Development of a method for the elemental analysis of milk powders using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and its potential use in geographic sourcing

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ARTICLE INFO

ABSTRACT

Milk has been reported as one of the most adulterated foodstuffs in the developed and developing world. One way to detect adulteration is to determine whether the country of origin on the label could be the actual country of origin. Such profiling may be accomplished through the use of elemental analysis techniques, however this is a preliminary study and this goal is not yet met. In this study, a laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) method was developed for the analysis of solid milk powder and compared to k_0-instrumental neutron activation analysis (k_0-INAA) for a reference milk material (IAEA-153) as well as several milk samples from different countries. The analytical figures of merit for both the LA-ICP-MS and the k_0-INAA analysis are reported. Precision of ~ 10% RSD or better was achieved for most elements for both techniques and bias of ~ 10% was achieved for both techniques for most elements with LA-ICP-MS producing lower limits of detection (~ 1 mg/kg) for Sr. The comparison of LA-ICP-MS to k_0-INAA showed overlap of the 95% confidence intervals for all comparison samples. A total of 68 authentic milk powder samples representing 5 different countries (Argentina, Russia, Singapore, Slovenia, and the United States) were analyzed to determine whether multivariate elemental differences between the countries were sufficiently larger than within country differences in order to visualize groupings by country. Principle component analysis (PCA) using Na, Mg, Ca, Rb, and Sr show different groups for the United States, Argentina, Singapore, and Slovenia samples of limited representation for each country. However the large number and geographic distribution of samples from Russia were not able to be distinguished from the samples from the United States and Slovenia.

1. Introduction

Milk is an essential food, however, it has been reported as one of the most adulterated foodstuffs [1]. One common adulteration is to fraudulently label the milk as produced in a country for illicit economic gain. A study organized by the International Atomic Energy Agency (IAEA) in collaboration with the Food and Agriculture Organization (FAO) (CRP D52038) has focused on the development and evaluation of different analytical methods to determine adulteration and geographic (country) origin. Given that milk is usually exported and imported as a powder, this study focuses on the development of laser-based methods for the analysis of solid milk powders.

The main composition of milk powder includes lactose, whey and casein proteins, and the elements Ca, Mg, K, Na, and P [2]. Milk powders also contain trace elements that can potentially be used for geographic provenance. A number of publications have reported the determination of geographic origin of food using elemental analysis and elemental profiling techniques [3–6]. Some elements that have been used for food sourcing are rubidium, cesium, and strontium. These elements may be useful for the analysis of milk powder since rubidium and cesium are easily mobilized in the soil and relocated into plants, and strontium is chemically similar to calcium, indicating that strontium can substitute for calcium in a wide range of naturally occurring minerals [3].

Past publications on the elemental analysis of bovine milk and milk powder have shown that the elemental concentrations in milk statistically differ by seasons, feed, and the location of the farm. Herwig et al. [7] found some correlations between the trace elemental concentration of feed and milk. Sola-Larrañaga and Navarro-Blasco [8] observed differences in milk composition with season. These differences in elemental profiles suggest that multi-elemental analysis of milk has the potential to be used to differentiate milk samples originating from farms with different feeding systems and environments and thus possibly by country if the within country variation is less than the between country variation. Potocnik et al. [9] was able to classify milk samples based on geographic region within Slovenia. Sacco et al. [10] was able to classify milk as being from southern Italy or foreign milk. Being able to determine if an imported milk has an elemental profile that is consistant with the country listed on the label is one step towards preventing milk adulteration.

The most commonly used techniques for the elemental analysis of milk (liquid) are inductively coupled plasma-optical emission spectroscopy (ICP-OES) [11,12] and inductively coupled plasma-mass spectroscopy (ICP-MS) [7,13]. However, for both of these methods, the sample usually must undergo an acid digestion procedure and dilution prior to analysis. Other researchers have reported the use of a specialized nebulizer and direct sampling of either a diluted milk sample or a milk sample treated with EDTA [12,14,15].

An alternative to these liquid sample introduction approaches is laser ablation (LA). A laser is used to generate fine particles of a solid sample that can be further analyzed by elemental techniques, thus eliminating the need for strong acids and dilutions, and allows for a larger representative sample to be characterized. Methods for preparation of solid milk samples have been previously developed for both laser induced breakdown spectroscopy (LIBS) and LA-ICP-OES [16–19]. These sample preparation methods have either reported problems with matrix effects or were limited to only the major elements Na, Ca, Mg, and K. To the authors' knowledge this is the first study to report the analysis of milk using LA-ICP-MS, which offers improved sensitivity compared to LIBS and LA-ICP-OES.

This paper mainly describes the development of a standard addition method for LA-ICP-MS that was evaluated using the milk powder reference material IAEA-153 (Trace Elements in Milk Powder, International Atomic Energy Agency, Vienna, Austria). The standard addition method is used here to estimate the elemental concentrations in an unknown sample by creating a calibration curve, which is extrapolated to the x-intercept. The calibration curves used in this study were created by adding increasing amounts of single-element standards to an aliquot of milk powder and plotting the instrument signal vs added concentration. Since all the calibration standards are made of the same milk powder, this method usually does not suffer from matrix effects. To further test the accuracy of the LA-ICP-MS method, the results for 13 samples were compared with a k_0-INAA method that was previously developed and evaluated [9]. This paper then looks at combining elemental data from other labs. Several laboratories from 5 countries (Argentina, Russia, Singapore, Slovenia, and the United States) provided elemental data for authentic milk powder samples. In order to assess the performance of each laboratory's methodology, each participant was asked to analyze IAEA-153. For this reference material, consistent results (within 95% confidence) were obtained. Finally, using the data submitted from the participating laboratories, the discrimination capabilities of the LA-ICP-MS elemental menu was evaluated to determine if differences between countries could be detected.

2. Materials and methods

2.1. Reference materials and sample collection

The following reference material was used: IAEA-153. Authentic and commercial milk samples were collected. Authentic is used to describe a milk sample where the origin such as country, region, or farm of production is known and documented. Commercial is used to describe samples purchased from a store where the exact origin is unknown. Authentic United States milk powder samples were shipped directly from a milk shed drying facility in Tulare, California. Each sample contained approximately 500 g and was marked as either skim or nonfat dairy milk. Commercial milk powder samples were also collected from local grocery stores. Authentic milk samples from other countries were either collected from farms within that country by the participating laboratory and dried in the laboratory using various techniques or collected directly from a drying facility. The samples collected at the farm level were approximately 2 g each.

2.2. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

2.2.1. Sample and calibration preparation

For the creation of calibration curves, single element ICP (CPI International, Santa Rosa, CA) and ICP-MS (Ricca Chemical Company, Pocomoke City, MD) standard solutions of Zn, Rb, Sr, and In at 1000 µg/mL and Na, Mg, Ca, Sc at 10,000 µg/mL were used.

Four representative samples of approximately 0.5 g of milk powder were accurately weighed to a precision of 0.1 mg into 17 × 100 mm polypropylene tubes. When sample mass was scarce, only 0.15 g of powder was used. Sc and In single element ICP-MS standard solutions were added ("spiked") as internal standards to each sample to a final concentration of 500 and 50 mg/kg, respectively.

Since the ICP element standards used are in nitric acid, partial digestion of the milk powders could occur. Calibration solutions were prepared that allowed the same amount of solution (160 µL for 0.5 g) to be added to each sample. The concentration of each element added to the four calibration standards can be found in Table 1.

Samples were mixed thoroughly with a vortex touch mixer (Fischer Scientific, Pittsburgh, PA) and dried in air at 80 °C in a PTFE-coated graphite HotBlock (Environmental Express, Charleston, SC) for up to 12 h.

To prepare the pellets, the dried milk powder samples were homogenized and pulverized to a fine powder using a high speed ball mixer mill (Glenmills, Clifton, NJ, USA) with a tungsten carbide ball and cups at 25 Hz for 15 min. For samples with a mass of 0.5 g, the samples were pressed into pellets of 13 mm in diameter in a 13 mm stainless steel die at 4 t for 2 min (Carver Benchtop Pellet Press, IN, USA). For samples with a mass of 0.15 g, the samples were pressed into pellets of 6 mm in diameter in a 6 mm stainless steel die at 2 t for 2 min.

2.2.2. Instrumental parameters

Laser ablation ICP-MS was performed using a quadrupole ELAN DRC II 6100 (Perkin Elmer LAS, Shelton, CT) connected to a 213 nm laser ablation system (New Wave Research Inc., Fremont, CA). The laser parameters were optimized using IAEA-153 to obtain the best signal to noise ratios and precision. The parameters were as follows: 100% energy (0.65 mJ), 10 Hz, 190 µm spot, 60 s dwell. Helium at 0.9 L/min

Table 1
The concentrations of each element added to each calibration standard in the standard addition method.

Element	Calibration Standard 1 (mg/kg)	Calibration Standard 2 (mg/kg)	Calibration Standard 3 (mg/kg)	Calibration Standard 4 (mg/kg)
Na	500	1000	2000	0
Mg	250	500	0	1000
Ca	500	1000	0	2000
Zn	60	30	10	0
Rb	20	10	5	0
Sr	10	5	2.5	0

was used as the ablation and carrier gas. Daily performance was tested using NIST SRM 612 (Trace Elements in Glass Matrix) (NIST, Gaithersburg, MD).

Isotopes that were mostly clear of interferences, easily measured, and preformed well during method optimization were selected. The isotopes measured included ^{23}Na, ^{24}Mg, ^{39}K, ^{44}Ca, ^{45}Sc, ^{66}Zn, ^{85}Rb, ^{88}Sr, and ^{115}In. The acquisition parameters for the pellets were as follows: transient signal output with 20 s gas blank, 60 s laser ablation, and 35 s of post-ablation blank, peak-hopping mode with a 20 s dwell for each isotope in the element menu, and 5 replicates per pellet

For integration of the transient signal, Plot2 (v2.2.10, Michael Wesemann Apps, Berlin, Germany) was used. For statistical evaluation of the data, Excel 2011 (v14.6.2, Microsoft Corporation, Redmond, Washington) and JMP (v13.0, SAS Institute Inc., Cary, North Carolina) were used.

2.3. k_0-INAA

2.3.1. Sample and calibration preparation

For k_0-INAA an aliquot (0.06–0.24 g) of milk powder sample was measured into a pure polyethylene ampoule (SPRONK system, Lexmond, Netherlands) so that the ampoule was full and sealed. For determination of intermediate and long-lived radionuclides, the milk powder and standard Al-0.1%Au (IRMM-530R) discs were stacked together and fixed in the polyethylene vial in sandwich form [9].

2.3.2. Instrumental parameters

The samples and standards were irradiated for 12 – 20 h in the carousel facility of the TRIGA Mark II research reactor at the Jožef Stefan Institute with a thermal neutron flux of 1.1×10^{12} cm^{-2} s^{-1}. After irradiation, the milk powder was measured after 4, 7 and 21 days cooling time on absolutely calibrated HPGe detectors with 40% and 45% relative efficiency. For peak area evaluation, the HyperLab 2002 program (Hyperlabs Software, Budapest, Hungary) was used. For elemental concentrations and effective solid angle calculations the software package Kayzero for Windows (DSM Research, Geleen, Netherlands) was applied.

3. Results and discussion

3.1. Development of the LA-ICP-MS method

The sample preparation steps were optimized so that the internal standards and element spikes were homogenized in the milk. Various milling times (2 mins, 5 mins, 10 mins, 15 mins, 30 mins) and different milk powder samples were tested to determine the amount of time needed to homogenize the element spikes.

Fig. 1 shows the transient signal for K, Na, Sc, and In after milling for 15 mins. K was not added to any of the samples so the signal shown represents the K content in the milk powder. Na is naturally present in milk powders and is also an element that was spiked in the samples. The signal depicted is a combination of the natural Na and a 1000 mg/kg spike. Sc and In are not normally present in milk or are present in a very small amount; these elements are spiked into the milk samples at 500 mg/kg and 50 mg/kg respectively. The element transient signals all follow the same trend indicating that the element spikes are homogenized in the sample.

Fig. 1 also shows the integration strategy for selecting the gas blank and signal ranges. The gas blank was subtracted from the signal. The blank-subtracted signal was normalized to an internal standard (K, Sc, or In). Three internal standards were selected and evaluated to assess which internal standard performed the best in terms of accuracy and precision for each element. IAEA-153 was used to assess the performance of each internal standard. All three internal standards produced accurate concentrations for Zn, Rb, and Sr. However, K performed the best for Na, Mg, and Ca. K normalization also produced more linear
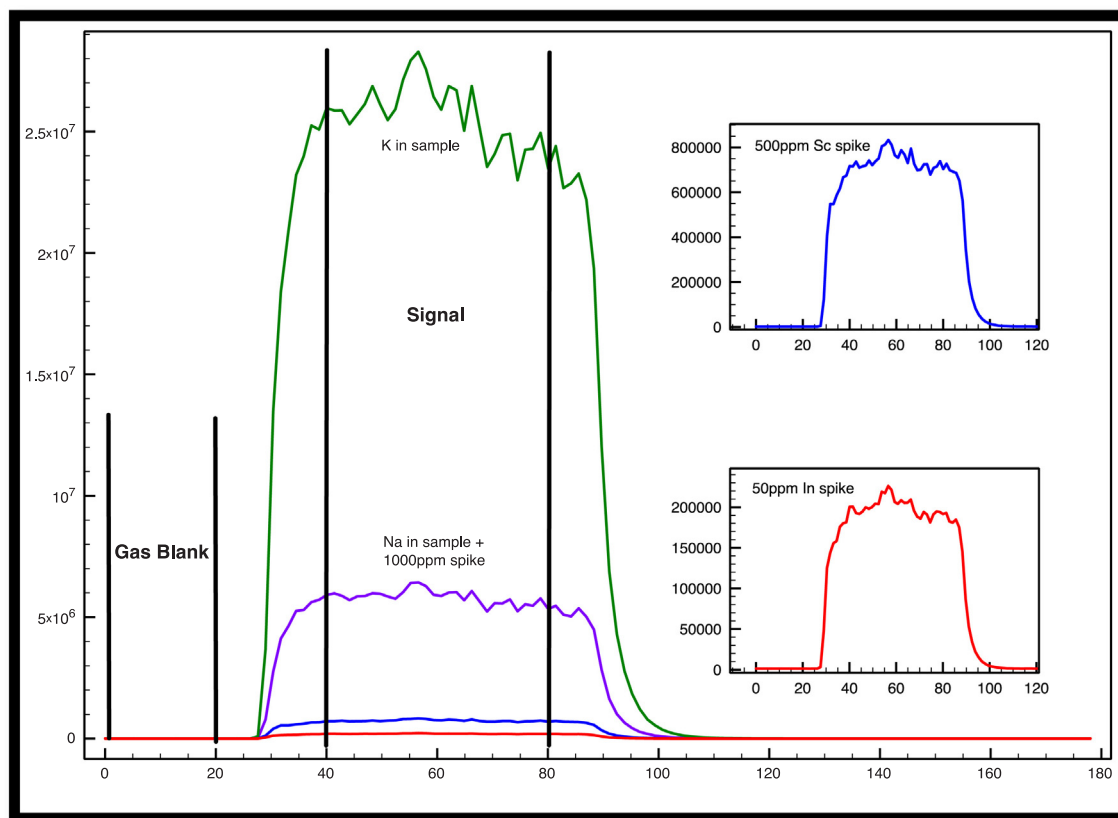

Fig. 1. For each replicate, a 20 s gas blank was integrated. For the signal, the first and last 10 s were ignored so only 40 s were integrated.
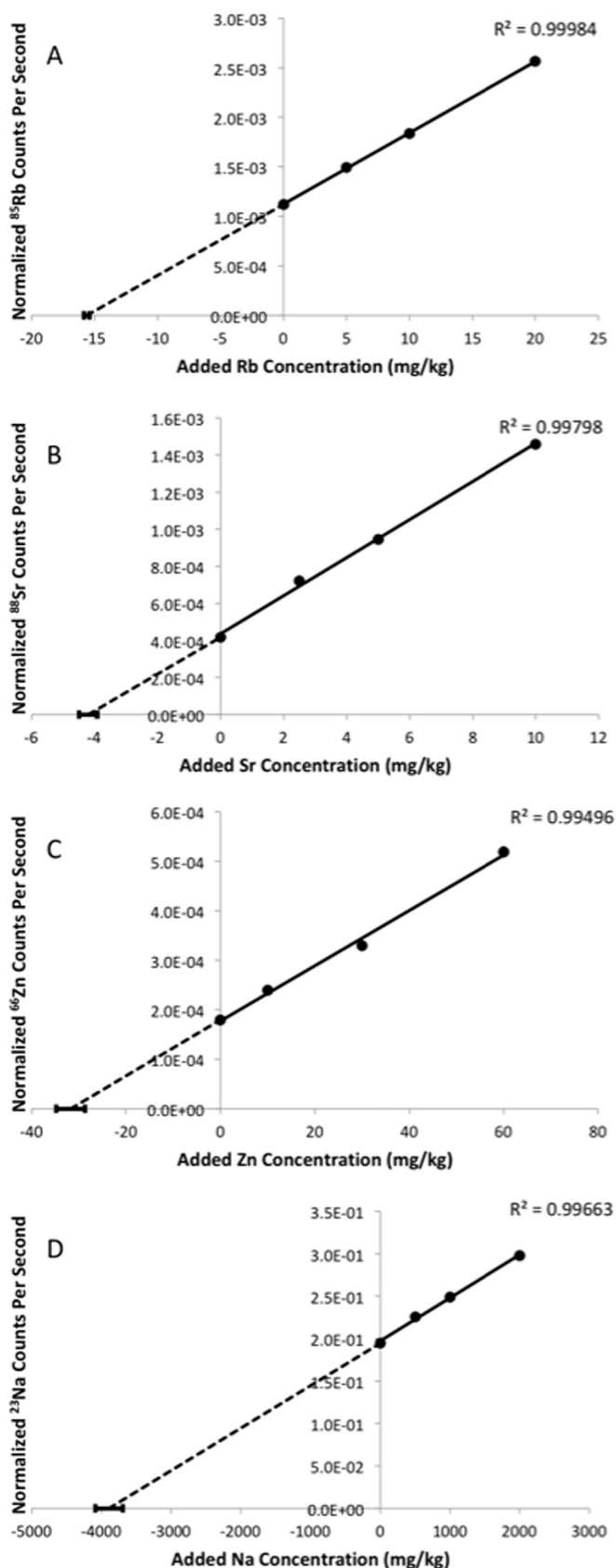
Fig. 2. Examples of calibration plots for some elements in IAEA-153 (A: Rubidium, B: Strontium, C: Zinc, and D: Sodium). Vertical error bars represent one standard deviation of the measured values over five replicates. Horizontal error bars on the extrapolated concentration represent the uncertainty S_{X_E}. In many cases, error bars cannot be seen over the data point due to the high precision.

calibration curves which resulted in smaller concentration uncertainties. In the end, all elements were normalized to K for this study.

The performance of the standard addition method was evaluated with IAEA-153. Fig. 2 shows the calibration curves created by plotting the normalized counts per second on the y-axis and added concentration (mg/kg) on the x-axis for select elements. The dotted line shows how the standard addition curve was extrapolated to determine the concentration in the original milk sample (negative x-intercept). All standard addition curves are very linear, R^2 greater than 0.99. The error bars for the data points are barely visible due to the high precision of the replicate measurements. The uncertainty of the extrapolated concentration, S_{X_E}, was calculated by using:

$$S_{X_E} = \frac{S_{y/x}}{b} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{b^2 \sum_i (x_i - \bar{x})^2}}$$

where b is the slope of the regression line, n is the number of points in the regression line. $S_{y/x}$ estimates the random errors in the y-direction

$$S_{y/x} = \sqrt{\frac{\sum_i (y_i - \hat{y}_i)^2}{n-2}}$$

where $\hat{y}$ are the fitted y values corresponding to each x-value and calculated from the regression equation [20]. S_{X_E} is displayed in Fig. 2 as a horizontal error bar on the x-intercept.

The accuracy, uncertainty, and limits of detection (LOD) of the method for all elements are reported in Table 2. The LODs were calculated using:

$$LOD = \frac{3 * S_{y/x}}{b}$$

Results indicate that the extrapolated concentrations (X_E) are in good agreement with the reported values for reference material IAEA-153. Only one element, Zn, fell outside the 95% confidence interval for unknown reasons.

The method performed well in terms of both accuracy and precision. Zn is the only element that fell outside the reported 95% confidence interval.

3.2. Comparison of LA-ICP-MS to k_0-INAA

k_0-INAA is a primary method for quantitative elemental analysis. It is often used to certify reference materials. It is used in this study to further assess the accuracy of the LA-ICP-MS method. Comparison of the LA-ICP-MS results for 13 powdered milk samples to k_0-INAA was done by comparing 95% confidence intervals for each technique. The element menu was limited to Na, Ca, Rb, and Sr for the comparison. Zn was excluded because it fell outside the 95% confidence interval for IAEA-153. Mg was not measured by k_0-INAA because it should be measured via ^{27}Mg, which is a short-lived radionuclide ($T_{1/2} = 9.462$ min). There were some samples that had a Sr concentration below the limit of detection for k_0-INAA. These samples are marked with < LOD. A better LOD for Sr was achieved with LA-ICP-MS than k_0-INAA (1 mg/kg vs 5 mg/kg).

Shown in Table 3 are the extrapolated concentrations (mg/kg) for

Table 2
Validation of the standard addition method using IAEA-153.

	Recommended Value IAEA-153 (mg/kg, 95% Confidence Interval)	Conc. (X_E, mg/kg)	Uncertainty (S_{X_E}, mg/kg)	Bias (%)	LOD (mg/kg)
Ca	12,870 (12,540–13,170)	**12,800**	465	− 0.5	148
Mg	1060 (1000–1150)	**1100**	66	3.7	91
Rb	14.03 (12.27–16.10)	**15.4**	0.2	9.8	0.3
Na	4180 (3870–4440)	**3870**	206	− 7.4	190
Sr	4.09 (3.49–4.73)	**4.18**	0.28	2.2	0.67
Zn	39.56 (37.66–41.23)	**31.3**	2.9	**20.9**	6.7

Table 3

Comparison of the LA-ICP-MS method to k_0-INAA. Results are given in mg/kg.

| Sample	LA-ICP-MS				k_0-INAA			
	Na	Ca	Rb	Sr	Na	Ca	Rb	Sr
USA 1	3750 ± 694	12,800 ± 2030	15.4 ± 1.3	4.21 ± 1.39	4310 ± 302	12,700 ± 904	17.4 ± 1.2	< LOD
USA 2	3960 ± 134	11,500 ± 1280	16.7 ± 2.5	7.59 ± 0.40	4060 ± 284	10,900 ± 786	17.0 ± 1.2	8.62 ± 1.70
USA 3	4050 ± 137	11,800 ± 1420	15.6 ± 0.4	7.83 ± 0.89	3970 ± 278	11,100 ± 800	16.5 ± 1.2	7.10 ± 1.38
ARGENTINA 1	4300 ± 1705	11,500 ± 5680	17.5 ± 8.6	6.87 ± 0.24	4330 ± 304	10,900 ± 800	17.3 ± 1.2	7.11 ± 2.24
ARGENTINA 2	2650 ± 98	7850 ± 1410	4.78 ± 1.54	16.9 ± 9.2	2770 ± 196	8890 ± 902	5.00 ± 0.46	17.4 ± 4.8
SLOVENIA 1	3480 ± 150	7640 ± 427	4.20 ± 1.30	19.5 ± 3.5	3700 ± 264	9060 ± 974	3.97 ± 0.40	27.4 ± 5.6
SLOVENIA 2	3730 ± 300	12,800 ± 4810	16.5 ± 1.7	3.05 ± 0.93	4110 ± 288	11,800 ± 884	17.9 ± 1.2	< LOD
SLOVENIA 3	4020 ± 624	13,500 ± 3080	16.4 ± 1.0	3.45 ± 1.81	4150 ± 292	12,000 ± 914	17.4 ± 1.2	< LOD
COMMERCIAL 1	3870 ± 567	13,700 ± 7300	13.4 ± 1.3	2.35 ± 1.82	4040 ± 292	12,900 ± 962	14.7 ± 1.0	< LOD
COMMERCIAL 2	3680 ± 122	11,100 ± 561	11.1 ± 0.8	5.10 ± 0.54	3650 ± 256	10,800 ± 774	11.3 ± 0.8	5.37 ± 1.58
COMMERCIAL 3	3740 ± 179	11,000 ± 1020	24.7 ± 1.7	7.98 ± 1.06	3960 ± 280	11,300 ± 862	25.9 ± 1.8	10.7 ± 2.4
COMMERCIAL 4	2870 ± 9	8400 ± 1580	9.40 ± 0.40	3.60 ± 0.51	2980 ± 208	8500 ± 666	9.71 ± 0.70	< LOD
COMMERCIAL 5	2700 ± 140	8630 ± 986	26.5 ± 0.4	3.99 ± 0.63	2690 ± 188	8050 ± 640	28.5 ± 2.0	< LOD
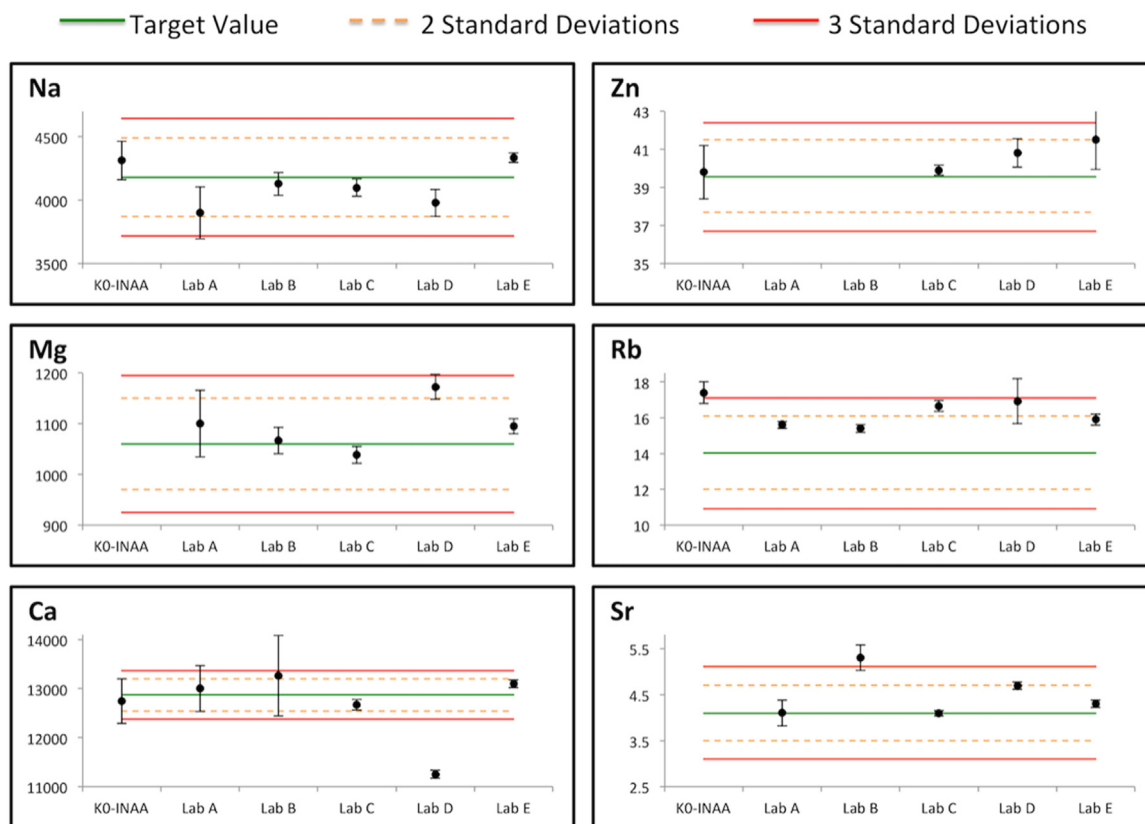
Fig. 3. Inter-comparison of select elements in IAEA-153. Results are given in mg/kg. Shown are the mean values determined by each lab for each element. Lab A used LA-ICP-MS. Labs B, D, E used solution ICP-MS. Lab C used ICP-OES for Na, Mg, Ca, Zn and ICP-MS for Rb and Sr.

LA-ICP-MS and 95% confidence intervals for both methods.

For LA-ICP-MS measurements, confidence intervals were calculated using:

$$X_E \pm t_{(n-2)} S_{X_E}$$

For this calculation, n is the number of calibration standards, 4, and t is the Student's t-distribution. The 95% confidence interval for k_0-INAA was calculated by multiplying the combined standard uncertainty by 2. All intervals for LA-ICP-MS overlapped with those for reported for k_0-INAA. The intervals for Ca and Na are large for LA-ICP-MS because there were only 4 calibration standards used for the standard addition. Increasing the number of standards, n, would decrease the 95% confidence interval.

Both LA-ICP-MS and k_0-INAA required minimum sample preparation, but k_0-INAA's sample preparation was quicker and easier. However, the cost and complexity of k_0-INAA make it unsuitable for routine milk analysis.

3.3. Inter-comparison

Research laboratories participating in the IAEA CRP from (Argentina, Russia, Singapore, Slovenia, and the United States) were asked to analyze IAEA-153 for Na, Mg, Ca, Zn, Rb, and Sr using their own methods, in order to evaluate their performance. The techniques used included LA-ICP-MS, solution ICP-MS, and ICP-OES. Although there are some differences between labs, each lab used a standard operating procedure that has previously been optimized. Fig. 3 shows the data from the 5 participating labs and how it compares to the reported
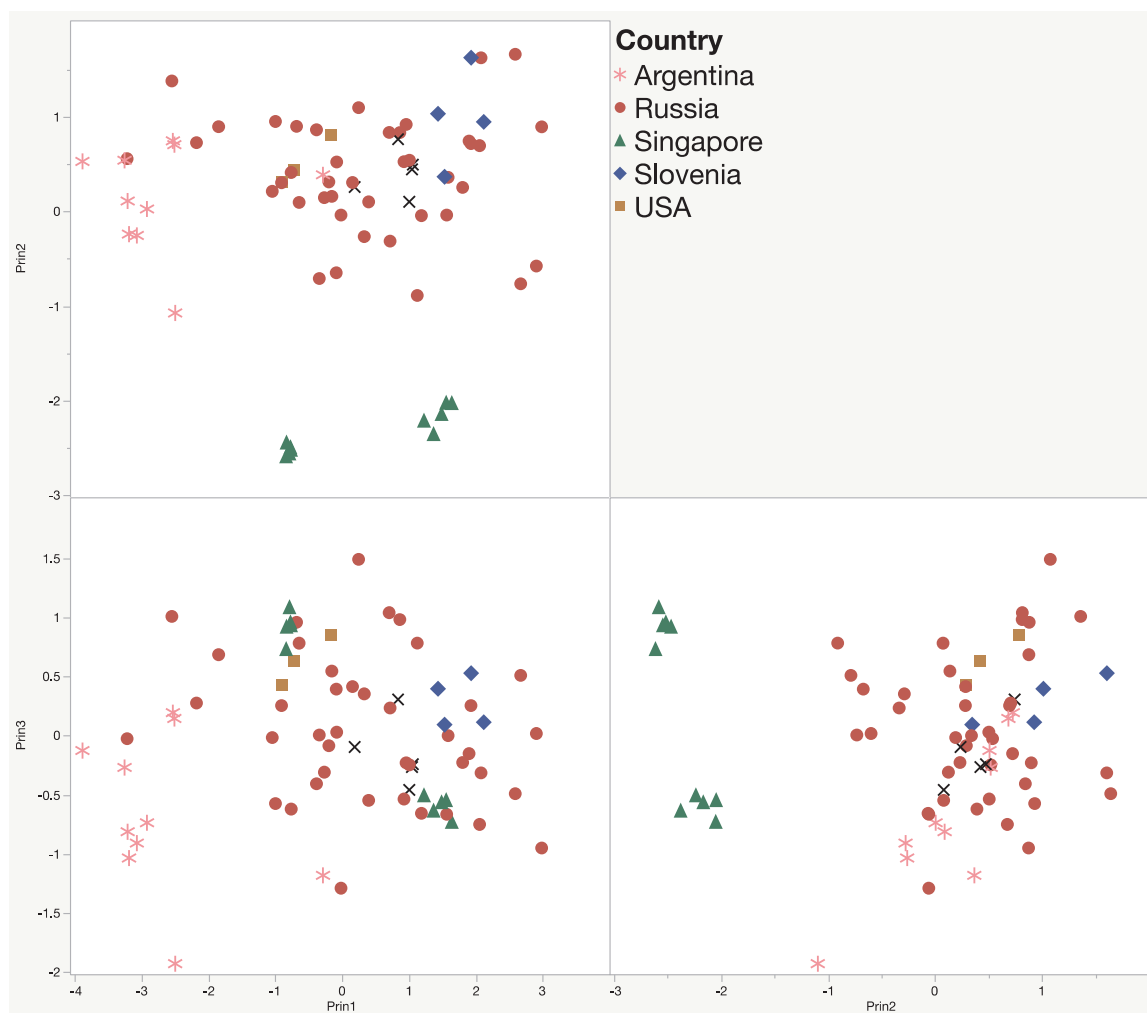
Fig. 4. A PCA plot depicting the authentic samples from Argentina, Russia, Singapore, Slovenia, and the United States. The black Xs represent the data for IAEA-153 submitted by each country. Component 1 accounts for 63.0% of the variation. Component 2 accounts for 26.4%. Component 3 accounts for 8.0%.

value for IAEA-153 and k_0-INAA. The red and yellow standard deviation lines were calculated from the IAEA-153 reference sheet. For most labs, the concentration of the element fell within ± 3 standard deviations. The [Zn] fell outside ± 3 standard deviations for labs A and B (not shown on Fig. 3) for unknown reasons. The [Ca] fell outside ± 3 standard deviations for lab D and the uncertainty of the measurement for lab B was high. For these reasons, Zn and Ca were excluded from the element menu for discrimination.

3.4. Preliminary study on elemental profiling

Each lab collected authentic milk samples, analyzed them using their own method, and submitted the data. Countries represented include: Argentina, Russia, Singapore, Slovenia, and the United States. For some countries, the data submitted represents a small area and not the entire country. For example, the United States data represents 3 samples from a milk shed. The Slovenia data represents 2 drying facilities, 2 samples from each. The data from Singapore represents 2 farms, 5 samples from each. The data from Argentina are from 1 to 3 farms within each of 4 distinct regions. The data spread from Russia is for 41 samples collected from farms located throughout the southern half of the entire country (~ 9000 km).

Principle component analysis (PCA) was used to evaluate the data from Argentina, Russia, Singapore, Slovenia, and the United States. To generate the PCA plots the following elements/ratios were used: Mg,

Rb, Sr, Na/Sr, Mg/Sr. These were selected, based on their discriminating capability, using stepwise linear discriminant analysis in JMP. The samples from Russia were not able to be distinguished from those from Argentina, the United States, and Slovenia, Fig. 4. This is mostly due to the expected large elemental variation observed within the many Russian samples due to the different geological sources, in comparison to the limited samples (and geographic representation) from Argentina, the United States, and Slovenia. Due to the high variation in the Russian samples, the PCA was redone excluding Russia to better evaluate the grouping between the remaining countries (Fig. 5). IAEA-153 was included in the PCA plots to further show that the IAEA-153 data clusters together even though it was analyzed by different methods in different labs.

4. Conclusion

This study presents the development of a standard addition LA-ICP-MS method for the analysis of powdered milk that yields accurate elemental concentrations for Na, Mg, Ca, Rb, and Sr without the need for acid digestion. The analytical approach developed for LA-ICP-MS may also be used for LIBS in the future, which would be a more convenient, faster, and economical tool that would especially be useful for developing countries.

To test the discriminating potential of this method, data from authentic milk powder samples from 5 countries were collected and
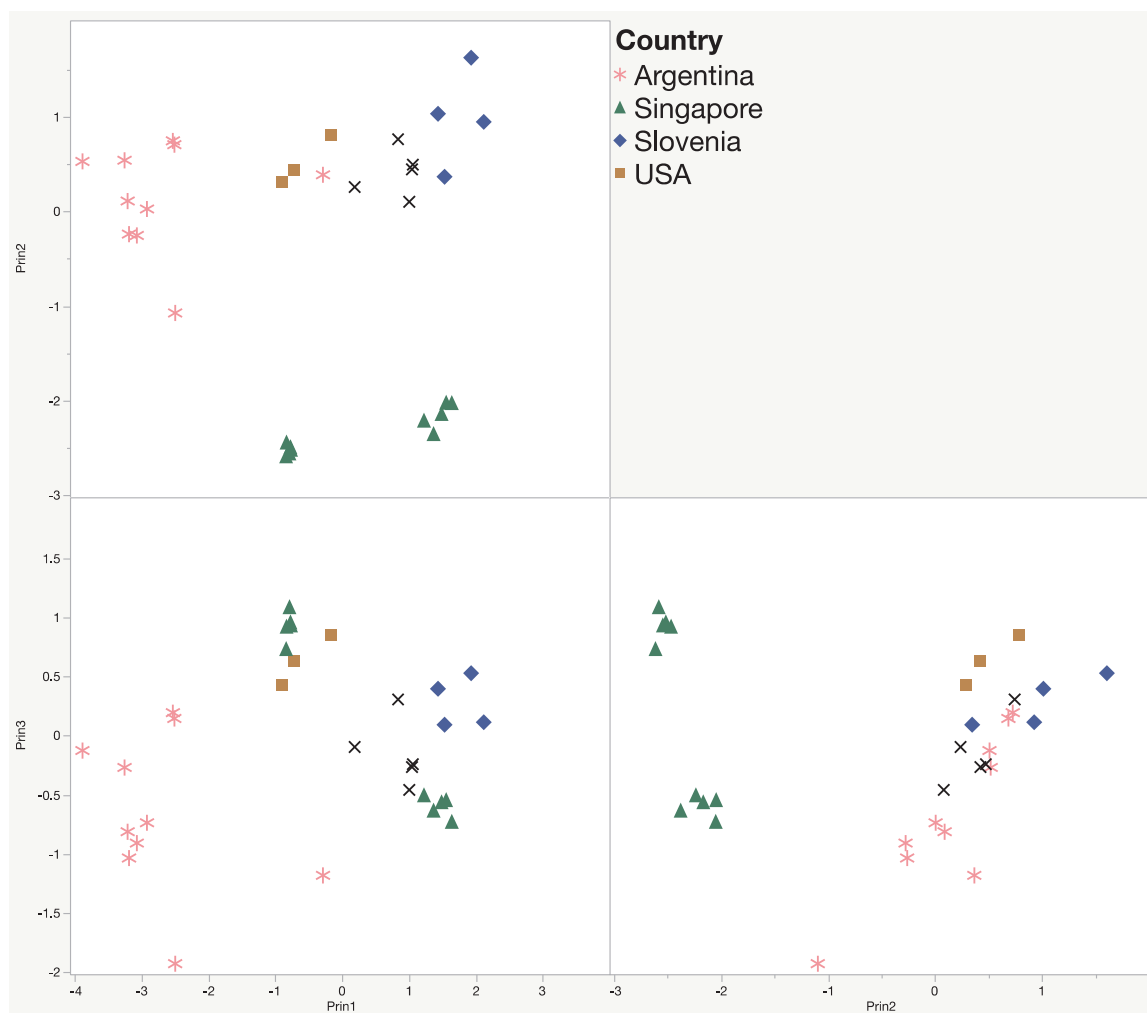
Fig. 5. A PCA plot depicting the authentic samples from Argentina, Singapore, Slovenia, and the United States. The black Xs represent the data for IAEA-153 submitted by each country. Component 1 accounts for 63.0% of the variation. Component 2 accounts for 26.4%. Component 3 accounts for 8.0%.

evaluated. The limited element menu was able to differentiate the samples from Singapore, Argentina, the United States, and Slovenia, from each other. However, the collected data represented a few localized areas and does not account for the total variation within every country. Samples collected from a large geographic area within Russia produces an expected large variation in the elemental profiles and therefore the limited element menu was not able to distinguish the Russian milk samples from those for Argentina, the United States, and Slovenia. The goal of being able to determine if a commercial milk originated from the country on the label has not been met. However, the few samples from Singapore appear to be very different from the samples from the drying facilities in the United States and Slovenia, and from the samples from Russia. If milk produced in Singapore was labeled as being made in the Russia, the elemental profile of that milk would not line up with that the current profile found in southern Russia. More samples would need be analyzed for each county to better account for the within country variation. The addition of isotope ratios, additional trace elements, or another discriminating factor may help in further distinguishing one country from another thus making it easier to determine if an unknown milk came from the country on the label.

The data from the participating laboratories suggests that database creation is a viable option and the addition of authentic samples from interested countries and geographic areas may provide a tool to detect fraudulently labeled commercial milk.

Acknowledgements

References

[1] M.S. Relsch, Momentum builds to keep fraudulent food off of store shelves, C&En (2014) 8–13.
[2] Y.W. Park, G.F.W. Haenlein, Milk and Dairy Products in Human Nutrition: Production, Composition and Health, John Wiley & Sons, Ltd., Chichester, West Sussex, UK, 2013.
[3] S. Kelly, K. Heaton, J. Hoogewerff, Tracing the geographical origin of food: the application of multi-element and multi-isotope analysis, Trends Food Sci. Technol. 16 (12) (2005) 555–567.
[4] L.M. Reid, C.P. O'Donnell, G. Downey, Recent technological advances for the determination of food authenticity, Trends Food Sci. Technol. 17 (7) (2006) 344–353.
[5] B. Peres, et al., Review of the current methods of analytical traceability allowing determination of the origin of foodstuffs, Food Control 18 (3) (2007) 228–235.

[6] D.M.A.M. Luykx, S.M. van Ruth, An overview of analytical methods for determining the geographical origin of food products, Food Chem. 107 (2) (2008) 897–911.

[7] N. Herwig, et al., Multi-element screening in milk and feed by SF-ICP-MS, Food Chem. 124 (3) (2011) 1223–1230.

[8] C. Sola-Larrañaga, I. Navarro-Blasco, Chemometric analysis of minerals and trace elements in raw cow milk from the community of Navarra, Spain, Food Chem. 112 (1) (2009) 189–196.

[9] D. Potocnik, et al., Multi-elemental composition of Slovenian milk: analytical approach and geographical origin determination, Acta Imeko 5 (1) (2016) 15–21.

[10] D. Sacco, et al., Discrimination between Southern Italy and foreign milk samples using spectroscopic and analytical data, Food Chem. 114 (4) (2009) 1559–1563.

[11] M.A. Brescia, et al., Chemometric determination of the geographical origin of cow milk using ICP-OES data and isotopic ratios. A preliminary study, Ital. J. Food Sci. 3 (2003) 329–336.

[12] P.J. McKinstry, H.E. Indyk, N.D. Kim, The determination of major and minor elements in milk and infant formula by slurry nebulisation and inductively coupled plasma - optical emission spectrometry (ICP-OES), Food Chem. 65 (2) (1999) 245–252.

[13] A. Ataro, et al., Quantification of trace elements in raw cow's milk by inductively coupled plasma mass spectrometry (ICP-MS), Food Chem. 111 (1) (2008) 243–248.

[14] K.M. Hua, M. Kay, H.E. Indyk, Nutritional element analysis in infant formulas by direct dispersion and inductively coupled plasma-optical emission spectrometry, Food Chem. 68 (4) (2000) 463–470.

[15] J.A. Nobrega, et al., Direct determination of major and trace elements in milk by inductively coupled plasma atomic emission and mass spectrometry, J. Anal. At. Spectrom. 12 (1997) 1243–1246.

[16] Z. Abdel-Salam, J. Al Sharnoubi, M.A. Harith, Qualitative evaluation of maternal milk and commercial infant formulas via LIBS, Talanta 115 (2013) 422–426.

[17] M. Ghezelbash, et al., Application of LIBS for identification and determination of element concentrations in milk, Iran. J. Nutr. Sci. Food Technol. 10 (1) (2015) 89–96.

[18] N. Gilon, et al., A matrix effect and accuracy evaluation for the determination of elements in milk powder LIBS and laser ablation/ICP-OES spectrometry, Anal. Bioanal. Chem. 401 (9) (2011) 2681–2689.

[19] W.Q. Lei, et al., Comparative measurements of mineral elements in milk powders with laser-induced breakdown spectroscopy and inductively coupled plasma atomic emission spectroscopy, Anal. Bioanal. Chem. 400 (10) (2011) 3303–3313.

[20] J.N. Miller, J.C. Miller, Calibration methods in instrumental analysis: regression and correlation, Statistics and Chemometrics for Analytical Chemistry, Pearson, Prentice Hall, 2010.