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Spectroscopie d’émission atomique par plasma micro-ondes (MP-AES)

Manuel de mesure des métaux dans le vin et les aliments

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Fonctionnement de la spectroscopie d'émission atomique par plasma micro-ondes

La spectroscopie atomique englobe plusieurs techniques analytiques permettant de déterminer la composition élémentaire d'un échantillon par l'examen de son spectre électromagnétique ou de son spectre de masse. Les techniques qui permettent d'identifier un élément d'après son spectre électromagnétique sont notamment la spectroscopie d'absorption atomique flamme (SAAF), la spectroscopie d'émission optique avec plasma à couplage inductif (ICP-OES) et la spectroscopie d'émission atomique par plasma micro-ondes (MP-AES). Les techniques qui sont capables d'identifier un élément d'après son spectre de masse sont notamment la spectrométrie de masse avec plasma à couplage inductif (ICP-MS) et la spectrométrie de masse triple quadripôle avec plasma à couplage inductif (ICP-QQQ).

Excitation atomique

La spectroscopie d'émission atomique par plasma micro-ondes est une technique basée sur l'émission atomique. Elle repose sur le fait que, quand un atome d'un élément donné est excité, il émet de la lumière selon un schéma caractéristique de longueurs d'onde (spectre d'émission) lorsqu'il retourne à son état fondamental. Les sources utilisées dans l'émission atomique peuvent être un plasma à micro-ondes (MP) ou un plasma d'argon à couplage inductif (ICP), les deux ayant une température élevée et sont donc d'excellentes sources d'excitation pour la spectroscopie d'émission atomique. Le plasma à micro-ondes fonctionnant à l'azote atteint des températures proches de 5 000 K. À cette température, l'émission atomique est forte, ce qui donne d'excellentes limites de détection et une excellente gamme dynamique linéaire pour la plupart des éléments.

À l'intérieur d'un système MP-AES, l'énergie micro-ondes issue d'un magnétron industriel robuste et fiable permet de former un plasma d'azote, lequel peut être extrait de l'air comprimé par un générateur d'azote Agilent (figure 1). Dans les faits, le MP-AES fonctionne avec de l'air.

Figure 1. Le générateur d'azote extrait l'azote de l'air comprimé pour alimenter le plasma.

L'utilisation d'un champ magnétique plutôt qu'un champ électrique pour l'excitation génère un plasma robuste et compatible avec une large gamme de types d'échantillon.

Un guide d'ondes micro-ondes optimisé crée des champs électromagnétiques concentrés au niveau de la torche (figure 2). Un champ axial magnétique et un champ radial électrique focalisent l'énergie micro-ondes et la contiennent de façon à produire un plasma.

Figure 2. Un guide d'ondes micro-ondes crée des champs électromagnétiques concentrés autour de la torche.

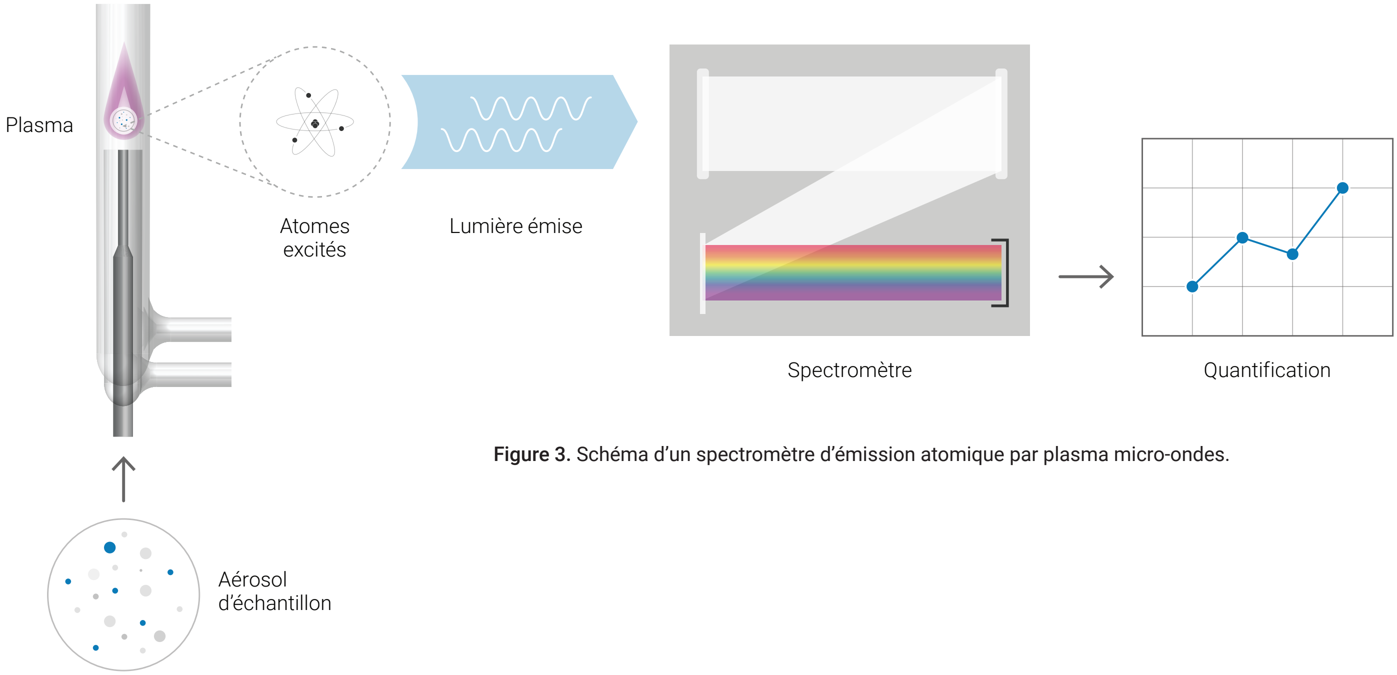

Figure 3. Schéma d'un spectromètre d'émission atomique par plasma micro-ondes.

Introduction de l’échantillon

Tout comme pour un instrument AA flamme, un aérosol est créé à partir d’un échantillon liquide à l’aide d’un nébuliseur et d’une chambre de nébulisation. L’aérosol est ensuite introduit au centre du plasma à haute température.

L’aérosol est asséché, décomposé puis atomisé. Les atomes continuent à être excités et émettent de la lumière à des longueurs d’onde caractéristiques de chaque élément lorsqu’ils retombent dans des états d’énergie plus basse (figure 3).

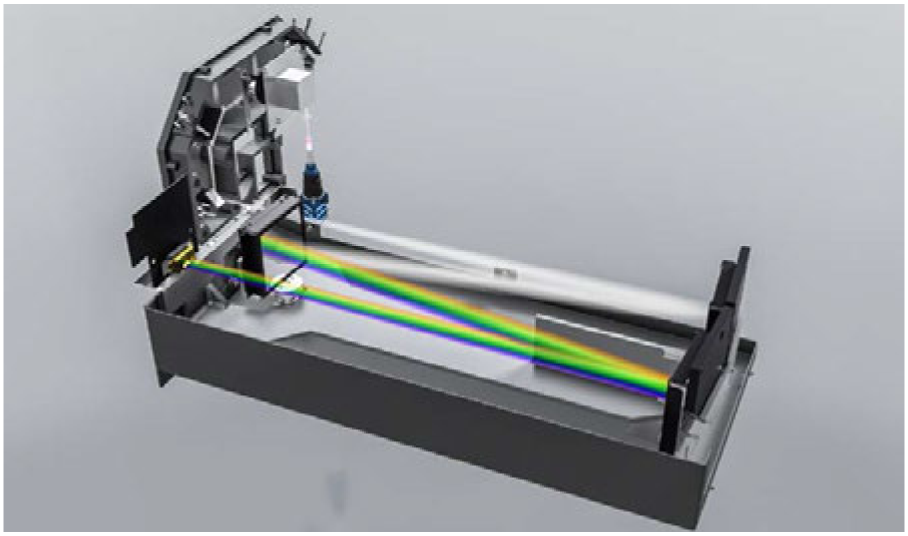

Figure 4. L’émission provenant du plasma est dirigée dans l’unité optique.

Unité optique

L’émission issue du plasma est dirigée vers un monochromateur à balayage rapide (figure 4). La gamme de longueurs d’onde sélectionnée est représentée sous forme d’image sur le détecteur à transfert de charge (CCD) de haute efficacité. Celui-ci mesure simultanément le spectre et le bruit de fond pour une justesse optimale.

Quantification

Tout comme l’AAS à flamme, la technique MP-AES permet de quantifier la concentration d’un élément présent dans un échantillon en comparant son émission à celle de concentrations connues de l’élément, représentées sur une courbe d’étalonnage. On obtient ainsi la concentration de l’élément dans l’échantillon.

Avantages de la technologie MP-AES

Faible coût de fonctionnement

L'alimentation en gaz est l'un des postes les plus onéreux de l'analyse élémentaire. Comme il fonctionne à l'air, l'instrument de MP-AES réduit considérablement le coût de fonctionnement et ne requiert aucune alimentation continue en gaz inflammables ou coûteux. Fini les bouteilles de gaz et autres lampes à acheter, et fini les frais de fonctionnement en veille. Lorsque le MP-AES est éteint, il ne consomme ni gaz ni électricité.

Sécurité

L'absence de gaz inflammables signifie la fin des fuites de gaz et de la commande et du transport de bouteilles. Supprimer tous ces risques fait de votre laboratoire un lieu de travail plus sûr.

Une meilleure performance que la spectroscopie d'absorption atomique

L'instrument de MP-AES est très sensible et offre des limites de détection en dessous du ppb. Il est également plus rapide et possède une gamme dynamique linéaire plus large que l'absorption atomique flamme (AA flamme) conventionnelle pour une analyse multi-élémentaire typique.

Traitement des matrices complexes

La robustesse de la source de plasma micro-ondes excitée par un champ électromagnétique du MP-AES simplifie l'analyse des matrices les plus difficiles, y compris les carburants et les solvants organiques, les échantillons géochimiques, les engrais et les aliments. Une torche en position verticale permet d'optimiser les performances pour les échantillons les plus complexes, et la visée axiale garantit d'excellentes limites de détection.

Utilisation à distance

Comme il ne nécessite que de l'électricité, l'instrument de MP-AES peut être placé au point d'échantillonnage plutôt que dans un laboratoire. Le délai de réponse est ainsi bien plus rapide, ce qui permet de produire des données en temps opportun et procure des avantages décisifs, comme éviter des déversements dans l'environnement ou éviter de fabriquer des produits défectueux.

Rapidité et simplicité d'utilisation

Les instruments Agilent de MP-AES sont accompagnés d'applets logicielles adaptées aux applications qui sont simples d'utilisation et qui chargent automatiquement la méthode prédéfinie pour un démarrage instantané de l'analyse, sans développement de méthode ni alignement préalable, et avec un minimum de formation.

Le chargeur de torche de l'instrument permet d'aligner la torche et de raccorder les arrivées de gaz de façon automatique, pour un démarrage rapide et des performances reproductibles.

Pourquoi passer de la SAAF à la MP-AES ?

Réduire les coûts de fonctionnement, renforcer la sécurité, améliorer la performance analytique et simplifier l'utilisation sont autant de défis essentiels auxquels sont confrontés les utilisateurs de la spectroscopie d'absorption atomique flamme (SAAF).

Avec l'introduction du spectromètre d'émission atomique par plasma micro-ondes (MP-AES) Agilent, ces défis ont été relevés, ce qui en fait l'instrument idéal pour les laboratoires souhaitant passer de la SAAF à une technique plus puissante, moins chère et plus sûre. De plus, grâce aux meilleures performances du MP-AES, le processus de préparation des échantillons peut aussi être grandement simplifié, ce qui permet d'économiser du temps et de l'argent.

Le MP-AES Agilent 4210 contient un modèle de guide d'onde et une torche capables d'analyser les échantillons avec une teneur en solides dissous jusqu'à 3 % sans compromettre les limites de détection.

Des coûts de fonctionnement réduits

Le plus gros poste de dépense lié au fonctionnement de la spectroscopie est le gaz. La SAAF utilise pour la flamme une combinaison d'air et d'acétylène, ou de protoxyde d'azote et d'acétylène. Alors que l'air peut être produit par un compresseur d'air, l'acétylène et le protoxyde d'azote sont fournis en bouteilles et doivent régulièrement être rechargés au fur et à mesure de leur consommation.

Le MP-AES 4210 utilise de l'azote extrait directement de l'air pour alimenter le plasma. Associé à un compresseur d'air, le générateur d'azote Agilent 4107 peut fournir la totalité de l'azote libre nécessaire avec une pureté supérieure à 99,5 %. Ceci réduit considérablement les coûts de fonctionnement durant toute la durée de vie de l'instrument.

Les économies potentielles liées à l'utilisation du MP-AES 4210 pour la détermination de Ca, Mg, Mn et K dans les jus de fruits sont illustrées en comparant un instrument de SAAF acheté avec un compresseur d'air et 1 an de consommables, à un MP-AES acheté avec un compresseur d'air, un générateur d'azote, un passeur automatique d'échantillons Agilent SPS 4 et 1 an de consommables (figure 1).

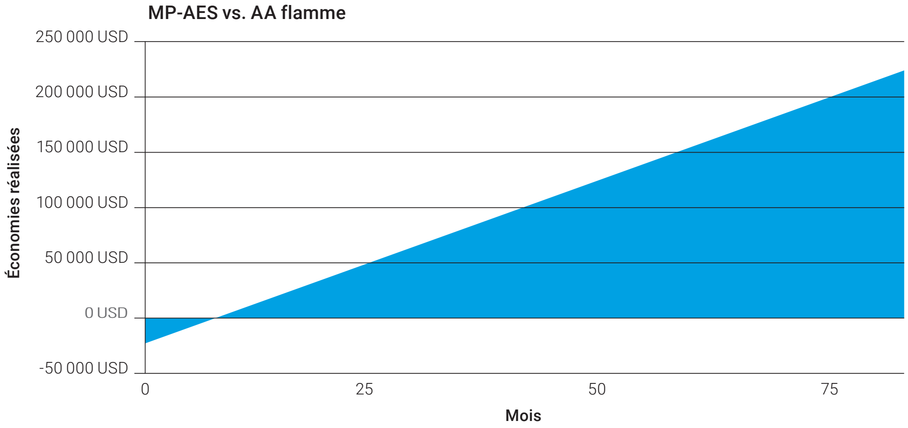

Figure 1. Estimateur de coût en ligne montrant les économies associées à l'utilisation du MP-AES pour la détermination de Ca, Mg, Na et K dans les jus de fruits.

Les hypothèses en matière de capacité d'analyse sont de 500 échantillons par semaine et de 4 éléments par échantillon.

Le calcul présuppose que le SAAF fonctionne sans passeur automatique d'échantillons, et que 3 éléments sont déterminés avec un mélange air/acétylène et 1 élément avec un mélange protoxyde d'azote/acétylène. Dans cet exemple, les résultats montrent une économie estimée à plus de 220 000 $ sur une durée de 7 ans[1]. Ce calcul repose sur un coût moyen global pour les gaz, et les résultats peuvent varier d'un pays à l'autre.

Une sécurité accrue

Une autre préoccupation majeure pour les utilisateurs de SAAF concerne les questions de sécurité liées à l'utilisation d'acétylène et de protoxyde d'azote, du stockage et de la manipulation des bouteilles à l'emploi d'une flamme dans l'instrument. La présence d'une flamme nue inquiète tous les laboratoires, en particulier ceux manipulant des solvants organiques. C'est pour cette raison qu'il n'est pas possible de faire tourner un SAAF sans surveillance.

Il est également courant de changer les brûleurs pour optimiser les performances lors de la détermination de la gamme complète d'éléments avec un SAAF. Même si les instruments de SAAF Agilent sont entièrement contrôlés par des dispositifs de sécurité veillant à ce que les bons brûleurs soient utilisés avec la bonne méthode, les brûleurs peuvent rester chauds après utilisation et doivent donc être manipulés avec précaution.

Le MP-AES 4210 permet de s'affranchir de ces complications. Le besoin d'acétylène et de protoxyde d'azote peut être supprimé, de même que les questions de stockage et de manipulation, et il n'est plus nécessaire de changer les brûleurs du fait des performances accrues du plasma d'azote qui fonctionne à plus haute température.

De meilleures performances analytiques

Le plasma du MP-AES 4210 fonctionne à environ 5 000 K, ce qui donne de meilleures limites de détection qu'avec un SAAF. Cette limite de détection améliorée signifie qu'il est possible d'analyser des éléments comme le phosphore, qui ont des limites de détection extrêmement élevées en SAAF.

Le tableau 1 donne les limites de détection instrumentales (IDL) de la MP-AES et de la SAAF pour les éléments contenus dans un échantillon de farine de riz. Les limites de détection plus basses pour P, Cu et Fe permettent de doser les éléments majeurs, mineurs et à l'état de traces en une seule et même mesure.

Tableau 1. Comparaison des limites de détection instrumentales (IDL) typiques du MP-AES 4210 et d'un SAAF

Élément	IDL typiques du 4210, lecture sur 10 s µg/L	IDL typiques en SAAF 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

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[1] Cet exemple a pour but de vous aider à comparer les coûts de fonctionnement et les économies réalisées entre le MP-AES et l'AA flamme. À notre connaissance, les formules et paramètres appliqués sont corrects, mais nous ne pouvons garantir les résultats. Les économies peuvent varier en fonction de facteurs tels le coût des gaz et de l'électricité au niveau local, les coûts de fonctionnement, le nombre d'éléments à analyser et leurs types. Pour ce calcul, les coûts de main d'œuvre ont été fixés à 25 USD/heure et le coût de l'électricité à 0,18 USD/kW.

Le modèle de guide d'onde et la torche du MP-AES 4210, associés au contrôle du débit massique et à l'humidification de la ligne de gaz de nébulisation, assurent une excellente stabilité à long terme pour les échantillons à matrice complexe, qui sont courants dans les échantillons miniers et environnementaux. L'introduction de solutions salines à forte concentration dans un brûleur de SAAF à air/acétylène sur une longue durée, par exemple 8 heures par jour, nécessite un entretien pour éviter les bouchages. La non-réalisation de cet entretien courant peut entraîner une dérive du signal.

La stabilité à long terme du MP-AES 4210 a été testée avec une solution de farine de riz digérée contenant 2 % de solides dissous (TDS). Les résultats sont présentés à la figure 2.

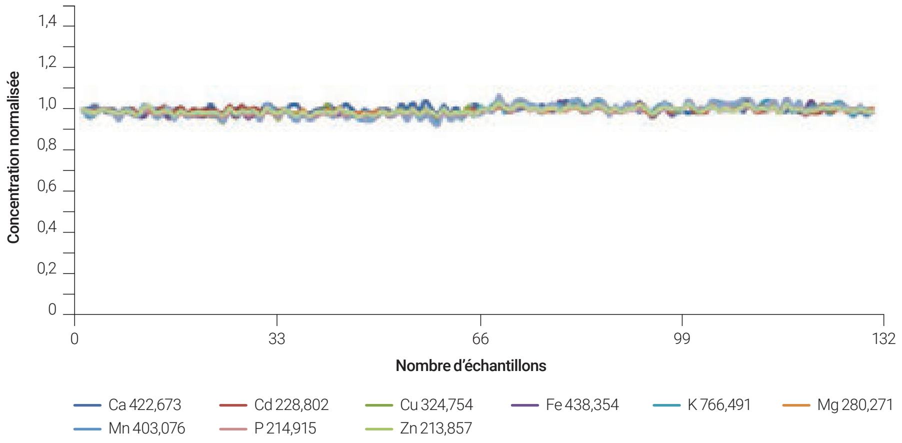


Figure 2. Farine de riz digérée contenant 2 % de solides dissous (TDS) et analysée pendant 8 h. Un nouvel étalonnage a été réalisé toutes les 2 h ; la stabilité résultante a été caractérisée par un RSD < 3 % pour tous les éléments. Une introduction d'échantillon multifonctions par défaut a été utilisée.

Le MP-AES 4210 possède aussi une gamme dynamique linéaire plus large qu'un SAAF. Le tableau 2 donne la gamme d'étalonnage linéaire et le coefficient de corrélation des principaux éléments d'un échantillon de jus de fruit pour le MP-AES 4210. Il donne aussi la gamme de travail optimale sur un instrument de SAAF pour les mêmes éléments. Les étalonnages du SAAF ont été réalisés avec le modèle « New Rational » par défaut. La plus grande plage linéaire du MP-AES par rapport au SAAF réduit les besoins de dilution pour les échantillons trop concentrés, ce qui simplifie l'analyse. Moins de dilutions signifie aussi que si des contaminants à l'état de trace doivent être dosés, il est peut-être encore possible de les détecter. En outre, grâce à une meilleure linéarité, il est possible d'obtenir une courbe d'étalonnage exacte avec moins d'étalons.

Simplification de la préparation des échantillons

Un facteur qui influence grandement les procédures de préparation d'échantillons sur un SAAF est l'existence d'interférences. La présence de composés impossibles à décomposer dans la flamme à basse température génère des interférences chimiques, et les éléments tels que Na et K peuvent être gênés par des interférences d'ionisation.

Tableau 2. Gamme de concentration linéaire du MP-AES 4210 et gamme de concentration optimale d'un SAAF pour des échantillons de jus de fruit.

Élément	Gamme de concentration linéaire (mg/L) du MP-AES 4210	Coefficient de corrélation linéaire de l'étalonnage du MP-AES	Gamme de travail optimale (mg/L) du SAAF
Ca 422,673	0 – 20	0,9999	0,01 – 10
Mg 518,360	0 – 100	0,99988	0,15 – 20 (pour Mg 202,6)
Na 589,592	0 – 20	0,99996	0,01 – 2,0
K 769,897	0 – 100	0,99968	1 – 6,0

Tableau 3. Conditions typiques de préparation des échantillons en SAAF et MP-AES

Élément	Éventuelles interférences chimiques	Préparation d'échantillon spécifique à la SAAF	Préparation d'échantillon spécifique à la MP-AES
Ca	Composés réfractaires Effets d'ionisation	Agent libérant du lanthane Tampon d'ionisation au césium	Aucune
Mg	Effets d'ionisation	Tampon d'ionisation au césium	Aucune
Na	Composés réfractaires Effets d'ionisation	Agent libérant du lanthane Tampon d'ionisation au césium	Aucune
K	Effets d'ionisation	Tampon d'ionisation au césium	Aucune

Tableau 4. Recouvrements de matériaux de référence certifiés (CRM) pour les principaux éléments d'un jus de pamplemousse, analysé par MP-AES. Aucun tampon d'ionisation n'a été nécessaire et une excellente exactitude a été obtenue pour K. De plus, aucun ajout de nitrate de lanthane n'a été réalisé et d'excellents recouvrements ont été atteints pour Ca.

Jus de pamplemousse T0842QC	Valeur certifiée (mg/L)		Valeur obtenue (mg/L)	% de recouvrement
	Valeur assignée	Gamme		
Calcium	145,6	123,6 – 167,6	158,3 ± 3,2	108,7
Magnésium	92,5	77,5 – 107,4	91,1 ± 0,6	98,5
Potassium	1 102	979 – 1 225	1 100 ± 14,7	99,8

Il existe diverses stratégies bien établies pour gérer ces interférences. Il est courant d'ajouter des agents libérant comme du strontium ou du lanthane pour résoudre ces interférences chimiques, ou bien d'utiliser une flamme au protoxyde d'azote, plus chaude. Les effets d'ionisation sont généralement résolus par addition d'un tampon d'ionisation à la solution, par exemple du sodium, du potassium ou du césium. Une autre stratégie consiste à extraire les éléments d'intérêt dans une phase organique afin de retirer les éléments interférents. Dans ce cas, l'échantillon doit faire l'objet d'une préparation distincte pour chaque élément.

Ces interférences chimiques sont éliminées grâce à la source de plasma plus chaude du MP-AES 4210. Ainsi, la préparation d'échantillon spécifique à chaque élément qui est requise sur le SAAF n'est plus nécessaire, ce qui simplifie grandement le processus de préparation des échantillons. À titre d'exemple, les éléments couverts dans l'analyse d'un jus de fruit sont indiqués ci-dessus avec une comparaison de la préparation d'échantillon nécessaire pour chaque élément (tableaux 3 et 4).

Conclusion

Le MP-AES 4210 d'Agilent est l'instrument idéal pour les clients souhaitant passer de la spectroscopie d'absorption atomique flamme (SAAF) à une autre technique. Utiliser de l'azote comme gaz source pour le plasma permet de réduire considérablement les coûts de fonctionnement, et l'élimination du protoxyde d'azote et de l'acétylène améliore grandement la sécurité. En outre, la température plus élevée de la source d'atomisation/ionisation du plasma d'azote améliore les limites de détection, la plage linéaire et la stabilité à long terme, et simplifie considérablement le processus de préparation des échantillons.

Accessoire pour MP-AES

Accessoires pour étendre les capacités

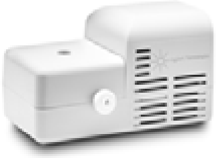
Agilent propose toute une gamme d'accessoires pour les instruments de MP-AES. Ils ajoutent des capacités supplémentaires aux instruments, ce qui vous permet d'optimiser le montage instrumental pour certaines applications particulières.

Système de vanne avancé (AVS 4)
Cette vanne de commutation à quatre ports permet d'atteindre de grandes cadences d'analyse et prolonge la durée de vie des composants, du fait de l'exposition réduite des composants du système d'introduction d'échantillon aux échantillons agressifs.

Système d'introduction d'échantillons multimode (MSIS)
Accessoire innovant pour ICP-OES et MP-AES qui permet d'introduire les échantillons en mode génération de vapeurs ou en mode nébulisation, ou dans les deux modes simultanément. Permet de détecter As, Se et Hg à des niveaux inférieurs au ppb.

Passeur automatique d'échantillons SPS 4
Le SPS 4, notre passeur automatique d'échantillons le plus rapide, permet de réaliser une analyse multi-élémentaire sans surveillance de jusqu'à 360 échantillons.

Générateur d'azote Agilent 4107
Le générateur d'azote extrait l'azote de l'air comprimé pour alimenter le plasma d'un instrument de MP-AES. Il fournit une alimentation continue en azote.



IsoMist
Chambre de nébulisation à température régulée qui offre une meilleure stabilité pour les solvants organiques volatils.

Module externe de contrôle du gaz (EGCM)
L'EGCM injecte de l'air dans le plasma pour réduire au minimum l'accumulation de dépôts de carbone, réduire le bruit de fond dans les applications organiques et permettre de doser le soufre.

Vin

La MP-AES permet de réaliser une analyse simple, rapide et automatisée des éléments du vin, sans aucune préparation des échantillons.

L'Organisation internationale de la vigne et du vin (OIV) a approuvé l'utilisation de la MP-AES pour l'analyse du fer, du cuivre, du potassium, du calcium et du manganèse dans les échantillons de vin. Ces éléments sont surveillés régulièrement pour contrôler la croissance des vignobles, la qualité des grains, la perte aromatique, et pour déterminer le risque d'oxydation. Les avantages de la MP-AES sont les suivants :

- Les échantillons de vin ne nécessitent aucune préparation, car ils sont dilués en ligne, pour des analyses directes et simples.
- La MP-AES peut être utilisée pour les mesures suivantes : cuivre 0,05-1 mg/L, fer 1-10 mg/L, potassium 15-1 200 mg/L, calcium 1-100 mg/L et manganèse 0,25-4 mg/L.
- Il est possible de mesurer facilement plus de 100 échantillons par jour.
- Aucun achat de gaz n'est requis et seul de l'azote est nécessaire pour l'analyse. Il s'agit donc d'une technique sans danger pour les laboratoires œnologiques.

La MP-AES peut aussi servir à mesurer des échantillons de plante ou de sol, pour déterminer :

- L'équilibre nutritionnel des vignes pendant la saison de croissance.
- Les besoins en nutriments élémentaires des vignes pour la saison à venir, pour pouvoir planifier les applications foliaires.
- Le potentiel agro-œnologique de sols sur lesquels on envisage une future plantation.

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

Application note

Food Safety

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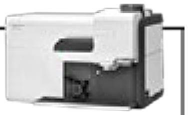

Introduction

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.

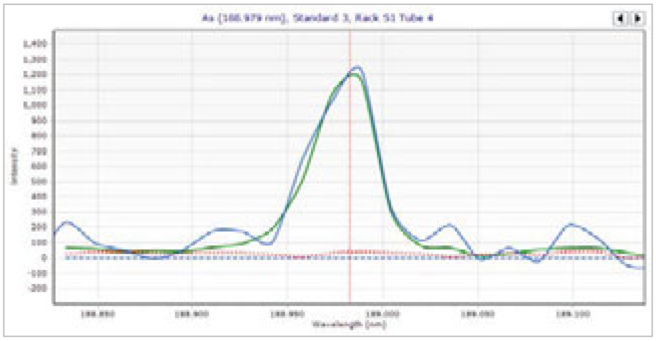

Figure 1. FLIC background correction applied to As (188.979 nm) calibration standard. Background and analyte peak (blue line), FLIC model applied to background and analyte peak (green line).

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.

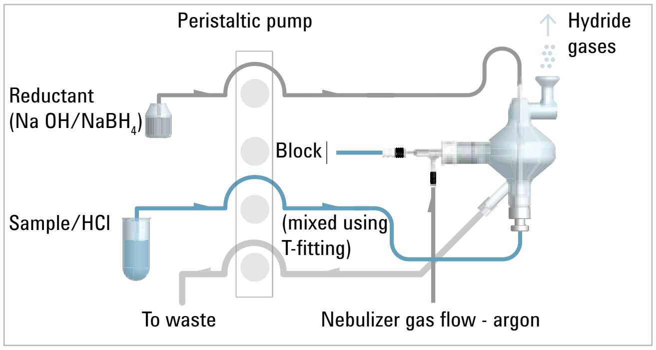

Figure 2. The MSIS setup for Vapor Generation mode.

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.

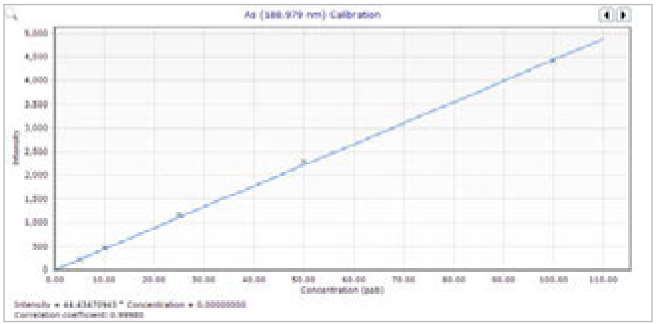

Figure 3. Calibration curve for As 188.979 nm showing excellent linearity across the 5-100 µgL^{-1} concentration range, illustrating the wide analytical range of the instrument.

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 µg L^{-1} CCV, (mean, n=7)	23.94	96
20 µg L^{-1} As (V)	20.59	103
20 µg 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

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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.

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]*

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

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.

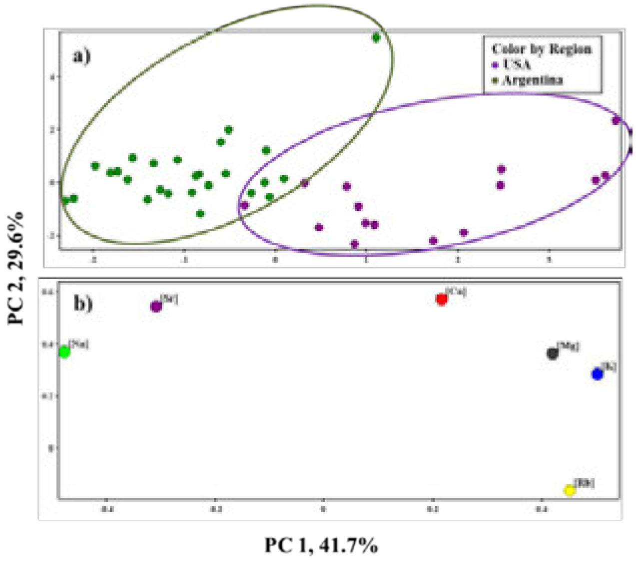

Figure 1. 2D PCA bi-plots using the 6 elements which differed significantly among the wine samples. (a) Product plot showing the wine samples color coded by geographical origin, (b) Loadings plot with 6 elements (Sr, Rb, Ca, K, Ca, Na and Mg). *Source: Nelson et al. [1].*

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.

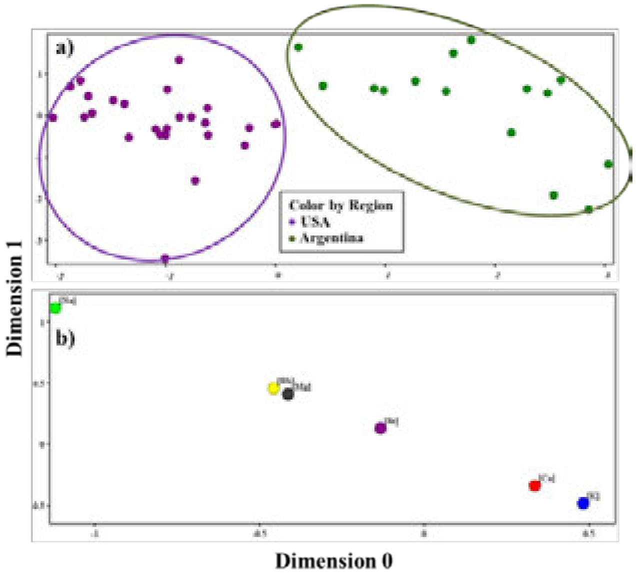

Figure 2. 2D PLS plots using the 6 elements which differed significantly among the wine samples. (a) Sample plot showing the separation of the wines according to geographical origin, with no overlap. (b) Element loadings plot. *Source: Nelson et al [1]*

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

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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.

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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Agroalimentaire et agriculture

Grâce à une cadence d’analyse élevée et à une mesure séquentielle rapide, le MP-AES Agilent est idéal pour les laboratoires de contrôle agroalimentaire.

Le MP-AES est l’équipement idéal des laboratoires sous contrat, pour lesquels le rendement est un facteur clé, ou pour les laboratoires d’analyse de petite et moyenne taille ayant pour mission de déterminer les teneurs en nutriments essentiels, en constituants majeurs, et en éléments toxiques présents à l’état de traces.

- Avec ses coûts de fonctionnement les plus bas, le système MP-AES vous offre un avantage compétitif majeur en réduisant les coûts de vos analyses tout en améliorant les performances.
- Oubliez les temps d’indisponibilité liés aux contraintes de réapprovisionnement en gaz et optimisez le rendement, la sécurité et la fiabilité de vos analyses, qui peuvent par ailleurs être effectuées sans surveillance.
- Réduisez la préparation des échantillons. Le plasma vertical à visée axiale permet d’analyser une large gamme d’échantillons, des minéralisats d’aliments ou de sols aux extraits de sols à fortes concentrations salines.
- Bénéficiez d’une meilleure stabilité à long terme avec l’humidification du gaz de nébulisation intégrée en standard sur le MP-AES.
- Augmentez la cadence de vos analyses par rapport aux systèmes AA flamme traditionnels et oubliez les changements fastidieux des brûleurs/gaz pour différents éléments.
- Le développement simple de méthodes et les procédures de démarrage rapide garantissent des performances optimales pour tous les utilisateurs.
- La fonctionnalité MultiCal permet d’analyser simultanément des composés à fortes et faibles concentrations.
- La couverture complète en longueurs d’onde permet d’éviter les interférences spectrales associées aux éléments majeurs en sélectionnant simplement une autre longueur d’onde.
- Obtenez une détection sub-ppb rapide des éléments As, Hg et Se avec le système d’introduction d’échantillons multimode (MSIS).
- Incluez P et S dans votre série d’analyses élémentaires avec de meilleures limites de détection, grâce à la technologie d’émission par plasma du 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 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.

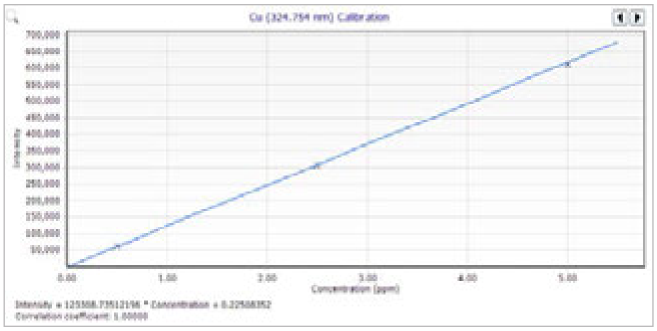
Results and discussion

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



Intensity = 125308.73512196 * Concentration + 0.22508352
Correlation coefficient: 1.00000

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.

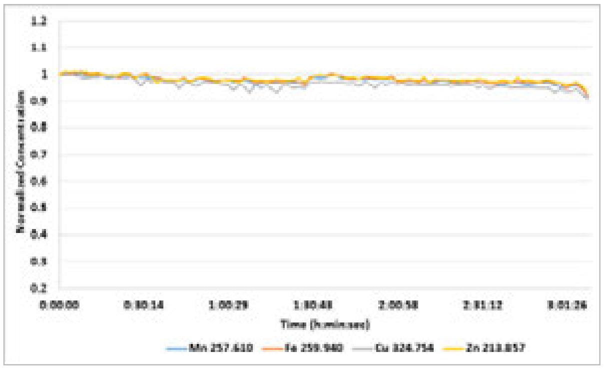


Figure 2. Normalized concentration of Cu, Fe, Mn and Zn in DTPA extracted soil sample, measured over 3 hours.

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

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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

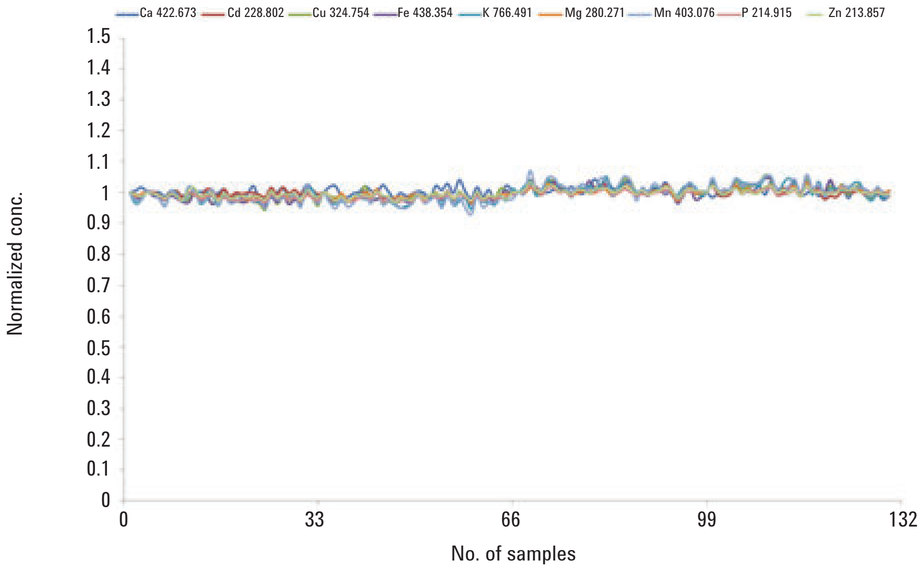

Figure 1. Normalized concentration of elements in a rice flour digest analyzed over an 8 hour time period, with recalibration every 2 hours.

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.

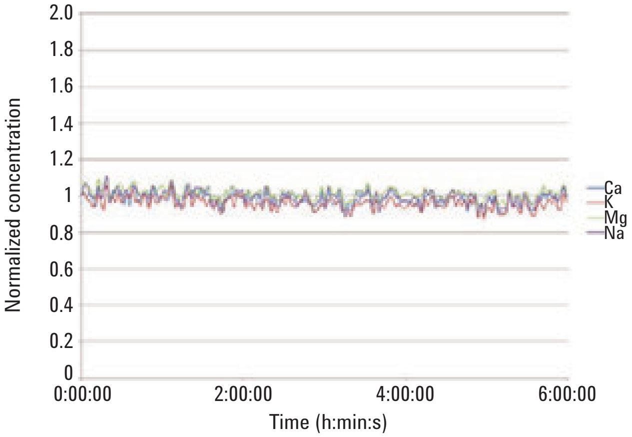
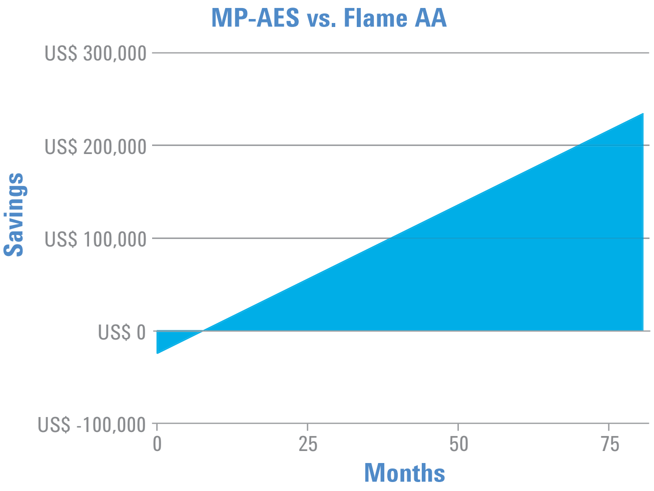


Figure 1. Normalized concentration of potassium in an apple juice sample over 6 hours

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.



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.

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[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.

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.

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

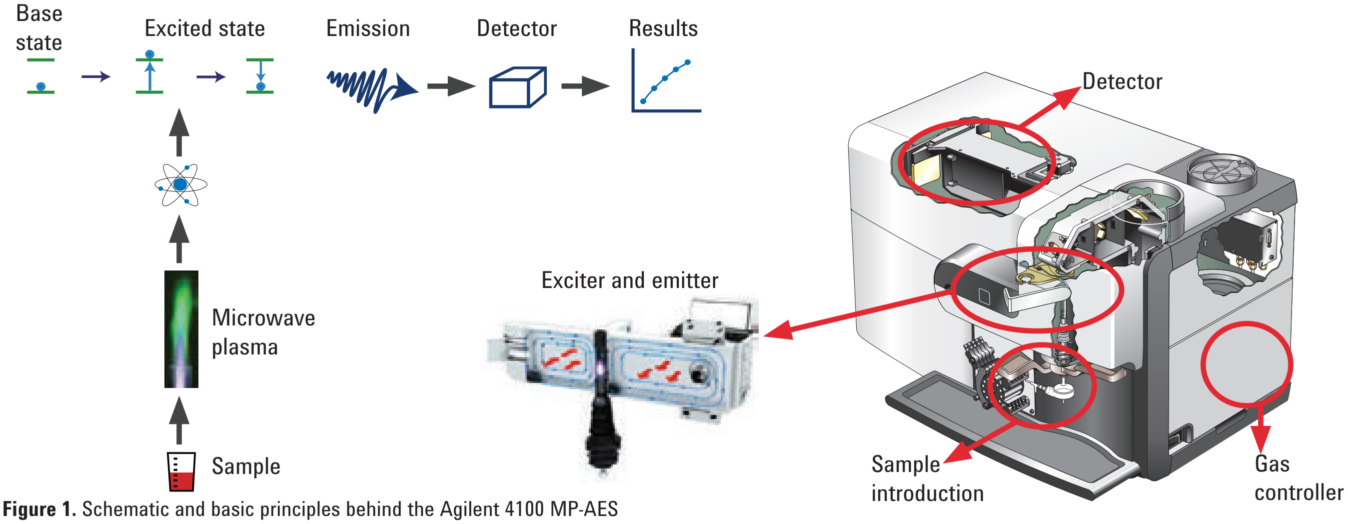

Figure 1. Schematic and basic principles behind the Agilent 4100 MP-AES

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.

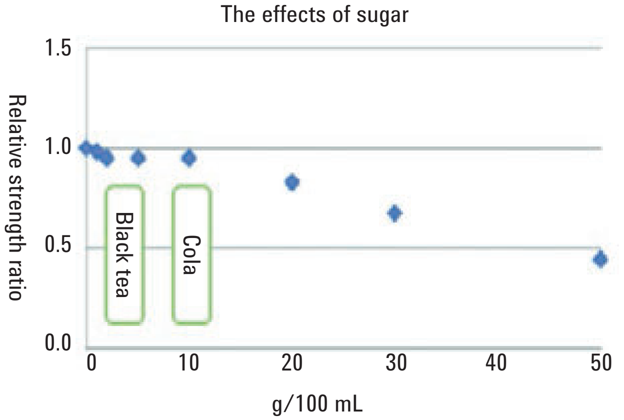

Figure 2. Variation in emission intensity due to differences in sugar concentration

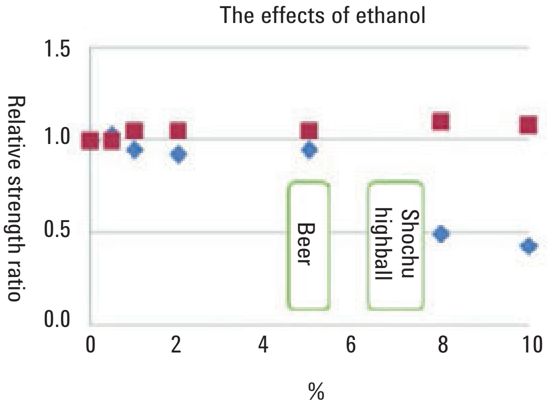

Figure 3. Variation in emission intensity due to differences in ethanol concentration, with and without adding air.
Red squares = with air, blue diamonds = without air

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.

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 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.

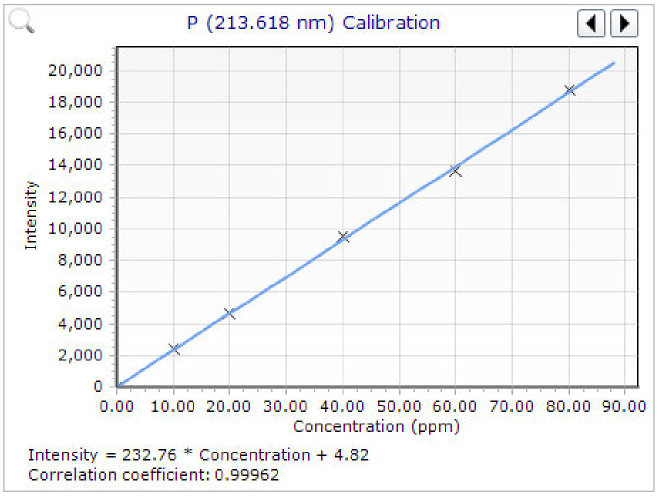
Table 2. Wavelength and working calibration concentration range

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.



Intensity = 232.76 * Concentration + 4.82
Correlation coefficient: 0.99962

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

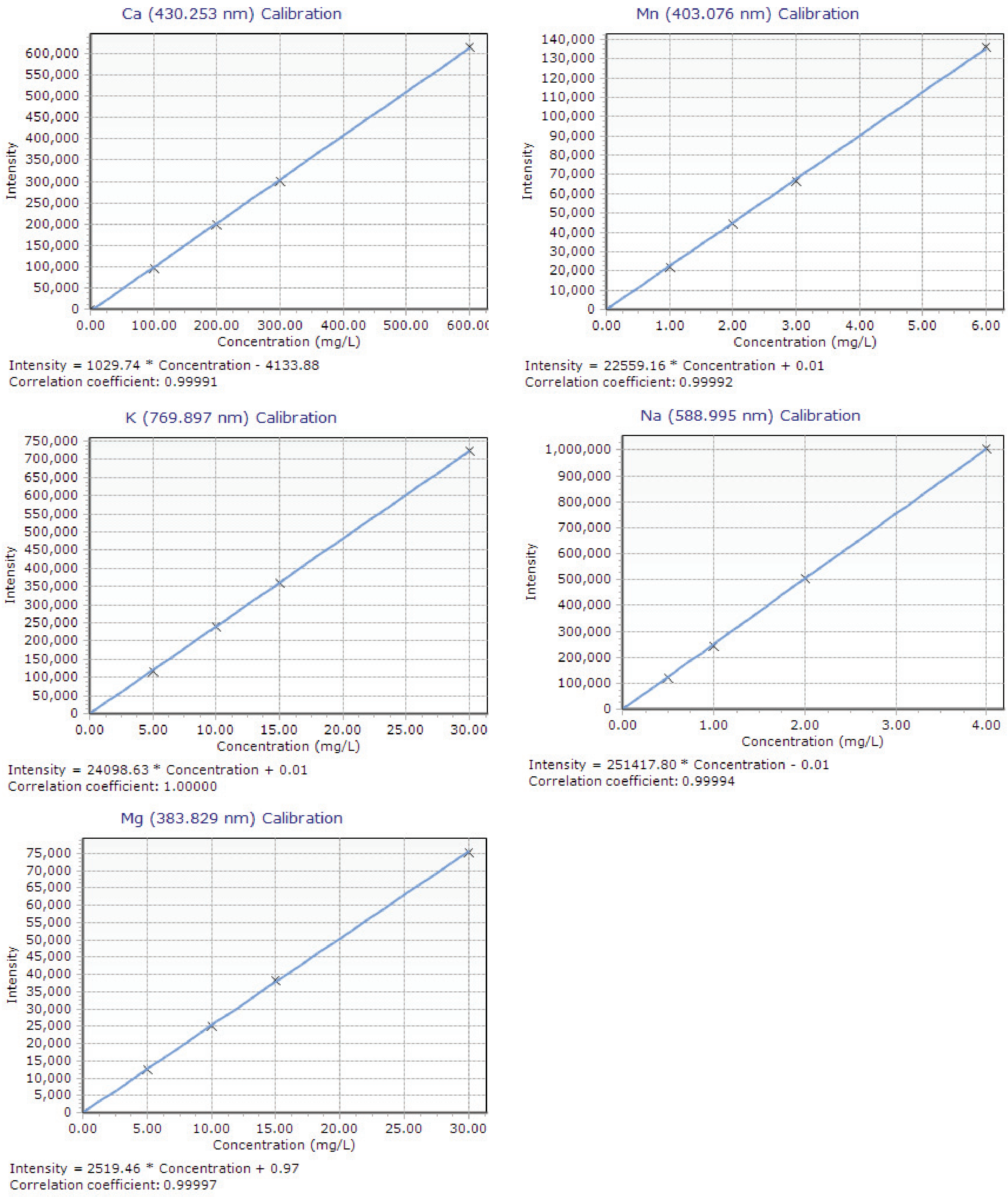
Results

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).



Ca (430.253 nm) Calibration

Intensity = 1029.74 * Concentration - 4133.88
Correlation coefficient: 0.99991

Mn (403.076 nm) Calibration

Intensity = 22559.16 * Concentration + 0.01
Correlation coefficient: 0.99992

K (769.897 nm) Calibration

Intensity = 24098.63 * Concentration + 0.01
Correlation coefficient: 1.00000

Na (588.995 nm) Calibration

Intensity = 251417.80 * Concentration - 0.01
Correlation coefficient: 0.99994

Mg (383.829 nm) Calibration

Intensity = 2519.46 * Concentration + 0.97
Correlation coefficient: 0.99997

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).

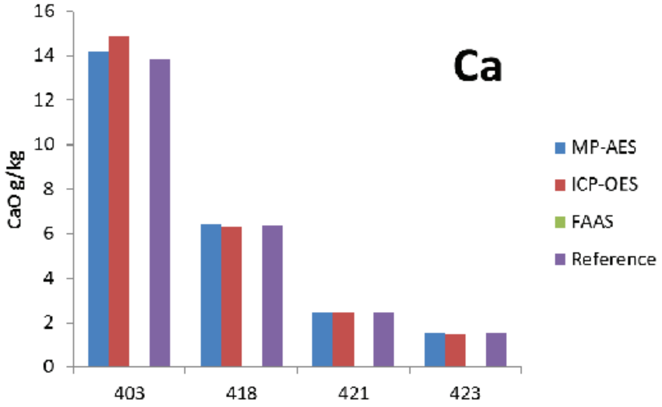


Figure 2. Reference results and Ca concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined)

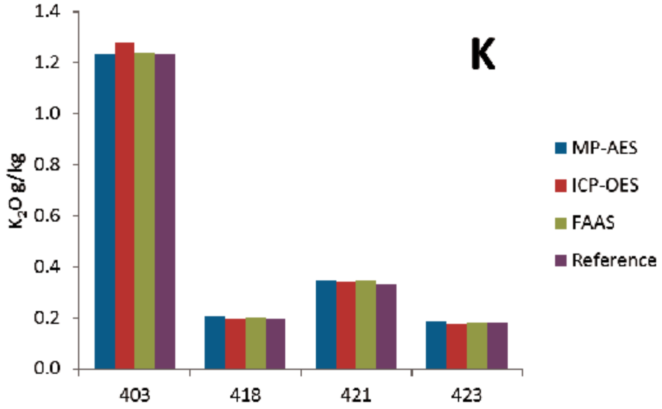


Figure 3. Reference results and K concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

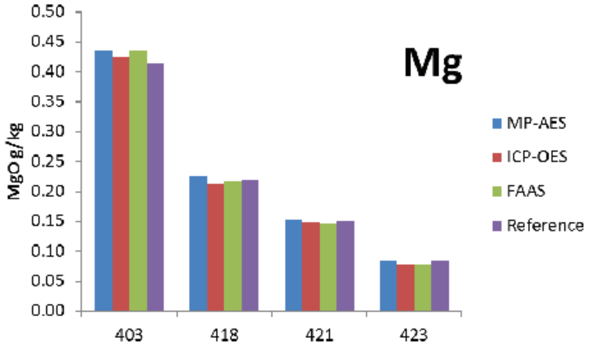


Figure 4. Reference results and Mg concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

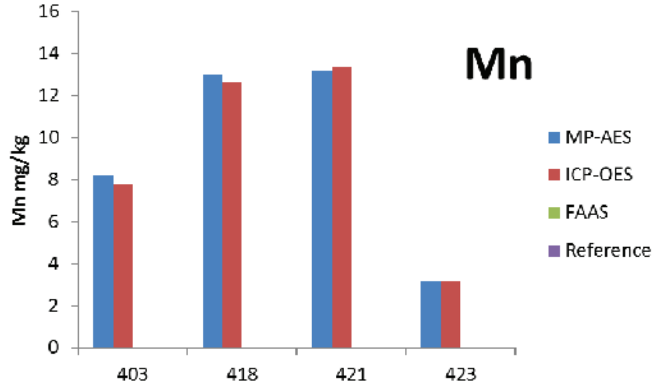


Figure 5. Mn concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined and no reference results available)

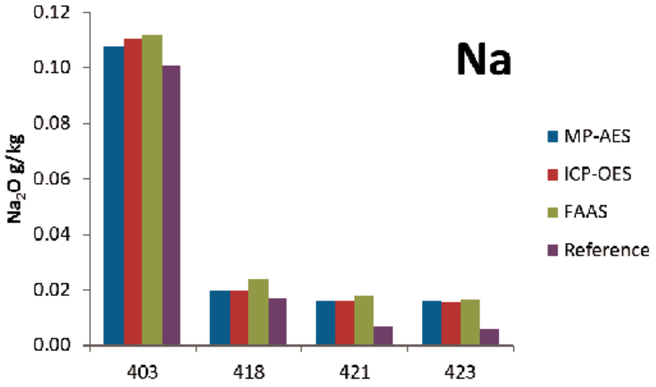


Figure 6. Reference results and Na concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

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Solutions de spectroscopie atomique

Spectroscopie atomique : l'importance du savoir

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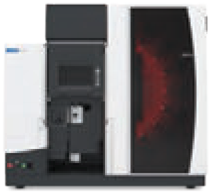
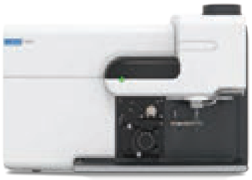


Spectroscopie d'absorption atomique (AA)

- Système à faible coût
- Productivité faible à modérée
- Analyse de ppt pour la SAAFG, et des forts ppb aux % pour la SAAF
- Environ 3 % de solides dissous pour la SAAF et jusqu'à 30 % pour le four graphite

La gamme dédiée à l'absorption atomique d'Agilent comprend aussi bien des modèles à flamme qu'à four graphite. L'AA flamme, peu coûteuse, offre un fonctionnement séquentiel rapide unique, une simplicité d'utilisation et une très bonne sensibilité, tandis que les modèles de SAAFG allient une grande sensibilité et une correction précise du fond par effet Zeeman pour vos échantillons les plus difficiles à analyser.



Spectroscopie d'émission atomique par plasma micro-ondes (MP-AES)

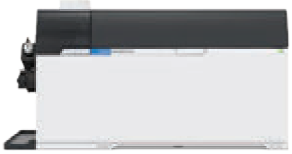
- Productivité modérée à haute
- De 100 ppb aux %
- Coûts de fonctionnement réduits
- Environ 3 % de solides dissous

Le MP-AES Agilent vous permet d'économiser de l'argent car il fonctionne à l'air. Les performances du MP-AES sont précises et fiables.

Spectroscopie d'émission optique avec plasma à couplage inductif (ICP-OES)

- Productivité maximale (< 30 s par échantillon) avec AVS 6/7
- De quelques ppb aux %
- Jusqu'à 30 % de solides dissous

Les systèmes d'ICP-OES Agilent sont les modèles les plus productifs au monde. Grâce à leur plasma vertical et à leurs émissions axiale et radiale, ils garantissent une excellente sensibilité et peuvent analyser les échantillons à matrice fortement chargée.



Spectrométrie de masse avec plasma à couplage inductif (ICP-MS et ICP-QQQ)

- Grande productivité (< 60 s par échantillon) avec ISIS 3
- De quelques ppq à plus de 1 000 ppm
- Jusqu'à 25 % de solides dissous

La gamme d'ICP-MS d'Agilent inclut à la fois un instrument pour l'analyse de routine et un modèle à haute performance offrant des limites de détection supérieures, une gamme dynamique plus large et une grande tolérance aux matrices chargées.

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