CEM CORPORATION

APPLICATION NOTES

Preparation of Mixed Food Samples for Trace Metals Analysis Using the CEM MARS 6 and Discover SP-D Systems

Abstract

Fast, accurate food testing is essential to ensuring the safety and quality of the food supply. As spectroscopic instrumentation has improved and lowered detection limits, CEM has made advances in microwave sample preparation technology to simplify the technique and ensure complete digestions. Several types of spiked food samples and reference standards were prepared for elemental analysis using the MARS 6™ and Discover® SP-D Systems, both manufactured by CEM Corporation. The samples and reference standards were digested in each of the systems, diluted, and analyzed, using inductively coupled plasma optical emission spectrometry (ICP-OES), with good recovery results. Recovery data for the food samples and reference standards prepared in each system is presented for multiple elements of interest including mercury, arsenic, cadmium and lead.

Introduction

With the continued globalization of trade, it has become increasingly important in recent years to ensure the safety of the food supply, as there have been numerous instances of metals contamination. This has led to increased demand for better analytical techniques and lower detection limits for elements of interest. Recent studies have shown that absorption of even low concentrations of some metals can have adverse effects on the human body. In lower concentrations, the symptoms of metals poisoning can include nausea and abdominal pain. In higher concentrations, metals contamination can lead to encephalopathy, cancer, and damage to the skeletal system and internal organs. Thus, the need for more advanced analyses and subsequent quality control of metals levels in food is crucial. With food manufacturers and food contract laboratories analyzing more samples and working to achieve lower detection limits than has been considered adequate in the past, already stretched laboratory resources are being strained.

In response, instrumentation manufacturers, such as ICP-OES and ICP-MS suppliers, have developed more sophisticated, user-friendly platforms that allow for higher throughput and simultaneous analysis of multiple elements in shorter periods of time. However, most food samples require some form of sample preparation prior to final analysis. In classical food analysis, the organic matrix was incinerated (usually in a muffle furnace at a controlled temperature) and the resultant inorganic residue was then digested in a weak acid. Another procedure often used involved heating the organic matrix in concentrated acids on a hot plate. With either procedure, there is a risk of losing volatile elements and both are time consuming. The introduction of microwave sample preparation systems in the mid-1980s significantly decreased digestion times, but traditional microwave systems required analysts to organize similar sample matrices into batches ranging from 2 to as many as 14 samples. This "batching" of samples into groups can inhibit sample throughput considerably.

With the introduction of the MARS 6™ Microwave Sample Preparation System and the Discover® SP-D Microwave Digestion System, CEM has addressed the limitations of traditional batch microwave digestion systems and afforded options to the industry that were previously unavailable. Both systems are engineered to provide a completely digested sample that will not require a filtration step. One system operates in a sequential format, while the other processes large batches of samples simul-

taneously. Both will minimize the labor involved in preparing food samples for acid digestion and vastly increase throughput. This paper will include discussion of sample preparation for microwave digestion and analyte recoveries from several types of spiked food samples and reference standards all of which were prepared for elemental analysis using the MARS 6 and Discover SP-D Systems. The samples and reference standards were digested in each of the systems, diluted, and analyzed, using inductively coupled plasma optical emission spectrometry (ICP-OES), with good recovery results. Recovery data for the food samples and reference standards prepared in each system is presented for multiple elements of interest including mercury, arsenic, cadmium, and lead.

Sample Preparation

Five types of samples were prepared for analysis: NIST SRM 1570a - Trace Elements in Spinach, NIST SRM 1849 - Infant/Adult Nutritional Formula, and three retail products from a local supermarket — ground beef, sliced ham, and sharp cheddar cheese. These samples were divided into two identical sets: one to be digested in the MARS 6 and one to be digested in the Discover SP-D. The NIST SRMs were digested without any preparation. For the retail products digested in the MARS 6, 1 g of each sample was frozen with liquid nitrogen and ground with an analytical mill to ensure a homogeneous sample. A sample size of 0.25 g was used in the Discover SP-D with the samples likewise frozen with liquid nitrogen and ground. The ground samples were stored in a freezer prior to use.

Reagents

- Nitric Acid – trace analysis grade
- Calibration Standards
  - o Mixed Standard in 2% HNO_3
    - 0.0250, 0.0375, 0.0500, 0.0625, 0.0750 ppm of As, Cd, Hg, and Pb
  - o Mixed Standard in 2% HNO_3
    - 0.320, 0.960, 1.64, 2.32, 3.00 ppm B
    - 1.52, 6.12, 10.76, 15.36, 20.00 ppm Mg
    - 12.00, 65.20, 118.4, 171.6, 225.2 ppm P
    - 0.200, 1.16, 2.12, 3.04, 4.00 ppm Zn
    - 0.040, 0.520, 1.04, 1.52, 2.00 ppm Mn
    - 0.080, 1.08, 2.04, 3.04, 4.00 ppm Fe
    - 0.0120, 0.132, 0.256, 0.376, 0.500 ppm Cu
- Spike Solution – 2.50 ppm of As, Cd, Hg, and Pb

Instrumentation

The first set of samples was digested in the CEM MARS 6 with One Touch™ Technology, a series of smart features that helps automate the digestion process. Sensors built into the floor of the cavity identify the number of samples run, as well as the vessel type. Using this information, along with the method chosen by the user, the MARS 6 then calculates the exact power necessary to complete the digest. The PowerMAX™ control system then precisely applies this energy in order to process up to 40 samples reproducibly and safely in under 45 minutes. In addition, the accuracy of the power delivery enables the mixing of the sample types and gives the system the ability to handle increased sample sizes of one gram or more. In order to maximize sample size and throughput, we used the 75-mL MARSXpress vessel in the 40-position turntable.

The MARS 6 delivers up to 1800W of microwave power, allowing for better digestions of larger batches of samples.

MARSXpress vessels feature a simple 3-part design.

The second set of samples was digested in the CEM Discover SP-D, the only sequential microwave digestion system available. By processing each sample individually, the system can run different sample types and acid matrices with individually programmed digestion conditions for each sample. Essentially, each vessel is a control vessel with pressure and temperature monitoring, ensuring the most reproducible digestions possible. The Discover SP-D only requires a standard 110V power source and house compressed air. The air rapidly cools the vessel after the run so that many samples can be digested individually in 10 minutes or less including cool down. The samples were digested in a 35-mL Pyrex® vessel with a snap-on cap using the method outlined below.

Digested and diluted samples were analyzed with an Agilent 720 ICP-OES.

Discover SP-D offers the easiest vessel assembly. Simply snap on the cap and place in autosampler.

The Discover SP-D with autosampler allows for unattended operation, even overnight.

Analytical Procedure

For the retail food products, a mass of 1.0 g of sample, 9 mL of HNO_3, and 1 mL of a 2.50 ppm spike solution was added to the 75-mL MARSXpress vessel. For the 35-mL Discover SP-D vessel, 9 mL of HNO_3 and 1 mL of a 2.50 ppm spike solution was added to 0.25 g of sample. The vessels were capped immediately after the addition of the reagents.

For the NIST SRM samples, a mass of 1.00 g was added to the 75-mL MARSXpress vessel and 0.25 g was added to the 35-mL Discover SP-D vessel with 10 mL of HNO_3 introduced to each of the vessels. The vessels were capped immediately after the addition of the reagents.

Methods were created in the MARS 6 and Discover SP-D. The following digestion conditions were used:

	Sample Type	Ramp Time (minutes)	Hold Time (minutes)	Digestion Temp (°C)
MARS 6 with 75-mL MARSXpress vessel	Organic	25	20	210
Discover SP-D with 35-mL vessel	Organic	5	5	210

Samples were cooled to room temperature and diluted to 50.0 mL with deionized water for ICP-OES analysis, using the analysis conditions below.

RF Power	1200 W
Plasma Flow	15 L/min
Auxiliary Flow	1.5 L/min
Nebulizer Flow	0.90 L/min
Instrument Stabilization Delay	15 seconds
Sample Uptake Delay	30 seconds
Pump Rate	12 RPM
Replicates	3
Replicate Read Time	100 seconds
Rinse Time	30 seconds (2% HNO_3)

Results

The results of the spike recovery study of retail food products are shown in the tables: MARS 6 Spike Recovery Results (in ppm) of 2.50 ppm Hg, As, Cd, and Pb and Discover SP-D Spike Recovery Results (in ppm) of 2.50 ppm Hg, As, Cd, and Pb.

The results shown in Tables 1 and 2 are of both volatile and non-volatile metals in ground beef, cheese, and sliced ham. Mercury and arsenic are commonly analyzed volatile metals. In the MARS 6, the spike recovery for mercury and arsenic was 99 – 108%, and in the Discover SP-D spike recoveries for these volatile elements was 100 – 115%. Cadmium and lead are commonly analyzed non-volatile metals and in the MARS 6 their spike recovery was 89 – 96%. The Discover SP-D spike recoveries for cadmium and lead were 101 – 104%. The Relative Standard Deviation (RSD) was less than 3% for all metals in the MARS 6 and less than 5% in the Discover SP-D. As observed in the recovery data, there was no loss of volatile or non-volatile metals.

Table 1.

MARS 6 Spike Recovery Results (in ppm) of 2.50 ppm Hg, As, Cd, and Pb

	Hg	As	Cd	Pb
Ground Beef 1	2.717	2.445	2.367	2.272
Ground Beef 2	2.701	2.541	2.399	2.302
Ground Beef 3	2.687	2.468	2.382	2.275
Average	2.702	2.485	2.383	2.283
% Recovery	108.07	99.38	95.30	91.32
RSD	0.55	2.02	0.67	0.72
Cheese 1	2.600	2.628	2.319	2.224
Cheese 2	2.624	2.695	2.355	2.342
Cheese 3	2.515	2.631	2.263	2.296
Average	2.580	2.651	2.312	2.287
% Recovery	103.19	106.05	92.49	91.49
RSD	2.22	1.43	2.00	2.60
Sliced Ham 1	2.614	2.457	2.382	2.223
Sliced Ham 2	2.644	2.499	2.386	2.231
Sliced Ham 3	2.649	2.527	2.394	2.283
Average	2.636	2.494	2.387	2.246
% Recovery	105.43	99.77	95.50	89.83
RSD	0.72	1.42	0.26	1.45

Table 2.

Discover SP–D Spike Recovery Results (in ppm) of 2.50 ppm Hg, As, Cd, and Pb

	Hg	As	Cd	Pb
Ground Beef 1	2.867	2.655	2.526	2.603
Ground Beef 2	2.825	2.566	2.545	2.570
Ground Beef 3	2.890	2.688	2.548	2.550
Average	2.861	2.636	2.540	2.574
% Recovery	114.43	105.45	101.59	102.97
RSD	1.15	2.39	0.47	1.04
Cheese 1	2.828	2.541	2.577	2.608
Cheese 2	2.790	2.418	2.531	2.501
Cheese 3	2.929	2.564	2.632	2.615
Average	2.88	2.5076	2.580	2.5745
% Recovery	113.96	100.31	103.20	102.99
RSD	2.52	3.13	1.96	2.48
Sliced Ham 1	2.704	2.662	2.549	2.486
Sliced Ham 2	2.908	2.504	2.5890	2.601
Sliced Ham 3	2.824	2.707	2.516	2.486
Average	2.812	2.624	2.551	2.524
% Recovery	112.48	104.97	102.05	100.97
RSD	3.65	4.06	1.43	2.63

As demonstrated in the results of the digestion of the NIST Standard Reference Materials (shown in Tables 3 and 4), MARS 6 and the Discover SP-D are well suited for the digestion of samples containing several metals over a large concentration range. The MARS 6 showed a recovery range of 90 - 106% with an RSD of 3%. The Discover SP-D showed a recovery range of 85 - 101% with an RSD of 4%.

Table 3.

MARS 6 NIST Standard Reference Material Recovery Results (in ppm)

SRM 1570a – Trace Elements in Spinach Leaves

	B	Ca	Cu	Fe	Mg	Mn	P	Zn
Sample 1	34.4	14060	12.1			71.1	5503	
Sample 2	34.4	13988	12.2			71.5	5539	
Sample 3	33.8	13786	11.8			69.7	5394	
Average	34.2	13945	12.1			70.8	5479	
Certified Value	37.6	15270	12.2			75.9	5180	
% Recovery	90.94	91.32	98.78			93.23	105.77	
RSD	1.07	1.02	1.48			1.38	1.37	

SRM 1849 – Infant/Adult Nutritional Formula

	B	Ca	Cu	Fe	Mg	Mn	P	Zn
Sample 1		4587	19.5	175.3	1473	49.1	3888	150.8
Sample 2		4422	18.9	169.0	1428	47.4	3762	145.4
Sample 3		4527	19.7	175.4	1482	49.2	3902	150.0
Average		4512	19.4	173.2	1461	48.6	3851	148.7
Certified Value		4900	20.3	177.1	1578	51	3782	152.3
% Recovery		92.08	95.43	97.82	92.59	95.22	101.82	97.65
RSD		1.85	2.04	2.15	1.97	2.02	2.00	1.96

Table 4.

Discover SP–D NIST Standard Reference Material Recovery Results (in ppm)

SRM 1570a – Trace Elements in Spinach Leaves

	B	Ca	Cu	Fe	Mg	Mn	P	Zn
Sample 1	33.9	12866	10.7			66.9	5024	
Sample 2	36.1	13343	11.3			69.8	5252	
Sample 3	36.5	12952	10.8			67.2	5105	
Average	35.5	13054	10.9			67.9	5127	
Certified Value	37.6	15270	12.2			75.9	5180	
% Recovery	94.41	85.48	89.75			89.52	98.97	
RSD	3.92	1.95	3.06			2.40	2.26	

SRM 1849 – Infant/Adult Nutritional Formula

	B	Ca	Cu	Fe	Mg	Mn	P	Zn
Sample 1		4666	18.4	167.8	1550	46.9	3813	145.0
Sample 2		4594	17.8	165.8	1526	46.1	3757	143.1
Sample 3		4695	18.1	167.4	1545	46.9	3816	144.8
Average		4652	18.1	167.0	1540	46.6	3795	144.3
Certified Value		4900	20.3	177.1	1578	51	3782	152.3
% Recovery		94.93	89.04	94.30	97.62	91.44	100.35	94.75
RSD		1.13	1.66	0.64	0.82	0.97	0.87	0.73

Conclusion

Testing for heavy metals contamination will continue to be crucial to maintaining the safety of the food supply and with laboratory resources already being stretched, a simple, fast, and accurate analysis is essential. Improvements in spectrometry equipment have necessitated similar technological advances in sample preparation. Both the MARS 6 and the Discover SP-D are well suited for the preparation of a wide variety of food matrices and offer a true choice in instrumentation based upon the flow of samples into the laboratory. Each system provides significant time savings and operates, to a large degree, unattended, freeing analysts to attend to other tasks. In addition, both systems reduce acid usage significantly as compared to hot plate methods. With samples digested in sealed containers, cross contamination is prevented and the recovery of even volatile elements is possible. As demonstrated by the data above, analyte recovery is accurate and reproducible.

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