Espectroscopia de emisión atómica de plasma de microondas (MP-AES)

Manual de análisis de metales en vino y alimentos

Índice

MP-AES: principio de funcionamiento

Principio de funcionamiento de la espectroscopia de emisión atómica de plasma de microondas

La espectroscopia atómica engloba diversas técnicas analíticas utilizadas para determinar la composición elemental de una muestra examinando su espectro electromagnético o su espectro de masas. Entre las técnicas que permiten identificar un analito elemental a partir de su espectro electromagnético se incluyen la espectroscopia de absorción atómica de llama (FAAS), la espectroscopia de emisión óptica por plasma acoplado inductivamente (ICP-OES) y la espectroscopia de emisión atómica de plasma de microondas (MP-AES). Asimismo, entre aquellas que posibilitan identificar los elementos por su espectro de masas se incluyen la espectrometría de masas por plasma acoplado inductivamente (ICP-MS) y la espectrometría de masas por plasma acoplado inductivamente de triple cuadrupolo (ICP-QQQ).

Excitación atómica

La espectroscopia de emisión atómica de plasma de microondas es una técnica de emisión atómica. Se sirve del fenómeno siguiente: una vez que se excita un átomo de un elemento específico, este emite luz con un patrón característico de longitudes de onda (un espectro de emisión) a medida que vuelve al estado base. Entre las fuentes de emisión atómica se incluyen las de plasma de microondas (MP) y plasma de argón acoplado inductivamente (ICP); ambas son fuentes de alta temperatura y, por lo tanto, excelentes fuentes de excitación para la espectroscopia de emisión atómica. El plasma de microondas con alimentación de nitrógeno alcanza temperaturas próximas a 5.000 K. A estas temperaturas, la emisión atómica es intensa y consigue unos límites de detección y un rango dinámico lineal excelentes para la mayoría de los elementos.

En el interior de un instrumento de MP-AES, la energía de microondas generada por un magnetrón industrial robusto y fiable se emplea para obtener plasma a partir de nitrógeno, que puede extraerse de aire comprimido mediante el generador de nitrógeno de Agilent (Figura 1). En efecto: el sistema de MP-AES funciona con aire.

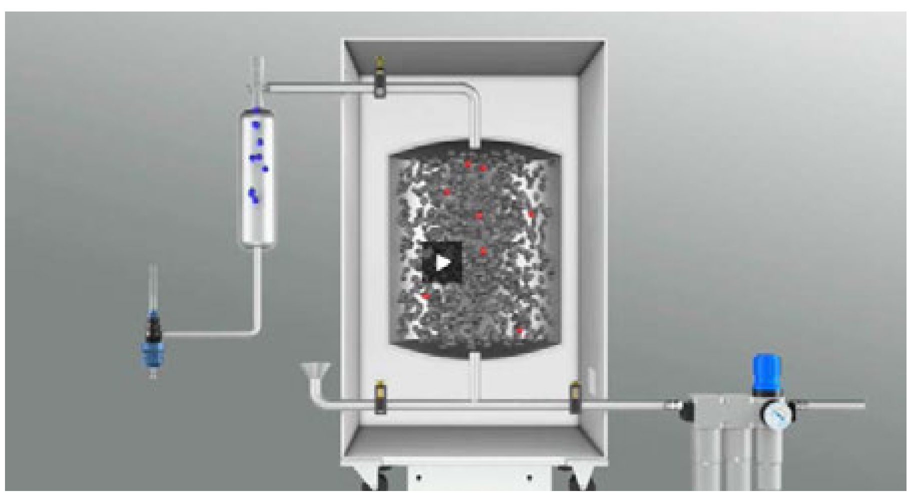


Figura 1. El generador de nitrógeno extrae nitrógeno a partir de aire comprimido para alimentar el plasma.

El uso de un campo magnético, en lugar de un campo eléctrico, para la excitación genera un plasma robusto que permite procesar una amplia variedad de tipos de muestras.

Una guía de microondas optimizada crea campos electromagnéticos concentrados en la antorcha (Figura 2). Un campo magnético axial y un campo eléctrico radial concentran y contienen la energía de microondas necesaria para crear el plasma.

Figura 2. La guía de microondas genera campos electromagnéticos concentrados alrededor de la antorcha.

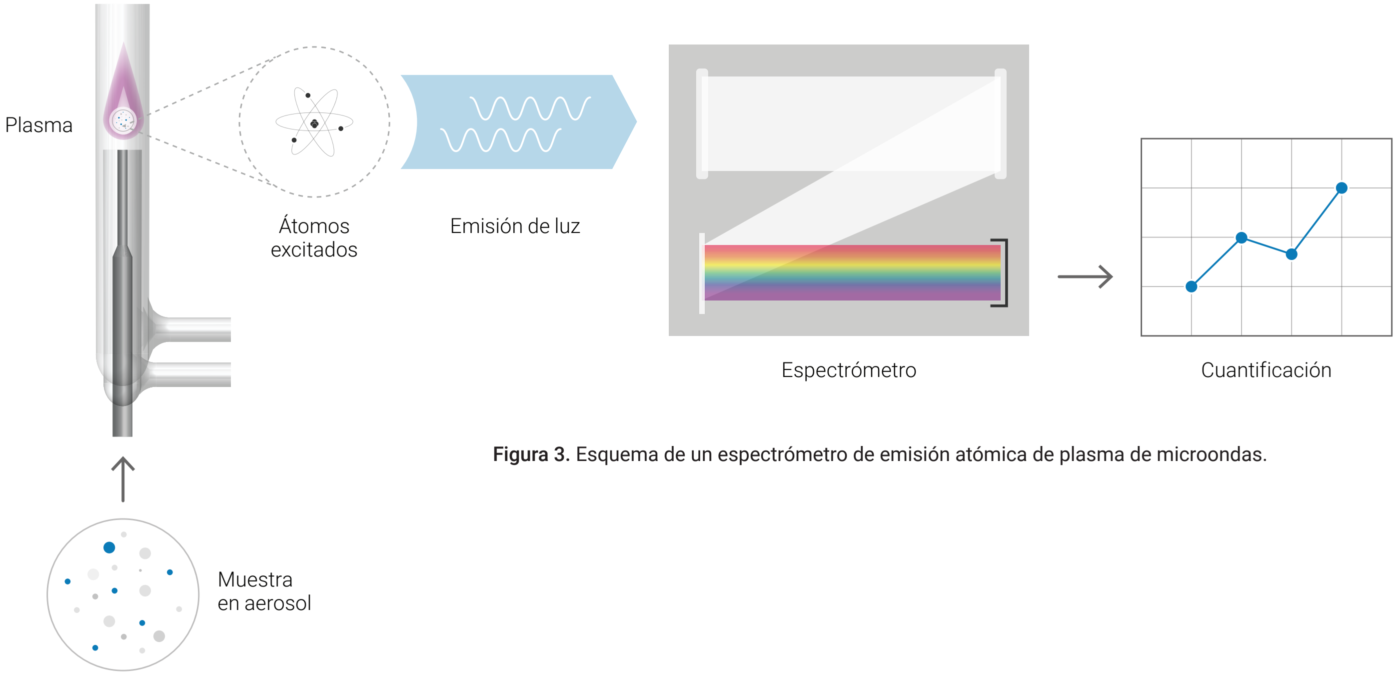


Figura 3. Esquema de un espectrómetro de emisión atómica de plasma de microondas.

Introducción de muestras

Al igual que en los instrumentos de AA de llama, se forma un aerosol a partir de una muestra líquida; para ello, se utilizan un nebulizador y una cámara de nebulización. Después, el aerosol se introduce en el centro del plasma caliente.

El aerosol se seca, se descompone y, por último, se atomiza. Los átomos mantienen la excitación y emiten luz con longitudes de onda características de cada elemento a medida que regresan a estados de menor energía (Figura 3).

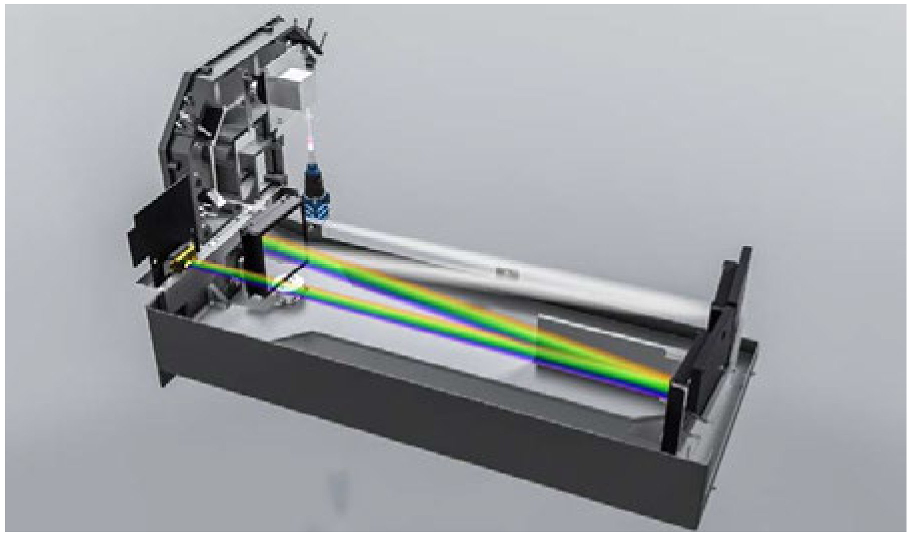


Figura 4. La emisión del plasma se dirige hacia el sistema óptico.

Sistema óptico

La emisión del plasma se dirige hacia un monocromador de mayor velocidad de barrido (Figura 4). El rango de longitud de onda seleccionado se aplica al detector de dispositivo de carga acoplada (CCD) de alta eficiencia. Esto permite medir los espectros y el ruido de fondo simultáneamente para conseguir una precisión óptima.

Cuantificación

Al igual que la AAS de llama, la MP-AES cuantifica la concentración de un elemento en una muestra comparando la emisión con los valores asociados a concentraciones conocidas del elemento, representadas en una curva de calibración. El resultado final es la concentración del elemento en la muestra.

Ventajas de la MP-AES

Bajo coste de propiedad

El suministro de gas es uno de los costes más elevados asociados al análisis elemental. Dado que el sistema de MP-AES funciona con aire, reduce considerablemente el coste de propiedad y elimina la necesidad de disponer de un suministro continuo de gases inflamables o caros. No es necesario comprar cilindros de gas o lámparas ni existen costes operativos asociados al modo de espera. Cuando un sistema de MP-AES está apagado, no consume gas ni electricidad.

Seguridad

Dado que no hacen falta gases inflamables, tampoco existirán fugas de gas ni será necesario pedir y transportar cilindros. La eliminación de todos estos riesgos convertirá su laboratorio en un lugar de trabajo más seguro.

Mayor rendimiento que la AA

Cualquier sistema de MP-AES ofrece una alta sensibilidad, unos límites de detección inferiores a las partes por billón (ppb) y mayor rapidez y un rango dinámico lineal más amplio que la absorción atómica (AA) de llama convencional para un análisis multielemental típico.

Procesamiento de matrices complejas

La robusta fuente de plasma por microondas excitada magnéticamente de un sistema de MP-AES permite procesar fácilmente matrices complejas, como combustibles y disolventes orgánicos, muestras geoquímicas, fertilizantes y alimentos. La antorcha está colocada en posición vertical para lograr el máximo rendimiento con muestras complejas e incluye un sistema de visión axial para optimizar los límites de detección.

Funcionamiento remoto

Dado que el sistema de MP-AES solamente requiere electricidad, se puede colocar cerca de un punto de muestreo, en lugar de en un laboratorio. Esto permite acortar mucho los plazos de medición, ofreciendo datos precisos que pueden aportar grandes beneficios, como prevenir vertidos al medio ambiente o la fabricación de productos con parámetros erróneos.

Rapidez y facilidad de uso

Los instrumentos de MP-AES de Agilent incluyen applets de software fáciles de usar que permiten cargar automáticamente un método predefinido para iniciar el análisis de inmediato, sin ningún desarrollo de métodos ni alineamiento y con unas necesidades de formación mínimas.

El cargador de la antorcha del instrumento permite su alineamiento automático y realiza la conexión de los tubos de gases, lo que agiliza la puesta en marcha y facilita un funcionamiento reproducible.

Motivos para cambiar de la FAAS a la MP-AES

La reducción de los costes operativos fijos, la mejora de la seguridad y el rendimiento analítico y la simplificación del funcionamiento son algunos de los principales desafíos a los que se enfrentan actualmente los usuarios de sistemas de espectroscopia de absorción atómica de llama (FAAS).

El lanzamiento del espectrómetro de emisión atómica de plasma de microondas (MP-AES) de Agilent ha permitido superar estos desafíos, lo que lo convierte en el instrumento idóneo para aquellos laboratorios que buscan cambiar de la FAAS a otra técnica más potente, económica y segura. Asimismo, el mayor rendimiento del sistema de MP-AES también posibilita simplificar sensiblemente el proceso de preparación de muestras, ahorrando con ello tiempo y dinero.

El sistema de MP-AES Agilent 4210 incorpora un diseño de guía de microondas y una antorcha que permiten analizar muestras con hasta un 3 % de sólidos disueltos totales, sin que eso afecte a los límites de detección.

Menores costes operativos

Los gases son el principal factor contribuyente a los costes operativos fijos. En la FAAS se utiliza una combinación de aire y acetileno, o bien de óxido nitroso y acetileno, para la llama. Mientras que el aire se puede suministrar mediante un compresor, el acetileno y el óxido nitroso deben adquirirse en cilindros, que deben reponerse con frecuencia a medida que se van agotando.

El sistema de MP-AES 4210 utiliza nitrógeno extraído directamente del aire para alimentar el plasma. El generador de nitrógeno Agilent 4107, combinado con un compresor de aire, suministra todo el nitrógeno libre necesario con una pureza superior al 99,5 %. Esto consigue una enorme reducción de los costes operativos a lo largo de la vida útil del instrumento.

El ahorro potencial asociado al uso del sistema de MP-AES 4210 para la determinación de calcio, magnesio, sodio y potasio en zumo de frutas se indica mediante la comparación de la compra de un sistema de FAAS con compresor de aire y consumibles para un año con la de un sistema de MP-AES con compresor de aire, generador de nitrógeno, muestreador automático SPS 4 y consumibles para un año (Figura 1).

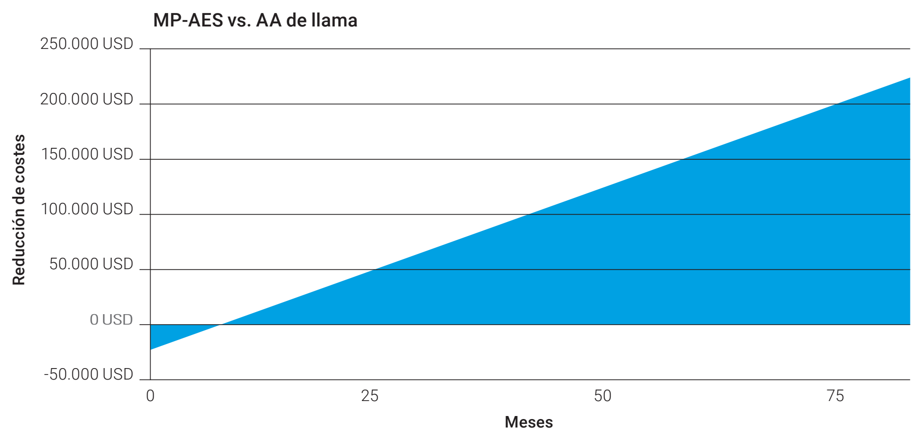


Figura 1. Calculadora de costes on-line que muestra el ahorro asociado al uso del sistema de MP-AES para la determinación de calcio, magnesio, sodio y potasio en zumo de frutas.

Los requisitos de análisis asumidos fueron de 500 muestras por semana y cuatro elementos por muestra.

Para el cálculo, se supuso que el sistema de FAAS funcionaba sin muestreador automático y que se determinaron tres elementos con aire y acetileno y un elemento con óxido nitroso y acetileno. En este ejemplo, el resultado muestra un ahorro estimado superior a 220.000 USD a lo largo de un período de evaluación de 7 años[1]. Para el cálculo se empleó un coste medio internacional del gas; los resultados pueden variar en función del país.

Mejora de la seguridad

Otro problema importante para los usuarios de sistemas de FAAS son los aspectos de seguridad relacionados con el uso de acetileno y óxido nitroso: desde el almacenamiento y la manipulación de cilindros hasta el uso de una llama en el instrumento. La presencia de una llama desnuda resulta problemática en todos los laboratorios y, en particular, en aquellos en los que se manipulan disolventes orgánicos; por este motivo, no es posible realizar análisis por FAAS sin supervisión.

A la hora de llevar a cabo análisis por FAAS, también es habitual cambiar los quemadores para mejorar el rendimiento al determinar el conjunto completo de elementos. A pesar de que los instrumentos de FAAS de Agilent disponen de enclavamiento completo para garantizar que se utilicen los quemadores adecuados para el método en cuestión, se debe actuar con precaución al manipular los quemadores, ya que pueden estar calientes después de usarlos.

El sistema de MP-AES 4210 elimina estos problemas. Evita tener que usar acetileno y óxido nitroso, así como los problemas asociados al almacenamiento y la manipulación; además, no es necesario cambiar el quemador gracias al mayor rendimiento del plasma de nitrógeno, que alcanza mayores temperaturas.

Mejora del rendimiento analítico

El plasma del sistema de MP-AES 4210 funciona a unos 5.000 K, lo que mejora los límites de detección en comparación con los sistemas de FAAS. La mejora de los límites de detección posibilita analizar elementos como el fósforo, cuyos límites de detección son muy altos en el caso de la FAAS.

La Tabla 1 muestra los límites de detección del instrumento (IDL) correspondientes a los sistemas de MP-AES y FAAS para elementos de una muestra de harina de arroz. Los límites de detección de fósforo, cobre y hierro son más bajos, lo que permite determinar los elementos mayoritarios, minoritarios y en cuanto a trazas con una única medición.

Tabla 1. Comparación de los límites típicos de detección del instrumento para el sistema de MP-AES 4210 y el sistema de FAAS.

Elemento	IDL típico del sistema 4210 (10 s de lectura) µg/l	IDL típico del sistema de FAAS µg/l
Ca	0,04	0,4
Mg	0,1	0,27
Na	0,1	0,26
K	0,6	0,76
P	66	26.000
Fe	1,7	7,3
Pb	2,5	14
Cu	0,5	1,2
Mn	0,2	1,0

1 Este ejemplo sirve para ayudarle a comparar los costes operativos y el ahorro que ofrece la MP-AES frente a la AA de llama. Las fórmulas y los parámetros aplicados son correctos hasta donde alcanza nuestro conocimiento; sin embargo, no ofrecemos garantías en relación con los resultados. El ahorro puede variar en función de factores como el coste local del gas y la electricidad, los costes de mano de obra y el número y el tipo de elementos. Para este cálculo, se consideró un coste de mano de obra de 25 USD/hora y un coste de la electricidad de 0,18 USD/kW.

El diseño de la guía de microondas y la antorcha del sistema de MP-AES 4210, combinado con el control del flujo másico y la humidificación de la línea de gas del nebulizador, consigue una excelente estabilidad a largo plazo en muestras con una matriz compleja, algo habitual en la minería y el sector medioambiental. La introducción de soluciones salinas de elevada concentración en un quemador de FAAS de aire y acetileno durante un período largo, como una jornada de trabajo de 8 horas, exigirá realizar mantenimiento para evitar obstrucciones. Si no se lleva a cabo esta tarea de mantenimiento rutinaria, podría producirse deriva de la señal.

La estabilidad a largo plazo del sistema de MP-AES 4210 se comprobó con una solución de harina de arroz digerida con un 2 % de TDS. Los resultados se muestran en la Figura 2.

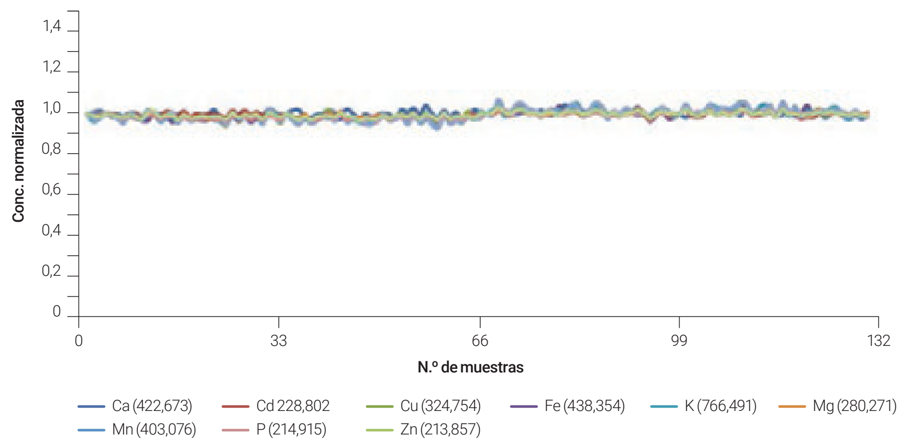


Figura 2. Análisis de harina de arroz digerida con un 2 % de TDS durante 8 horas. Se realizó una recalibración cada 2 horas y la estabilidad resultante fue <3 % de la RSD para todos los elementos. Se utilizó de forma predeterminada un sistema polivalente de introducción de muestras.

El sistema de MP-AES 4210 también ofrece un rango dinámico lineal más amplio que el del sistema de FAAS. En la Tabla 2 se presentan el rango de calibración lineal y el coeficiente de correlación del sistema de MP-AES 4210 para los elementos mayoritarios de una muestra de zumo de frutas. Asimismo, se muestra el rango óptimo de trabajo del sistema de FAAS para esos mismos elementos. Para las calibraciones del sistema de FAAS se empleó el modelo New Rational predeterminado. La mayor amplitud del rango lineal del sistema de MP-AES frente al sistema de FAAS reduce la necesidad de realizar diluciones de muestras que estén fuera del rango, lo que simplifica el análisis. La reducción de las diluciones también hace que, si existen contaminantes a nivel de trazas que haya que determinar, siga siendo posible detectarlos. Además, la mejora de la linealidad consigue que se necesiten menos patrones de calibración para obtener una curva de calibración exacta.

Simplificación de la preparación de muestras

Un factor que influye enormemente en los procedimientos de preparación de muestras de la FAAS es la presencia de interferencias. La presencia de compuestos que la llama de baja temperatura no pueda descomponer provoca interferencias químicas y hace que elementos como el sodio y el potasio sufran interferencias de ionización.

Tabla 2. Rango de concentración lineal del sistema de MP-AES 4210 y rango óptimo de concentración del sistema de FAAS para muestras de zumo de frutas.

Elemento	Rango de concentración lineal del sistema de MP-AES 4210 (mg/l)	Coeficiente de correlación lineal de la calibración del sistema de MP-AES	Rango óptimo de trabajo del sistema de FAAS (mg/l)
Ca (422,673)	0-20	0,9999	0,01-10
Mg (518,360)	0-100	0,99988	0,15-20 (para Mg [202,6])
Na (589,592)	0-20	0,99996	0,01-2,0
K (769,897)	0-100	0,99968	1-6,0

Tabla 3. Requisitos habituales de preparación de muestras para las técnicas de FAAS y MP-AES.

Elemento	Posibles interferencias químicas	Preparación de muestras específica para la técnica de FAAS	Preparación de muestras específica para la técnica de MP-AES
Ca	Compuestos refractarios Efectos de ionización	Agente de liberación de lantano Tampón de ionización de cesio	Ninguna
Mg	Efectos de ionización	Tampón de ionización de cesio	Ninguna
Na	Compuestos refractarios Efectos de ionización	Agente de liberación de lantano Tampón de ionización de cesio	Ninguna
K	Efectos de ionización	Tampón de ionización de cesio	Ninguna

Tabla 4. Recuperaciones de los elementos mayoritarios de materiales de referencia certificados (CRM) en zumo de pomelo, analizados mediante MP-AES. No fue necesario usar supresores de ionización y se obtuvo una exactitud excelente para el potasio. Asimismo, no se añadió nitrato de lantano y se consiguieron valores de recuperación excelentes para el calcio.

Zumo de pomelo T0842QC	Valor certificado (mg/l)		Valor detectado (mg/l)	Recuperación (%)
	Valor asignado	Rango		
Calcio	145,6	123,6-167,6	158,3 ± 3,2	108,7
Magnesio	92,5	77,5-107,4	91,1 ± 0,6	98,5
Potasio	1102	979-1.225	1.100 ± 14,7	99,8

Existen distintas estrategias consolidadas para abordar estas interferencias. Es habitual añadir agentes de liberación, como estroncio o lantano, para resolver las interferencias químicas; también se puede recurrir a usar una llama de óxido nitroso, que alcanza mayores temperaturas. Los efectos de ionización se suelen resolver añadiendo un tampón de ionización a la solución, como sodio, potasio o cesio. Otra estrategia es extraer los elementos de interés en una fase orgánica para eliminar los elementos interferentes. Eso obliga a realizar una preparación individual de la muestra para cada uno de los elementos contenidos en ella.

La temperatura más elevada de la fuente de plasma del sistema de MP-AES 4210 elimina estas interferencias químicas. Esto evita tener que llevar a cabo la preparación de muestras específica para cada elemento propia de la FAAS, lo que simplifica enormemente el proceso de preparación de muestras. A modo de ejemplo, los elementos estudiados en un análisis de zumo de frutas se muestran más arriba junto con una comparación de la preparación de muestras necesaria para cada elemento (Tablas 3 y 4).

Conclusión

El sistema de MP-AES Agilent 4210 es el instrumento idóneo para aquellos clientes que buscan pasar de la espectroscopia de absorción atómica de llama (FAAS) a otra técnica. El uso de nitrógeno como fuente de gas para el plasma reduce enormemente los costes operativos; asimismo, no requiere usar sustancias peligrosas, como óxido nitroso y acetileno, lo que mejora sensiblemente la seguridad. Además, la fuente de atomización/ionización de plasma de nitrógeno de alta temperatura mejora los límites de detección, el rango lineal y la estabilidad a largo plazo, y simplifica en gran medida el proceso de preparación de muestras.

Accesorios de MP-AES

Ampliación de las capacidades mediante el uso de accesorios

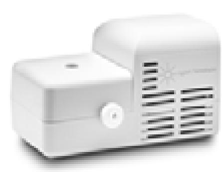
Agilent ofrece una gama de accesorios para instrumentos de MP-AES. Aportan capacidades adicionales al instrumento para permitirle optimizar la configuración para aplicaciones específicas.

Sistema avanzado de válvula (AVS 4)
Esta válvula de conmutación de cuatro puertos permite obtener una alta productividad de análisis de muestras y alarga la vida útil de los componentes gracias a la menor exposición de los componentes de introducción de muestras a muestras agresivas.

Sistema de introducción de muestras multimodo (MSIS)
Este innovador accesorio para instrumentos de ICP-OES y MP-AES permite la introducción de muestras mediante los modos de generación de vapor o de nebulización, o bien mediante ambos modos al mismo tiempo. Posibilita la detección de concentraciones de arsénico, selenio y mercurio inferiores a las ppb.

Muestreador automático SPS 4
El SPS 4 es nuestro muestreador automático más rápido y permite realizar un análisis multielemental de hasta 360 muestras sin supervisión.

Generador de nitrógeno 4107
El generador de nitrógeno extrae nitrógeno a partir de aire comprimido para alimentar el plasma del instrumento de MP-AES. Proporciona un suministro continuo de nitrógeno.



IsoMist
Una cámara de nebulización con control de temperatura que ofrece mayor estabilidad para disolventes orgánicos volátiles.

Módulo de control de gas externo (EGCM)
El módulo EGCM inyecta aire en el plasma para minimizar la acumulación de residuos de carbono, reduce el ruido de fondo en las aplicaciones con compuestos orgánicos y permite realizar determinaciones de azufre.

Vino

El sistema de MP-AES permite realizar un análisis sencillo, rápido y automatizado de elementos presentes en el vino (sin necesidad de preparación de muestras).

La Organización Internacional de la Viña y el Vino (OIV) ha aprobado el uso de la MP-AES para el análisis de hierro, cobre, potasio, calcio y manganeso en muestras de vino. Estos elementos se monitorizan de forma frecuente para controlar el crecimiento de las vides, la calidad de la uva y la pérdida de aroma, así como para determinar el riesgo de oxidación. La MP-AES ofrece las siguientes ventajas:

- No requiere preparación de muestras, ya que la muestra se diluye on-line, lo que hace que el análisis resulte sencillo y directo.
- La MP-AES se puede utilizar para medir: cobre (0,05-1 mg/l), hierro (1-10 mg/l), potasio (15-1.200 mg/l), calcio (1-100 mg/l) y manganeso (0,25-4 mg/l).
- Capacidad de medición de 100 o más muestras al día con facilidad.
- No es necesario comprar gases, ya que solo se necesita nitrógeno para el análisis. Esto hace que resulte una técnica segura para su uso en laboratorios enológicos.

El sistema de MP-AES también se puede utilizar para analizar muestras de plantas y suelos, ya que posibilita determinar:

- El balance nutricional de las vides durante la temporada de crecimiento.
- Las necesidades de nutrientes de las vides para la siguiente campaña, con el fin de planificar aplicaciones foliares.
- El potencial agroenológico de los suelos en los que se esté considerando establecer plantaciones.

Routine analysis of total arsenic in California wines using the Agilent 4200/4210 MP-AES

Application note

Food Safety

Authors

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Verified for Agilent
4210 MP-AES

Introduction

Arsenic (As) is a naturally occurring element found throughout the world. The environmental levels of As have been increasing due to natural sources, such as volcanic activity, and anthropogenic sources, such as smelting. The continuous release of As into the ecosystem has formed an accumulation of the element in the food chain.

Wine is a globally consumed beverage where total levels of As are regulated between 100-200 µg L^{-1}, depending on the country in question [1]. However, there are countries, such as the United States, that do not regulate levels of all elements in wine. This necessitates investigating total As levels in wine produced in the United States to identify potential contamination, beyond the levels regulated by other countries.

Measuring total arsenic levels in wine with various spectrometric techniques typically deliver insufficient sensitivity due to the element's relatively high ionization potential. However, the use of vapor generation techniques to form volatile forms of As allow for a more sensitive detection of As.

This study investigates the use of the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) coupled with the Multimode Sample Introduction System (MSIS) accessory to measure total As in wine samples from the California region. This application is also applicable for Agilent's 4210 MP-AES instrument.

The MP-AES offers high sensitivity, with superior performance in comparison to Flame Atomic Absorption Spectroscopy. The instrument uses nitrogen to sustain the plasma, either extracted from the ambient air (using a nitrogen generator) or supplied via a nitrogen Dewar. Compared with acetylene-based instruments, the MP-AES is much safer to run, as no flammable gases are required. Operating costs are also significantly less. The addition of the MSIS accessory assists with the production of hydride species which are separated from the liquid and introduced to the plasma, delivering better performance and lower detection limits, than with conventional nebulization.

Experimental

Instrumentation

All measurements were performed using the Agilent 4200 MP-AES fitted with the MSIS accessory, MicroMist glass nebulizer and Easy-fit torch.

The As 188.979 nm line was selected for analysis and the read time optimized in the easy to use MP Expert software that controls the instrument. The instrument operating and method settings are given in Table 1.

The Agilent MP Expert software allows for correction of background and spectral interferences. The Fast Linear Interference Correction (FLIC) background correction (refer to Figure 1) was used to correct for the complex structured background by modeling with the solution blank of 10% HCl and 5% ethanol as the interferent.

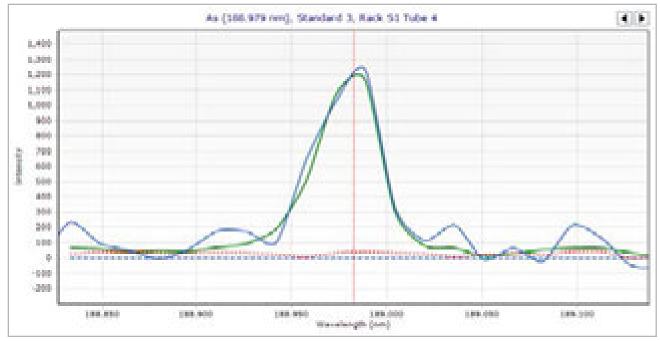

Figure 1. FLIC background correction applied to As (188.979 nm) calibration standard. Background and analyte peak (blue line), FLIC model applied to background and analyte peak (green line).

Table 1. Agilent 4200 MP-AES operating and method conditions.

Parameter	Setting
As wavelength (nm)	188.979
Pump speed (rpm)	20
Sample pump tubing	Black-black
Hydride reagent tubing	Black-black
MSIS waste tubing	Black-white
Read time (sec)	20
Number of Replicates	3
Sample uptake delay (s)	40
Nebulizer flow (L/min)	0.45
Fast pump during uptake	On
Stabilization time (s)	20
Background correction	FLIC
Calibration Fit	Linear
Nitrogen gas source	Agilent 4107 Nitrogen Generator

Samples

Forty commercially available wines, originating from various areas in California, were analysed in this study (Table 2). The wine varieties included: Pinot noir, Merlot, Cabernet Sauvignon, Rosé, Chardonnay, white Zinfandel, Sauvignon blanc, a white blend, sparkling wine and port-style wine.

Table 2. Wine samples used in the study, with corresponding sample number and regional origin.

Sample#	Wine type	Region
1	Cabernet Sauvignon	South Coast
2	Cabernet Sauvignon	Sonoma County
3	Cabernet Sauvignon	Lodi/Woodbridge Grape Commission
4	Cabernet Sauvignon	South Coast
5	Cabernet Sauvignon	Sierra Foothills
6	Cabernet Sauvignon	Napa County
7	Cabernet Sauvignon	Sierra Foothills
8	Cabernet Sauvignon	Napa County
9	Cabernet Sauvignon	Greater Bay Area
10	Cabernet Sauvignon	North Coast
11	Cabernet Sauvignon	North Coast
12	Cabernet Sauvignon	South Central Coast
13	Cabernet Sauvignon	Greater Bay Area
14	Cabernet Sauvignon	Sonoma County
15	Cabernet Sauvignon	Lodi/Woodbridge Grape Commission
16	Cabernet Sauvignon	North Central Coast
17	Cabernet Sauvignon	South Central Coast
18	Cabernet Sauvignon	South Coast
19	Cabernet Sauvignon	South Central Coast
20	Cabernet Sauvignon	Sonoma County
21	Cabernet Sauvignon	Sierra Foothills
22	Cabernet Sauvignon	South Central Coast
23	Cabernet Sauvignon	North Central Coast
24	Cabernet Sauvignon	North Coast
25	Cabernet Sauvignon	Greater Bay Area
26	Cabernet Sauvignon	Napa County
27	Cabernet Sauvignon	Sierra Foothills
28	Pinot Noir	Appellation Central Coast
29	White Blend	San Joaquin County
30	Rosé	Contra Costa County
31	Rosé	Lodi/San Joaquin County
32	Chardonnay	Santa Barbara County
33	White Zinfandel	Napa and Sonoma
34	Chardonnay	Central Coast
35	Chardonnnay	Napa County
36	Merlot	Napa County
37	White Zinfandel	Napa and Lodi
38	Sauvignon Blanc	Oakville/Napa County
39	California Brut sparkling wine	Sonoma County
40	Petite Sirah port-style wine	Clarksburg/Yolo County

Sample preparation

All wine samples were diluted by a factor of three with Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany) then further diluted with hydrochloric acid (34-37.5%, Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) for a total acid concentration of 10%. This resulted in a final 3.3-fold wine dilution. Each wine was prepared in triplicate with the exception of sample 37, which was prepared with 5 replicates due to high residual sugar content.

Four wine samples were selected and prepared as spiked samples for additional analysis. Low and high concentration spikes were used at 10 μgL^{-1} and 50 μgL^{-1} and prepared in triplicate.

Calibration standards and reagents

A 1,000 μgL^{-1} single element calibration standard of As (VHG Labs, Manchester, NH, USA) was used to prepare working standards at 5, 10, 25, 50 and 100 μgL^{-1}. As (III) and As (V) calibration standards from SPEX CertiPrep (Metuchen, NJ, USA) were used as check standards to validate the method at 20 μgL^{-1} each. All calibration standards were matrix-matched with a 10% hydrochloric acid (34-37.5% Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) and 5% ethanol (v/v) (200 proof, Gold Shield Distributors, Hayward, CA) solution.

Two separate solutions were created for hydride generation. The first consisted of 1.2% Sodium Borohydride ($NaBH_4$, 98%, J.T. Baker, Center Valley, PA, USA) and 1.0% Sodium Hydroxide (NaOH, ACS Grade, EMD Chemicals Inc., Gibbstown, NJ) in Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany). The second was a 1:1 solution of HCl (34-37.5%, Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) and Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany).

A reduction solution of 25% (w/v) potassium iodide (ACS Grade, BDH Chemicals, West Chester, PA) was used to reduce As species prior to analysis. As (III) and As (V) are the most prevalent forms of As in wines. This reduction step aims to change the valence state of As from As (V) to As(III), because As (V) does not readily form a metal hydride. The potassium iodide solution was added to all samples and standards to create a final concentration of 1%. Best results were obtained when it was added at least 3 hours prior to analysis.

The setup of the MSIS (in Vapor Generation mode) for this analysis is displayed in Figure 2. The sample and 50% HCl solution were mixed using a 'tee' fitting after the peristaltic pump and the combined sample/HCl line was connected to the bottom of the MSIS. The reductant, $NaOH/NaBH_4$ solution, line was attached to the top of the MSIS. The unused sample line to the nebulizer was blocked during analysis as conventional nebulization was not required.

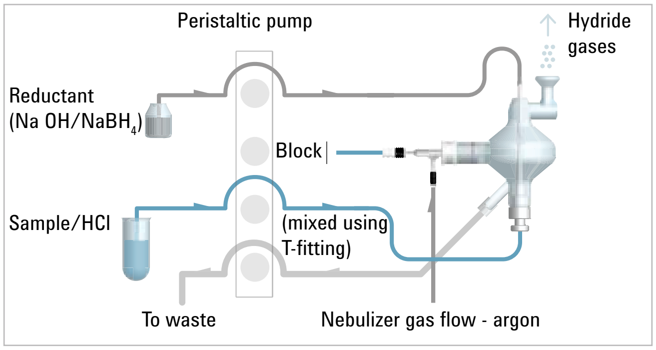

Figure 2. The MSIS setup for Vapor Generation mode.

Results and discussion

Calibration

The five-point calibration curve for As (188.979 nm) is shown in Figure 3. It shows excellent linearity with a calibration coefficient of greater than 0.999 and less than 6% error on each calibration point.

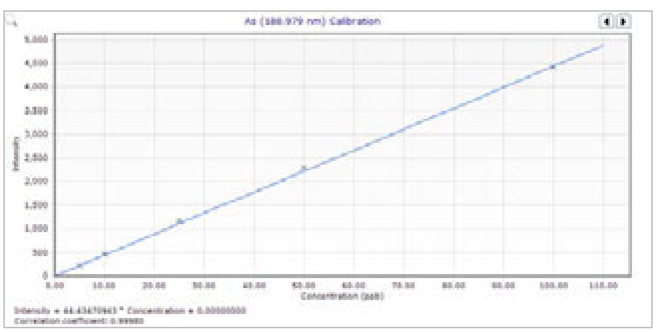

Figure 3. Calibration curve for As 188.979 nm showing excellent linearity across the 5-100 μgL^{-1} concentration range, illustrating the wide analytical range of the instrument.

Method Detection Limit

The Method Detection Limit (MDL) for As was determined from the analysis of ten replicate measurements of the blank solution. The results displayed in Table 3, show that the calculated MDL (confidence interval of 99.5%) for As was 0.34 μgL^{-1}.

Table 3. The calculated MDL and standard deviation results for As 188.979 nm.

Element	Concentration (μgL^{-1})
Mean (n=10)	0.01
SD	0.10
MDL (0.995)	0.34
MDL (0.99)	0.29
MDL (0.95)	0.19

Method validation

To check the validity of the method, Quality Control (QC) samples were run after the calibration and throughout the analytical run. The Continuing Calibration Verification (CCV) and Continuing Calibration Blanks (CCB) were measured every 10 samples. The initial calibration verification block included a 20 μgL^{-1} As (III) and As (V) sample. This was done to validate the calibration and confirm the efficiency of the KI reduction step of As (V) to As (III) prior to analysis. All CCV recoveries were within ± 10% of the assigned values (Table 4).

Table 4. QC recoveries of CCB, CCV and 20 μgL^{-1} As (V) and As (III) samples.

Solution	Concentration (μgL^{-1})	Recovery (%)
CCB, (mean, n=7)	0.46	-
25 $\mu g\ L^{-1}$ CCV, (mean, n=7)	23.94	96
20 $\mu g\ L^{-1}$ As (V)	20.59	103
20 $\mu g\ L^{-1}$ As (III)	19.92	99.6

Analysis of wine samples

The method described above was applied to the analysis of 40 Californian wine samples. The results obtained for each sample are the average of 3 replicates and can be found in Table 5, along with the standard deviation and relative standard deviation (%RSD). As concentrations in the wine samples ranged from below the MDL to 48.81 μgL^{-1}, well below the range of 100-200 μgL^{-1} regulated in many countries.

Table 5. The quantitative results for total As (188.979 nm) concentration in 40 Californian wines using the 4200 MP-AES.

Sample	Mean Concentration (µgL^{-1}) (mean, n=3)	Standard Deviation	Relative Standard Deviation (%)
1	1.03	0.88	0.85
2	<MDL	0.71	N/A
3	1.48	2.12	1.43
4	1.43	0.84	0.59
5	<MDL	0.21	N/A
6	<MDL	0.40	N/A
7	<MDL	0.77	N/A
8	<MDL	0.74	N/A
9	<MDL	0.74	N/A
10	43.81	1.13	0.03
11	2.92	3.55	1.22
12	<MDL	1.17	3.95
13	<MDL	3.91	1.90
14	6.63	1.14	0.17
15	6.09	1.45	0.24
16	3.24	1.89	0.58
17	<MDL	0.22	N/A
18	2.33	1.33	0.57
19	<MDL	2.11	14.06
20	<MDL	1.52	6.70
21	0.75	0.92	1.23
22	<MDL	2.51	N/A
23	10.16	1.15	0.11
24	<MDL	1.63	N/A
25	<MDL	1.74	N/A
26	<MDL	1.66	N/A
27	<MDL	0.22	N/A
28	3.96	0.52	0.06
29	1.37	1.16	0.85
30	<MDL	0.71	N/A
31	<MDL	0.47	N/A
32	27.04	1.21	0.04
33	31.17	4.72	0.15
34	4.53	0.37	0.08
35	9.86	0.23	0.02
36	3.44	0.46	0.13
37	17.84 (mean, n=5)	0.63	0.04
38	11.23	0.28	0.02
39	9.76	0.24	0.02
40	2.64	0.90	0.34

<MDL = below Method Detection Limit

Analysis of spiked wine samples

Four wines, representing various total As concentrations, were selected for a spike recovery study. Two spikes were completed for each sample at 10 and 50 µgL^{-1}. This equates to spikes of 33 and 165 µgL^{-1} in the sample. The recoveries for each spike were within ± 10%, with the exception of one which had a recovery of 111%. Results seen in Table 6, show excellent recovery for As using the MP-AES at low and high µgL^{-1} levels.

Conclusions

The Agilent 4200 MP-AES coupled with the MSIS accessory provided an easy and accurate analysis of total As in wine. The MSIS technology increased sensitivity to levels lower than single digit µgL^{-1}. The resulting MDL would be approximately 100 times lower when compared to using direct nebulization. All 40 wine samples analyzed were found to have As concentrations less than the levels regulated by most countries worldwide.

The complex background on the calibration and samples was easily corrected with Agilent's Fast Linear Interference Correction (FLIC), improving analytical accuracy.

The nitrogen-based plasma significantly reduces operating costs when nitrogen is supplied with the use of a Agilent 4107 Nitrogen Generator. The generator extracts nitrogen from compressed air. Alternatively, nitrogen can be supplied by Dewar.

The Agilent 4200 MP-AES with MSIS accessory proved to be a reliable, cost-effective instrument for quantifying total As in wine.

Table 6. The percent recovery results for the four As spiked wine samples at 10 and 50 µgL^{-1}, the results shown represent the concentration in the original sample, calculated accounting for the dilution factor.

Sample#	Spiked concentration (µgL^{-1})		Measured spiked concentration (µgL^{-1})	Measured unspiked concentration (µgL^{-1})	Recovery (%)
8	33	Ave	32.25	-1.53	102.36
		%RSD	0.03	-0.48	
8	165	Ave	153.26	-1.53	93.82
		%RSD	0.01	-0.48	
23	33	Ave	42.76	10.16	98.81
		%RSD	0.01	0.11	
23	165	Ave	164.79	10.16	93.72
		%RSD	0.01	0.11	
28	33	Ave	39.54	3.96	107.82
		%RSD	0.01	0.06	
28	165	Ave	161.48	3.96	95.46
		%RSD	0.04	0.06	
32	33	Ave	57.63	27.04	92.68
		%RSD	0.00	0.04	
32	165	Ave	211.12	27.04	111.56
		%RSD	0.01	0.04	

Reference

C. K. Tanabe, H. Hopfer, G. Gilleland, A. Liba, S. E. Ebeler and J. Nelson. Total arsenic analysis in Californian wines with hydride generation – microwave plasma – atomic emission spectroscopy (HG-MP-AES). *J. Anal. At. Spectrom*, 2016

Elemental profiling of Malbec Wines for geographical origin using an Agilent 4200 MP-AES

Application note

Food testing

Authors

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Introduction

Red wine produced from the Malbec grape is increasing in popularity in the United States. However, the US is a relatively small producer of the wine compared to Argentina, where it is the most extensively planted grape variety in the country. With rising imports into the US from Argentina there are growing concerns relating to the validation of the geographical origin of this wine.

Typically ICP-MS is used to distinguish between wines originating from different regions by comparing the relative concentrations of mineral elements, which are characteristic of the soil composition of the region of production. In this study, a cost-effective approach has been taken using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) to measure 6 elements (Sr, Rb, Ca, K, Na and Mg). Agilent's Mass Profiler Professional (MPP) integrated chemometrics software and another data analysis package were used to model the MP-AES results to distinguish the geographical origin of 41 Malbec wine samples produced in Argentina and the USA.

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Experimental

Samples

Malbec grapes from the 2011 vintage were sourced from 41 different geographical sites; 26 from the Mendoza region of Argentina and 15 from California, USA. In order to reduce the impact of the wine making process on the elemental composition of each wine, and to preserve any elemental differences arising from the geographical origin, two central winemaking facilities only were used to produce the wine. Table 1 lists all the samples, with their detailed geographical origin. Details of the winemaking procedure can be found in the original study [1].

Calibration standards and reagents

Single-element calibration standards (Ca, K, Mg, Na at 10,000 mg/L, and Sr at 1,000 mg/L) were purchased from VHG Labs (Manchester, NH, USA), Rb 1,000 mg/L was from SPEX CertiPrep (Metuchen, NJ, USA), and concentrated nitric acid was obtained from JT Baker (Instra-Analyzed grade, Center Valley, PA, USA). The ionization buffer solution (100,000 mg/L Cs; Agilent, Santa Clara, CA, USA) was diluted to 2,000 mg/L in 1% HNO_3 prior to use. Ultrapure water (18 MΩcm, EMD Millipore Bellerica, MA, USA) and Uvasol spectroscopy grade ethanol from Merck (Whitehouse Station, NJ, USA) were used for the calibration solutions and dilutions.

Instrumentation

An Agilent 4200 MP-AES fitted with a MicroMist concentric nebulizer and baffled cyclonic spray chamber was used throughput the study. An External Gas Control Module (EGCM) was used to inject air into the nitrogen plasma to prevent carbon present in the wine samples from building up on the torch. This ensures stable results over the course of the analysis and reduces the background emissions generated by the organic species present in the sample. A 2,000 mg/L cesium (Cs) Ionization Buffer solution was constantly mixed with the sample stream immediately before entering the spray chamber, using a simple mixing tee.

Each element (Sr, Rb, Ca, K, Na and Mg) was monitored at a specific wavelength to ensure interference-free detection. EGCM and read time settings were optimized for each element. The instrument was calibrated and tuned daily using an Agilent wave calibration solution.

All wine samples were analyzed in triplicate after a 1:50 dilution in 5% HNO_3. A 6-point calibration between 0 and 500 mg/L was carried out for each element in matrix-matched calibration solutions (5% HNO_3 and 0.2% ethanol) to account for matrix interferences of the ethanolic wine solutions.

The sample introduction and calibration parameters used are given in Table 2 and 3 respectively.

Statistical data analysis

Data analysis of the concentrations of the 6 monitored elements monitored in each of the Malbec wines was carried out in RStudio (version 0.98.501, Boston, MA) and Agilent's Mass Profiler Professional (MPP; version 12.61). Multivariate analysis of variance (MANOVA) and individual univariate analysis of variance (ANOVA) for each element were run in RStudio. Elements that differed significantly among the wines were further used in an untargeted Principal Component Analysis (PCA) within the MPP software to visualize the sample differences. As a final analysis, Partial Least Squares – Discriminate Analysis (PLS-DA) was used for the geographical classification of the wines, according to country and to region within a country.

Table 1. Samples included in the study. For each wine sample, the district, department, and altitude is shown. *Denotes samples from the Yolo region - the only US region outside a recognized American Viticultural Area (AVA). *Source: Nelson et al [1].*

Sample code	District	Department / AVA or County	Altitude (meters above sea level)	Sample code	District	Department / AVA or County	Altitude (meters above sea level)
M1	La Consulta	San Carlos	999	M22	El Peral	Tupungato	1235
M2	Perdriel	Luján	964	M23	El Peral	Tupungato	1235
M3	La Consulta	San Carlos	999	M24	El Peral	Tupungato	1241
M4	La Consulta	San Carlos	999	M25	Gualtallary	Tupungato	1354
M5	La Consulta	San Carlos	999	M26	Gualtallary	Tupungato	1353
M6	Las Compuertas	Luján	1022	C1	Yountville	Napa	Not available
M7	Las Compuertas	Luján	1022	C2	Mount Veeder	Napa	315
M8	Las Compuertas	Luján	1022	C3	Mount Veeder	Napa	510
M9	Altamira	San Carlos	1024	C4	Mount Veeder	Napa	497
M10	Altamira	San Carlos	1043	C5	Oak Knoll District	Napa	25
M11	Altamira	San Carlos	1096	C6	Alexander Valley	Sonoma	58
M12	Altamira	San Carlos	1047	C7	Alexander Valley	Sonoma	68
M13	Altamira	San Carlos	1043	C8	Alexander Valley	Sonoma	53
M14	Altamira	San Carlos	1024	C9	Hames Valley	Monterey	214
M15	Gualtallary	Tupungato	1342	C10	Monterey County	Monterey	154
M16	Altamira	San Carlos	1052	C11	Lodi	San Joaquin	61
M17	El Peral	Tupungato	1235	C12	Winters*	Yolo	88
M18	Lunlunta	Maipú	931	C13	Winters*	Yolo	77
M19	Lunlunta	Maipu	930	C14	Winters*	Yolo	70
M20	El Peral	Tupungato	1235	C17	Red Hills	Lake	648
M21	El Peral	Tupungato	1235				

Table 2. 4200 MP-AES operating conditions. *Source: Nelson et al [1]*

<table>
<tr><th>Parameter</th><th colspan="6">Value</th></tr>
<tr><td>Element</td><td>Sr</td><td>Rb</td><td>Mg</td><td>Ca</td><td>Na</td><td>K</td></tr>
<tr><td>Monitored wavelength (nm)</td><td>407.771</td><td>780.027</td><td>279.553</td><td>396.847</td><td>589.592</td><td>769.897</td></tr>
<tr><td>EGCM setting</td><td>Low</td><td>Low</td><td>Med</td><td colspan="3">High</td></tr>
<tr><td>Pump rate (rpm)</td><td colspan="6">10</td></tr>
<tr><td>Sample tubing</td><td colspan="6">Org-Grn</td></tr>
<tr><td>Ionization buffer tubing</td><td colspan="6">Org-Grn</td></tr>
<tr><td>Waste tubing</td><td colspan="6">Blue-Blue</td></tr>
<tr><td>Read time (s)</td><td colspan="2">5</td><td colspan="4">2</td></tr>
<tr><td>Number of replicates</td><td colspan="6">3</td></tr>
<tr><td>Sample uptake delay (s)</td><td colspan="6">50</td></tr>
<tr><td>Stabilization delay (s)</td><td colspan="6">20</td></tr>
<tr><td>Fast pump during uptake</td><td colspan="6">Yes</td></tr>
<tr><td>Background correction</td><td colspan="6">Auto</td></tr>
</table>

Table 3. Calibration parameters used for wine sample analysis. *Source: Nelson et al [1]*

Element	λ (nm)	Calibration Range (mg/L)	Background Correction	Calibration fit	Correlation Coefficient
Sr	407.771	0-5	auto	linear	0.9999
Rb	780.027	0-5	auto	linear	0.9997
Mg	279.553	0-5	auto	linear	0.9998
Ca	396.847	0-5	auto	linear	0.9999
Na	589.592	0-5	auto	linear	0.9999
K	769.897	0-20	auto	linear	0.99999

Results and discussion

Three sigma detection limits were determined by analyzing 10 sample blanks. All 6 of the elements monitored were detected in the 41 different wine samples at concentrations above their limits of detection (LODs), as shown in Table 4. All elements also differed significantly among the wine samples in a multi- and univariate analysis of variance at an α level of 5%. Thus, all 6 elements were included in the subsequent PCA and PLS-DA analyses.

Figure 1a shows a clear separation of the wines by country of origin, with only a slight overlap of two US wines. The component loadings plot (Figure 1a) shows that the elemental differences in Na and Sr primarily account for the separation by country of origin.

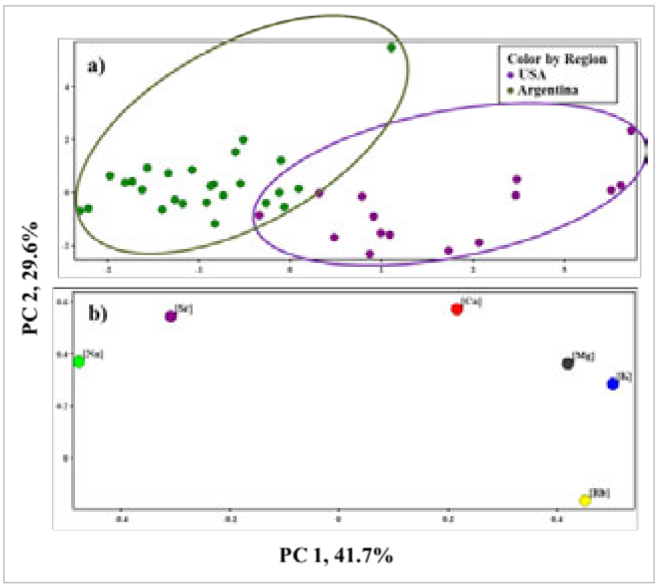

Figure 1. 2D PCA bi-plots using the 6 elements which differed significantly among the wine samples. (a) Product plot showing the wine samples color coded by geographical origin, (b) Loadings plot with 6 elements (Sr, Rb, Ca, K, Ca, Na and Mg). *Source: Nelson et al. [1].*

However, an almost 100% correct classification of the wines according to their country of origin was obtained using PLS-DA (Figure 2). Using cross-validation, the prediction accuracy for the USA wines was 93.3% and 96.2% for the Argentina wines, leading to an overall accuracy of 95.1% for the PLS-DA model (Table 5). The incorrectly classified wines (M1 for the Argentina wines and C12 for the USA wines), were most likely due to their higher/lower levels in Na, Mg, and K (M1 was low in Na, Mg, and K; C12 was high in Mg) compared to the other wines in the same class. Excellent classification was achieved. If a larger set of samples had been available, we would have tested to see how the model performs with complete unknown samples.

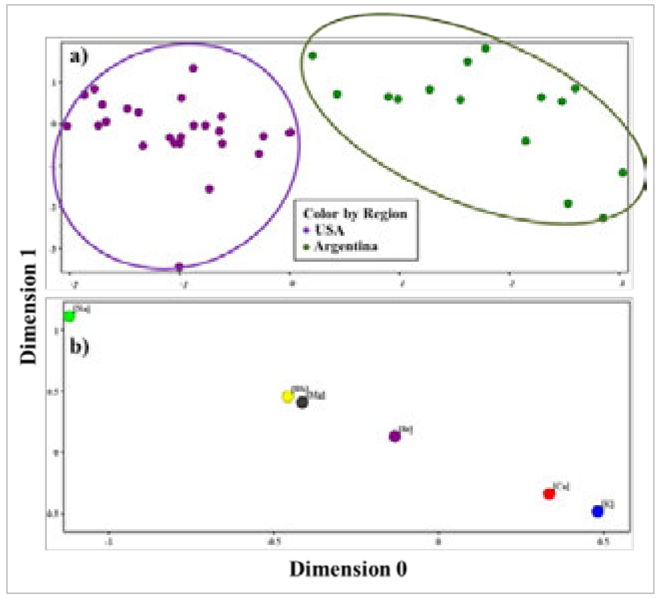

Figure 2. 2D PLS plots using the 6 elements which differed significantly among the wine samples. (a) Sample plot showing the separation of the wines according to geographical origin, with no overlap. (b) Element loadings plot. *Source: Nelson et al [1]*

Table 4. Detection limits (DL) and elemental concentrations for the wines from Argentina and the USA. Shown are mean $\bar{x}$, standard error of the mean $\sigma_{\bar{x}}$, and the minimal (min) and maximal (max) concentrations. Concentrations (mg/L) are given for the elements that differed significantly among the five wineries ($P \leq 0.05$). *Source: Nelson et al [1]*

		Wines from California, USA		Wines from Mendoza, Argentina	
	DL	$\bar{x} \pm \sigma_{\bar{x}}$	min – max	$\bar{x} \pm \sigma_{\bar{x}}$	min – max
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sr	0.0018	0.45 ± 0.02	0.24 - 0.83	0.77 ± 0.04	0.23 - 1.59
Rb	0.0004	3.37 ± 0.03	0.57 - 7.83	0.99 ± 0.02	0.55 - 2.19
Mg	0.0012	80.87 ± 0.42	61.75 - 144.86	72.87 ± 0.54	53.55 - 116.29
Ca	0.0016	51.78 ± 0.19	43.26 - 74.01	50.46 ± 0.25	33.22 - 95.08
Na	0.0007	4.90 ± 0.09	3.38 - 8.46	37.48 ± 0.48	13.71 - 121.87
K	0.0020	1444.42 ± 10.53	1120.94-2219.84	1181.22 ± 15.45	976.85-1989.12

Table 5. Result of the cross validation (leave one out algorithm) for the PLS-DA run on the 2 countries. *Source: Nelson et al [1]*

	USA (predicted)	Argentina (predicted)	Accuracy
Argentina (true)	1 (= M1)	25	96.2%
USA (true)	14	1 (= C12)	93.3 %
Overall accuracy			95.1 %

Conclusions

The Agilent 4200 MP-AES is an easy-to-use, low cost instrument suitable for geographical origin analysis of wine samples when combined with a data analysis package such as Agilent's Mass Profiler Professional (MPP). Six elements, Sr, Rb, Mg, Ca, Na, and K, were useful for broad classification of geographic origin of Malbec wines from Argentina and the US, with 14 out of 15 US samples correctly classified and only 1 out of 26 of the Argentinian wines wrongly classified.

Reference

1. Jenny Nelson, Helene Hopfer, Greg Gilleland, Daniel Cuthbertson, Roger Boulton, Susan E Ebeler. Elemental Profiling of Malbec Wines Made Under Controlled Conditions by Microwave Plasma Atomic Emission Spectroscopy. Am. J. Enol. Vitic. Published ahead of print April 2015

Determination of metals in wine using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer

Application note

Food Testing and Agriculture

Authors

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Introduction

The concentrations of certain metals in wine are of great interest because of their influence on the wine-making process. Strict analytical control of the trace element content is required during the entire wine making process. For example, metals such as potassium, calcium, and iron can produce precipitates, cause cloudiness, or affect the taste.

The wine maker needs to properly control the production process so that the quality of the product can be assured. During vintage, when monitoring trace elements is most critical, sample turnaround time (and to a lesser extent sample throughput) becomes important. Most wine labs are small to medium in size, and hence value ease of use and reduced infrastructure requirements.

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Metals in wine can be determined by a number of analytical techniques[1-10]. The most common technique used is Flame Atomic Absorption (FAA), while ICP-OES is sometimes used in larger central laboratories where extra sample throughput is required, although having elemental analysis capabilities close to the winery during vintage is generally preferred.

This work describes an alternative, safer and cheaper analytical method for the determination of metals in wine using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES).

Which measurement technique is right for you?

There are many factors to be taken into account when selecting the right analytical technique. In many cases several techniques will provide adequate detection range, so the technique of choice will depend on factors such as sample throughput requirements, ease-of-use, infrastructure required, and on-going operating costs.

The MP-AES offers significantly reduced on-going operating costs over both FAA and ICP-OES by running on nitrogen that can be supplied via a nitrogen generator. This eliminates the need for on-going gas resupply and avoids flammable gases (required for FAA), enhancing safety and allowing unattended, overnight operation. The reduced infrastructure required for MP-AES also makes it well suited to remote sites where supply of expensive specialty gases can be difficult.

The 4100 MP-AES fits between FAA and ICP-OES in many aspects such as detection power, dynamic range, and speed of analysis. For these key performance metrics, the MP-AES offers a unique alternative to both FAA and ICP-OES.

These features make the MP-AES an attractive technique for many small to medium size laboratories, particularly those at remote locations, and for an increasing number of laboratories requiring the lowest possible on-going operating costs.

Experimental

Instrumentation

The measurements were performed on an Agilent 4100 MP-AES using a dewar nitrogen supply. The 4100 MP-AES is a compact bench-top microwave plasma atomic emission spectrometer that generates a robust, magnetically-excited nitrogen plasma. Operating the instrument with the optional Agilent 4100 Nitrogen Generator further reduces the operating costs.

The sample introduction system used for this application consisted of a standard torch, a double pass glass cyclonic spraychamber and an inert OneNeb nebulizer.

The determination of Ca, K, Na and Mg benefits from the use of an ionization suppressant. The ionization suppressant was mixed with the sample via a T piece placed before the nebulizer. The on-board three channel peristaltic pump was used to deliver the sample through the sample introduction system. A 0.1% w/v Cs (CsCl Analar, Merck) solution was used as an ionization suppressant.

The External Gas Control Module (EGCM) was used to inject air into the plasma when running the diluted wine matrix that contained a small amount of alcohol. The air injection prevents any carbon build up in the torch, ensuring stable results when running these samples over a long time period.

The air injection also reduces the background emissions generated by the organics present in the sample. The EGCM is automatically controlled by the instrument software, and as such requires minimal user interaction.

Because the amount of alcohol in diluted wine samples is low, the air injection rate is selected at a lower rate than the default setting for each wavelength.

The instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Parameter	Value				
Element	Ca	K	Na	Mg	Fe
Wavelength (nm)	396.847	769.897	589.592	285.213	371.993
EGCM setting	Low	Low	Low	Low	Medium
Nebulizer	OneNeb				
Spraychamber	Double pass glass cyclonic				
Pump rate	15 rpm				
Sample tubing	Orange/green				
Waste tubing	Blue/blue				
Read time	1-10 seconds*				
Number of replicates	3				
Sample uptake delay	15 seconds				
Stabilization delay	20 seconds				
Fast pump during uptake	On				
Background correction	Auto				

*Can be varied based on sample concentrations

For comparison purposes, the samples were also measured on an Agilent 725 radially-viewed ICP-OES instrument and an Agilent 240FS FAA spectrometer.

Standard and Sample Preparation

A variety of wine samples were selected for this study, covering both red and white varieties.

- Wine 1 : Shiraz
- Wine 2 : Cabernet Sauvignon
- Wine 3 : Chardonnay
- Wine 4 : Sauvignon Blanc
- Wine 5 : Viognier

Additionally, two certified reference materials were analyzed to validate the method:

- Red wine: TM-Wine-R1A (Spex CertiPrep)
- White wine: TM-Wine-W1A (Spex CertiPrep)

For MP-AES and ICP-OES analysis, the samples were degassed in an ultrasonic bath, then diluted 1 in 10 (v/v) with 5% HNO_3 (Suprapur, Merck). Standards and blank were prepared in 5% v/v HNO_3 and 2% v/v ethanol (Merck) to matrix match the alcohol content of the wine samples. Care must be taken when adding ethanol into 5% HNO_3. Ethanol should be added gradually drop-wise with a Pasteur pipette.

For AA analysis, the samples were also degassed and further sample preparation for AA depends on the element of interest.

- For Ca samples were diluted 1 in 10 with 5% HNO_3 and 2000 mg/L Sr (Strontium chloride, Laboratory reagent, BDH).
- For K and Na samples were diluted 1 in 10 with 5% HNO_3 and 1000 mg/L Cs.
- For Mg and Fe samples were diluted 1 in 10 with 5% HNO_3.

The standards and blanks were matrix matched with the samples, as described above.

Results

Method detection limit

Method detection limit (MDL) is expressed as 3 times the standard deviation of 10 replicate measurements of the blank. Analytical wavelengths used and the MDL by MP-AES are listed in Table 2.

Table 2. Method detection limits (MDL) by MP-AES

Element	Wavelength (nm)	MDL (µg/L)
Ca	396.847	8
K	769.897	110
Na	589.592	15
Mg	285.213	11
Fe	371.993	15

Certified Reference Material and Wine Samples

The accuracy of the measurement of metals in wine samples by MP-AES was verified by the analysis of the certified red and white wine reference material. Good agreement was obtained with certified values, with recoveries between 94% and 110% (see Table 3). Results for the analysis of wine samples by all three techniques can be seen in Table 4. For the five wines analyzed, the MP-AES results are in good agreement with the AA and ICP-OES results.

Table 3. Analysis of CRM samples by MP-AES

Element	Measured mg/L	Certified-TM-Wine-W1A mg/L	% Recovery
Ca	79 ± 1	82.2 ±2	96
K	980 ± 23	939 ± 142	104
Na	27.6 ± 0.4	25.1 ± 3	110
Mg	119 ± 1	123 ± 3	97
Fe	2.03 ± 0.01	1.97 ± 0.2	103

Element	Measured mg/L	Certified-TM-Wine-R1A mg/L	% Recovery
Ca	47 ± 0.31	50 ±2	94
K	1160 ± 32	1120 ± 142	104
Na	21.0 ± 0.4	22.4 ± 3	96
Mg	127 ± 1	123 ± 3	103
Fe	2.43 ± 0.03	2.49 ± 0.2	98

Table 4. Comparison of the analysis of wine sample by three techniques

Element	Concentration (mg/L)		
	4100 MP-AES	240FS AA	725 ICP-OES
Wine 1			
Ca	52	52	54
K	1205	1116	1112
Na	37	37	35
Mg	148	149	150
Fe	1.2	1.1	1.0
Wine 2			
Ca	6.6	6.9	6.9
K	1206	1197	1154
Na	30	34	32
Mg	103	100	102
Fe	2.2	2.2	2.0
Wine 3			
Ca	56	59	59
K	900	848	839
Na	34	33	31
Mg	87	86	90
Fe	0.9	0.9	0.7
Wine 4			
Ca	70	70	77
K	756	718	741
Na	10	11	9.0
Mg	78	77	83
Fe	0.4	0.4	0.3
Wine 5			
Ca	32	31	34
K	689	627	661
Na	48	48	45
Mg	121	125	134
Fe	1.8	1.7	1.7

Conclusion

The MP-AES is an accurate and reliable technique for this application and is an ideal alternative to FAA and ICP-OES. Results for certified samples were in good agreement with the CRM reference values and results for various wine samples were in good agreement across all three techniques.

The MP-AES also offers significant benefits over the commonly used FAA, including enhanced productivity through greatly simplified sample preparation and unattended multi-element analysis, higher performance through improved detection limits and greater linear dynamic range, and lower cost of ownership and operating costs by running on nitrogen and eliminating flammable gases such as acetylene and nitrous oxide.

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Alimentos y agricultura

Gracias al gran número de muestras analizadas y a la medida secuencial rápida, el sistema de MP-AES de Agilent resulta idóneo para los laboratorios de control alimentario.

El sistema de MP-AES es perfecto para los laboratorios que funcionen por contrato, donde la rapidez es fundamental, incluidos aquellos laboratorios pequeños y medianos que necesiten determinar nutrientes esenciales, elementos mayoritarios y elementos tóxicos a nivel de trazas. Ofrece las siguientes ventajas:

- El sistema de MP-AES tiene un coste de propiedad mínimo, lo que le supondrá una ventaja frente a sus competidores, ya que reduce el coste por análisis y aumenta el rendimiento.
- Eliminación de los tiempos de inactividad asociados a la espera de recargas de gas y mayor agilidad en el procesamiento de las muestras gracias al análisis seguro, fiable y sin supervisión.
- Simplificación del proceso de preparación de muestras. El plasma vertical de visión axial permite procesar una amplia variedad de muestras, desde alimentos y digestiones de suelos a extractos de suelos con alto contenido salino.
- Aumento de la estabilidad a largo plazo gracias a la humidificación de gas del nebulizador integrada de serie en el sistema de MP-AES.
- Aumento del número de muestras analizadas en comparación con los sistemas de AA de llama convencionales; además, podrá olvidarse de tener que volver a cambiar quemadores o gases para diferentes elementos.
- Desarrollo de métodos y puesta en marcha rápidos, lo que permite que todos los usuarios consigan un rendimiento óptimo.
- La función MultiCal le permite analizar elementos con concentraciones altas y bajas en un mismo análisis.
- Gracias a la completa cobertura de longitudes de onda, podrá evitar las interferencias espectrales de los elementos mayoritarios con tan solo elegir otra longitud de onda.
- Detección rápida de concentraciones de arsénico, mercurio y selenio inferiores a las ppb gracias al sistema de introducción de muestras multimodo (MSIS).
- Inclusión del fósforo y el azufre en el conjunto de análisis elementales y mejora de los límites de detección gracias a la tecnología de emisión de plasma del sistema de MP-AES.

Determination of available micronutrients in DTPA extracted soils using the Agilent 4210 MP-AES

Application note

Food safety and agriculture

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Introduction

Micronutrient soil analysis is commonly conducted in agricultural laboratories to assess the quality of soil for plant development and crop yield. Micronutrients such as copper, iron, manganese and zinc can be extracted from soil using solutions containing chelating agents such as diethylenetriaminepentaacetic acid (DTPA).

Typically, the determination of micronutrients in soils is conducted using Flame Atomic Absorption Spectroscopy (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES); however, with agriculture

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labs increasingly under pressure to reduce operating costs and improve safety, Microwave Plasma Atomic Emission Spectroscopy (MP-AES) is gaining recognition as a suitable alternative to these techniques.

Why use MP-AES over traditional techniques?

The advantages of MP-AES for the analysis of environmental samples, including soils include:

- Lower running costs and improved safety.
  MP-AES uses nitrogen gas from either a Dewar or extracted from air using the Agilent 4107 Nitrogen Generator. Eliminating the need for expensive and hazardous gases such as acetylene allows for unattended analysis. It is the ideal instrument for laboratories looking to reduce on-going operating costs or with safety concerns.

- Excellent analytical performance for difficult samples.
  The stable microwave plasma is capable of analyzing complex matrices such as DTPA soil extracts or soil digests containing high total dissolved solids (TDS), as well as aqueous solutions.

- Multi-elemental analysis.
  MP-AES offers improved analytical performance, lower detection limits and a wider calibration range compared to Flame Atomic Absorption Spectroscopy.

- Ease of use.
  MP-AES uses intuitive MP Expert software and plug-and-play hardware to simplify instrument setup, method development and analytical performance, with minimal training. Additionally, application specific software applets can be created in MP expert from pre-set templates, further simplifying analysis.

This application note describes the determination of micronutrients Cu, Fe, Mn and Zn in soils following DTPA extraction using the Agilent 4210 MP-AES.

Experimental

Instrumentation

All measurements were performed using the Agilent 4210 MP-AES with it's integrated humidifier accessory and SPS 4 autosampler. The instrument was set up with the standard sample introduction system comprising the Agilent OneNeb Series 2 nebulizer, double-pass glass cyclonic spray chamber and Easy-fit torch. Instrument method parameters and analyte settings are listed in Table 1.

Table 1. Agilent 4210 MP-AES instrument and method parameters.

Parameter	Value			
Element	Cu	Fe	Mn	Zn
Wavelength (nm)	324.754	259.940	257.610	213.857
Nebulizer	OneNeb Series 2			
Nebulizer flow rate (L/min)	0.75			
Pump rate (rpm)	15			
Sample pump tubing	Orange/Green Solvaflex			
Waste pump tubing	Blue/blue Solvaflex			
Read time (s)	3			
Number of replicates	3			
Sample uptake delay (s)	35			
Rinse time (s)	20			
Stabilization time (s)	10			
Background correction	Auto			
Gas source	Dewar nitrogen			

Standard and sample preparation

The soil samples were supplied dried and ground. The extraction solution comprised 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M calcium chloride dihydrate ($CaCl_2.2H_2O$) and 0.1 M triethanolamine (TEA).

1.97 g of DTPA, 1.47 g $CaCl_2.2H_2O$ and 13.3 mL TEA were dissolved separately in distilled water and combined. The pH was adjusted to 7.3 using conc. HCl and the volume made up to 1 L with distilled water.

10 g of soil was weighed and 20 mL of the DTPA extraction solution was added. After shaking for 120 minutes, the sample was filtered using filter paper.

Multi-element calibration standards were prepared at the following concentrations: 0.5, 2.5 and 5.0 µg/mL of Cu and Zn, 5.0, 25.0 and 50.0 µg/mL of Mn and 25.0, 50.0 and 100.0 µg/mL of Fe. All calibration blanks and standards were prepared in the DTPA extraction solution.

Results and discussion

Working concentration range

Linear calibrations were obtained for all four elements with calibration coefficients greater than 0.999 (Table 2) and less than 10% calibration error for each point. As an example, Figure 1 shows the calibration curve for Cu 324.754 nm and the calibration error for each calibration point (Table 3).

Table 2. Wavelength and working calibration concentration range.

Element and line (nm)	Concentration range (µg/mL)	Concentration coefficient
Cu 324.754	0.5-5	1.000
Fe 259.940	10-100	0.999
Mn 257.610	5-50	0.999
Zn 213.857	0.5-5	0.999

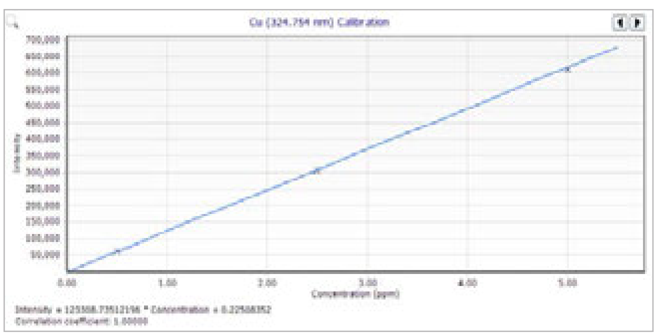

Figure 1. The calibration curve for Cu 324.754 nm shows excellent linearity across the calibrated range with a correlation coefficient of 1.00000.

Table 3. Calibration error (%) for each calibration point for Cu 324.754 nm.

Standards	Calibration error (%)
Blank	0.00
Standard 1	1.31
Standard 2	0.59
Standard 3	0.94

Method detection limits

Three sigma method detection limits (MDL) were determined from ten replicate measurements of the 0.5 µg/mL spiked blank DTPA extraction solution during the analytical run. The results shown in Table 4 are the average of 3 analytical runs.

Table 4. Agilent 4210 MP-AES element wavelengths used for analysis and MDLs at a sampling weight of 10 g for the DTPA extraction.

Element	Wavelength (nm)	MDL (mg/kg)
Cu	324.754	0.06
Fe	259.940	0.03
Mn	257.610	0.03
Zn	213.857	0.05

Spike recoveries

To verify the accuracy of the method, a DTPA-extracted soil sample was spiked with Cu, Fe, Mn and Zn at 5, 40, 20 and 5 mg/kg concentration levels respectively. The recoveries for the spiked sample are given in Table 5. The recovery results were within ± 10% of the expected value for all 4 analytes which highlights the suitability of the method for the application.

Table 5. Agilent 4210 MP-AES spike recoveries for all elements in the DTPA extracted soil sample.

Element and line (nm)	DTPA extracted soil sample (mg/kg)	Spiked concentration (mg/kg)	Measured concentration (mg/kg)	Recovery (%)
Cu 324.754	0.43	5	4.58	92
Fe 259.940	22.81	40	36.46	91
Mn 257.610	6.56	20	18.09	90
Zn 213.857	0.23	5	4.62	92

Long term stability

Long term stability of the Agilent 4210 MP-AES was measured by analyzing a DTPA extracted soil sample approximately every 2 minutes over 3 hours of continuous measurement. Figure 2 shows that excellent stability was achieved, with measurement precision <2% RSD for all elements (see Table 6), over the 3-hour period.

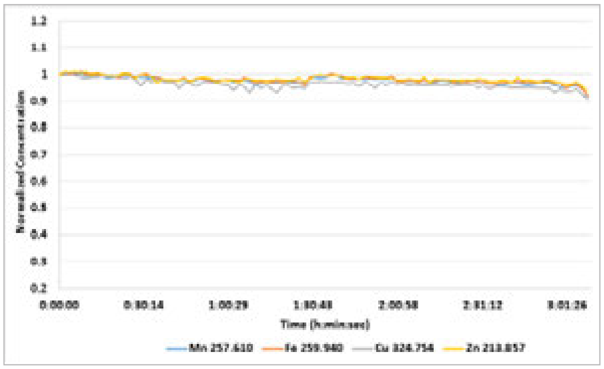

Figure 2. Normalized concentration of Cu, Fe, Mn and Zn in DTPA extracted soil sample, measured over 3 hours.

Table 6. Agilent 4210 MP-AES long term stability results (% RSD) for Cu, Fe, Mn and Zn in DTPA extracted soil sample.

Element	Wavelength (nm)	%RSD
Cu	324.754	1.77
Fe	259.940	1.45
Mn	257.610	1.38
Zn	213.857	1.21

Conclusions

The Agilent 4210 MP-AES proved suitable for the cost-effective analysis of micronutrients in DTPA extracted soil samples. As the microwave plasma is generated from nitrogen gas, it eliminates the need for expensive and flammable gases, which reduces operational costs and improves lab safety. Compared to FAAS, the high plasma temperature (5000 K) of MP-AES provides a higher sample matrix tolerance, lower detection limits and an expanded working concentration range.

The method used in this study demonstrated:

- High analytical performance with excellent MDLs and spike recoveries for all elements within ± 10% of the target values.
- Excellent linearity across a wide concentration range.
- Excellent long term stability, with less than 2% RSD over a 3-hour period.

Determination of major elements in milk using the Agilent 4200 MP-AES

Application note

Food testing & agriculture

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Introduction

Milk is one of the most important food commodities in the world and its consumption has grown, particularly in developing countries which have experienced strong economic growth and urbanization in recent decades.

As a substantial source of several nutrients such as proteins, enzymes, fats, vitamins and essential elements (also known as minerals), milk plays a key role during all phases of human life. Rapid growth during infancy and early childhood creates high demand for the nutrients that milk provides. This development phase requires a balanced amount of different elements, as mineral deficiencies may impair body development whilst excessive mineral intake may increase the osmotic load and cause complications in the developing kidneys of a child.

Essential elements such as Ca, K, Mg, Na and P have several physiological functions in the tissue structure of humans and other animals, such as maintaining osmotic/electrolyte balance, and acting as a cofactor for many enzymes. Deficiencies in these essential elements causes disturbances in the physiological system in any stage of life and, for this reason, such elements must be monitored to ensure the nutritional value of foods. The accurate analysis of essential elements is particularly important in extensively consumed products, such as milk.

Several atomic spectroscopy techniques are routinely used for elemental quantification in milk and dairy products, in particular flame atomic absorption spectrometry (FAAS) and recently microwave plasma atomic emission spectrometry (MP-AES).

The recent introduction of microwave plasma atomic emission spectrometry was a breakthrough revolution in entry-level atomic spectroscopy techniques. The easy to use Agilent 4200 MP-AES has better performance and speed than a FAAS and requires no hazardous and expensive gases. This improves safety and reduces the cost of analysis.

This work shows the performance of the Agilent 4200 MP-AES for quantification of Ca, K, Mg, Na and P in fresh and powdered milk after acid digestion, with quality assurance performed by analysing a Certified Reference Material (CRM) and applying some of the concepts from the US EPA Contract Laboratory Program.

Experimental

Instrumentation
For this study a microwave plasma atomic emission spectrometer, the Agilent 4200 MP-AES (Agilent Technologies, Santa Clara, CA) was used for elemental determination of digested milk samples. Acid digestion was carried out using an UltraWAVE Single Reaction Chamber Microwave Digester (Milestone Inc., Shelton CT).

Standards and reagents
Analytical grade concentrated nitric acid (HNO_3 67-69%) and hydrochloric acid (HCl 32-35%) were used for sample digestion. The 18.2 MΩ deionized water used was obtained from a Milli-Q™ Water System (Millipore, Darmstadt, Germany). Calibration and accuracy verification standards were prepared using Agilent (Agilent Technologies, Santa Clara, CA) and Spex (SPEX CertiPrep, Metuchen, NJ) Calibration Standards. Method validation was achieved by analyzing the accuracy verification standards and a milk powder Certified Reference Material (CRM), NIST 1549a (NIST, Gaithersburg, MD).

Microwave sample digestion
Seven different powdered and liquid milk samples were purchased from a supermarket in California, USA and digested before analysis by MP-AES (refer to Table 4).

To prepare the milk samples for microwave digestion approximately 0.25 g of each powdered milk, 0.50 g of the powdered NIST 1549a CRM and 1 g of each fresh milk sample was accurately weighed and transferred to a 15 mL Teflon digestion vial. Before capping the vials, 6 mL of nitric acid and 1 mL of hydrochloric acid was added to each. A blank solution was also prepared, containing 6 mL of nitric acid and 1 mL of hydrochloric acid. Each milk sample and blank solution was prepared in triplicate in accordance with this procedure. Similarly, seven samples of the NIST 1549a CRM were prepared and digested in order to evaluate the accuracy of the analytical procedure.

At least two of the sample vials in each batch of 14 samples digested contained the NIST 1549a CRM. One blank solution was included in each batch.

Microwave digestion of the samples was carried out in accordance with the following procedure: The digestion chamber was initially pressurized to 40-45 mTorr with industrial grade nitrogen gas, before the temperature and pressure were gradually increased to 240 °C and 150 bar respectively over 20 minutes. These values were maintained for a further 15 minutes (the duration of the digestion) to ensure complete digestion.

Upon completion of the program each digested sample was diluted to a final volume of 10 mL with deionized water, before a further 10 times dilution with a solution of 2% nitric acid.

Elemental determination
The Agilent 4200 MP-AES has superior performance compared to FAAS in terms of detection limits, linear range, and sample throughput. The 4200 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The use of nitrogen improves safety by eliminating expensive, hazardous gases and also results in low operational costs. The nitrogen plasma reaches around 5,000 K and eliminates the chemical interferences that are common in FAAS, such as the formation of refractory $CaPO_4$. This means that the element-specific sample preparation often required in FAAS can be simplified to a single sample preparation for all elements. The more powerful excitation source also enables phosphorus determinations, which is not possible on FAAS.

The instrument features mass flow control of the nebulizer gas, and a torch loader mechanism which automatically connects all gases. Method parameters can be automatically optimized in the MP Expert software, which also features automatic background correction.

Method conditions for digested milk sample analysis in the 4200 series MP-AES are listed in Table 1.

Table 1. MP-AES 4200 operational conditions for Ca, K, Mg, Na, P determination in digested milk

Common Conditions	
Background Correction	Auto
Nebulizer	Micromist
Spray Chamber	Double pass glass cyclonic
Pump Speed	10 rpm
Read Time	2 s
Replicates	3
Stabilization Time	20 s
Viewing Position	0

Elemental Conditions		
Element	Wavelength (nm)	Nebulizer Flow (L/min)
Ca	422.673	0.4
K	766.491	0.8
Mg	285.213	0.4
Na	588.995	0.4
P	214.915	0.35
Y (Internal Standard)	371.029	0.4

Results and Discussion

Concentrations working range and method detection limit

Calibrations for all elements were between 5 and 100 ppm, and the correlation coefficient was greater than 0.999 for all wavelengths. Method detection limits (MDL) were calculated as 3 times the standard deviation of 10 consecutive blank readings (3σ). From the MDL, the method quantification limit (MQL) was calculated as 3.33 x MDL. The MDL and MQL are summarized in Table 2.

Table 2. Method Detection Limits (MDL) and Method Quantification Limits (MQL) in mg/L.

Element/ Wavelength (nm)	MDL	MQL(1)
Ca 422.673	0.002	0.007
K 766.491	0.067	0.223
Mg 285.213	0.002	0.007
Na 588.995	0.117	0.351
P 214.915	0.318	1.059

(1) Quantification limits in sample must take into account the different dilution factors applied in powdered milk or fresh milk.

Quality Control

Two strategies were adopted to validate the method:

1. Analysis of the NIST 1549a milk CRM in seven independent digestions, analyzed among unknown samples.

2. Analysis of Initial Calibration Blank and Initial Calibration Verification solutions (ICB & ICV) immediately after the method calibration, followed by Continuing Calibration Blank and Continuing Calibration Verification (CCB & CCV) solutions every 10 samples. The ICB/CCB and ICV/CCV analyses totalled four runs each.

The results from this analysis, shown in Table 3, highlight the ability of the MP-AES to reliably analyze digested milk samples with excellent accuracy, precision and minimal carryover between solutions.

Table 3. Summarized results and recoveries of NIST 1549a CRM, ICB/CCB and ICV/CCV samples.

	Ca	K	Mg	Na	P
CRM Reference Value (mg/kg)	8810 ± 240	11920 ± 430	892 ± 62	3176 ± 58	7600 ± 500
CRM Measured Conc. (n=7) ± SD (mg/kg)	9031 ± 195	11683 ± 566	928 ± 15	3373 ± 108	7360 ± 96
CRM Recovery (%)	102.5	98.0	104.1	106.2	96.8
ICB/CCB (n=4) Average ± SD (mg/kg)	0.020 ± 0.001	0.780 ± 0.155	0.004 ± 0.001	0.411 ± 0.212	< MDL
ICV/CCV (n=4) Recovery %	99.9	102.6	96.7	101.9	99.7

Table 4. Analysis results of powdered and fresh milk digested samples by Agilent 4200 MP-AES.

Samples	Ca mg/kg (RSD)	K mg/kg (RSD)	Mg mg/kg (RSD)	Na mg/kg (RSD)	P mg/kg (RSD)
Powdered Instant Nonfat Milk	11953 (4.5%)	15296 (3.6%)	1242 (4.4%)	4141 (3.5%)	9611 (1.0%)
Powdered Nonfat Milk	11058 (3.8%)	16057 (6.6%)	1176 (1.9%)	4167 (5.4%)	9223 (1.1%)
Powdered Organic Buttermilk	9659 (1.5%)	27253 (1.37%)	1116 (3.8%)	4069 (3.7%)	8489 (2.3%)
Powdered Sweet Cream Buttermilk	8287 (6.6%)	14421 (8.8%)	1053 (5.9%)	4784 (7.5%)	7920 (5.9%)
Powdered Whole Milk	8592 (3.1%)	15157 (3.1%)	1218 (1.0%)	3010 (3.3%)	7750 (0.9%)
Fresh Whole Milk	1150 (2.9%)	1687 (1.9%)	109 (0.9%)	407 (1.9%)	898 (0.8%)
Fresh Nonfat Milk	1182 (1.6%)	1726 (0.6%)	112 (1.3%)	412 (0.4%)	904 (0.6%)

Sample Analysis

To evaluate the performance of the method with real samples, digested powdered and fresh milk samples were also analyzed (shown in Table 4). These results demonstrate the ability of this method to analyze a diverse collection of real samples with good precision, easily covering the vast range of major element concentrations determined (e.g. from 1150 to 11953 mg/kg for Ca).

Conclusion

An accurate and robust method has been developed for the determination of major elements in digested milk samples on the 4200 MP-AES. The detection limits achieved were found to be well below those required for milk analysis, and excellent recoveries were obtained for the CRM (between 110—90%) and ICV/CCV (between 105—95%).

The 4200 MP-AES is the ideal instrument for those looking to move away from FAAS and extend their laboratory’s analytical capabilities. Recognized benefits of the MP-AES include reduced running costs, enhanced productivity through numerous ease-of-use features and simplified sample preparation, improved safety, and higher analytical performance such as better detection limits and greater linear dynamic range.

References

[1] Khan, N.; Jeong, I. S.; Hwang, I. M.; Kim, J. S.; Choi, S. H.; Nho, E. Y.; Choi, J. Y.; Park, K. S.; Kim, K. S; Analysis of minor and trace elements in milk and yogurts by inductively coupled plasma-mass spectrometry (ICP-MS), *Food Chemistry* 147 (2014) 220–224.

[2] US EPA Contract Laboratory Program, Statement of Works for Inorganics, Multi-Media, Multi-Concentration, Document Number ILMO 4.0.

Determination of major, minor and trace elements in rice flour using the 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Food testing

Authors

John Cauduro

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Introduction

The analysis of foodstuffs, such as rice, is of particular interest for nutrient elements present at high concentrations, and also for toxic elements such as cadmium that can be present at trace levels. The analysis is important to ensure product quality and safety, as well as determining product origin. Food scares related to contamination not only constitute a health risk but also undermine consumer confidence. This can lead to lost earnings through reduced sales and loss of credibility through adverse publicity.

Flame Atomic Absorption Spectroscopy (FAAS) is well established for the analysis of foods, but with lab budgets coming under increasing pressure and current market trends for lower cost of ownership, improved performance, ease of use, and safety, many FAAS users are looking to transition to another technique to expand their analytical capabilities.

Agilent has expanded its atomic spectroscopy portfolio to include the Microwave Plasma-Atomic Emission Spectrometer. The Agilent 4200 MP-AES is the second generation microwave plasma instrument that features an improved waveguide design that is capable of running samples with high total dissolved solids without compromising detection limits. The 4200 MP-AES significantly reduces running costs through the use of nitrogen as its plasma gas. The use of nitrogen also increases safety, by removal of flammable gases, and allows unattended operation of the instrument. The 4200 MP-AES is easy to use, and is able to achieve lower detection limits than a standard FAAS, as well as being able to determine additional elements such as phosphorus.

This application describes the analysis of rice flour for cadmium and other major, minor and trace elements on the 4200 MP-AES.

Experimental

Instrumentation

The innovative 4200 MP-AES features a second generation waveguide and torch, with mass flow controlled nebulizer gas flow. The 4200 MP-AES has a robust toroidal plasma with a central channel temperature of ~5,000 K which eliminates many of the chemical interferences that are present in FAAS and also expands the concentration working range of the 4200 MP-AES when compared the FAAS. This means that the element specific sample preparation that is commonplace when using FAAS is not necessary when using the 4200 MP-AES, improving ease of use and reducing cost. The 4200 MP-AES also achieves lower detection limits than FAAS, particularly for phosphorus, which enables the analysis of extra elements. By running on nitrogen, the 4200 MP-AES offers reduced operating costs and increased lab safety compared to flame AA, through the avoidance of flammable and costly gases such as acetylene, and nitrous oxide.

The analysis was carried out using a 4200 MP-AES equipped with the standard sample introduction setup consisting of the OneNeb nebulizer and a double pass spray chamber. An SPS 3 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended.

The MP-AES features continuous wavelength coverage which allows the analyst to select wavelengths that are appropriate for the expected concentration range, and free from spectral interferences. Method conditions for the selected wavelengths are shown in Table 1 and common method conditions are shown in Table 2.

Table 1. Agilent 4200 MP-AES operating parameters

Element	Wavelength	Read time (s)	Nebulizer Flow (L/min)
P	214.915 nm	2	0.55
Cd	228.802 nm	10	0.55
Mg	280.271 nm	1	0.55
Zn	213.857 nm	5	0.55
Mn	403.076 nm	3	0.55
K	766.491 nm	1	0.55
Cu	324.754 nm	2	0.75
Fe	438.354 nm	5	0.75
Ca	422.673 nm	1	1.00

Sample preparation

NIES CRM No.10c Rice Flour (NIES, Japan) was analyzed to validate the analytical method. The rice flour samples were digested using a Milestone Ethos microwave digestion system[1]. Samples were prepared in duplicate with approximately 0.5 g of rice flour CRM accurately weighed into separate TFM vessels. This was followed by the addition of 7 mL of HNO_3 and 1 mL of H_2O_2 and placed in the microwave digestion unit. The samples were digested using the preloaded digestion methods, allowed to cool, and then made up to 25 mL with deionized water. The final solution contained 2% total dissolved solids. No ionization suppressants or matrix modifiers were required for the analysis.

Calibration range

The calibration concentration range of the standard solutions are summarized in Table 3. As the working range of 4200 MP-AES far exceeds that of FAAS (by up to 20x in some instances), only one dilution of the sample is required to measure the complete set of elements. The calibration fit for all wavelengths used was linear.

Results and Discussion

Method detection limits (MDLs)

MDLs were determined from the analysis of 10 digested blank samples. The MDLs (3σ) for the selected analytical wavelengths are listed in Table 4.

Table 2. Common method conditions

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	30 seconds
Rinse time	60 seconds
Stabilization time	10 seconds
Fast Pump during Uptake and Rinse	On (80 rpm)
Nebulizer	OneNeb
Spray chamber	Double pass cyclonic
Autosampler	Agilent SPS 3
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Table 3. Working concentration range of the 4200 MP-AES standard solutions

Element	Wavelength	Concentration range	
P	214.915 nm	0–100	ppm
Cd	228.802 nm	0–1.0	ppm
Mg	280.271 nm	0–40	ppm
Zn	213.857 nm	0–4.0	ppm
Mn	403.076 nm	0–1.0	ppm
K	766.491 nm	0–100	ppm
Cu	324.754 nm	0–1.0	ppm
Fe	438.354 nm	0–1.0	ppm
Ca	422.673 nm	0–4.0	ppm

Table 4. Agilent 4200 MP-AES element wavelength and MDL (mg/kg in sample)

Element/ Wavelength (nm)	Ca 422.673	Cd 228.802	Cu 324.754	Fe 438.354	K 766.491	Mg 280.271	Mn 403.076	P 214.915	Zn 213.857
MDL (mg/kg)	0.10	0.16	0.05	0.44	3.0	0.06	0.05	13	0.15

Analysis of certified reference material

Results of the analysis of major, minor and trace elements in rice is listed in Table 5. The measured values (average result on two different 4200 MP-AES instruments carried out in duplicate) are in good agreement with the certified values for all CRM samples. The results demonstrate the capability of the 4200 MP-AES to achieve excellent results across a wide concentration range in a sample with 2% dissolved solids.

Long term stability

A digested rice flour sample was repeatedly analyzed under method conditions over 8 hours to test the long term stability of the method. The test was performed under controlled laboratory environmental conditions within the instrument operating specification, with a recalibration every 2 hours. The resulting stability plot is show in Figure 1. Excellent stability of < 3 % RSD for all elements was achieved, demonstrating the capability of the 4200 MP-AES, OneNeb nebulizer and mass flow controlled nebulizer gas flow to handle 2% total dissolved solids.

Table 5. Results of NIES No.10c Rice Flour. All results in mg/kg in the solid sample.

Element/ Wavelength (nm)	Ca 422.673	Cd 228.802	Cu 324.754	Fe 438.354	K 766.491	Mg 280.271	Mn 403.076	P 214.915	Zn 213.857
Mean	96.0	1.96	4.13	11.50	2700	1174	37.35	3139	22.02
SD	2.5	0.11	0.29	1.03	105	23	1.04	92	0.48
Certified value	95	1.82	4.1	11.4	2750	1250	40.1	3350	23.1
2SD certified	2	0.06	0.3	0.8	100	80	2.0	80	0.9
% difference	101.0	107.7	100.8	100.9	98.2	93.9	93.1	93.7	95.3

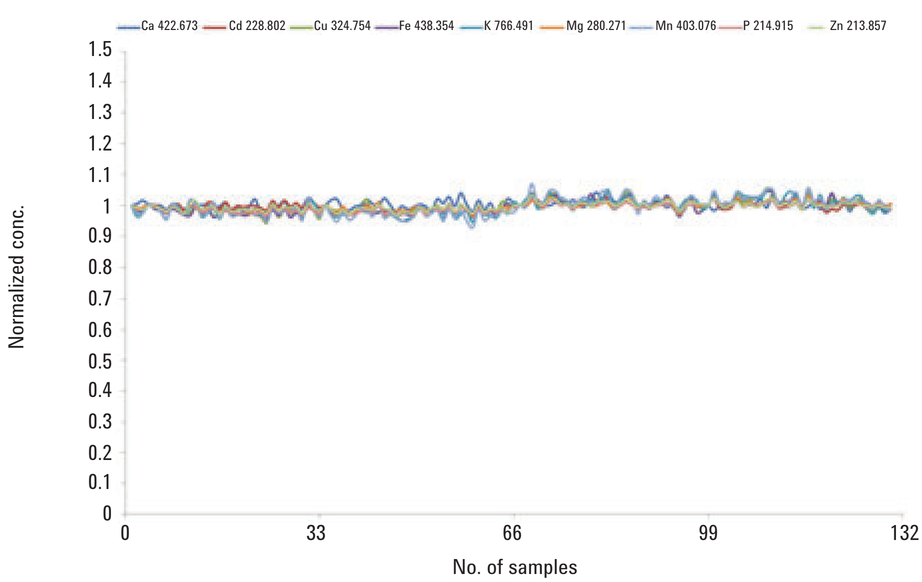

Figure 1. Normalized concentration of elements in a rice flour digest analyzed over an 8 hour time period, with recalibration every 2 hours.

Conclusion

A method for the determination of major, minor and trace elements in rice flour has been described. The next generation 4200 MP-AES achieved recoveries in a rice CRM of +/- 10 % of the assigned value, with MDLs sufficient for the analysis and excellent long term stability.

The excellent analytical performance, including phosphorus which is not practical by FAAS, multi-element unattended operation, improved safety and ease of use make the 4200 MP-AES the ideal alternative for FAAS users looking to transition to a new technique. Furthermore, the sample preparation process can be simplified, with no modifiers or ionization suppressants required due to the higher temperature excitation source of the MP-AES.

Reference

1. Milestone Application Note. Food/Feed. Rice Flour. ID HPR-FO-39. Milestone Ethos with internal temperature sensor, HPR1000/10S high pressure segmented rotor.

Determination of major elements in fruit juices using the Agilent 4200 MP-AES with the Agilent 4107 Nitrogen Generator

Application note

Food testing

Authors

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Introduction

Major elements such as calcium, magnesium, sodium and potassium are essential nutrients in food and the routine monitoring of the levels of these elements in fruit juices is a common quality control process. Flame Atomic Absorption Spectroscopy (FAAS) is well suited to this application as it delivers the performance required for the analysis at a reasonable price. However, with the introduction of the Agilent Microwave Plasma-Atomic Emission Spectrometer (MP-AES), several of the analytical challenges of using FAAS for this application have been overcome, making it the ideal instrument for laboratories looking to transition away from FAAS to a more powerful and safer technique.

The 4200 MP-AES main operating gas, nitrogen, is supplied from an Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). This greatly reduces the running costs and eliminates the safety concerns associated with specialty gases required by FAAS such as acetylene and nitrous oxide. The nitrogen-based plasma source of the 4200 MP-AES operates at a higher temperature than the flame source of a FAAS, avoiding the chemical interferences present in FAAS (especially for elements such as Ca). This eliminates the time consuming, element specific sample preparation and burner head changeover that is required when analyzing Ca, Na, K and Mg in the same sample by FAAS. The analysis of this application by MP-AES also removes the need for costly and time consuming modifiers and ionization suppressants. The plasma source in the MP-AES also leads to improved performance with respect to detection limits and linear dynamic range when compared to FAAS, which is important in an analysis where the elements can be present over a wide range of concentrations. With no flammable gases required, the MP-AES is able to operate unattended which increases sample throughput.

This application note describes the analysis of fruit juice samples using an Agilent 4200 MP-AES running with an Agilent 4107 Nitrogen Generator.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES, with nitrogen supplied from an Agilent 4107 Nitrogen Generator. The sample introduction system consisted of a double pass spray chamber and OneNeb nebulizer.

The instrument was controlled by the powerful and easy-to-use MP Expert software. The MP-AES features continuous wavelength coverage and MP Expert features an extensive wavelength database that allows the selection of wavelengths that are appropriate for the concentration range required for the analysis. For instance, in this application, the less sensitive Mg 518.360 nm line was preferred over the more sensitive Mg 285.213 line.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Value			
Element	Ca	Mg	Na	K
Wavelength	422.673	518.360	589.592	769.897
Nebulizer	OneNeb			
Nebulizer flow rate	Default (0.75 L/min)			
Spray chamber	Double pass glass cyclonic			
Pump rate	15 rpm			
Sample pump tubing	Orange/green			
Waste pump tubing	Blue/blue			
Autosampler	Agilent SPS 3			
Read time	1 second			
Number of replicates	3			
Fast pump during uptake	On			
Sample uptake delay	30 seconds			
Rinse time	40 seconds			
Stabilization time	20 seconds			
Background correction	Auto			
Gas source	Agilent 4107 Nitrogen Generator			

Standard and sample preparation

Two quality control (QC) test materials were analyzed to validate the method:

- Apple Juice T1650QC (certified by FAPAS*)
- Grapefruit Juice T0842QC (certified by FAPAS*)

*FAPAS – The Food and Environmental Research Agency, York, UK.

Materials were purchased from Graham B Jackson (Aust) P/L.

Additionally, a commercially available apple juice was analyzed in the long term stability studies.

All fruit juice samples were diluted 20x with 5% HNO_3 (ACS Grade, Merck). No other modifiers or ionization suppressants were required.

Standards were prepared from a 10,000 mg/L multi element standard (Inorganic Ventures). All calibration blanks and standards were prepared in 5% HNO_3.

Results

Working range

The working concentration range of the standard solutions are summarized in Table 2. As the working range of MP-AES far exceeds that of FAAS (by up to 20 times in some instances), only one dilution of the sample is required to measure the complete set of elements.

Table 2. Working concentration range of the 4200 MP-AES standard solutions

Element	4200 MP-AES concentration range (mg/L)	Correlation coefficient
Ca 422.673	0–20	0.99990
Mg 518.360	0–100	0.99988
Na 589.592	0–20	0.99996
K 769.897	0–100	0.99968

Recoveries

Table 3 shows the concentration and recovery results of the four elements in the two fruit juices. The recovery results for Ca, Mg, Na, K in the fruit juices using this method were within +/- 10% of the assigned value. All results measured in this study were within the certified ranges of the two quality control test materials.

Table 3. Recovery results of 4 elements in the fruit juices using the 4200 MP-AES with the nitrogen generator

Apple Juice T0840QC	Certified value (mg/L)		Found (mg/L)	% Recovery
	Assigned value	Range		
Magnesium	49.0	40.3–57.8	49.9 ± 0.6	102
Sodium	21.2	16.9–25.4	22.2 ± 0.5	105
Potassium	1044	926–1161	1039 ± 29.7	100

Grapefruit Juice T0842QC	Certified value (mg/L)		Found (mg/L)	% Recovery
	Assigned value	Range		
Calcium	145.6	123.6–167.6	158.3 ± 3.2	109
Magnesium	92.5	77.5–107.4	91.1 ± 0.6	99
Potassium	1102	979–1225	1100 ± 14.7	100

Long term stability

A commercial apple juice solution (diluted 20x with 5% HNO_3) was repeatedly analyzed over a period of 6 hours. The resulting stability plot is shown in Figure 1. All elements have an RSD of less than 4% over 6 hours. With the OneNeb nebulizer and mass flow controlled nebulizer gas flow, excellent stability results were obtained for a sample with a complex high sugar matrix.

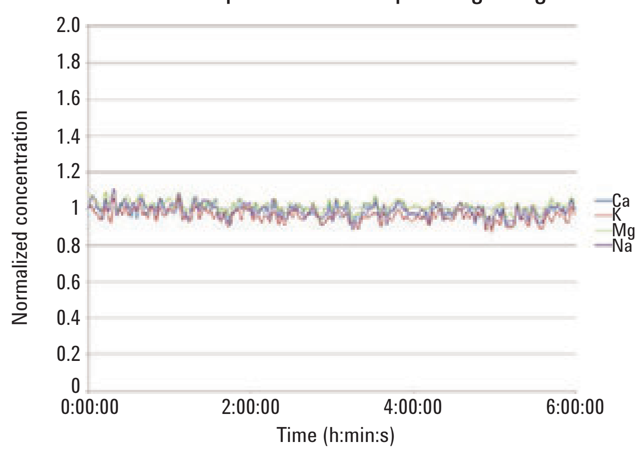
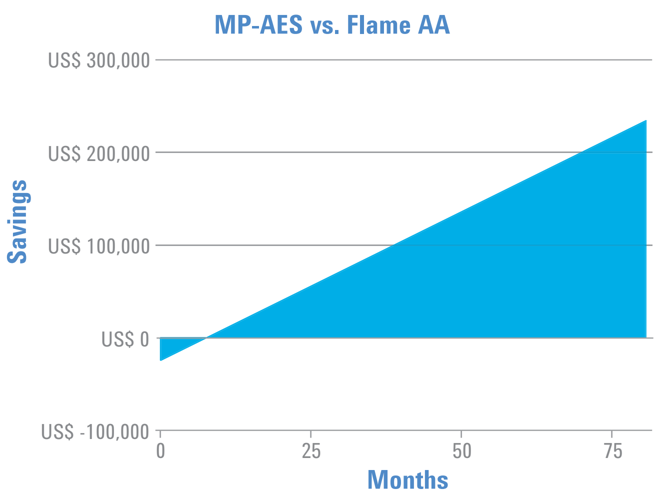


Figure 1. Normalized concentration of potassium in an apple juice sample over 6 hours

Cost savings with the 4200 MP-AES

The potential cost saving of using the 4200 MP-AES for this application was estimated by comparing an FAAS purchased with an air compressor and 1 year of consumables to an MP-AES purchased with air compressor, nitrogen generator, SPS 3, and 1 year of consumables. The analysis requirements were assumed to be 500 samples per week and 4 elements per sample. The calculation assumes that the FAAS is run without an autosampler and that 3 elements are analyzed with air/acetylene and 1 element with nitrous oxide/acetylene. In this example the results show an estimated cost saving of greater than US $220,000 over a 7 year evaluation period[1]. A global average gas cost was used in this calculation and results will vary from country to country.



[1]This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements. For this calculation operator labor costs were set to USD $25/hour and electricity costs were set to USD $0.18 per kW.

Conclusion

A simple and rapid method using MP-AES has been developed to analyze Ca, Mg, Na and K in fruit juice. The recoveries obtained from the analysis of the two QC test materials were within +/- 10% of the assigned values and within the certified concentration range. Using the standard sample introduction system supplied with the 4200 MP-AES, excellent long term stability was obtained over a 6 hour period.

The 4200 MP-AES is the ideal instrument for those customers who are looking to transition away from FAAS and extend their laboratory's analytical capabilities. Recognized benefits of MP-AES include reduced running costs, enhanced productivity through numerous ease-of-use features and simplified sample preparation, improved safety, and higher analytical performance such as better detection limits and greater linear dynamic range.

Analysis of aluminum in beverages using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Food Testing

Authors

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Abstract

Aluminum present in a beverages can affect the taste. This application note describes the determination of aluminum in beverages using an Agilent 4100 MP-AES. Beverages contain a variety of matrix constituents, including salt, sugar, and alcohol. A study was performed to determine how these matrix constituents affect aluminum measurements, and what could be done to reduce such effects. It was determined that sufficient analysis is possible so long as the matrix concentration and alcohol concentration are known to some extent.

Agilent Technologies

Introduction

At present, absorption spectrophotometry, atomic absorption spectrophotometry and inductively coupled plasma-atomic emission spectroscopy have been adopted for performing elemental analyses of food. Aluminum content in food and beverages is restricted by municipal water supply quality standards to a maximum of 0.2 mg/L on the basis of the Japanese Waterworks Law. When flame atomic absorption spectroscopy (FAAS) is utilized, low sensitivity for aluminum and high matrix constituents in the beverage can cause problems with burners getting clogged. This study was conducted to see if an MP-AES, instead of an FAAS, could be used for beverage analysis.

Experimental

Instrumentation

The measurements were performed on an Agilent 4100 MP-AES. The 4100 MP-AES is a compact bench-top spectrometer that generates a robust, magnetically-excited nitrogen plasma.

A 2.45-GHz air-cooled magnetron is used to generate a magnetic field around a torch. The skin effect of that magnetic field causes plasma to form in the shape of a donut, just as with inductively coupled plasma, and it becomes possible to introduce liquid samples at a steady rate (see Figure 1). The nitrogen used to generate the plasma can be supplied via a simple air compressor and the Agilent 4107 Nitrogen Generator.

A clear advantage of in-house gas generation is the reduced costs of operation and maintenance compared to conventional gas resupply.

The sample introduction system used for this application consisted of a standard torch, a single pass cyclonic spray chamber and a glass concentric nebulizer.

Table 1 lists the instrument operating conditions.

Table 1. Agilent 4100 MP-AES operating conditions

Parameter	Value
Microwave power	1.0 kW
Pump speed	15 rpm
Integration time	3 seconds

Standard and Sample Preparation

Samples included:

- Barley tea
- Green tea
- Black tea
- Coffee
- Cola
- Sports drink
- Beer
- Shochu highball

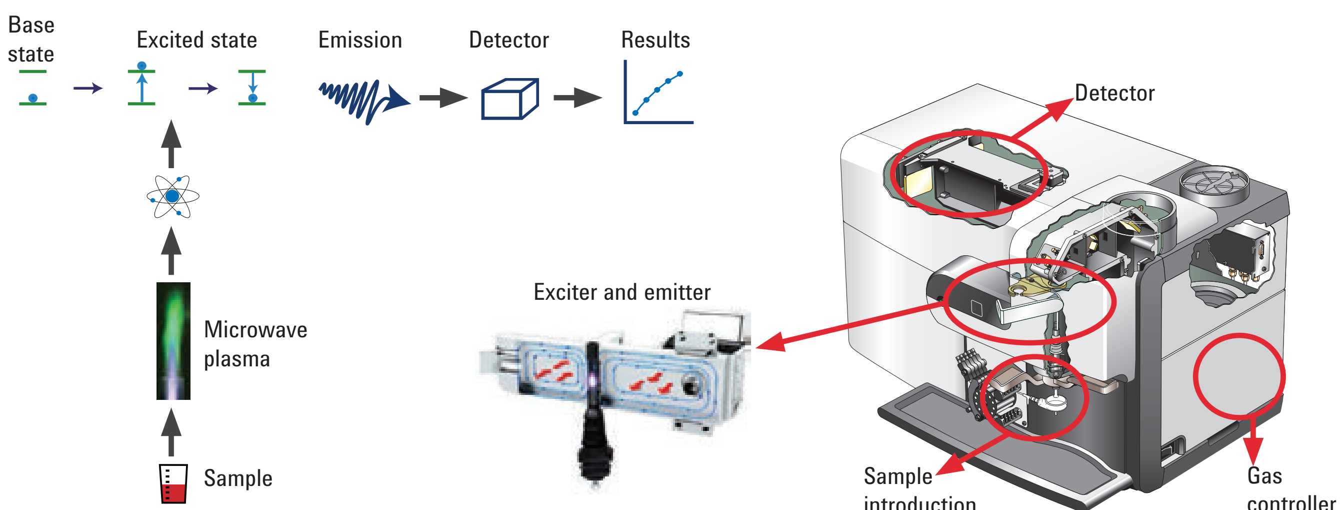

Figure 1. Schematic and basic principles behind the Agilent 4100 MP-AES

Results

Quantitative lower limits and stability

The quantitative lower limits and stability in aqueous solutions and in ethanol were measured. A 0.1% nitric acid solution and ethanol diluted at 0.2 mg/L was prepared using standard solutions.The quantitative lower limit was assumed to be a concentration ten times the standard deviation (σ) obtained from repeatedly measuring the blank ten times. The stability was calculated by repeatedly measuring each of the 0.2 mg/L solution ten times (see Table 2).

Table 2. Method detection limits (MDL) by MP-AES

Aluminum	Limit of quantification (µg/L)	Stability at 0.2 mg/L (%RSD)
Aqueous solution	1.9	1.4
Ethanol (100%)	7.9	0.7

The results for limit of quantification and stability confirm that microwave plasma atomic emission spectroscopy is sufficiently applicable for the analysis of aluminum in beverages.

The effects of sugar

With the emission intensity of aluminum at 0.2 mg/L with a sugar concentration of 0 g/100 mL given a value of 1, the effects of varying the sugar concentration between 0 and 50 g/100 mL were measured. The sugar concentrations of the samples were: approx. 2–5 g/100 mL for black tea (with sugar), and 11 g/100 mL for cola (see Figure 2).

The measurements show that sugar concentrations up to approximately 10 g/100 mL do not have a significant effect. Additional standards and matrix matching are needed for concentrations above 10 g/100 mL. The samples examined had a sugar concentration of about 11 g/100 mL, so the analysis was performed using the absolute calibration method.

The effects of ethanol

An additional study was conducted to see if the 4100 MP-AES could be used to determine aluminum content in alcoholic beverages sold in aluminum cans. Subjecting alcohol to plasma produced a relatively large amount of carbon in relation to the concentration of alcohol. Carbon can cause the torch injector to become blocked. To prevent this, air was mixed with the support gas before subjecting it to the plasma.

With the emission intensity of aluminum in a 0.2 mg/L solution set to 1, the effects of varying the ethanol content from 0 to 10% in the solution were examined (see Figure 3).

There were no significant variations either with or without air at ethanol concentrations of about 5%, but emission intensity declined at concentrations above 5% with no air added. Beer is approximately 5% alcohol, while some shochu highballs are higher, at about 8%. For that reason, the sample analysis was performed with air added.

Aluminum was added to each sample, and the results of the recovery tests are given in Table 3.

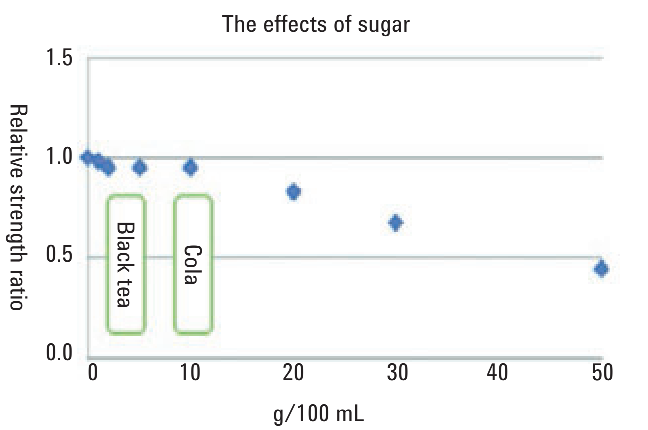

Figure 2. Variation in emission intensity due to differences in sugar concentration

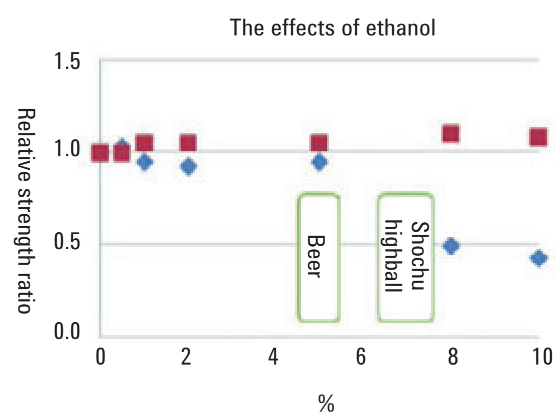

Figure 3. Variation in emission intensity due to differences in ethanol concentration, with and without adding air.
Red squares = with air, blue diamonds = without air

Table 3. Aluminum addition recovery tests

Al	Unspiked (mg/L)	0.2 mg/L added (mg/L)	Recovery rate (%)
Barley tea	0.00	0.22	110
Coffee	0.01	0.23	109
Sports drink	0.01	0.22	105
Cola	0.05	0.24	96
Beer	0.04	0.23	96
Shochu highball	0.01	0.22	105
Al	**Unspiked (mg/L)**	**1.0 mg/L added (mg/L)**	**Recovery rate (%)**
Green tea	1.14	2.12	99
Black tea	2.45	3.38	98

Conclusion

This study has shown that the limit of quantification for aluminum is 1.9 µg/L in aqueous solutions and 7.9 µg/L in ethanol, which adequately meets municipal water supply quality standards as stated in the Japanese Waterworks Law. Favorable results with regard to stability were also obtained. The results of the examination for the effects of beverage matrices (sugar and alcohol) showed that direct measurements without matrix matching can be done for concentrations of about 10 g/100 mL of sugar in beverages, and that the Agilent 4100 MP-AES can also easily and rapidly analyze samples with differing alcohol concentrations if air is mixed in. Thus, it has been demonstrated that the MP-AES has low running costs, is easy to operate, and can perform analyses of aluminum in beverages.

Cost-effective analysis of major, minor and trace elements in foodstuffs using the 4100 MP-AES

Application note

Foods and beverages

Author

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Introduction

Whether the goal is food safety, ensuring quality or establishing provenance, measuring the trace element content of foods and beverages that we all consume is of paramount importance. While some elements are essential for our well being at low concentrations, others like lead and chromium are highly toxic and more still are being linked to viral, neurological and other diseases. Food scares related to contamination or poor quality not only constitute a health risk, they also undermine consumer confidence. This can lead to lost earnings through reduced sales and loss of credibility through adverse publicity.

Atomic spectroscopy is well established for the analysis of metals in foods and the technique employed often depends on the requirements of the application in terms of elements of interest, expected concentrations, and number and type of samples. Other important procurement factors that influence instrument selection include purchase and operational budget for consumables, gases, power and labor, as well as service and maintenance costs.

Agilent Technologies

With lab budgets coming under increasing pressure, Agilent has expanded its atomic spectroscopy portfolio to include the 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). MP-AES is a new analytical technique that uses a microwave-induced nitrogen plasma to provide elemental analysis, with significantly reduced running costs through the use of nitrogen as its plasma gas.

Experimental

This work describes the analysis of various certified and standard reference materials per the sample descriptions below:

- NIES CRM No.7 Tea Leaves: from National Institute of Environmental Studies (NIES), Japan.
- NIES CRM No.10c Rice Flour: from National Institute of Environmental Studies (NIES), Japan.
- NIST SRM 1577 Bovine Liver: from National Institute of Standards and Testing, USA.
- CRM-Wheat Flour: from High Purity Standards, USA
- CRM-Milk Powder: from High Purity Standards, USA
- CRM-Oyster Tissue: from High Purity Standards, USA

Sample preparation

A simple acid digestion method was used to prepare three of the samples. Initially, 0.25 g of the tea leaves CRM, 0.5 g of bovine liver SRM and 1 g of rice flour CRM were weighed into separate 250 mL beakers. This was then followed by the addition of 10 mL of HNO_3 and each beaker was covered with a watch glass. The samples were heated on a hot plate until completely dissolved. After cooling to room temperature, each digest was transferred to a 100 mL volumetric flask and made up to the required volume by adding Milli-Q water.

Pre-prepared sample solutions of CRM-Wheat Flour, CRM-Milk Powder and CRM-Oyster Tissue in 4% HNO_3 were purchased from High Purity Standards, USA.

Working standards and a blank were matrix-matched with the samples.

Instrumentation

The innovative 4100 MP-AES with its proprietary Microwave Excitation Assembly is a sequential atomic emission spectroscopic technique capable of fast, unattended multi-element analysis at varying concentration levels using a nitrogen plasma. The unique Microwave Excitation Assembly focuses and contains the microwave energy that is created via a concentrated axial magnetic field around the torch. This creates a robust toroidal plasma that allows the stable introduction of liquid samples. With a central channel temperature of ~5,000 K, MP-AES is highly suited to spectroscopic analysis, as it creates high intensity atomization emission lines. In addition to simplified spectra, nitrogen-MP-AES offers reduced operating costs and increased lab safety compared to flame AA, through the avoidance of costly and highly flammable gases such as acetylene.

The analysis was carried out using an Agilent 4100 MP-AES equipped with a standard MP-AES torch, concentric nebulizer, and glass cyclonic spray chamber.

Operating parameters are shown in Table 1.

Table 1. Agilent 4100 MP-AES operating parameters

Instrument parameter	Setting
Nebulizer pressure	160–180 kPa
Read time	3 s (10 s for MDL)
Number of replicates	3 (10 for MDL)
Stabilization time	15 s
Background correction	Auto

Results

Method detection limits

The Method Detection Limits were determined from the analysis of digested blank samples. The selected analytical wavelengths and method detection limits (3σ) are listed in Table 2.

Table 2. Agilent 4100 MP-AES element wavelength and method detection limits (ppb)

Element	Wavelength (nm)	MDL (ppb)
Al	396.152	0.5
Ba	455.403	0.02
Ca	445.478	14
Cd	228.802	1.2
Co	340.511	4
Cr	425.433	0.5
Cu	327.396	0.4
Fe	371.993	3
K	769.897	3
K	404.414	280
P	213.618	100
Pb	405.781	5
Pb	368.343	12
Mg	518.361	4
Mn	403.076	0.5
Mo	379.825	1.5
Na	589.592	3
Na	568.821	140
Ni	341.476	2
Ni	352.453	2
Sr	407.771	0.01
Zn	213.857	4

Analysis of foodstuffs

Results of the analysis of major, minor and trace extractable elements in six different foodstuffs are listed in Tables 3 to 8. The measured values (carried out in triplicate) are in good agreement with the certified values for all CRM and SRM samples.

Table 3. Results of NIES No.7 Tea Leaves

Element	Measured values	Certified values
	wt%	**wt%**
Ca	0.314 ± 0.013	0.320 ± 0.012
Mg	0.150 ± 0.004	0.153 ± 0.006
K	1.861 ± 0.074	1.86 ± 0.07
	mg/kg	**mg/kg**
Ba	5.76 ± 0.57	5.7*
Cd	nd	0.03 ± 0.03
Co	nd	0.12*
Cr	nd	0.15*
Cu	7.13 ± 0.81	7 ± 0.3
Pb	nd	0.8 ± 0.03
Ni	6.03 ± 0.63	6.5 ± 0.3
Sr	3.63 ± 0.43	3.7*
Zn	34 ± 3	33 ± 3

* Reference values only

Table 4. Results of NIES No.10c Rice Flour

Element	Measured values	Certified values
	wt%	**wt%**
Mg	0.127 ± 0.006	0.125 ± 0.008
K	0.279 ± 0.012	0.275 ± 0.010
P	0.300 ± 0.010	0.335 ± 0.008
	mg/kg	**mg/kg**
Al	1.49 ± 0.13	1.5*
Ca	95.4 ± 7.0	95 ± 2
Cd	1.83 ± 0.14	1.82 ± 0.06
Co	nd	0.007*
Cr	nd	0.08*
Cu	4.03 ± 0.32	4.1 ± 0.3
Fe	10..6 ± 0.15	11.4 ± 0.8
Mo	nd	1.6 ± 0.1
Ni	nd	0.30 ± 0.03
Sr	0.2	0.2*
Zn	21.8 ± 1.0	23.1 ± 0.8

* Reference values only

Table 5. Results of NIST 1577 Bovine Liver

Element	Measured values	Certified values
	wt%	**wt%**
Na	0.247 ± 0.006	0.243 ± 0.013
K	1.00 ± 0.08	0.97 ± 0.06
	mg/kg	**mg/kg**
Ca	131	123*
Cd	nd	0.27 ± 0.04
Co	nd	0.18*
Cu	185 ± 6	193 ± 10
Fe	266 ± 5	270 ± 20
Pb	nd	0.34 ± 0.08
Mg	625 ± 45	605*
Mn	10.4 ± 1.41	10.3 ± 1
Mo	nd	3.2*
Sr	0.15 ± 0.07	0.14*
Zn	125 ± 4	130 ± 10

* Reference values only

Table 6. Results of CRM-Wheat Flour

Element	Measured values (mg/kg)	Certified values (mg/kg)
Al	0.83 ± 0.02	0.85 ± 0.01
Ca	9.64 ± 0.97	9.5 ± 0.1
Cd	nd	0.0015*
Co	nd	0.001*
Cr	0.013 ± 0.001	0.014*
Cu	0.09 ± 0.008	0.1 ± 0.002
Fe	0.81 ± 0.04	0.90 ± 0.01
K	62.5 ± 0.5	65 ± 0.7
P	61.1 ± 1.7	65 ± 0.7
Pb	0.05 ± 0.001	0.050 ± 0.003
Mg	20.8 ± 0.1	20.0 ± 0.2
Mn	0.36 ± 0.02	0.4 ± 0.008
Ni	nd	0.009 ± 0.001
Zn	0.47 ± 0.05	0.50 ± 0.01

* Reference values only

Table 7. Results of CRM-Milk Powder

Element	Measured values (mg/kg)	Certified values (mg/kg)
Al	nd	0.020 ± 0.002
Ca	131 ± 9	130 ± 1
Co	nd	0.0004*
Cr	nd	0.0003*
Cu	0.006 ± 0.001	0.007 ± 0.001
Fe	0.018 ± 0.002	0.020 ± 0.001
K	178 ± 6	170 ± 2
P	98.7 ± 1.3	100 ± 1
Pb	nd	0.002*
Mg	11.9 ± 0.2	12 ± 0.1
Mn	0.003 ± 0.002	0.003*
Na	48.7 ± 2.6	50 ± 1
Zn	0.48 ± 0.05	0.50 ± 0.01

* Reference values only

Table 8. Results of CRM-Oyster Tissue

Element	Measured values (mg/kg)	Certified values (mg/kg)
Al	2.92 ± 0.07	3*
Ca	15.0 ± 0.49	15*
Cd	nd	0.03*
Co	nd	0.004*
Cr	nd	0.007*
Cu	0.56 ± 0.05	0.6*
K	100 ± 0.96	100*
P	79.1 ± 0.9	80*
Pb	nd	0.005*
Mg	12.1 ± 0.2	12*
Mn	0.18 ± 0.01	0.2*
Na	48.9 ± 0.8	50*
Ni	nd	0.01*
Zn	8.3 ± 0.4	9*

* Reference values only

Conclusions

MP-AES offers any food testing facilities dependant on acetylene-based instrumentation a real alternative in terms of sensitivity, multi-element capability and speed of analysis, while cutting operating costs and improving the safety of the lab environment through the use of non-flammable nitrogen.

This study shows that following a quick and simple acid digestion sample preparation procedure (required for three of the six diverse food samples), all six certified and standard reference materials can be analyzed for trace and major element concentrations with good accuracy by MP-AES. The addition of the Agilent 4107 Nitrogen Generator is also possible in order to perform this analysis with significantly lower gas costs or for analysis in remote locations where sourcing of gases is costly or difficult.

Total metals analysis of digested plant tissue using an Agilent 4200 Microwave Plasma-AES

Application note

Agriculture

Authors

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Introduction

Plant growth and development largely depends on the composition and concentration of mineral nutrients available in the plant leaves and other tissues. These essential nutrients are divided into macronutrients (required in larger quantities because of their structural roles in the plant) and micronutrients (required in smaller quantities because they tend to be involved in regulatory roles in the plant). A deficiency or enrichment of nutrients may result in decreased plant productivity, crop yield or plant quality.

Analysis of the total metal content in plants is often carried out by Flame Atomic Absorption Spectrometry (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). More recently, agricultural testing labs looking to upgrade or replace their FAAS with a more powerful technique are looking to Microwave Plasma–Atomic Emission Spectrometry (MP-AES) with its many advantages. MP-AES is a multi-element technique that offers better detection limits over a wider working analytical range than FAAS and more elements are available for analysis by MP-AES, including

Agilent Technologies

phosphorus, an expensive and widely used major nutrient in soil fertilization.

For laboratories that have difficulty in sourcing gases, are looking to reduce operating costs or are under pressure to improve safety by removing flammable gases, the MP-AES is ideal as it uses nitrogen gas, that can be generated from air.

This application note describes the sample preparation procedure and analytical method used to determine Cu, Fe, Mn, Zn, Na, K, Ca, Mg, B and P in a plant reference material using the Agilent 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES with nitrogen plasma gas supplied via an Agilent 4107 Nitrogen Generator. The generator alleviates the need and expense of sourcing analytical grade gases. The sample introduction system comprised a double-pass cyclonic spray chamber and the OneNeb nebulizer.

An Agilent SPS 3 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended. The instrument operated in a fast sequential mode and featured a Peltier-cooled CCD detector. Background and spectral interferences could be simutaneously corrected easily and accurately using Agilent's MP Expert software. Method parameters are given in Table 1.

Table 1. MP-AES method parameters

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	35 seconds
Rinse time	30 seconds
Stabilization time	15 seconds
Fast Pump during uptake and rinse	On (80 rpm)
Autosampler	Agilent SPS 3
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Samples

Botanical reference material (RM) ASPAC 80 Pasture was obtained from the Australasian Soil and Plant Analysis Council (ASPAC, Carapook, VIC, Australia).

Sample preparation

Microwave digestion was used to prepare the ASPAC 80 RM for total metals analysis of Cu, Fe, Mn, Zn, Na, K, Ca, Mg, B and P by MP-AES. 7 mL of HNO_3 and 1 mL H_2O_2 was added to 0.18 g of the sample. A preloaded method for the MARS (CEM, Corporation, USA) microwave was used to digest the sample. Once cooled, the solution was diluted to 50 mL using ultrapure water. No further sample preparation was required and no modifiers or ionization buffers were added.

Wavelength selection and calibration range

Details of wavelength selection and calibration range are given in Table 2. Continuous wavelength coverage allows lines to be chosen that have appropriate sensitivity for the concentration range, and avoid spectral interferences.

Table 2. Wavelength and working calibration concentration range

Element and wavelength (nm)	Calibration range (ppm)
Cu 324.754	1–5
Fe 259.940	5–25
Mn 257.610	5–25
Zn 213.857	1–5
Na 568.820	2–100
K 766.491	1–100
Ca 445.478	20–100
Mg 383.829	1–100
B 249.772	0.25–1.0
P 213.618	10–80

Results and discussion

Calibration

A typical calibration curve for phosphorus is displayed in Figure 1. The curve shows excellent linearity across the concentration range. The large linear dynamic range means that less sample dilutions are needed which improves productivity and reduces the risk of sample contamination.

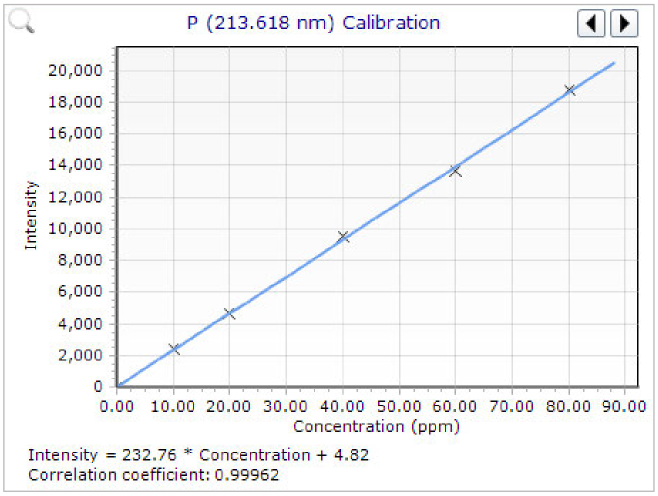

Figure 1. Calibration curve for phosphorus

Sample analysis

The plant RM sample was analyzed for all elements in a single measurement. The quality of the MP-AES results was evaluated by comparing them with the reference values for ASPAC 80. Table 3 shows good accuracy was achieved for all elements over a wide concentration range. The ability of the MP-AES to determine all elements in a single sample measurement greatly simplifies the workflow when compared to an FAAS, and eliminates the need for lamp changes, measurements in absorption and emission, and in the case of B and P, analysis of the samples by other techniques.

Table 3. MP-AES results for total metals content of plant reference material ASPAC 80.

Element	Wavelength nm	Measured value µg/g	Reference value µg/g	Accuracy %
Cu	324.754	13.6	14.7 ± 1.2	93
Fe	259.940	316.13	324 ± 32	98
Mn	257.610	125.8	138 ± 10	91
Zn	213.857	54.6	58.1 ± 5.3	94
Na	568.263	2512	2460 ± 210	102
K	766.491	27302	26700 ± 1850	102
Ca	445.478	10563	11100 ± 600	95
Mg	383.829	3239	3350 ± 220	97
B	249.772	21.65	23.7 ± 3.4	91
P	213.618	3223.35	2970 ± 250	109

Conclusions

The study shows the effectiveness of the Agilent 4200 MP-AES for the analysis of total metal content of a plant-based reference material following microwave digestion. Elements that are difficult to analyze by FAAS such as B and P were included, with all data acquired in a single run. Accurate determinations over a wide concentration range were obtained showing the suitability of MP-AES for the application. When compared to an FAAS, the workflow on the MP-AES is also simplified by eliminating the need for multiple sample preparations, lamp changes and measurements in absorption and emission modes.

Current trends in the market for lower detection limits, lower cost of analysis, improved ease of use and improved safety, are all met by the Agilent 4200 MP-AES. The instrument uses nitrogen, eliminating expensive and hazardous gases such as acetylene, increasing safety, and allowing for unattended operation of the instrument, even in remote locations. When the N_2 is supplied using the Agilent 4107 Nitrogen Generator that extracts N_2 from air, running costs are greatly reduced compared to an FAAS or ICP-OES that rely on a constant supply of analytical grade gases.

With greater sensitivity, linear dynamic range, and sample throughput compared to FAAS, the Agilent 4200 MP-AES is the ideal replacement for labs looking to extend their analytical capabilities.

Determination of exchangeable cations in soil extracts using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer

Application note

Agriculture

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Introduction

Accurate, routine testing of nutrients in soil samples is critical to understanding its potential fertility. Many of the nutrients that are vital to plants are exchangeable cations. These are ions loosely attached to and/or adsorbed onto clay particles and organic matter in soil that may become available to plants. Determination of these cations is of great interest for agronomic diagnostic and soil sustainability, enabling more accurate assessment and management of nutrient requirements [1, 2]. If the results indicate there is a nutrient imbalance, then this can be corrected for by the application of a suitably formulated fertilizer.

This application note describes an analytical method for the determination of Ca, K, Mg, Mn and Na in soils using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). A chemical extraction with 1 M ammonium acetate is recommended (standard NF X 31-108) [1, 2, 3]. In this work, results obtained with MP-AES are compared to those obtained by other well-proven, validated techniques flame atomic absorption spectrometry (FAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES), and with inter-laboratory results to demonstrate the reliability and accuracy of MP-AES data.

Which measurement technique is right for you?

There are many factors to be taken into account when selecting the right analytical technique. In many cases several techniques will provide adequate detection range, so the technique of choice will depend on factors such as sample throughput requirements, ease-of-use, infrastructure required, and on-going operating costs. In the case of this application, it has been more common for smaller laboratories with low sample throughput requirements to use FAAS, while some larger laboratories (with higher sample throughput requirements) may use ICP-OES.

The 4100 MP-AES fits between FAAS and ICP-OES in many aspects such as detection power, dynamic range, and speed of analysis. For these key performance metrics, the MP-AES offers a unique alternative to both FAAS and ICP-OES.

There are also some clear differentiating benefits of the MP-AES technology over these more traditional options. By eliminating the need for on-going gas resupply, the MP-AES offers significantly reduced on-going operating costs over both FAAS and ICP-OES — and avoids flammable gases (required for FAAS), hence enhancing safety and allowing unattended, overnight operation. The reduced infrastructure required for MP-AES also makes it well-suited to remote sites where supply of gases can be difficult and/or expensive. These features make the MP-AES an attractive technique for many small to medium size agricultural laboratories, particularly those at remote locations, and for an increasing number of laboratories requiring the lowest possible on-going operating costs.

Experimental

Instrumentation

The 4100 MP-AES revolutionizes the way analysts conduct multi-elemental analysis. Using a microwave plasma that is based on nitrogen, supplied from a compressed air supply and the Agilent 4107 Nitrogen Generator, the 4100 MP-AES does not require flammable or expensive gases such as acetylene, nitrous oxide or argon. This improves lab safety, results in a significant reduction in operating costs and allows installation in mobile labs or remote locations where gas supplies may not be available.

Additionally, the 4100 MP-AES has been designed to improve the analytical performance and productivity when compared with FAAS, with good sensitivity and detection limits down to sub ppb levels over a wide linear range.

Instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	OneNeb
Spray chamber	Glass cyclonic single-pass
Sample tubing	White-white
CsCl tubing	Orange-yellow
Waste tubing	Blue-blue
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Fast pump during sample uptake	Yes
Pump speed	15 rpm

The analysis of soil samples was also carried out by ICP-OES and FAAS. Conditions of analysis are as described in Table 2.

Table 2. Global conditions of analysis

Instrument	Dilution	Comments
Agilent 4100 MP-AES	On-line with CsCl 1.5%	OneNeb nebulizer
Agilent 280 FS AAS	SIPS 20. Dilution factor set by element	CsCl as modifier for Na and K, La/CsCl as modifier for Mg
Agilent 725 ICP-OES	No dilution	OneNeb nebulizer

Material

Soil samples were provided (air-dried and sieved <2 mm) by the French inter-laboratory comparisons organization BIPEA (Inter-professional Bureau of Study and Analysis, France). All samples have been recently analyzed in proficiency testing, so that the reference values and standard deviations for CaO, K_2O, MgO and Na_2O concentrations in ammonium acetate were known. Note: manganese was not included in the testing scheme but has been included in this investigation.

The reference numbers of the soil samples used were 403, 418, 421 and 423.

Sample preparation

As described in the standard NF X 31-108, 1 M ammonium acetate adjusted to pH 7, was used as extractant. The total concentration of dissolved salt was 77 g/L.

For each soil, 50 mL of 1 M ammonium acetate was added to 2.5 g of soil. The mixture was shaken by rotation in a room at 20 °C ±2 °C over 1 hour. After extraction, the samples were filtered using a filter paper and the clear solutions were analyzed immediately.

Standard preparation

Four multi-element standard solutions were prepared in 1 M ammonium acetate. Table 3 provides details of the calibration concentration range for each analyte. Single element stock solutions from Merck Germany were used. Table 4 displays selected wavelengths and calibration parameters used for analysis.

Cesium chloride was used as an ionization buffer. This was added on-line via a 'Y' piece to avoid manual spiking of standards and samples.

Table 3. Calibration standards used for soil extraction analysis (mg/L)

	Ca	K	Mg	Mn	Na
Blank	0	0	0	0	0
Standard 1	100	5	5	1.0	0.5
Standard 2	200	10	10	2.0	1.0
Standard 3	300	15	15	3.0	2.0
Standard 4	600	30	30	6.0	4.0

Table 4. Agilent 4100 MP-AES wavelengths and calibration parameters selected for analysis

Element	Wavelength (nm)	Read time (s)	Nebulizer pressure (kPa)	Background correction
Ca	430.253	3	240	Auto
K	769.897	3	240	Auto
Mg	383.829	3	240	Auto
Mn	403.076	3	240	Auto
Na	588.995	3	240	Auto

Results

Calibration

The calibration curves for Ca, K, Mg, Mn and Na on the MP-AES are displayed in Figure 1. Results show good linearity. This highlights the better linear dynamic range achieved with the 4100 MP-AES as compared to FAAS. Less sample dilutions are then needed when using MP-AES avoiding sample contamination and enhancing productivity.

Sample analysis

The accuracy of the results obtained by MP-AES was evaluated by two methods: i) comparison of the MP-AES results with results obtained with another analytical technique (FAAS and/or ICP-OES) and ii) calculation of z-scores for the MP-AES results with data from the inter-laboratory test (reference results and corresponding standard deviations).

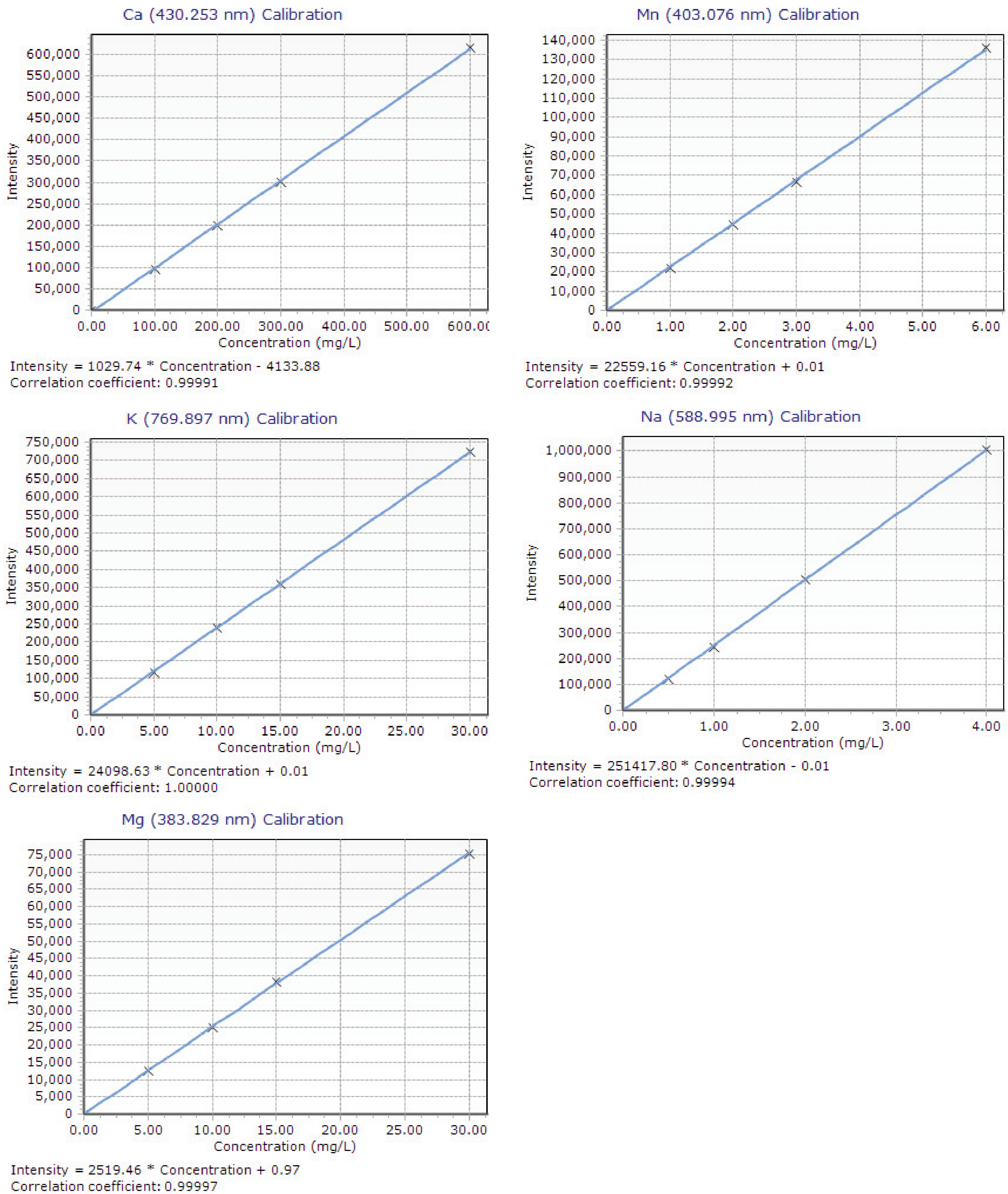

Figure 1. Typical MP-AES calibration curves for Ca, Mn, K, Na and Mg

Comparison of MP-AES with ICP-OES and/or FAAS

Figures 2 to 6 show for all cations an excellent agreement between the 4100 MP-AES results and those from other spectrometric techniques. The correlation of the analytical results between the different techniques was made and linear regressions are observed: coefficients of determination are $0.995 < R^2 < 0.999$ and the slopes are between 0.969 and 1.043 (Table 5).

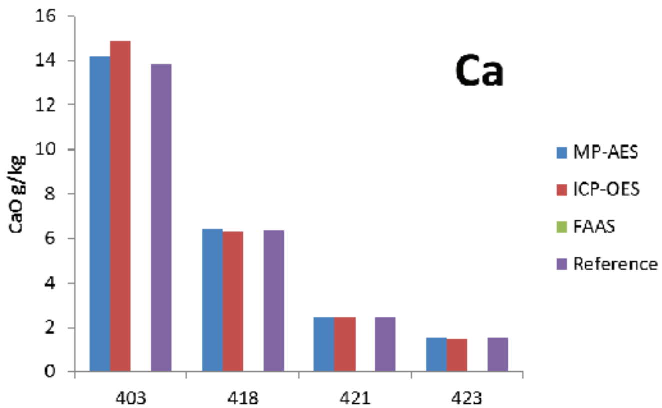

Figure 2. Reference results and Ca concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined)

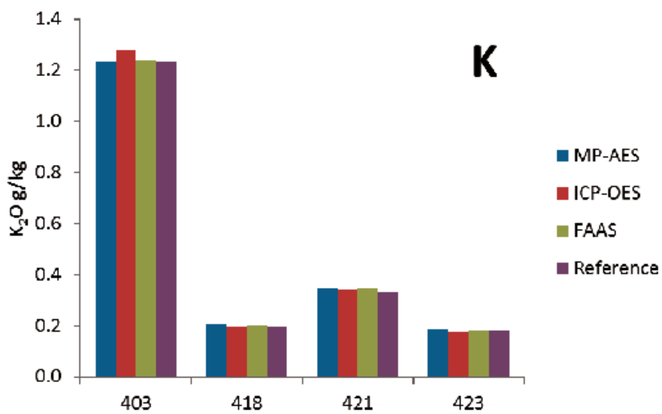

Figure 3. Reference results and K concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

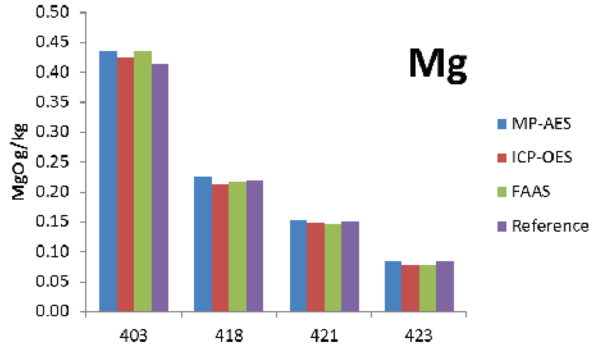

Figure 4. Reference results and Mg concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

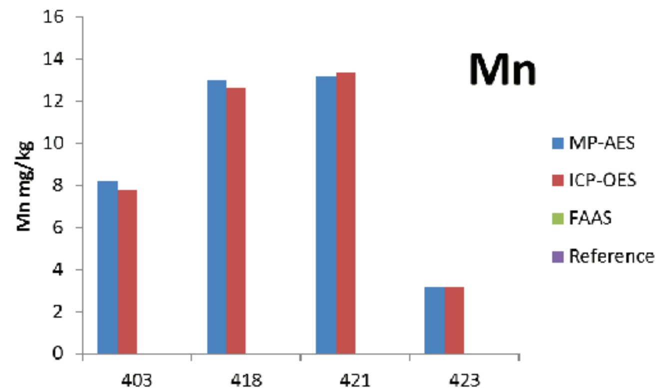

Figure 5. Mn concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined and no reference results available)

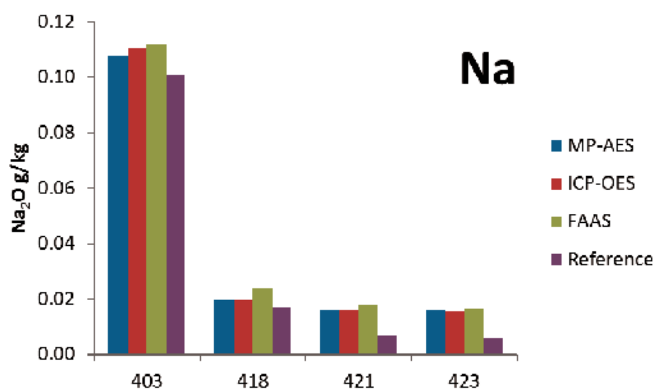

Figure 6. Reference results and Na concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

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Soluciones de espectroscopia atómica

Espectroscopia atómica El valor del conocimiento

Contar con la información correcta en el momento adecuado puede ayudarle a abrirse paso entre las complejidades cotidianas de sus muestras, las necesidades de instrumentos, la normativa y otras exigencias de tiempo y recursos, así como a hacer frente a dificultades inesperadas. Lo más valioso que puede ofrecer una solución analítica es la tranquilidad de saber que obtendrá las respuestas que necesita, cuando las necesita. A partir de aportes de clientes de todo el mundo, Agilent ha creado una gama innovadora de espectroscopia atómica, que abarca instrumentos, consumibles, patrones, servicios, software y más, para llevar esa tranquilidad a su laboratorio.

Espectroscopia de absorción atómica (AA)

- Bajo coste del sistema.
- Productividad baja o moderada.
- Detección de ppt para los sistemas de GFAAS. Detección de valores altos de ppb o % para los sistemas de FAAS.
- Alrededor de un 3 % de sólidos disueltos totales para la FAAS y hasta un 30 % para los sistemas de cámara de grafito.

La gama de sistemas de absorción atómica de Agilent incluye modelos de llama y de cámara de grafito. La AA de llama de bajo coste ofrece una exclusiva capacidad secuencial rápida, un funcionamiento sencillo y una sensibilidad muy elevada; por su parte, los sistemas de GFAAS proporcionan alta sensibilidad y corrección del ruido de fondo por efecto Zeeman para las muestras más complejas.

Espectroscopia de emisión atómica de plasma de microondas (MP-AES)

- Productividad moderada o alta.
- Entre 100 ppb y %.
- Bajo coste operativo.
- Alrededor de un 3 % de sólidos disueltos totales.

El sistema de MP-AES de Agilent le ahorra dinero, ya que funciona con aire. El sistema de MP-AES ofrece un rendimiento exacto y fiable.

Espectroscopia de emisión óptica por plasma acoplado inductivamente (ICP-OES)

- Productividad máxima (<30 s por muestra) con el accesorio AVS 6/7.
- Entre valores bajos de ppb y %.
- Hasta un 30 % de sólidos disueltos totales.

El sistema de ICP-OES de Agilent es el más productivo del mundo en su categoría. Gracias al uso de plasma vertical para la emisión axial y radial, proporciona una sensibilidad excelente y capacidad para muestras con alto contenido de matriz.

Espectrometría de masas por plasma acoplado inductivamente (ICP-MS e ICP-QQQ)

- Alta productividad (<60 s por muestra) con el accesorio ISIS 3.
- Entre valores bajos de ppq hasta valores superiores a 1.000 ppm
- Hasta un 25 % de sólidos disueltos totales.

La gama de sistemas de ICP-MS de Agilent incluye tanto un instrumento adecuado para análisis de rutina como un modelo de alto rendimiento con mejores límites de detección, un rango dinámico más amplio y tolerancia alta de matriz.

El sistema de ICP-QQQ de Agilent con modo MS/MS proporciona una exactitud excepcional para aplicaciones avanzadas.

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