Talanta 112 (2013) 43–48

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper, iron, manganese and zinc in animal feed and fertilizer

Wei Li [a], Patrick Simmons [b], Doug Shrader [b], Timothy J. Herrman [a,c], Susie Y. Dai [a,d,*]

[a] *Office of the Texas State Chemist, Texas A&M AgriLife Research, Texas A&M University, 445 Agronomy Rd., College Station, TX 77843, United States*
[b] *Agilent Technologies, Santa Clara, CA 95051, United States*
[c] *Department of Soil and Crop Sciences, Texas A&M University, College Station, TX 77843, United States*
[d] *Department of Veterinary Pathobiology, Texas A&M University, College Station, TX 77843, United States*

ARTICLE INFO

Article history:
Received 3 January 2013
Received in revised form
12 March 2013
Accepted 13 March 2013
Available online 30 March 2013

Keywords:
Microwave plasma

ABSTRACT

Quantitative analysis of elements in agricultural products like animal feed and fertilizers by a new instrument using microwave plasma-atomic emission spectroscopy (MP-AES) technology was demonstrated in this work. Hot plate and microwave digestion were used to digest the sample matrices and the consequent digests were subject to atomic absorption spectroscopy (AA), inductive coupled plasma optical emission spectroscopy (ICP-OES) and MP-AES analysis. The detection limit, accuracy and dynamic range for each instrument, were compared and matrix effects were evaluated with respect to the fertilizer and feed materials. The new MP-AES platform can offer comparable or better performance compared to AA and/or ICP-OES with respect to routine analysis for a regulatory program.

1. Introduction

Deficiency of metals, minerals and nutrients can cause serious problems in both animals and plants. Minerals in the form of inorganic salts are essential nutrients for animals and plants so mineral supplementation is a common practice in agriculture. Iron deficiency can lead to anemic issues in young pigs since iron is an essential constituent of proteins like hemoglobin and myoglobin in muscle tissues. Whereas, manganese may be deficient in chickens and other poultry species, leading to signs of perosis. Perosis symptoms in birds can cause enlarged hock joints and labored movement [1]. Plants also require macro and micro nutrients for germination and growth. Nitrogen and phosphate have been commonly applied as fertilizers, but deficiencies in other elements can still cause severe symptoms in plants. For instance, copper and Zinc are important for plants. Copper deficiency can cause chlorosis and a lack of Zinc can cause stunted growth in leaves.

Common agricultural practices include comprehensive analysis of animal feed and fertilizers for mineral elements and AA and ICP-OES have been widely used for element analysis [2]. Flame AA has been one of the major techniques used for element determination in animal feeding stuff and plant fertilizer analysis. The official European Commission (EC) method for iron, cooper, manganese and zinc analysis in animal feeding stuff is based on acidic digestion of the feeding stuff followed by atomic absorption spectroscopy measurement [3]. Determination of various elements in plant fertilizer has also been carried out by AA (AOAC Official Method 965.09 [4]). Compared to AA, atomic emission spectroscopy has higher throughput with the capacity for multi-element monitoring. For emission spectroscopy systems, various excitation sources have been used to produce the excited atoms which emit the light used for element measurement. Emission sources include flames, electrical arc/spark and plasma instruments. Particularly the plasma based systems have been broadly used, in which the plasma is produced based on different mechanisms. Inductively coupled plasma instruments have been successfully used to determine about 70 elements in different sample matrices [5]. In general, the sample aerosol is desolvated in the plasma, then vaporized and dissociated, followed by excitation of the atoms or ions present in the sample. The element is identified by the specific wavelength emitted and the concentration of the element present is determined by the intensity of the peak. ICP-OES systems usually consist of a pneumatic nebulizer, a spray chamber, a radio frequency generator and a torch. Generation of the plasma is achieved by igniting argon gas in an intense electromagnetic field, causing collisions between neutral argon gas and charged particles. This results in high temperature plasma with temperatures approaching 10,000 °C. The operation of such a plasma depends upon a continuous supply of argon gas, which can be expensive in the long term [6].

---

[*] Corresponding author at: Texas A&M University, Office of the Texas State Chemist, Texas A&M AgriLife Research, 445 Agronomy Rd, College Station, TX 77843, United States. Tel.: +1 979 645 1121x146; fax: +1 979 845 1389.
E-mail address: susie@otsc.tamu.edu (S.Y. Dai).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.03.029

Another way to generate and sustain the plasma is to utilize microwave induced plasma (MP), in which the plasma is powered by a lower cost magnetron and waveguide. Since their invention over 30 years ago, MP systems have been applied to spectroscopic analysis [7] and the development of MP instrumentation has been researched by many groups [8–14]. The coupling of a MP with optical emission spectroscopy, gas chromatography and mass spectrometry has enabled the MP technology to be applied to various analytical fields where the MP has been used as an excitation source for OES or an ionization source for the mass spectrometry [15–20]. However, most of the developments have been constrained in specific research groups since the majority of the applications are based on in-house instrumentation designs. Wide application of the MP technical can only be visualized once MP sources are commercially available. In 1995, a commercially available helium microwave induced plasma was introduced allowing chemical composition determination of micro- and nano-particles [21]. Even though commercial microwave induced plasma-optical emission spectroscopy had been introduced in the 80s and 90s [7], broad applications were not seen with those commercial MP instruments. Utilization of argon and helium plasmas has been used for spectroscopic analysis, with various applications in different matrices [19,22,23]. Furthermore, the usage of nitrogen and air as plasma gas has also been studied [24,25] and the comparison of detection limits of several MP systems to the ICP source has demonstrated that MP performance approaches that of the ICP sources [26].

Reported here is the utilization of the newest commercially available instrument (4100 MP-AES) based on the microwave induced plasma-atomic emission spectroscopy for element analysis in a variety of materials, specifically for agricultural sample matrices. The nitrogen plasma is sustained at atmospheric pressure and takes sample aerosol from a conventional pneumatic nebulizer. The study presents the implementation of the nitrogen microwave plasma-atomic emission spectroscopy (MP-AES) technique to analyze agricultural materials including animal feed and fertilizers. The performance of the MP-AES was compared to that of traditional AA and ICP-OES analysis. The analysis of micro nutrients iron, zinc, copper and manganese are presented and matrix effects are discussed with respect to the different instrumental techniques.

2. Material and methods

2.1. Instruments and apparatus

The AA instrument was a Varian SpectrAA220 FS (Varian, Palo Alto, CA) equipped with a standard nebulizer and Mark 7 spray chamber and burner. The ICP-OES instrument was a Varian Vista Pro (Varian, Palo Alto, CA) equipped with a cross-flow nebulizer and Scott Spray chamber. The MP-AES was an Agilent 4100 MP-AES (Agilent, Santa Clara, CA) equipped with a standard glass concentric nebulizer and cyclonic spray chamber. A MARSXpress microwave digestion system (CEM Corporation, Matthews, North Carolina) was used for digestion of feed materials.

2.2. Reagents and materials

Reagent grade chemicals were used unless otherwise specified and deionized water (17 MΩ or higher) was used to prepare the reagents and materials. Nitric acid and hydrochloride acid solutions are all of trace metal grade and obtained from VWR (Radnor, Pennsylvania). A total of 18 feed materials and 15 fertilizer materials were collected from local manufacturers. The feed matrices included beef cattle, horse, poultry, sheep and goat feed, dog and cat food, and wild animal feed. For the beef cattle, horse, poultry, sheep and goat feed categories, three feed materials were collected for each category. For the wild animal feed category, two sample materials were collected. For dog and cat food, total of four sample materials were collected. The fertilizer matrices included liquid fertilizer, mineral mixture and specialty fertilizer. For liquid fertilizer, four sample materials were collected. For mineral mixture, five sample materials were collected. For the specialty fertilizer category, six sample materials were collected. Choice of material selection is based on the typical animal species fed on commercial feed and typical commercial fertilizer encountered on the market. The blank was defined as the sample matrix with the target element levels below the limit of detection by MP-AES analysis.

2.3. Sample extraction

Feed materials: One gram of feed materials were weighed and transferred into individual 55 mL microwave digestion vessels. Ten mL of 15.9 N trace metal grade HNO_3 was added to each vessel. After standing for 12 h, the samples were processed by microwave digestion as follows: ramp temperature from ambient to 200 °C over 20 min, then hold at 200 °C for 20 min. After digesting, they were allowed to cool to approximately 50 °C or lower before handling. The digestion was transferred to a 50 mL volumetric flask, then the solution volume was adjusted to 50 mL and filtered for instrumental analysis.

Fertilizer materials: One gram of fertilizer materials were weighed and transferred into a 200 mL volumetric flask. Ten mL of 12 N trace metal grade HCl was added into the flask and the flask was heated on a hot plate until only 1 to 3 mL of solution remained. Twenty mL of 2.0 N HCl was added to the flask and the solution was boiled for 3 to 5 min. Seventy five mL of DI water was then added to the flask and the solution was boiled again, and then cooled to room temperature. The solution volume was then adjusted to 200 mL and filtered for instrumental analysis.

Dilution: Feed and fertilizer digests were diluted with 0.5 N HNO_3 solutions before instrumental analysis. To meet the calibration curve range, appropriate dilution factors were applied to the samples so that they would fall within the calibration ranges shown in Table 1.

Table 1
Quantitation wavelength and calibration curve for different instruments. (Wavelengths were selected to obtain highest signal/noise ratios for target elements and considering interference).

	MP-AES		ICP-OES		AA	
	Detection wavelength (nm)	Calibration curve range (μg/g)	Detection wavelength (nm)	Calibration curve range (μg/g)	Detection wavelength (nm)	Calibration curve range (μg/g)
Cu	324.754	0.01–10	324.754	0.02–5	324.8	0.05–2
Fe	259.940	0.02–10	259.940	0.01–5	248.3	0.1–2
Mn	257.610	0.01–10	257.610	0.01–5	279.5	0.1–2
Zn	213.857	0.01–4	213.857	0.01–5	213.9	0.2–2

Table 2
Instrument parameters.

MP-AES	Nitrogen (L/min)	22.5
	Air (L/min)	25
	Argon (L/min)	N/A*
	Nebulizer (kPa)	200
	Intermediate (kPa)	170
	Outer (kPa)	170
	Pump Speed (rpm)	15
	Stabilization Time (s)	10
	Sample Uptake Time (s)	12
	Rinse time (s)	30
ICP-OES	RF power (W)	1.3
	Plasma gas flow (L/min)	16.5
	Auxiliary gas flow (L/min)	2.25
	Nebulizer gas flow (L/min)	0.7
	Replicates	3
	Replicate time (s)	10
	Stabilization time (s)	30
AA	Acetylene (L/min)	13.5
	Air (L/min)	2.0
	Smoothing	5
	Replicates	3

* Argon is used only to ignite the plasma (consumption is about 50 mL each time) and then is automatically switched over to nitrogen.

3. Experimental section

Table 1 shows the wavelengths for elemental analysis used for each instrument. Experimental parameters for different instrumental analysis are listed in Table 2. For MP-AES analysis, viewing positions and Nebulizer pressures were not included in the table because those parameters are optimized before running each experimental batch using a 500 ng/g four element mixed solution. Data points were obtained in triplicate. The instrument utilized MP Expert software version 1.0.1.42902.

The instrumental Limit of Detection (LOD) and Limit of Quantitation (LOQ) were determined based on sample replicates measurement. Seven replicates were fortified at 50 ng/mL in blank solution (0.5 N HNO_3) for each instrumental experiment. LOD and LOQ values were determined using the formulas below:

$$\text{LOD} = 3 \times s$$

$$\text{LOQ} = 10 \times s$$

where s is the standard deviation of seven replicates.

The linear calibration curve was established for each instrument of Cu, Fe, Mn and Zn. The concentration range was determined when the linear regression correlation coefficient is bigger than 0.99.

In order to establish MP-AES as a viable alternative for AA and ICP-OES, the same extract from the original sample was shared between three instruments to avoid sample variation and extraction variations. The analyses results yield three data sets and a one way ANOVA analysis was performed to evaluate the statistical difference within the data sets.

4. Results and discussion

4.1. MP-AES spectrum of copper, iron, manganese and zinc

The mechanism of MP-AES spectroscopy is similar to that of the ICP-OES. The major difference is the plasma generation. Instead of using the inductively coupled argon plasma, the MP-AES uses nitrogen plasma which is sustained by a lower power microwave source operating at atmospheric pressure. A wide variety of gases can be used for plasma generation, which may impact the plasma properties such as temperature and excitation mechanisms. One desirable gas used in the plasma generation is nitrogen, which is nonflammable and economical. However, compared to argon plasma, nitrogen plasma is cooler and features different performance characteristics. The high temperature in the ICP argon plasma favors formation of excited ions, which actually produces more emission spectral lines. The abundant multiple emission lines offer more wavelengths for measurement but at the same time can potentially produce more spectral interferences. With the nitrogen plasma, since the temperature is lower, most of the elements are in the atomic state resulting in a simpler spectrum than the argon plasma. Table 1 shows the wavelength lines for four elements (Cu, Fe, Mn and Zn) used in the MP-AES analysis for quantitation purposes. The spectral line and intensities need to be carefully tested for each element to achieve the maximum sensitivity and eliminate possible interferences. For example, it was discovered that for Fe, the optimized spectra line is at 259.94 nm. However, there is an adjacent line at 259.84 nm for Fe with reduced intensity. In the same wavelength range, Sb can potentially be an interference, producing a spectral line at 259.81 nm. Thus, analysis of Fe is based on the spectral line at 259.94 nm and the spectral line of 259.84 nm was not used. Studies by other groups have also reported similar spectral line selections [25]. In one of the previous MP studies, Zhang et al. [25] also selected 324.754 nm for Cu and 213.856 nm for Zn. Spectral lines selected for Mn were 403.076 nm, 279.482 nm and 259.373 nm. The MP source used in the Zhang's study is based on the Okamoto cavity. In our study for Mn analysis, the spectral line of 403.076 nm produced a similar intensity and quantitation calculation as 257.610 nm, and spectral line 257.610 nm was chosen as the reference line.

The spectral lines used for the ICP-OES and AA analyses were also listed in Table 1. The same wavelength was used for each element in the MP-AES and the ICP-OES measurement. The ranges for each element calibration curve are listed in Table 1 as well. The listed wavelengths proved to be proper for the dynamic range of the calibration curve for each element.

Table 1 also lists the linear concentration range of the calibration curve established on each instrument. Even though it had been common practice to use rational extrapolation for analyte concentration determination, the direct comparison for the linear range is meaningful regarding the dynamic range evaluation. The results suggested that for the elements Fe, Cu, and Mn, the MP-AES provides a wider linear range than the other two platforms, with AA showing the narrowest linear range.

4.2. Limit of detection and limit of quantification

The LOD and LOQ of the MP-AES method for each element are listed in Table 3. Even though there is rich information about the LOD and LOQ for ICP-OES in the literature, in order to do a direct comparison for this work, the LOD and LOQ were determined by calculating the standard deviation for the 50 ng/mL solution measurement. In the present work, the LOD and LOQ are defined as 3 and 10 times the standard deviation of seven repeated measurements of the 50 ng/mL solution, respectively. As indicated by our analysis, the LOD and LOQ for MP-AES are comparable to that of ICP-OES. Of particular note is that the LOD and LOQ of MP-AES for Mn are lower than those of the ICP-OES. It is apparent that both the MP-AES and the ICP-OES have lower LOD and LOQ than the AA instrument by more than 10 fold. Theoretically, it would be ideal if a sample blank is available so that the detection limit in the real sample matrix for animal feed and fertilizer could be evaluated. However, it is difficult to find such sample matrices that are free of the four elements. The small difference in the LOD and LOQ suggested that the performance of MP-AES would be similar to that of ICP-OES. It has been proposed that water may play a role in the analyte line emission intensities. In ICP analysis, water may lead to an increase of the intensity. However, with microwave induce plasma, water may only absorb energy and decrease the emission line intensity. In the current analysis, both the MP-AES and the ICP-OES utilize the nebulization process to remove the water in the aerosol; the vaporization of water may not be efficient enough so the two instruments share the similar LOD and LOQ.

4.3. Matrix effect

Matrix effects were evaluated for both the animal feed and fertilizer matrices. Different digestion protocols were applied to feed and fertilizer materials. A hot plate digestion procedure was applied to fertilizers and a microwave digestion protocol was applied to feed materials, resulting in better digestion efficiency for each matrix. Animal feeds are made from a variety of agricultural crops and have complicated compositions, which introduce great challenges for feed analysis. Mineral supplements are often added to produce the complete feed. In the current study, a variety of animal feeds were evaluated by the MP-AES technique. Representative feeds for beef cattle, horse, poultry, dog and cat, and wild animal were chosen to test the matrix effect as shown in Tables 4–7. Feed ingredients like minerals were treated as fertilizer for the digestion protocol. As presented in the procedure for sample digestion, the dilution of the original digest is different for feed and fertilizer. Further dilution was conducted when necessary.

One critical parameter that impacts the final result of MP-AES analysis and minimizes the matrix effect is the dilution factor following the original digestion. The original digest is usually too concentrated for the MP-AES analysis. In order to get an optimized dilution factor for the MP-AES analysis, several dilution factors were tested. Interestingly, different elements showed different matrix effects. In order to directly compare the analysis results, the same digest was shared for all instruments. When comparing AA and the MP-AES analysis and using the AA measurement as the target value, the measurement of Cu was not dependent on the dilution factor. In other words, the analysis results for Cu were consistent within the AA and MP-AES measurements regardless of the dilution factor used for analysis. However, significant matrix effects were observed for other elements and a serious matrix effect was observed for Fe in some feed samples. In one sheep and goat feed digested sample, if the original 10 fold diluted sample was analyzed, there was significant signal suppression in the MP-AES analysis, resulting in a 19% suppression of the MP-AES result compared to the AA measurement. The analyses of Zn and Mn showed less matrix effect with either a high dilution factor (40) or low dilution factor (10).

Table 3
Comparison of instrumental limit of detection (LOD) and limit of quantification (LOQ).

	MP-AES		ICP-OES		AA	
	LOD (ng/mL)	LOQ (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)
Cu	2.2	7.4	1.7	5.8	12.6	42.1
Fe	4.1	13.7	1.8	6.0	25.4	84.6
Mn	1.5	5.0	5.4	18.0	23.6	78.5
Zn	2.3	7.6	1.8	6.0	41.3	137.8

Note: 50 ng/mL solution was used for determination of LOD and LOQ.

Based on the calibration solution range, there was an optimized dilution for samples analyzed. However, it is hard to accommodate measurements for all four elements since those four elements (Cu, Fe, Zn and Mn) may be present in the samples at very different concentrations depending on the particular feed or fertilizer. Generally, it was discovered that a dilution factor of 40 is strong enough to have the target element concentration in the range of the calibration curve, at the same time eliminating interference from the sample matrix.

4.4. Survey of animal feed, feed ingredients and fertilizer using AA, ICP-OES and MP-AES

In this comparison study, all samples were digested and then subjected to MP-AES, ICP-OES and AA measurements. Selected analysis results for each feed and fertilizer category are presented in Tables 4–7. The one way ANOVA statistical analysis has yielded the *p* value, when data from all three instruments are available, for each feed/fertilizer category and all of the *p* values are presented in Tables 4–7. The *p* values that are greater than 0.05 suggested that there were no statistically significant differences between the measurements between MP-AES, ICP-OES and the AA platforms. However, a few tests did show the *p* value being smaller than 0.05, which suggested that data from the three instruments are different. When the *p* value is smaller than 0.05, close examination of the data suggested that one of the instruments yielded the results differently than the other two instruments. For example, when measuring iron in the beef cattle feed, MP-AES gave the result of 315.0 ± 4.2 ppm, higher than those measured by ICP-OES (306.1 ± 6.3 ppm) and AA (291.5 ± 25.2 ppm). When measuring copper in the wild animal feed, ICP-OES gave a result of 24.9 ± 0.8 ppm, higher than those measured by MP-AES (20.7 ± 1.7 ppm) and AA (21.4 ± 2.1 ppm). Nevertheless, the results from the three instruments were very consistent, which indicates comparable performance of the MP-AES to the AA and ICP-OES analysis. As discussed previously, different elements showed varied matrix effects in the analysis. The most important practice is using a large dilution factor of the original digest. However, for elements that may exist at low levels in the agricultural material,

Table 4
Comparison of copper analysis by MP-AES, ICP-OES and AA.

Copper	**MP-AES**		**ICP-OES**		**AA**		***P***
Matrix	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	
Beef cattle	18.0 ± 0.6	3.4	16.0 ± 0.7	4.5	15.6 ± 1.1	6.9	0.023
Horse feed	13.3 ± 0.5	3.9	12.7 ± 0.7	5.1	11.8 ± 1.0	8.8	0.156
Poultry feed	16.7 ± 1.3	7.5	15.0 ± 1.0	6.8	15.3 ± 1.5	10.0	0.283
Sheep and goat feed	16.9 ± 0.5	2.7	16.9 ± 0.3	2.0	16.3 ± 1.4	8.4	0.582
Wild animal feed	20.7 ± 1.7	8.0	24.9 ± 0.8	3.4	21.4 ± 2.1	9.8	0.040
Dog and cat food	33.3 ± 0.6	1.7	27.6 ± 1.7	6.0	28.9 ± 4.0	13.7	0.069
Liquid fertilizer	438.7 ± 15.6	3.6	436.7 ± 13.2	3.0	436.7 ± 22.0	5.0	0.987
Mineral mixture	2108.0 ± 27.9	1.3	1975.5 ± 84.3	4.3	2002.0 ± 147.6	7.4	0.298
Specialty fertilizer	382.9 ± 4.6	1.2	334.4 ± 11.5	3.4	352.3 ± 34.5	9.8	0.077

Table 5
Comparison of iron analysis by MP-AES, ICP-OES and AA.

Iron	MP-AES		ICP-OES		AA		P
Matrix	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	
Beef cattle	315.0 ± 4.2	1.3	306.1 ± 6.3	2.1	291.5 ± 25.2	8.6	0.241
Horse feed	155.3 ± 4.2	2.7	156.7 ± 6.2	4.0	161.9 ± 7.8	4.8	0.445
Poultry feed	177.0 ± 8.8	5.0	182.8 ± 1.8	1.0	178.4 ± 17.7	9.9	0.818
Sheep and goat feed	219.2 ± 4.5	2.1	223.2 ± 4.4	2.0	227.0 ± 11.0	4.8	0.470
Wild animal feed	388.4 ± 14.7	3.8	416.5 ± 7.8	1.9	398.0 ± 35.0	8.8	0.359
Dog and cat food	365.7 ± 3.6	1.0	331.5 ± 11.0	3.3	338.3 ± 40.2	11.9	0.262
Liquid fertilizer	3614.8 ± 28.6	0.8	3668.9 ± 180.7	4.9	3668.9 ± 289.2	7.9	0.929
Mineral mixture	6252.7 ± 98.7	1.6	5916.8 ± 125.1	2.1	6235.5 ± 375.2	6.0	0.224
Specialty fertilizer	26991.6 ± 493.5	1.8	25424.5 ± 809.7	3.2	25856.5 ± 2429.2	9.4	0.467

Table 6
Comparison of manganese analysis by MP-AES, ICP-OES and AA.

Manganese	MP-AES		ICP-OES		AA		P
Matrix	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	
Beef cattle	203.3 ± 2.7	1.3	174.8 ± 8.1	4.7	–	–	
Horse feed	126.7 ± 3.0	2.3	115.3 ± 2.5	2.2	–	–	
Poultry feed	138.3 ± 7.7	5.6	122.0 ± 1.4	1.1	–	–	
Sheep and goat feed	100.2 ± 2.2	2.2	88.5 ± 3.0	3.4	–	–	
Wild animal feed	340.1 ± 19.1	5.6	318.9 ± 3.4	1.1	–	–	
Dog and cat food	52.3 ± 1.5	2.9	42.1 ± 1.6	3.7	–	–	
Liquid fertilizer	1656.5 ± 49.7	3.0	1954.6 ± 16.6	0.8	1954.6 ± 99.4	5.1	0.002
Mineral mixture	6693.8 ± 96.4	1.4	6093.0 ± 133.9	2.2	6093.0 ± 535.5	8.8	0.101
Specialty fertilizer	1494.5 ± 31.6	2.1	1299.5 ± 59.8	4.6	1299.5 ± 119.6	9.2	0.037

Table 7
Comparison of zinc analysis by MP-AES, ICP-OES and AA.

Zinc	MP-AES		ICP-OES		AA		P
Matrix	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	Results (ppm)	RSD (%)	
Beef cattle	151.3 ± 1.3	0.9	143.6 ± 2.2	1.5	147.3 ± 7.0	4.8	0.171
Horse feed	90.2 ± 2.3	2.5	79.7 ± 3.0	3.8	76.4 ± 5.9	7.8	0.013
Poultry feed	101.3 ± 4.9	4.9	87.9 ± 4.1	4.6	88.3 ± 5.3	6.0	0.023
Sheep and goat feed	107.9 ± 3.1	2.9	98.2 ± 5.4	5.5	97.6 ± 6.4	6.6	0.087
Wild animal feed	213.7 ± 10.2	4.8	199.9 ± 6.4	3.2	190.2 ± 14.0	7.4	0.091
Dog and cat food	220.1 ± 3.0	1.4	196.2 ± 4.4	2.2	201.8 ± 22.0	10.9	0.141
Liquid fertilizer	10976.7 ± 109.8	1.0	11370.0 ± 109.8	1.0	11375.0 ± 486.9	4.3	0.244
Mineral mixture	3611.3 ± 45.3	1.3	3548.3 ± 124.5	3.5	3631.4 ± 136.8	3.8	0.648
Specialty fertilizer	1662.2 ± 25.4	1.5	1581.8 ± 33.2	2.1	1646.9 ± 149.6	9.1	0.542

the dilution practice will not be detected. For some of the feed materials, AA analysis cannot quantify manganese as the concentration level is below the detection limit of AA.

The official EC method for determination of Fe, Cu, Mn and Zn in feeding stuffs is documented in the Eighth Commission Directive 78/633/EEC of June the 15, 1978 [26]. The method uses AA and a hydrochloride acid digestion. The reported detection limit in that method is 20 mg/kg for Fe, 10 mg/kg for Cu, 20 mg/kg for Mn and 20 mg/kg for Zn. Official AOAC methods use AA to monitor the elements listed above; AOAC official method 965.09 [4] measures minor nutrients in fertilizers and AOAC official method 968.08 [27] and 999.10 [28] measure metals and other elements in plants, pet foods and fortified food. Official AOAC methods 985.01 [4] and 2011.14 [29] also use ICP spectroscopic methods to quantify elements in similar matrices. AA and ICP methods have been well established and are widely adopted in agricultural analytical laboratories. Our data suggests that the new instrumentation of MP-AES is a potential alternative for AA and ICP-OES in those official methods.

5. Conclusions

The MP-AES and ICP-OES show better sensitivity than the AA instrument in the comparison study. Meanwhile, the one way ANONA analysis revealed that the performance of MP-AES is comparable to that of the ICP-OES measurement, with respect to the sample matrices tested. Compared with the commercial ICP-OES which typically uses argon as the plasma gas, the MP-AES relies on using nitrogen as the plasma gas, which may provide a more economical alternative to traditional ICP-OES for routine analysis in agricultural analytical laboratories.

References

[1] D.C. Church, Livestock Feeds and Feedings, third ed., Prentice Hall, Englewood Cliffs, New Jersey, 1991.
[2] K.W. Jackson, T.M. Mahmood, Anal. Chem. 66 (12) (1994) 252–279.
[3] Eighth Commission Directive 78/633/EEC of June 1978 Establishing Community Mehtods of Analysis for the Official Control of Feedingstuffs. In Official Journal No. L206, 29.07.78, pp 43–55.

[4] Official Methods of Analysis Method 985.01 Metals and Other Elements in Plants and Pet Foods, AOAC International, Gaithersburg, MD, 2005.
[5] J. Nolte, ICP Emission Spectroscopy, A Practical Guide, Wiley-VCH, Weinheim, Germany, 2003.
[6] A. Montaser, D.W. Golightly, Inductively Copupled Plasma in Analytical Atomic Spectrometry, VCH Publishers, Inc, New York, 1992.
[7] K.J. Jankowski, E. Reszke, Microwave Induced Plasma Analytical Spectrometry, first ed., Royal Society of Chemistry, Warsaw, Poland, 2010.
[8] H. Kawaguch, M. Hasegawa, A. Mizuike, Spectrochim. Acta, Part B B27 (5) (1972) 205–210.
[9] K. Fallgatt, V. Svoboda, Appl. Spectrosc. 25 (3) (1971) 347–352.
[10] F.E. Lichte, R.k. Skogerbo, Anal. Chem. 45 (2) (1973) 399–401.
[11] M. Moisan, C. Beaudry, P. Leprince, IEEE Trans. Plasma Sci. 3 (2) (1975) 55–59.
[12] A.T. Zander, G.M. Hieftje, Anal. Chem. 50 (9) (1978) 1257–1260.
[13] M.D. Calzada, M.C. Quintero, A. Gamero, J. Cotrino, J.E.S. Uria, A. Sanzmedel, Talanta 39 (4) (1992) 341–347.
[14] J.F. Camuna, M. Montes, R. Pereiro, A. SanzMedel, C. Katschthaler, R. Gross, G. Knapp, Talanta 44 (4) (1997) 535–544.
[15] K. Jankowski, R. Parosa, A. Ramsza, E. Reszke, Spectrochim. Acta, Part B 54 (3-4) (1999) 515–525.
[16] D.J. Douglas, J.B. French, Anal. Chem. 53 (1) (1981) 37–41.
[17] Y. Okamoto, J. Anal. At. Spectrom. 9 (7) (1994) 745–749.
[18] Y. Su, Y. Duan, Z. Jin, Anal. Chem. 72 (22) (2000) 5600 -5.
[19] H. Matusiewicz, M. Slachcinski, Microchem. J. 82 (1) (2006) 78–85.
[20] H. Matusiewicz, M. Slachcinski, J. Anal. At. Spectrom. 25 (8) (2010) 1324–1333.
[21] H. Takahara, M. Iwasaki, Y. Tanibata, IEEE Trans. Instrum. Meas. 44 (3) (1995) 819–823.
[22] H. Matusiewicz, M. Slachcinski, Microchem. J. 86 (1) (2007) 102–111.
[23] J.A.C. Broekaert, V. Siemens, Spectrochim. Acta, Part B 59 (12) (2004) 1823–1839.
[24] T. Maeda, K. Wagatsuma, Microchem. J. 76 (1-2) (2004) 53–60.
[25] Z.N. Zhang, K. Wagatsuma, Spectrochim. Acta, Part B 57 (8) (2002) 1247–1257.
[26] M.R. Hammer, Spectrochim. Acta, Part B 63 (4) (2008) 456–464.
[27] Official Methods of Analysis Method 968.08, Minerals in Animal Feed and Pet Food, AOAC International, Gaithersburg, MD, 1968.
[28] Official Methods of Analysis Method 999.10, Lead, Cad mium, Zinc, Copper, and Iron in Foods, AOAC International, Gaithersburg, MD, 1999.
[29] Official Methods of Analysis Method 2011.14, Calcium, Copper, Iron, Magnesium, Manganese, Potassium, Phosphorus, Sodium, and Zinc in Fortified Food Products, AOAC International, Gaithersburg, MD, 2011.