

The Direct Analysis of Milk Powder on the Liberty Series II ICP-OES with the Axially-Viewed Plasma

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

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Introduction

The analysis of milk is important because milk is an indicator of environmental contamination, a significant pathway for toxic metal intake by humans and a source of essential nutrients. Previously, milk liquid and milk powder analysis was carried out using flame and graphite furnace atomic absorption spectrometry and even anodic stripping voltammetry [1]. Inductively coupled plasma atomic emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are now preferred for routine determinations because of the rapid multi-element analysis capabilities of these techniques.

Generally, milk samples are prepared by either wet digestion or dry ashing [1-5]. These are time consuming and involve procedures using potentially hazardous chemicals. Direct slurry nebulization combined with standard additions calibration has also been reported for ICP-MS with varying success [5,6]. The accuracy of standard additions is greatly influenced by calibration linearity and the presence of spectral interference. The ICP-MS technique has the advantage of sensitivity but is unable to analyze high dissolved solid contents for long periods of time and the instrumentation is more expensive than ICP-OES.

This work describes the direct analysis of milk powder using standard quantitative calibration with aqueous standards. Viscosity effects of the milk powder solutions are corrected for using scandium (361.384 nm—ionic line) as an internal standard. Major, minor and trace elements were determined in a single analysis. Less sensitive lines are used for the determination of major elements allowing both major and minor elements to be determined from a single sample solution.

Many of the major constituents in milk powder such as Na, K and Ca are easily ionized elements (EIE) that have been reported to cause ionization interferences. Ionization interferences tend to cause a reduction in signal intensity with increasing concentration of EIE and the effect is prominent at interferent concentrations at or above 100 mg/L. The atomic lines of Na and, K, and to a lesser extent Ca (422.673 nm) and Li, exhibit signal enhancement with increasing concentrations of



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EIE. The effect can be easily minimized or eliminated on a radially-viewed ICP-OES by adjusting the viewing height. For the more sensitive axially-viewed ICP-OES, many reports of interferences due to EIE have been described [7,8]. In one report, scandium used as an internal standard was found to compensate for part of the signal depression [8]. Ionization interferences on the axially-viewed plasma have been found to be reduced by lowering the nebulizer pressure and increasing the power. Increasing the power increases the electron density in the plasma thus reducing the effect of electrons contributed by the EIE. Generally, when analyzing samples that contain high levels of EIE, it is recommended that all standards have similar levels of EIE added (matrix matching).

An alternative is to saturate the plasma with a high concentration of another EIE such as caesium. Therefore, the effect of adding caesium as an ionization suppressant to the standards and samples was also investigated.

The accuracy and validity of the method was assessed by the use of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 8435 Whole Milk Powder.

Experimental

Instrumental

An Agilent Liberty Series II ICP-OES with the axially-viewed plasma was used for the analysis.

The Liberty Series II ICP features a 40 MHz free running RF generator, a 0.75 m Czerny-Turner monochromator with a 1800 grooves/mm holographic grating used in up to four orders. The resolution of the optical system ranges from 0.018 nm in the 1st order to 0.006 nm in the 4th order.

The instrument was controlled with a Digital Equipment Corporation (DEC) Venturis computer with an Intel Pentium processor and Agilent's Plasma 96 software running under Microsoft's Windows 95 operating system.

The instrument operating conditions are listed in Table 1.

Table 1: Instrument Operating Conditions

Power	1.30 kW
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Sturman- Masters
Torch	Standard axial torch with 2.3 mm id injector
Nebulizer	V-groove
Nebulizer pressure	240 kPa
Pump tube	Inlet - PVC grey-grey, 1.30 mm id Outlet - PVC, blue-blue, 1.65 mm id
Pump speedrate	15 rpm
Sample uptake rate	1.5 mL/min
Integration time	1 second for Ca, K, Mg, Na, P, S and Sr 3 seconds for Ba, Fe, Mn, Zn and Sc
No. of replicates	3
Sample delay time	25 seconds
Fast pump	On
Stabilization time	20 seconds
Background correction	Polynomial plotted background
PMT voltage	600 V

For the determination of sulfur, an Auxiliary Gas Module-2 (AGM-2) is required. The AGM provides a nitrogen purge for the monochromator to extend the working wavelength range from 189 nm down to 175 nm.

To make sure that the milk powder sample was evenly mixed and in suspension while being aspirated, the solution was continuously stirred with a magnetic stirrer.

Standard Preparation

Aqueous standards were prepared from Custom-Grade Multi-element Solutions Var Cal 1, Var Cal 2 and Var Majors 1 (Inorganic Ventures, Inc.) and from 1000 mg/L single element standards (Spectrosol, BDH Chemicals). The standards were made up in 18 M Ω Milli-Q water with 0.5% v/v HNO₃ and 0.002% v/v Triton X100 prepared from a 1% w/v Triton X100 solution. Scandium was added to each solution as an internal standard with a final concentration of 0.5 mg/L.

The following calibration standards were prepared.

Table 2. Calibration Standards

Standard	Concentration (mg/L)	Elements
Standard 1	0.2	Ba, Mn, Zn, Sr
Standard 2	1.0	Ba, Mn, Zn, Sr, Fe
Standard 3	5.0	Mg, Fe
Standard 4	25	Mg, Na, Ca
Standard 5	100	Na, Ca, K
Standard 6	200	K
Standard 7	13.350 and 32.614	S and P, respectively
Standard 8	66.752	S
Standard 9	163.069	P

Rinse and calibration blank solutions were prepared from 18 MΩ Milli-Q water with 0.5% HNO₃ and 0.002% Triton X100.

Sample Preparation

Solutions were prepared from an instant full cream milk powder sample purchased at a local supermarket and SRM 8435 Whole Milk Powder.

Milk powder solutions containing 0.5% and 4% w/v were prepared for both samples. The sample was accurately weighed and then transferred into a volumetric flask. The flask was filled approximately 3/4 full with 18MΩ Milli-Q water and gently shaken until the milk powder was evenly mixed. Triton X100 was added to give a concentration of 0.002%. Acid was not added to the sample solutions as it causes the precipitation of protein. Scandium (0.5 mg/L) was added as an internal standard.

The scandium bulk standard was stabilized with acid and it was necessary to dilute the scandium by preparing a secondary standard before adding it to the milk powder solutions because even a small concentration of acid will cause the precipitation of protein. Adding dilute ammonia solution to the samples to adjust the pH to 7.5 [6] can overcome this problem, but it was not required in this case.

The solutions were made up to the mark and placed in an ultrasonic bath for 5 minutes. The solutions were then shaken vigorously for 1 minute.

A separate rinse containing 0.002% v/v Triton X100 and no acid was used for rinsing between samples.

For the study of the effect of the addition of an ionization suppressant, 1% w/v Cs as CsCl was added to all sample, standard and rinse solutions. Caesium was chosen as an ionization suppressant as it has a low energy of ionization, is not very sensitive by ICP-OES and, therefore, spectral interference is generally not a problem. Caesium chloride is available in a very pure form and does not build up in the torch injector tube as readily as other alkali salts.

Results and Discussion

Milk Powder Analysis

The results presented in Tables 3–6 represent the concentrations of constituent elements in the milk powder on a dry weight basis. Moisture content in the two milk powder samples was determined by accurately weighing the undried samples and then reweighing the samples after drying in an air oven for 4 hours at 85 °C. Moisture content was small and represented only 1.3% and 1.9% of the total weight for the full cream milk powder sample and NIST SRM 8435, respectively.

The mean results of the triplicate analyses for the determination of major constituent elements in milk powder without the addition of 1% w/v Cs are listed in Table 3.

The mean results of the triplicate analyses for the determination of minor and trace constituent elements in milk powder without the addition of 1% w/v Cs are listed in Table 4.

The mean results of the triplicate analyses for the determination of major constituent elements in milk powder with the addition of 1% w/v Cs are listed in Table 5.

The mean results of the triplicate analyses for the determination of minor and trace constituent elements in milk powder with the addition of 1% w/v Cs are listed in Table 6.

The effect of ionization interference from the EIE can be seen for K and Sr and to a smaller extent Ca, in Tables 3 and 4. Ionic lines were used for Ca and Sr and signal suppression for these lines was evident as a value lower than the certified value was found. With the addition of Cs to all solutions, Tables 5 and 6, a value very close to the certified value was found for both lines.

For K, without the addition of Cs, a lower than expected result was found. This is unexpected because signal enhancement is usually observed for K. An explanation for this could be that standard 5 contained reasonably high levels of other EIE and therefore the signal enhancement for K in standard 5 was higher than that for the sample. The sample was remeasured for K using separate standards for K. The measured K concentrations for the full cream milk powder sample and SRM 8435 Whole Milk Powder were 1.14 and 1.26 wt%, respectively. These results are closer to the certified value for the SRM, but are still unexpectedly lower. With the addition of Cs, the result for K was very close to the certified value.

Na was also expected to be affected by the presence of other EIE but this was not evident in this analysis. This is probably due to the presence of other EIE's in both the standards and samples.

The remaining elements did not appear to be greatly affected by the EIE because much of the signal depression was corrected by the internal standard.

For the 4% milk powder solutions without added Cs, EIE concentration was approximately 1000 mg/L and ionization inter-

ference is reportedly [8] quite significant at these levels. Despite this, results very close to the certified values were found for Ba, Fe and Mn. This suggests the internal standard not only successfully corrected for the different viscosity of the samples but also corrected for ionization interference for these elements.

Table 3. Major Elements in Milk Powder Without the Addition of Caesium

Element	Wavelength (nm)	0.5% Milk powder sample (wt%)	0.5% S.R.M. 8435 Whole milk powder (wt%)	S.R.M. 8435 Certified value (wt%)
Ca	315.887	0.849 ± 0.033	0.876 ± 0.008	0.922 ± 0.049
K	769.896	0.844 ± 0.044	0.975 ± 0.020	1.363 ± 0.047
Na	588.995	0.277 ± 0.010	0.376 ± 0.004	0.356 ± 0.040
P	213.618	0.761 ± 0.031	0.784 ± 0.019	0.780 ± 0.049
S	180.731	0.263 ± 0.019	0.268 ± 0.006	0.265 ± 0.035

Table 4. Minor and Trace Elements in Milk Powder Without the Addition of Caesium

Element	Wavelength (nm)	0.5% Milk powder sample (mg/kg)	4% Milk powder sample (mg/kg)	0.5% S.R.M. (mg/kg) 8435 Whole milk powder (mg/kg)	4% S.R.M. 8435 Whole milk powder (mg/kg)	S.R.M. 8435 Certified value (mg/kg)
Mg	285.213	754 ± 23		808 ± 22		814 ± 76
Sr	407.771	4.65 ± 0.04		3.77 ± 0.03		4.35 ± 0.50
Zn	213.856	27.5 ± 1.5		25.5 ± 0.8		28.0 ± 3.1
Ba	455.403		0.70 ± 0.03		0.57 ± 0.02	0.58 ± 0.23
Fe	259.940		2.30 ± 0.05		1.70 ± 0.03	1.8 ± 1.1
Mn	257.610		0.242 ± 0.001		0.151 ± 0.004	0.17 ± 0.05

Table 5. Major Elements in Milk Powder With the Addition of 1% (w/v) Caesium

Element	Wavelength (nm)	0.5% Milk powder sample (wt%)	0.5% S.R.M. 8435 Whole milk powder (wt%)	S.R.M. 8435 Certified value (wt%)
Ca	315.887	0.931 ± 0.019	0.899 ± 0.021	0.922 ± 0.049
K	769.896	1.304 ± 0.032	1.397 ± 0.024	1.363 ± 0.047
Na	588.995	0.298 ± 0.004	0.378 ± 0.004	0.356 ± 0.040
Na	330.237	0.280 ± 0.004	0.360 ± 0.007	0.356 ± 0.040
P	213.618	0.775 ± 0.017	0.758 ± 0.004	0.780 ± 0.049
S	180.731	0.252 ± 0.007	0.254 ± 0.006	0.265 ± 0.035

Table 6. Minor and Trace Elements in Milk Powder With the Addition of 1% (w/v) Caesium

Element	Wavelength (nm)	0.5% Milk powder sample (mg/kg)	4% Milk powder sample (mg/kg)	0.5% S.R.M. (mg/kg) 8435 Whole milk powder (mg/kg)	4% S.R.M. 8435 Whole milk powder (mg/kg)	S.R.M. 8435 Certified value (mg/kg)
Mg	285.213	761 ± 14		775 ± 13		814 ± 76
Sr	407.771	5.53 ± 0.05		4.40 ± 0.07		4.35 ± 0.50
Zn	213.856	30.0 ± 0.7		26.3 ± 0.5		28.0 ± 3.1
Ba	455.403		0.79 ± 0.02		0.62 ± 0.01	0.58 ± 0.23
Fe	259.940		2.23 ± 0.07		1.76 ± 0.06	1.8 ± 1.1
Mn	257.610		0.269 ± 0.004		0.167 ± 0.007	0.17 ± 0.05

Long Term Stability

The long term stability was determined for the most concentrated milk powder solution to show that good stability can be obtained over a reasonable period of time for a solution containing a high content of dissolved and undissolved solids. The effect of internal standardization on long term stability was also studied.

Long term stability was evaluated by continuously aspirating 4% instant full cream milk powder solution over a period of time. A one minute rinse was performed at the maximum pump rate of 50 rpm (fast pump) between measurements.

The precision of the measurements over one and a half hours with internal standardization correction ranged from 1.2 and 2.0 %RSD.

The long term stability plots for major constituents Ca and Mg and minor constituents Ba, Mn and Sr with and without internal standardization are displayed in Figures 1 and 2, respectively.

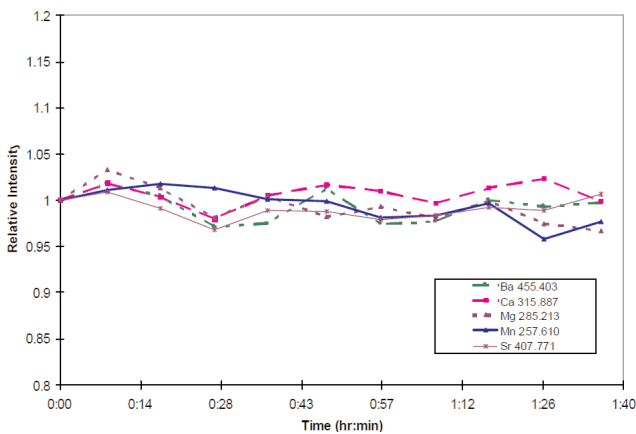


Figure 1. Signal stability over one and a half hours for a 4% full cream milk powder solution with internal standardization.

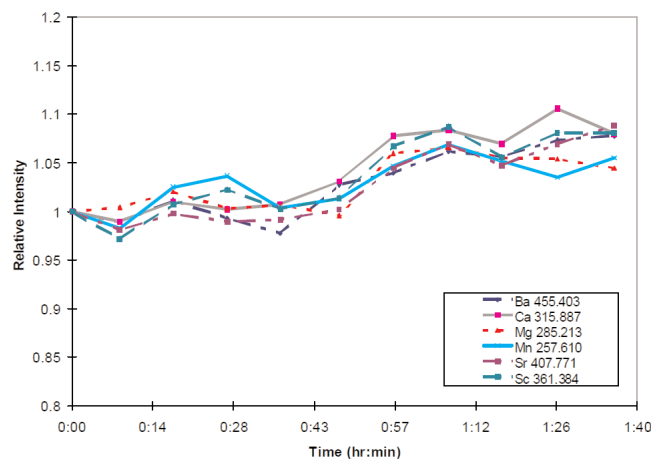


Figure 2. Signal stability over one and a half hours for a 4% full cream milk powder solution without internal standardization.

After the milk powder solution had been aspirated for over one and a half hours, the injector tube showed signs of blockage due to deposition of the milk powder. Figure 2 shows the effect of the build up of milk powder on the signal. Not only does the internal standard correct for viscosity effects and some ionization interferences, from Figure 1 it can be seen that it is also very effective in compensating for drift caused by the gradual build up of milk powder in the injector tube of the torch.

Five replicates were measured at an integration time of three seconds for each line. The precision for each measurement ranged from 0.1 to 1.6 %RSD for the major constituent elements and 0.2 to 3.0 %RSD for minor and trace constituent elements.

Sample Delay and Stabilization Times

When differing matrices are aspirated into a spray chamber, some time must be allowed so that the solution can reach the plasma and for the signal to stabilize. The time required to allow the system to stabilize when switching from aqueous solutions to the milk powder solutions was studied.

This was evaluated by firstly aspirating the rinse solution followed by a 4% full cream milk powder solution. The pump speed was set to 50 rpm (fast pump speed), which is the pump rate used during the sample delay stage, and the signal was monitored for Sc.

A plot of the signal over a short period of time is displayed in Figure 3.

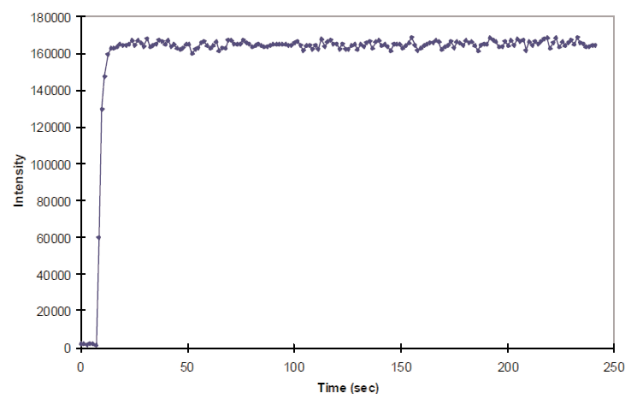


Figure 3. Stabilization profile for a 4% full cream milk powder solution.

When switching from the rinse solution to the 4% milk powder solution, the signal was found to stabilize after 20–25 seconds. Therefore, for the analysis of the milk powder solutions, a sample delay time of 25 seconds was used. The stabilization time was set to 20 seconds. The stabilization time is the time allowed for the pump to slow down from full speed to the analysis pump speed—in this case, 15 rpm.

It was observed that the presence of Triton X100 detergent, which is often used for slurry nebulization to help keep the sample in suspension, greatly reduced the stabilization time.

Summary

The concentrations of various elements of both nutritional and environmental interest in milk powder samples were determined on the Liberty Series II with the axially-viewed plasma.

Aqueous calibration solutions were used and the scandium internal standard successfully corrected for the viscosity effects of the samples, improved the long term stability of the analysis and corrected for some ionization interferences due to the high levels of EIE.

The time required for the system to stabilize after switching from aqueous solutions to the milk powder solutions was found to be very short.

The addition of caesium as an ionization suppressant eliminated ionization interferences and the need for dilution, allowing both major and minor constituents to be measured in a single solution. For the determination of trace elements such as strontium where a more concentrated milk powder solution is required, the addition of caesium becomes an important factor.

With the addition of 1% caesium, all measured values are in very good agreement with the certified values for the standard reference material, validating the accuracy of the method.

References

1. P. D. Kluckner, D. F. Brown, R. Sylvestre, "Analysis of milk by plasma emission spectrometry". ICP Information Newsletter, **1981**, 7, 83.
2. R. C. Munter, R. A. Grande, P. C. Ahn, "Analysis of animal tissue and food materials by inductively coupled plasma emission spectrometry in a university research service laboratory". ICP Information Newsletter, **1979**, 5, 368.
3. N. W. Barnett, L. S. Chen, G. F. Kirkbright, "Determination of trace concentrations of lead and nickel in freeze-dried human milk by atomic absorption spectrometry and inductively coupled plasma emission spectrometry". Analytica Chimica Acta, **1983**, 149, 115-121.

4. J. Borkowska-Burnecka, E. Szmigiel, W. Zyrnicki, "Determination of major and trace elements in powdered milk by inductively coupled plasma atomic emission spectrometry". Chemia Analityczna (Warsaw), **1996**, 41, 625-632.
5. S. E. Emmett, "Analysis of liquid milk by inductively coupled plasma mass spectrometry". Journal of Analytical Atomic Spectrometry, **1988**, 3, 1145-1146.
6. J. R. Dean, L. Ebdon, R. Massey, "Selection of mode for the measurement of lead isotope ratios by inductively coupled plasma mass spectrometry and its application to milk powder analysis". Journal of Analytical Atomic Spectrometry, **1987**, 2, 369-374.
7. C. Dubuisson, E. Poussel, J-M. Mermet, "Comparison of axially and radially viewed inductively coupled plasma atomic emission spectrometry in terms of signal-to-background ratio and matrix effects". Journal of Analytical Atomic Spectrometry, **1997**, 12, 281-286.
8. I. B. Brenner, A. Zander, M. Cole, "Characterization of an axially and radially viewed inductively coupled plasma - influence of Na and Ca". Journal of Analytical Atomic Spectrometry, In Press.

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