anton-Paar Multiwave 3000 Microwave Digestion System.

A laboratory grade muffle furnace was used for ashing purpose.

PerkinElmer, NIST® traceable calibration standards in acid for atomic spectroscopy was used as the stock standards for preparing working standards. All these working standards were prepared daily with ASTM® type I water acidified in Suprapur® nitric acid, in polypropylene vials (Sarstedt®) on volume-by-volume dilution. Micropipettes with disposable tips (Eppendorf®, Germany) were used for pippetting solutions. Certified Reference Standard for trace metals in fish from High Purity Standards (Lot # 0801404) was used for validating the developed method. Multielement ICP standard for trace metal ions in 5% HNO_3, from Spex Certiprep® (New Jersey, USA), prepared at midpoint of the calibration curve for all elements was used as quality control check standard. The acids used (nitric acid and hydrofluoric acid) were of Suprapur® grade, from Merck® in Germany.

Sample Preparation

Three different dry fish and seafood samples were brought directly from the local fish market and were kept sealed in resealable polypropylene bags. The samples were kept at room temperature and before sampling was dried at 65 ˚C in a laboratory oven until they attained constant weight.

For microwave digestion, about 0.50 g of homogenized and dried samples of fish was accurately weighed directly into the PTFE-TFM digestion vessels. To each sample, 5.0 mL of concentrated nitric acid, 2.0 mL of hydrogen peroxide and 1.0 mL water were added. The analytical reagent blanks were also prepared and these contained only the acids. The vessels were sealed and placed into the Rotor 8 for the microwave digestion. After the digestion process, the digestate liquids were transferred to the 50.0 mL auto-sampler polypropylene vials and laboratory ASTM® Type I water was added to a final total volume of 20.0 mL.

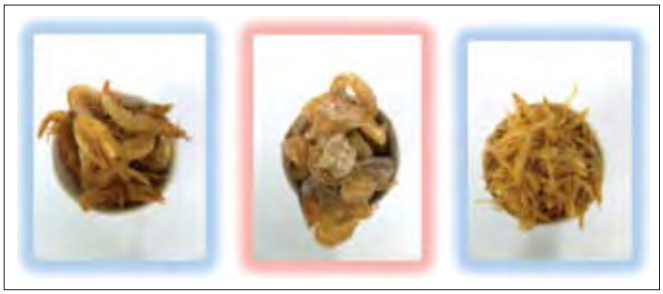

Figure 3. Samples.

For dry ashing, quartz crucibles used were rinsed with 20% nitric acid and then dried. Samples were homogenized using an agate mortar and pestle and then 10.0 g sample was taken in the crucibles. The samples were dried at 100 ˚C in a laboratory oven. These crucibles were then placed in the muffle furnace at ambient temperature. The temperature was then raised at the rate of 50 ˚/hour to 450 ˚C and let the dish stand for 8 hours or overnight. Then it was wet-ashed with 1.0-3.0 mL of water and evaporated on a hot plate. This procedure is repeated until the product is completely ashed. The ash should be white/grey or slightly colored. 5.0 mL of 6.0 M HCl was added to the crucible to completely cover the ash. The ash was evaporated on the hot plate and the residue was redissolved in 10.0-30.0 mL of 0.10 M nitric acid. The crucible was swirled with care so that all ash comes in contact with the acid. The crucible was covered with a watch glass and left standing for 1-2 hours. The solution in the crucible was stirred thoroughly with a stirring rod and then transferred into the plastic bottle. The sample reagent blank was also prepared in the same way.

Results and Discussion

The official AOAC methods were compared for their performance in digesting the fish samples.

Microwave digestion offers complete dissolution of the samples with less possibility of contamination from the environment, in less than 60 minutes including the cooling step. The conventional muffle furnace ashing method normally results in the loss of some more volatile analytes like cadmium and lead, and it is extremely tedious usually lasting more than 24 hours.

The analysis results shows close agreement between the values obtained for sample duplicates with microwave digestion. A four point calibration which includes three standards and one blank were created for both Flame and GFAA measurements. With both Flame and GFAA techniques, excellent correlation coefficients better than 0.999 were obtained. The quality control check standard recoveries (Prepared at midpoint of calibrations) were excellent and were within 95-105%. The recovery of various metal ions from the high purity standard certified reference material for fish were excellent.

The AAnalyst 800 uses a transversely heated stabilized temperature platform system to ensure the minimum influence of matrix interferences possible. The longitudinal Zeeman background correction combined with other STPF conditions further ensured interference-free analysis of lead and cadmium in various fish and seafood samples. The big difference between the concentration values obtained by microwave digestion and muffle furnace ashing shows that analytes are lost during ashing.

Conclusions

The patented THGA tube used in the AAnalyst 800 system provides a uniform temperature distribution along its entire length. This eliminates cooler temperatures at the tube ends and removes most interferences. With the THGA tube design, accuracy and sample throughput are improved by reducing the need for the time-consuming standard additions technique. With the longitudinal Zeeman-effect background correction, the amount of light throughput is doubled by eliminating the need for a polarizer in the optical system. All other commercial Zeeman designs incorporate inefficient polarizers that reduce light throughput and diminish performance. With this unique design, the AAnalyst 800 provides the lowest detection limits available.

In conventional furnace systems, the heating rate during atomization depends on the input-line voltage. As voltage varies from day to day, season to season or among laboratory locations, so does the heating rate. The AAnalyst high-performance systems use enhanced power control circuitry to maintain a uniform heating rate, so no matter where a system is located, one can be sure that it provides outstanding, consistent performance.

The AAnalyst 800 produces highly accurate, fast and reproducible results with difficult matrices such as fish and seafoods. The developed method has been validated by using reference material and the method has been successfully applied for the analysis of different fish and seafood samples.

The capability of PerkinElmer/Anton-Paar Multiwave 3000 microwave digestion system to digest the fish and seafood samples in accordance with AOAC Method 999.10 was demonstrated. The samples prepared with microwave digestion were compared with samples prepared by conventional dry ashing in accordance with AOAC Method 999.11. The capability of AAnalyst 800 to perform the analysis of fish samples for trace metal contamination with both flame and graphite furnace AAs was demonstrated. Microwave digestion proved to be very effective, time saving and an accurate way of preparing samples of fish and seafood for analysis of trace metal ions. As analytes are lost during the conventional ashing process, microwave digestion is the preferred technique for sample preparation for fish and seafood samples.

Table 1. **Instrumental Conditions for the Flame Analysis on the AAnalyst 800.**

Element	Cu	Fe	Zn
Wavelength (nm)	324.8	248.3	213.9
Slit (nm)	0.7	0.2	0.7
Mode	AA	AA	AA-BG
Flame	Air-Acetylene	Nitrous Oxide-Acetylene	Air-Acetylene
Burner	10 cm Universal	10 cm Universal	10 cm Universal
Calibration	Linear Through Zero	Linear Through Zero	Linear Through Zero
Lamp	HCL	HCL	HCL
Lamp Current (mA)	15	30	10
Standards (mg/L)	1.0, 2.5, 5.0	1.0, 2.5, 5.0	0.05, 0.10, 0.25
Spike Conc. (mg/L)	2.5	2.5	0.10
Read Time (sec)	3.0	3.0	3.0
Replicates	3	3	3
Air Flow (L/min)	17.0	7.0 (Nitrous Oxide)	17.0
Acetylene Flow (L/min)	2.0	16.0	2.0

Table 2. **Instrumental Conditions for the Furnace Analysis on the AAnalyst 800.**

Element	Pb	Cd
Wavelength (nm)	283.3	228.8
Slit (nm)	0.7	0.7
Mode	AA-BG	AA-BG
Processing	Peak Area	Peak Area
Read Time (sec)	5.0	5.0
Replicates	3	3
Lamp	EDL	EDL
Lamp Current (mA)	440	230
Injection Temperature °C	90	90
Sample Volume, µL	20	20
Matrix Modifier Volume, µL	5	5
Calibration Equation	Linear with Calculated Intercept	Linear with Calculated Intercept
Standards (µg/L)	10.0, 25.0, 50.0	0.50, 1.0, 2.0
Spiked Concentration (µg/L)	25.0	1.0

Table 3. **Graphite Furnace Temperature Programs.**

Element	Step	Temp °C	Ramp Time (sec)	Hold Time (sec)	Internal Gas Flow (mL/min)	Gas Type
Pb	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	850	10	20	250	Argon
	4	1600	0	5	0	Argon
	5	2450	1	3	250	Argon
Cd	1	110	1	30	250	Argon
	2	130	15	30	250	Argon
	3	500	10	20	250	Argon
	4	1500	0	5	0	Argon
	5	2450	1	3	250	Argon

Table 4. **Analysis of Certified Reference Material for Fish (Lot # 0801404).**

Metal	Certified Value (µg/mL)	% Recovery from Diluted Solution
Cu	50.0 ±0.5%	100
Zn	1000.0 ±0.5%	97
Fe	100.0 ±0.5%	101
Pb	10.0 ±0.5%	103
Cd	5.0 ±0.5%	102

Table 5. **Spike and QC Recovery Studies.**

Metal	QC 1 (%)	QC 2 (%)	Spike Recovery (%)
Cu	106	108	99
Fe	100	100	107
Zn	101	95	102
Pb	100	102	92
Cd	104	107	105

Table 6. **Method Detection Limits (MDLs).**

Metal	MDL (mg/kg)
Cu	0.2
Fe	0.8
Zn	0.1
Pb	1.6 (µg/kg)
Cd	0.1 (µg/kg)

Table 7. **Results of Analysis of Fish Samples (In mg/kg).**

Metal	Fish I (MDS)	Fish I (Muffle) Furnace)	Fish II (MDS)	Fish II (Muffle Furnace)	Fish III (MDS)	Fish III (Muffle Furnace)
Cu	17	6.7	39	12	86	20
Fe	215	33	153	48	360	57
Zn	53	21	61	19	95	31
Pb	0.13	0.04	0.14	0.08	0.14	0.06
Cd	0.11	0.04	0.20	0.07	0.33	0.11

References

1. AOAC Method 999.10.

2. AOAC Method 999.11.

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APPLICATION NOTE

Atomic Absorption

The Determination of Total Mercury in Fish and Agricultural Plant Materials Using Thermal Decomposition and Amalgamation Coupled with Atomic Absorption

Summary

Mercury has long been recognized as a serious global pollutant that has a significant impact upon our ecosystem. Unlike most other pollutants, it is highly mobile, non-biodegradable, and bio-accumulative and as a result has to be closely monitored to ensure its harmful effects on local populations are minimized. Approximately 50 tons of mercury particulates are emitted into the atmosphere every year by a variety of different man-made and natural sources including coal-fired power plants, solid waste incineration plants, volcanoes and forest fires. When the mercury falls back to earth it is deposited on the land and gets into the soil, river sediments and water ecosystems, where it is converted into the highly toxic organo mercury compound, methyl mercury (CH_3Hg^+). This toxicant enters both the plant and aquatic system food chain, and eventually ends up in the crops, vegetables and seafood we consume.

This application note will focus on a rapid test method for determining mercury directly in food materials and agricultural crops using the principles of thermal decomposition, amalgamation and detection by atomic absorption described in EPA Method 7473 and ASTM Method 6722-01. Because there is no sample dissolution required, this novel approach can determine the total mercury content in these types of samples in less than five minutes, which is significantly faster than the traditional wet chemical reduction method for quantifying mercury.

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Introduction

Mercury is distributed throughout the environment in a number of different forms. It exists mainly as elemental mercury vapor in the atmosphere, while most of the mercury found in water, sediments, soil, plants, and animals is in the inorganic and organic forms of the element. Natural sources of mercury come from volcanoes, forest fires and the weathering of mercury-bearing rocks. However, this is small compared to the vast amount of mercury which is generated from anthropogenic sources (human activities), such as fossil fuel combustion, solid waste incineration, mining and smelting, manufacture of cement and the use of mercury cells in the commercial production of chlorine.

Of all the anthropogenic activities, by far the largest polluters are coal-fired power plants, which release approximately 50 tons of elemental mercury into the atmosphere each year via the effluent generated by the combustion process.[1] Once released, the mercury particulates fall back down to the ground and get absorbed by soils, where it eventually gets into commercial farming crops and vegetables. It also enters surface waters, such as lakes, rivers, wetlands, estuaries and the open ocean, where it is converted to organic mercury (mainly methyl mercury – CH_3Hg^+) by the action of anaerobic organisms. The methyl mercury bio-magnifies up the aquatic food chain as it is passed from a lower food chain to a subsequently higher food chain level through feeding and eventually finds its way into the fish we eat.

As a result of this, the EPA considers there is sufficient evidence for methyl mercury to be considered a developmental toxicant that can potentially change the genetic material of an organism and thus increases the frequency of mutations above the natural background level.[2] At particular risk are women of childbearing age because the developing fetus is the most sensitive to the toxic effects of methyl mercury. It has been proved that children who are exposed to methyl mercury before birth may be at increased risk of poor performance on neuro-behavioral tasks, such as those measuring attention, fine motor function, language skills, visual-spatial abilities and verbal memory.

For that reason the EPA initiated the Clean Air Interstate Rule (CAIR)[3] and the Clean Air Mercury Rule (CAMR)[4] in March 2005, which is a two-phase plan to reduce the amount of mercury emission from coal-fired power stations from 48 tons to 15 tons by the year 2018, requiring new and improved mercury-specific control technology for power utilities.

Study

The goal of this study was to evaluate a novel approach for the direct determination of total mercury in a range of food and plant SRMs (standard reference material) using aqueous calibration standards. The samples evaluated are shown in Table 1.

Table 1. **The standard reference materials evaluated in this study.**

Sample Matrix	SRM Name
Tuna	BCR 463
Dogfish Muscle	NRC Dorm 2
Dogfish Liver	NRC Dolt 3
Spinach Leaves	NIST 1570A
Apple Leaves	NIST 1515
Wheat Flour	NIST 8437

Instrumentation

The SMS™ 100 mercury analyzer (PerkinElmer Inc., Shelton, CT) was used for the study. This is a dedicated mercury analyzer for the determination of total mercury in solid and liquid samples using the principles of thermal decomposition, amalgamation and atomic absorption described in EPA Method 7473[5] and ASTM Method 6722-01.[6] The SMS 100 uses a decomposition furnace to release mercury vapor instead of the chemical reduction step used in traditional liquid-based analyzers. Both solid and liquid matrices can be loaded onto the instrument's autosampler and analyzed without acid digestion or sample preparation prior to analysis. Because this approach does not require the conversion of mercury to mercuric ions, lengthy sample pretreatment steps are unnecessary. As a result, there is no need for reagents such as highly corrosive acids, strong oxidizing agents or reducing chemical, which means, no hazardous waste to be disposed of.

Principles of Operation

A small amount of the solid material (0.05-1.00 gms, depending on the mercury content) is weighed into a nickel sample boat. The boat is heated in an oxygen rich furnace, to release all the decomposition products, including mercury. These products are then carried in a stream of oxygen to a catalytic section of the furnace. Any halogens or oxides of nitrogen and sulfur in the sample are trapped on the catalyst. The remaining vapor is then carried to an amalgamation cell that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamation cell is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through an absorbance cell positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at the 253.7 nm wavelength as a function of the mercury concentration in the sample. A detection limit of 0.005 ng (nanogram) of mercury is achievable with a 25 cm path length cell, while a 2 cm cell allows a maximum concentration of 20 µg (microgram) of mercury. A schematic of the SMS 100 is shown in Figure 1.

Operating Conditions

Table 2 shows the instrumental operating conditions for all the SRMs.

Table 2. **The SMS 100 operating conditions for all the SRMs.**

Parameter	Setting
Sample Weight	0.500 gm (weighed accurately)
Sample Boat	Nickel
Drying Temp/Time	300 °C for 45 sec
Decomposition Temp/Time	800 °C for 150 sec
Catalyst Temp	600 °C
Catalyst Delay Time	60 sec
Gold Trap Temp	600 °C for 30 sec
Measurement Time	90 sec
Oxygen Flow Rate	300 mL/min

Calibration

The SMS 100 measurement process involves the thermal generation of mercury vapor from the sample, which means the instrument can either be calibrated with aqueous standards or directly with solid certified reference materials. However, it is not critical that the calibration standards are of a similar matrix to the sample, because under similar operating conditions, different sample matrices generate similar absorbance values. This is shown by the straight line calibration graph in Figure 2 obtained from different concentrations of mercury in widely different samples, such as oyster tissue, dogfish, coal[7] and sediment samples.[8]

For this study, all the food and plant SRMs were calibrated against standards made up in dilute nitric acid. Calibration graphs of 0-50 ng and 50-500 ng of mercury were generated from 0.1 and 1.0 ppm aqueous standards in 10% nitric acid respectively, by injecting different weights into a nickel sampling boat. The 0-50 ng calibration was obtained using the high sensitivity 25 cm optical path length cell, while the optional 2 cm cell was used for the 50-500 ng. The 0-50 ng calibration plot is shown in Figure 3, while the 50-500 ng plot is shown in Figure 4. The low calibration plot was then used to determine mercury in the spinach, apple leaves and wheat flour samples, while the high calibration plot was used for the tuna and dogfish samples,

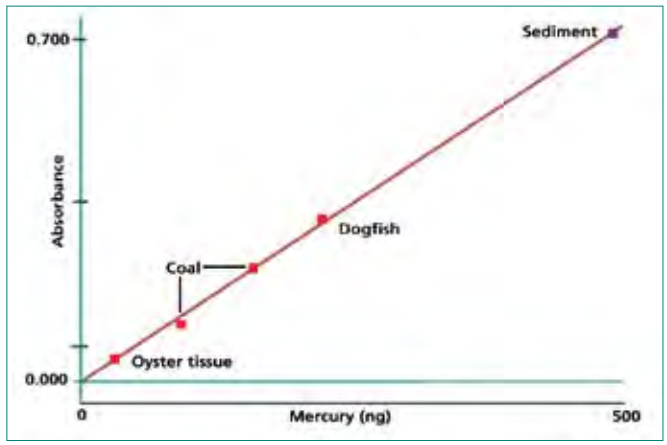

Figure 2. Under similar operating conditions, different sample matrices generate similar absorbance values as shown by the straight line calibration graph obtained from different concentrations of mercury in widely different samples.

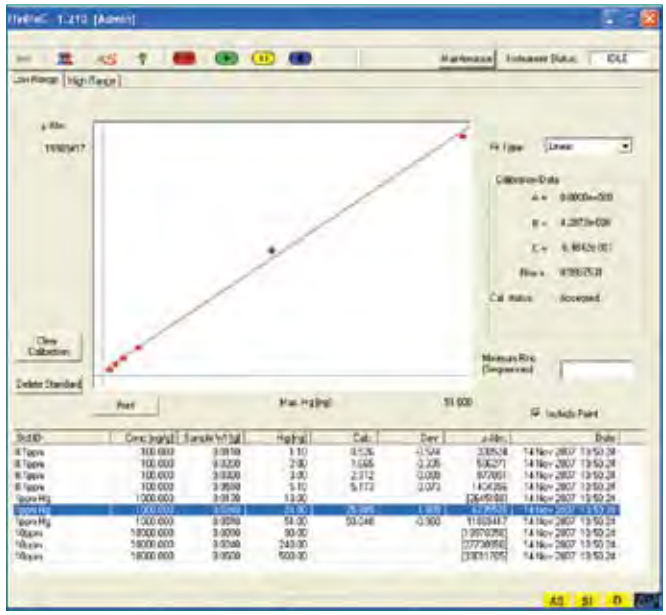

Figure 3. 0-50 ng mercury calibration plot in 10% nitric acid used for the spinach, apple leaves and wheat flour samples.

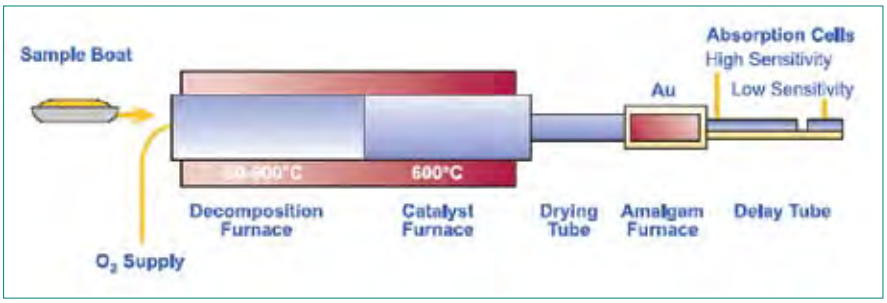

Figure 1. A schematic of the SMS 100 mercury analyzer.

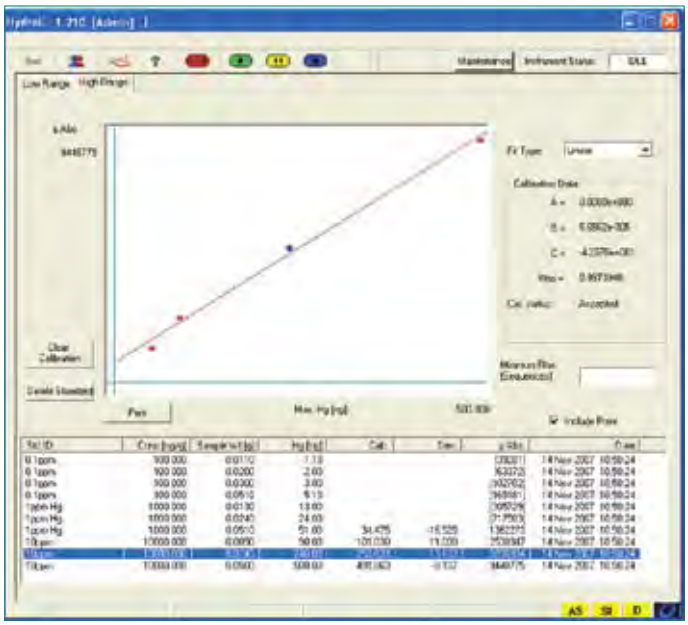

Figure 4. 50-500 ng mercury calibration plot in 10% nitric acid used for the tuna and dogfish samples.

Results

The SMS 100 results for all the SRMs evaluated are shown in Table 3.

***Table 3.* Results of the direct determination of mercury in a range of fish and plant material SRMs using the SMS 100.**

Sample Matrix	CRM Name	Certified Conc. (ppm)	Conc. Found (ppm)	Recovery (%)
Tuna	BCR 463	2.85	3.04	105
Dogfish Muscle	NRC Dorm 2	4.64	4.73	102
Dogfish Liver	NRC Dolt 3	3.37	3.51	104
Spinach Leaves	NIST 1570A	0.030	0.033	109
Apple Leaves	NIST 1515	0.044	0.046	104
Wheat Flour	NIST 8437	0.004	0.0042	105

Conclusion

The study shows that the thermal decomposition, amalgamation and atomic absorption technique gives excellent correlation with standard reference materials for the determination of mercury in a range of fish and plant material SRMs. The fact that a sample can be analyzed in approximately 5 minutes using aqueous calibration standards, means the lengthy sample preparation steps associated with traditional wet chemical-based mercury analyzers can be avoided.

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