Elemental Analysis of Nutrients in Dairy Manure by Automated X-ray Fluorescence Spectrometry

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Abstract

We have determined that X-ray fluorescence (XRF) spectrometry can be used as a rapid and precise method for quantitative elemental analysis of macro and micro nutrients in dairy manure. The elements chosen for this study were N, P, K, Ca, Mg, S, Zn, Mn, Fe, Cu, Al, Na, B, and C. The wavelength-dispersive XRF spectrometer was calibrated by comparing its results with a panel of dried dairy manure samples with analyses from inductively coupled plasma (ICP) obtained from three independent certified laboratories. In addition, the XRF results for C, N, and S were compared with those from a high-temperature combustion (HTC) analyzer dedicated to measurements of these three elements. Then the performance of the calibrated XRF was tested against a separate panel of dairy manure samples collected at fifteen different sampling points at a manure processing plant. Subsamples from these samples were analyzed for the 14 elements of interest by a certified laboratory. The close agreement between the XRF results and those of the certified laboratory established that XRF can be used as a simple and precise method for the elemental analysis of dairy manure.

Keywords: Elemental analysis; X-ray fluorescence spectrometry; Dairy manure; Combustion analysis; Inductively coupled plasma spectroscopy; Calibration standard

Abbreviations: XRF: X-ray fluorescence; AAS: Atomic absorption spectroscopy; ICP-OES: Inductively coupled plasma optical emission spectrometry; HTC: High temperature combustion; TKN: Total Kjeldahl nitrogen; MLD: Maple Leaf Dairy.

Introduction

Each year the US dairy industry produces more than 200,000 million pounds of milk along with approximately 55 billion pounds of excreted manure [1]. Dairy manure poses a potential environmental problem because its high content of phosphorous and nitrogen can have negative impacts (such as eutrophication and algae blooms) to nearby land and water systems [1]. It is therefore desirable to process dairy manure, not only to remove excess nutrients so as to minimize the environmental impacts but also to recover nutrients of economic value for use where they are needed. A typical manure processing plant utilizes multiple steps, such as a rotating screen unit to remove excess fibers and an anaerobic digester unit to produce biogases [1]. Consequently, it is of importance to monitor and evaluate the nutrient contents of the manure at each processing step to determine the efficiency of these units in terms of solids removal and nutrients recovery. Traditional methods for analyzing major and trace elements in manure are based on acid digestion and homogenization of individual samples followed by determination of nitrogen by the total Kjeldahl nitrogen (TKN) method [2] and other elements by atomic absorption spectrophotometry (AAS) [3] or inductively coupled plasma optical emission spectrometry (ICP-OES) [4]. These methods are also widely used to analyze the elemental composition of environmental samples, such as fertilizers, soil sediments, and plant tissues [5-9]. While these methods are well established, the associated sample preparation procedures can be time-consuming and/or hazardous [10]. X-ray fluorescence spectrometry (XRF) has gained popularity in the field of elemental analysis, not only because its accuracy and precision are comparable to those of other spectroscopic methods, but also because of its simple sample preparation [10]. XRF spectrometry uses X-ray excitation to identify the elements present in samples and quantify their concentrations by measuring the intensity of characteristic energies emitted from particular elements [11]. Numerous studies have compared the analytical results obtained by AAS, ICP, and XRF for metals in soil, sediment, and biological samples, and these studies have shown that XRF spectrometry offers results comparable to those traditional methods [12-15]. Although XRF has been widely used to characterize many environmental samples, to our knowledge, no studies have reported the application of XRF technology to identify and quantify nutrients contained dairy manure. We developed a specific method to rapidly and simultaneously quantify the concentrations of macro and micro nutrient elements present in dairy manure samples using a commercial wavelength-dispersive XRF spectrometer [11]. A set of reference samples was created from dairy manure collected at various locations in the manure processing plant at Maple Leaf Dairy (MLD) Farm (Cleveland, WI). These samples were sent to three different independent laboratories for analysis of 13 elements present in dairy manure, namely, N, P, K, Ca, Mg, S, Zn, Mn, Fe, Cu, Al, Na, and B. The results obtained from these laboratories were used together with the concentration data for C and N of the reference samples analyzed by a high-temperature combustion (HTC) analyzer [16] in our laboratory to calibrate the XRF instrument and to develop a protocol for the analysis of dairy manure.

To validate the protocol, we collected a new set of samples from fifteen different sampling points in the manure processing plant at MLD Farm. A subsample from each sample was sent to a certified laboratory for analysis of 14 elements of interest, and another subsample from each sample was analyzed by the calibrated XRF instrument to measure the concentrations of these elements. The XRF results were in close agreement with those from the conventional methods. Thus we conclude that XRF offers an approach to quickly identify and quantify nutrients in raw and processed dairy manure with simpler sample preparation, better precision and reasonable accuracy.

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Materials and Methods

Sample collection and preparation

Samples were collected at different locations in the manure processing pipeline at MLD Farm following sampling procedures described in the handbook on "Recommended Methods of Manure Analysis" [17]. The total solid content of each sample was determined by weighing before and after drying at 95°C in a Fisher Isotemp™ model 6925 oven (Fisher Scientific, Pittsburgh, PA). An investigation of the optimal drying times and temperatures for dairy manure and their effects on the final analytical results revealed that manure could be safely dried for 48 h in the oven at that temperature. After drying, each sample was ground for 30-60 s using a Chemplex model 5000 gyrating grinder (Chemplex Industries, Inc., Palm City, FL). Samples with large amounts of fiber (by visual inspection) were ground for longer time periods (2- 3 min) to achieve better homogeneity, whereas samples with little fiber required a shorter time (45 s). This grinding process produced powder with particles of less than 100-mesh size. For XRF measurement, precisely 6 g of each ground sample was transferred to a 50 mm diameter flat disc placed in a steel pressing cup and covered with a Chemplex SpectroCertified® thin film sample support made of Mylar polyester film. The powder was then pressed into a uniform pellet of 5 mm thickness using a Herzog hydraulic cup press model TP40 (Herzog Automation Corp., Cleveland, OH) set to a hydraulic force of 300 kN. For each manure sample, 2 pellets were prepared. The resulting pellets must have a flat and smooth surface, because surface roughness can negatively affect the peak intensities of the measured elements.

Determination of C, N and S via combustion method

The concentrations of C, N, and S in dairy manure samples were measured by using a Vario MAX cube high temperature combustion (HTC) analyzer (Elementar Americas, Inc., Mt. Laurel, NJ, USA). Approximately 300 mg of each dry manure sample prepared according to methods described above was weighed and put into a ceramic crucible. The crucible was then loaded into a chamber in which the sample was oxidized completely and instantaneously at high temperature (1200°C) into gaseous compounds such as CO_2, NO_2, N_2, and SO_2, which can be detected and quantified [2]. This method was used to measure the concentrations of C, N, and S in both the reference and test samples as detailed below.

XRF calibration and measurement

The samples collected at fifteen different locations in the manure processing pipeline at MLD Farm were prepared according to the procedures described above. From each of these reference samples, subsamples were taken to prepare two pressed pellets for XRF analysis, and other subsamples were sent to three different laboratories for total elemental analysis by the standard methods (ICP spectrometry and TKN). The concentrations of all fourteen elements were measured by standard ICP-OES with the exception of nitrogen, which was determined by both the total Kjedahl nitrogen (TKN) and combustion methods, and carbon, which was measured by combustion method using our HTC analyzer. Whereas the reference concentrations for nitrogen were averages of the values determined from the combustion and TKN methods, those for the other 12 elements were determined from the ICP measurements (Supplemental Table S1). Although combustion data were obtained for S, they were not used because we found that they were significantly different from the ICP results (Supplemental Table S1). The reference chemical concentrations for these 14 elements were then used to calibrate the XRF spectrometer.

The XRF instrument used in this work was a wavelength-dispersive XRF spectrometer (Bruker AXS, Inc.) equipped with eight crystal analyzers and a rhodium tube, which was run at 40 kV, 170 mA, and 4 kW. The spectrometer was controlled by SPECTRA^{plus} V2 software, which supports calibration of the instrument from reference data. Specifically, by scanning the reference samples, an XRF spectrum was obtained for each sample, and from this spectrum, characteristic peaks were identified and selected for the elements of interest. All 14 elements in this study were identified using K spectra [11]. These intensity peaks were matched with the concentration data of corresponding elements for each reference sample, which consequently provided a plot of measured intensity vs. known concentration for each element. Regression analysis was performed automatically on these data points to derive the correlation between the intensity and concentration for each element in the manure samples. Further correction factors (such as matrix correction and preparation methods) were applied on a case-by-case basis to improve the fit. Some sample points were omitted because of inconsistency in the reference data results from the three laboratories (Supplemental Table S1). As a result, a new method was created specifically for dairy manure, and it was then used for subsequent analyses of other dairy manure samples. The total measurement time for each subsequent sample was 18 min, including the time loss incurred by automatic changing from sample to sample.

As with other analytical methods, it was important to establish calibration specifications for each element determined by the XRF instrument, including the lower limit of detection (LLD), limit of detection (LOD), the standard error of calibration (SEC), calibration ranges and the limit of quantification (LOQ). The lower limit of detection (LLD), which is defined as three times of the standard counting error of the background intensity [18,19], was automatically calculated by the software. The LOD was estimated by (Eq. 1), where $t_{1-\alpha,\upsilon}$ is the quantile of the one-side Student's t distribution with α probability and υ degrees of freedom [16]. The SEC, which was also generated by the software, is defined by (Eq. 2), where C_i^{XRF} and C_i^{chem} are the concentrations of the ith standard measured by the XRF and reference methods, respectively, and n is the number of standards [20]. The calibration range for a particular element is defined as a range with the lower limit being the LOD and the upper limit being the highest concentration of the calibration standards. In practice, analysts often report the limit of quantification, which is estimated as three times the limits of detection, to represent the lowest elemental concentration that can be reliably detected by the analytical method [18].

$$\text{LOD} \approx t_{1-\alpha 9}\text{LLD} \tag{1}$$

$$\text{SEC} = \frac{\sum_{i=1}^{n}(C_i^{XRF} - C_i^{chem})^2}{n-1} \tag{2}$$

Validation of XRF method

In order to test if the elemental concentrations analyzed by the calibrated XRF instrument were comparable to those measured by other standard methods, such as ICP-OES, fifteen new samples were collected at MLD Farm and prepared according to the procedures described above. For each test sample, two pellets were prepared and analyzed in duplicate with the XRF spectrometer using the calibrated method. Duplicate test samples were also analyzed by the HTC analyzer, and the remaining material from each test sample was divided into two parts and sent to an independent laboratory for analysis. Consequently, a total of 30 samples were analyzed by XRF, HTC analyzer, TKN and ICP-OES. The correlation between these methods was examined by

plotting the concentration data obtained from one method versus the data from the other method. In addition, the Bland-Altman method [21] for comparing two analytical methods was employed to analyze the agreement between pairs of methods. This method of comparison plots the mean-difference and the 95% limits of agreement as estimated from the ± 1.96 standard deviation of the mean difference between the two methods for each element of interest. The statistical analyses were performed using the R package MethComp (version V.1.22.2) [22].

Results and Discussion

Reference samples and XRF calibration

Because standard samples for dairy manure are not available, we created a set of reference samples from dairy manure collected at MLD farm and sent them to three independent laboratories for elemental analysis. Even though the data from these independent laboratories were obtained by the same analytical methods, namely total Kjeldahl nitrogen (TKN) and inductively coupled plasma optical emission spectrometry (ICP-OES), the measurements varied considerably, with minimum, median, and the maximum coefficients of variation being 1%, 9%, and 34% respectively (Table 1). In addition, the magnitude of the variation depended on the type of element. For example, whereas the coefficients of variation between the three laboratories for Al ranged from 6% to 34%, they ranged from 1% to 10% for Mn. Different reasons could account for this variation. First of all, the instruments and operating procedures that were used to analyze the reference samples at these laboratories might be different even though the methods were similar (analytical variation). Each laboratory might have its own set of operating parameters established for the instrument, which could produce slightly different results. Secondly, the samples analyzed by these laboratories might not have been exactly identical (biological variation) even though they were homogenized using the same procedures. The ICP method often uses a very small sample for analysis, and thus sample inhomogeneity could lead to irreproducible results [10,17]. Although this type of variation exists, we found the median coefficient of variation to be on the order of 1% (Supplemental Table S2), which is smaller than the analytical variation between the larger duplicate samples of dairy manure sent to independent laboratories (see "Validation of XRF method" section).

Considerable care was taken in developing the procedure used to calibrate the XRF spectrometer for elemental analysis of dairy manure samples. We found it important to specify the sample size (6 g of solid was used with or without binder material) to ensure that the concentration was properly normalized and quantified. Because of the inherent variation in the reference data, it appeared reasonable to remove data points that were inconsistent (outliers) when constructing the plots of intensity vs. known concentrations for the 14 elements of interest during the calibration process. Manual optimization (such as setting background intensity, setting concentration ranges) was often necessary to ensure good correlation between measured intensity and known concentration for each element in manure sample. Whereas the calibration curves displayed excellent correlations for Na, K, Al, and Fe (squared correlation coefficients greater than 0.98) and good correlations for P, Mn, Zn, Ca, Cu, and S (squared correlation coefficients from 0.9 to 0.98), the correlation for other elements (C, B, and Mg) were not as high (0.87 - 0.90) and lower for N (0.74) (Supplemental Figure S1). This indicated that the calibration method should be used with reservation to quantify nitrogen. Whether this is a problem inherent to this method or to manure samples exclusively was not clear. Therefore, further investigation needs to be carried out with other biological and/or geochemical samples to determine if nitrogen in these samples can be quantified with XRF methods.

It is important to note that the calibration charts (Table 2) are specific to the dairy manure samples collected at MLD farm. Analyses of manure samples of different types (e.g., non-dairy manure) or from different farms may require a different set of calibration standards. Nevertheless, the sample preparation protocol and calibration procedures described here should apply to any manure sample.

Validation of the XRF method developed for manure analysis

We used the XRF method described above to measure the concentrations of N, P, K, Ca, Mg, Na, C, S, Zn, B, Mn, Fe, Cu, and Al in separate samples of dairy manure (Supplemental Table S3). The XRF results were compared with concentration data obtained by analyzing the same samples using standard methods (TKN, ICP-OES, and combustion) (Supplemental Table S2 and S4) to determine how well these methods correlate with one another. Figures 1, 2 and 3 show the correlation between average concentrations measured by XRF and

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
Al	0.06	0.34	0.12	0.23	0.10	0.18	0.10	0.12	0.07	0.16	0.18	0.09	0.09	0.11	0.14
B	0.04	0.13	0.03	0.13	0.06	0.13	0.10	0.13	0.12	0.05	0.07	0.12	0.09	0.14	0.15
Ca	0.03	0.06	0.07	0.08	0.04	0.08	0.06	0.11	0.10	0.03	0.10	0.11	0.09	0.09	0.07
Cu	0.13	0.11	0.18	0.10	0.22	0.21	0.12	0.18	0.09	0.09	0.18	0.04	0.14	0.05	0.17
Fe	0.06	0.17	0.09	0.01	0.12	0.11	0.08	0.08	0.05	0.06	0.10	0.14	0.13	0.15	0.20
K	0.06	0.12	0.05	0.10	0.01	0.10	0.05	0.09	0.05	0.06	0.09	0.09	0.05	0.03	0.08
Mg	0.11	0.14	0.07	0.08	0.10	0.14	0.12	0.13	0.07	0.09	0.12	0.11	0.19	0.08	0.15
Mn	0.05	0.02	0.02	0.10	0.01	0.07	0.06	0.03	0.04	0.06	0.03	0.07	0.08	0.07	0.01
N	0.17	0.14	0.10	0.12	0.08	0.10	0.04	0.07	0.05	0.09	0.10	0.06	0.06	0.05	0.09
Na	0.13	0.13	0.12	0.12	0.15	0.17	0.12	0.12	0.12	0.11	0.19	0.12	0.11	0.09	0.07
P	0.08	0.09	0.05	0.05	0.06	0.08	0.09	0.05	0.05	0.04	0.01	0.04	0.08	0.05	0.06
S	0.07	0.02	0.09	0.04	0.05	0.06	0.06	0.08	0.10	0.06	0.08	0.09	0.08	0.05	0.08
Zn	0.15	0.16	0.14	0.10	0.10	0.16	0.15	0.15	0.09	0.08	0.17	0.10	0.28	0.10	0.14

S1, S2… S15 are 15 reference samples sent to three independent laboratories. Coefficients of variation were calculated as the ratio of the standard deviation to the mean.

Table 1: Coefficients of variation in reference samples among three laboratories for 13 elements in dairy manure.

Elements	LLD (ppm)	LOD (ppm)	SEC (%)	Max concentration (%)	LOQ (ppm)
B	0.1	0.2	0.0004	0.01	0.5
C	216.4	368.1	1.4	45.1	1104.2
N	794.9	1352	0.2	2.9	4056.1
Na	14.5	24.6	0.1	5.2	73.7
Mg	10.9	18.5	0.2	2.3	55.6
Al	0.8	1.4	0.006	0.2	4.1
P	1.1	1.9	0.07	1.6	5.6
S	0.8	1.3	0.03	0.8	3.8
K	5.7	9.6	0.2	11.1	28.8
Ca	12.1	20.5	0.2	3.3	61.5
Mn	0.6	1	0.002	0.04	3.1
Fe	0.8	1.3	0.005	0.2	3.8
Cu	0.3	0.5	0.001	0.02	1.5
Zn	0.3	0.4	0.002	0.05	1.3

Lower limit of detection (LLD) of the XRF instrument, limit of detection (LOD), standard error of calibration (SEC), maximum concentration of standard, and limit of quantification (LOQ) are reported for each element. The units are either in wt/wt % or ppm (parts-per-million). In this study, LOD is calculated for 30 duplicate standards with 95% probability.
Table 2: Statistical specifications for calibration standard charts for 14 elements measured by XRF instrument.

standard methods. The correlation coefficients were quite high for P, K, Ca, Na, Zn, Mn, Fe, Cu, Al, and S. For C, the plot (Figure 1) showed excellent correlation between concentrations determined by XRF and combustion. In contrast, the XRF/ICP and XRF/TKN correlations for B, Mg, and N, respectively, were poorer; this may reflect the poor agreement of the data used to calibrate the XRF spectrometer for these elements. For N, the XRF/TKN and XRF/combustion showed very similar correlation coefficients (0.7), and the TKN/combustion correlation was higher (0.97) (Figure 3). For S, XRF/ICP was highly correlated (0.99), whereas both XRF/combustion and combustion/ICP correlated poorly (0.6) (Figure 3). These results show that while the XRF method is suitable for many elements, it may not be the best method for B, N, and Mg.

When comparing two analytical methods it is often important to define the acceptance limits of differences between the two methods. Whether one analytical method can be replaced by another heavily depends on the application for which they are to be used. It is beyond the scope of this study to determine limits of differences between XRF and standard ICP methods for each element in manure as this requires prior knowledge of applicable environmental regulations for land and water systems. Therefore, we computed the 95% limit of agreement between XRF and conventional methods for various elements, a metric widely adopted for the comparison of analytical methods [21]. In this analysis, the smaller the interval between the upper and lower 95% limits relative to the magnitude of the mean concentration the better the two methods agree. According to this metric, XRF and ICP showed excellent agreement for the macronutrients K, Na, and S (Figures 4 and 6) and micronutrients such as Fe and Cu (Figure 5). The level of XRF/ICP agreement was slightly lower for other elements (Figures 4, 5 and 6). As shown above from the correlation plots, the TKN/combustion methods showed better agreement than either XRF/TKN or XRF/combustion methods for measuring N (Figure 6). This result justifies our use of combustion data in constructing the calibration curves for N. As noted above for S, XRF/ICP showed much tighter agreement than
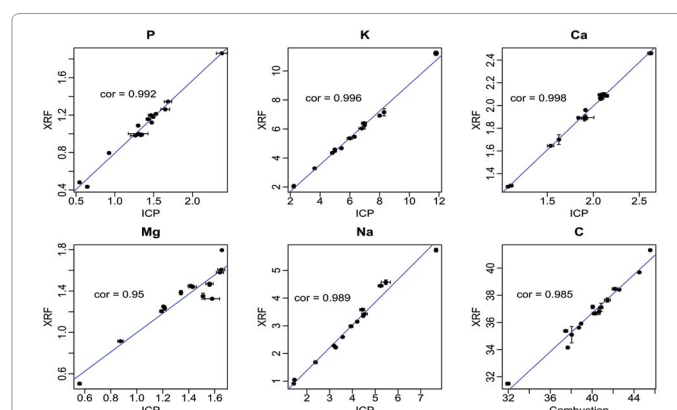

Figure 1: Correlation of concentrations derived from X-ray (XRF), inductively coupled plasma (ICP), and combustion methods for macronutrients in dairy manure. The concentrations measured by the test method (XRF) are plotted against the concentrations measured by the standard method (ICP) for P, K, Ca, Mg, and Na. For C, the concentrations measured by XRF are plotted against the concentrations measured by the combustion method. Each data point represents the average concentration from duplicate samples. The vertical and horizontal error bars indicate standard deviations of the concentrations measured by the corresponding methods. Solid blue lines represent the linear relationship between two methods and the correlation values (cor) indicate how closely the data obtained from two methods agree.

Figure 2: Correlation of concentrations derived from X-ray (XRF) and inductively coupled plasma (ICP) methods for micronutrients in dairy manure. The concentrations measured by the test method (XRF) are plotted against the concentrations measured by the standard method (ICP) for Zn, B, Mn, Fe, Cu, and Al. Each data point represents the average concentration from duplicate samples. The vertical and horizontal error bars indicate the standard deviations of the concentrations measured by the corresponding methods. Solid blue lines represent the linear relationship between two methods and the correlation values (cor) indicate how closely the data obtained from two methods agree.
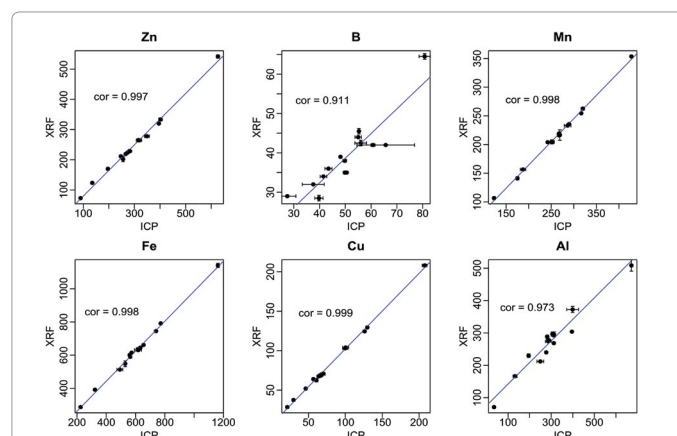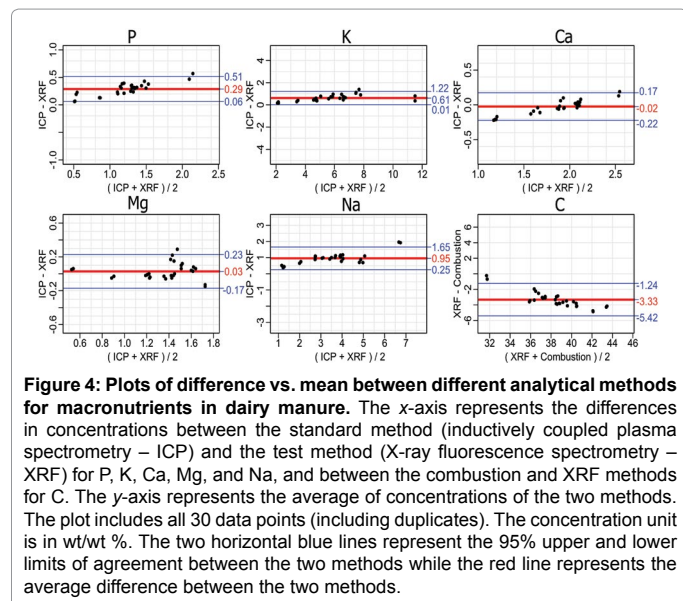
either XRF/combustion or ICP/combustion; this result justifies our use of ICP data, rather than combustion data, in calibrating XRF for S. Similarly for C, the good agreement between XRF and combustion justifies our use of combustion data in calibrating the XRF spectrometer (Figure 4). Furthermore, we noticed that for P, K, Na, Zn, B, Mn, and S, the concentration values from ICP were higher than those from XRF (Figures 4, 5 and 6) as indicated by the positive lower limits.

Overall the XRF method displayed better precision than the ICP and combustion methods as indicated by the smaller error bars in the correlation plots (Figures 1, 2 and 3). As noted above, the ICP method often uses very small samples (milligrams) compared with the XRF method (grams), and therefore sample inhomogeneity can lead

Figure 3: Correlation of concentrations derived from X-ray (XRF), total Kjeldahl nitrogen (TKN), inductively coupled plasma (ICP), and combustion methods for nitrogen and sulfur in dairy manure. The concentrations measured by the test method (XRF) are plotted against the concentrations measured by the combustion method, and standard methods for N (TKN) and S (ICP). Each data point represents the average concentration from duplicate samples. The vertical and horizontal error bars indicate the standard deviations of the concentrations measured by the corresponding methods. Solid blue lines represent the linear relationship between two methods, and the correlation values (cor) indicate how closely the data obtained from two methods agree.
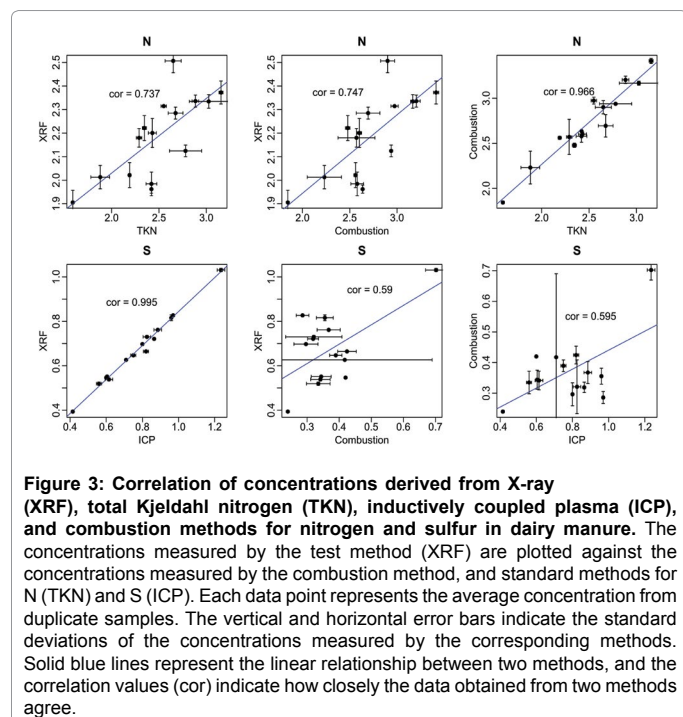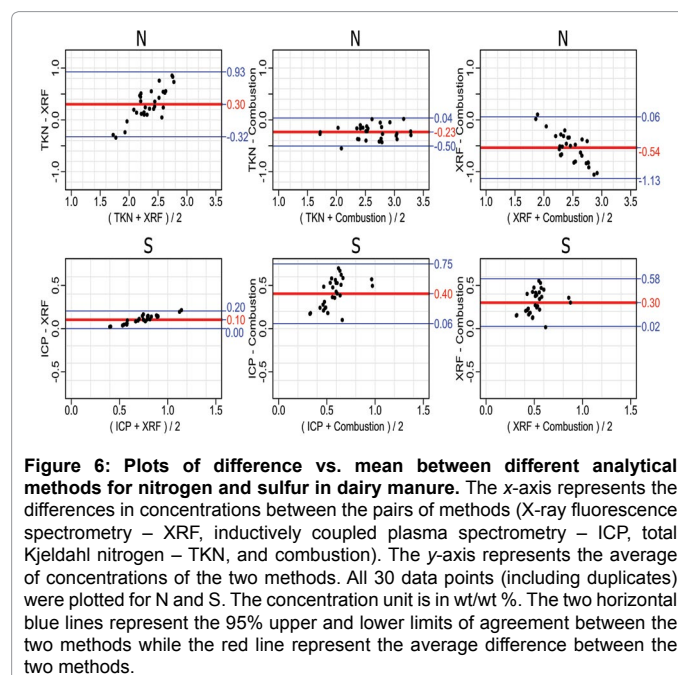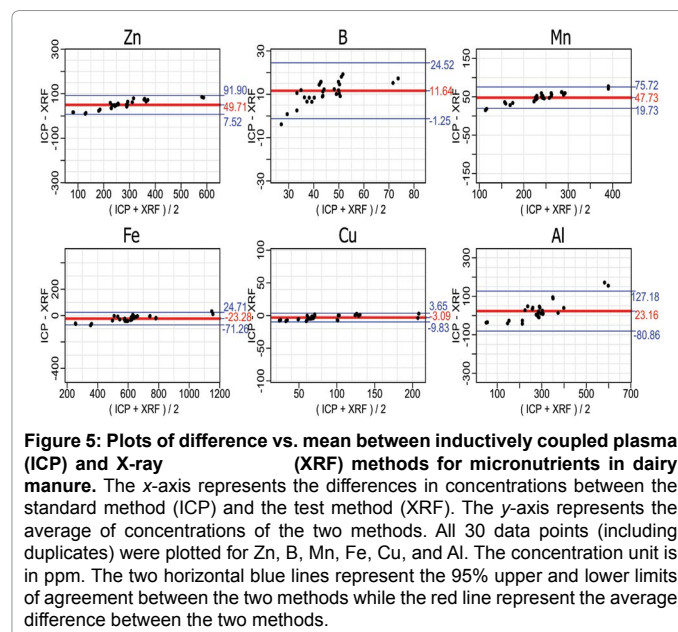

Figure 4: Plots of difference vs. mean between different analytical methods for macronutrients in dairy manure. The x-axis represents the differences in concentrations between the standard method (inductively coupled plasma spectrometry – ICP) and the test method (X-ray fluorescence spectrometry – XRF) for P, K, Ca, Mg, and Na, and between the combustion and XRF methods for C. The y-axis represents the average of concentrations of the two methods. The plot includes all 30 data points (including duplicates). The concentration unit is in wt/wt %. The two horizontal blue lines represent the 95% upper and lower limits of agreement between the two methods while the red line represents the average difference between the two methods.

Figure 5: Plots of difference vs. mean between inductively coupled plasma (ICP) and X-ray (XRF) methods for micronutrients in dairy manure. The x-axis represents the differences in concentrations between the standard method (ICP) and the test method (XRF). The y-axis represents the average of concentrations of the two methods. All 30 data points (including duplicates) were plotted for Zn, B, Mn, Fe, Cu, and Al. The concentration unit is in ppm. The two horizontal blue lines represent the 95% upper and lower limits of agreement between the two methods while the red line represent the average difference between the two methods.

Figure 6: Plots of difference vs. mean between different analytical methods for nitrogen and sulfur in dairy manure. The x-axis represents the differences in concentrations between the pairs of methods (X-ray fluorescence spectrometry – XRF, inductively coupled plasma spectrometry – ICP, total Kjeldahl nitrogen – TKN, and combustion). The y-axis represents the average of concentrations of the two methods. All 30 data points (including duplicates) were plotted for N and S. The concentration unit is in wt/wt %. The two horizontal blue lines represent the 95% upper and lower limits of agreement between the two methods while the red line represent the average difference between the two methods.

to irreproducible results [10]. Our reference data showed variation between results from different facilities using the same methodology (ICP and TKN) on subsamples of the same sample, and these variations limited our ability to compare XRF with standard methods. In most cases, the difference between XRF and ICP was on the same order of magnitude as the differences in the ICP data from the different facilities.

Conclusions

This is the first study to our knowledge to compare analytical methods for elemental analysis of dairy manure. We describe here the development of XRF as a rapid analytical method for the determination and monitoring of major and trace nutrient elements in dairy manure. We found that the XRF method not only has great precision but also gives good accuracy in comparison with a standard method (ICP) for

K, Na, Fe, Cu, and S. Although the limits of agreement are larger for other elements, XRF results may be acceptable for routine manure analysis. An advantage of XRF for manure analysis is that, unlike wet chemistry methods, it requires no chemical preparation or complicated pretreatment. The XRF protocol described here should be applicable to the elemental analysis of other environmental samples, such as biomass and plant tissues.

Acknowledgements

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