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RESEARCH ARTICLE

Assessment of the ED-XRF technique to quantify mineral elements in nonlyophilised milk and cheese

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The interest in analytical methods that accurately measure or predict the elemental profile of dairy foods has been steadily rising. The purpose of this study was to assess the robustness of the energy-dispersive X-ray fluorescence (ED-XRF) technique for the prediction of mineral elements in milk and cheese, avoiding any sample preparation steps. Results highlighted relatively low accuracy of the ED-XRF technique for the quantification of milk mineral elements, with coefficients of determination in validation (R^2_v) from 0.03 (magnesium) to 0.39 (phosphorus). Greater accuracies were obtained for the quantification of cheese minerals, with R^2_v from 0.26 (sodium) to 0.69 (calcium).

Keywords Inductively coupled plasma optical emission spectrometry, Energy-dispersive X-ray fluorescence, Milk, Cheese, Calcium, Potassium.

INTRODUCTION

Mineral elements play an important role in both mental health and physical human health. Minerals act as catalysts for many physiological processes, including muscle contraction, transmission of nerve impulses and absorption of food nutrients (Franzoi *et al*. 2019).

Minerals represent a small fraction of milk (Manuelian *et al*. 2018) and are found in different chemical forms: inorganic ions and salts, or in association with proteins, nucleic acids, fat and carbohydrates (Franzoi *et al*. 2019). It is well recognised that milk and cheese mineral elements are important for bone and tooth health (Visentin *et al*. 2019) and some minerals (calcium, phosphorus and magnesium) play an important role in milk processing and transformation due to their influence on micelle structure and stability as these both greatly impact milk coagulation properties and curd rheology (Bijl *et al*. 2013). Indeed, calcium, phosphorus and magnesium negatively correlate with clotting time, while they have a positive association with curd firmness and titratable acidity (Toffanin *et al*. 2015; Visentin *et al*. 2018). Moreover, some elements such as sodium, chloride and potassium are considered indicators for the screening of serious animal diseases such as mastitis in dairy cows (Summer *et al*. 2009).

Therefore, the interest in analytical methods that accurately measure or predict the elemental profile of dairy foods has been steadily increasing. Among the reference methods, the most commonly used to determine the mineral profile in food matrices are inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The ICP-OES is one of the most effective tools for the simultaneous determination of macroelements in dairy products (de Andrade *et al*. 2022). The ICP-MS is highly sensitive and allows for the analysis of microelements and isotope ratios with very low detection limits (Ammann 2007; Parsons and Barbosa 2007). Among predictive analyses, the most used for the study of the elemental composition of dairy foods are mid-infrared spectroscopy (MIRS) and energy-dispersive X-ray fluorescence (ED-XRF). These techniques accurately predict macroelements such as calcium, potassium and phosphorus, while giving

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reasonable accuracy for minerals present in minor quantities in dairy products (i.e. sodium, magnesium and sulphur). Even though these techniques are less precise and relatively expensive, they nonetheless provide high-throughput results and require minimal sample preparation without the need for specialised personnel (De Marchi *et al*. 2018). In particular, the ED-XRF technique provides the opportunity to perform analysis without prior sample digestion and to quantify major minerals and trace elements simultaneously. The ED-XRF technique is based on X-ray impulse, which passes through the sample to be analysed. In response to this impulse, sample minerals emit a fluorescent radiation, which is specific for each element (qualitative analysis). Also, by measuring the intensity of the emitted radiation it is possible to determine the amount of each mineral in the matrix (quantitative analysis; Brouwer 2003). To date, analytical protocols adopted for the determination of mineral elements in milk thorough ED-XRF comprise sample lyophilisation (Perring and Andrey 2003; McCarthy *et al*. 2020). It is not clear to which extent the quantification of mineral elements through ED-XRF is affected when analysing raw samples, excluding the lyophilisation step.

Therefore, the purpose of this study was to assess the robustness of the ED-XRF technique applied to the quantification of mineral elements in milk and cheese, avoiding any sample preparation steps.

MATERIALS AND METHODS

Reagents and analytical apparatus

Ultrapure water (18.2 MOhm/cm resistivity at 25°C) was obtained through PURELAB flex 1 (ELGA LabWater, Veolia Water Solutions & Technologies, Pordenone, Italy). Minerals used for calibration and as internal standards, including calcium (Ca), phosphorus (P), magnesium (Mg), sodium (Na), potassium (K), sulphur (S) and iridium (Ir), were purchased from CPAchem (CPAchem Ltd., Stara Zagora, Bulgaria) at the highest available purity. Detection and quantification of mineral elements were performed through Spectro Arcos ICP-OES (Spectro Analytical Instruments, Kleve, Germany). All solutions and solvents were tested for mineral contamination through ICP-OES analysis. Mineral content was always below the limit of detection of the instrument.

Sample collection

Individual milk samples ($n = 205$) of Holstein Friesian cows were collected in February 2021, in a single test day and on a single commercial dairy herd (Belluno, Italy). Samples (50 mL) were collected in plastic tubes and immediately added with 200 µL of preservative (bronopol, 2-bromo-2-nitropropan-1,3-diol; D&F Inc., Dublin, CA, USA) to avoid bacterial growth and proliferation. Within 6 h, milk samples were stored and kept at −20°C until analyses were performed.

Cheese samples ($n = 63$) included 15 Grana Padano samples from the Breeders Association of Piemonte Region (ARAP, Cuneo, Italy), 12 Grana Padano samples from the Breeders Association of Veneto Region (ARAV, Padova, Italy), 24 Pecorino samples from the Breeders Association of Sardinia Region (ARAS, Sardegna, Italy), 5 Asiago samples from the Latterie Vicentine dairy company (Vicenza, Italy), 4 Casatella samples from the Sant'Andrea dairy company (Treviso, Italy) and 3 Caciotta samples from the Soligo dairy company (Treviso, Italy). All cheese samples were grounded and stored in a 50-mL plastic tube at −20°C until analyses.

Sample mineralisation and ICP-OES analysis

Sample mineralisation and ICP-OES analysis were carried out in the laboratory of Eurolab S.r.l. (Vicenza, Italy). Milk samples were thawed in a thermostatic bath (15 min, 40°C) and gently mixed 20 times by inversion to promote sample homogenisation, whereas cheese samples were defrosted at room temperature (6 h, 22°C). Quantification of Ca, K, P, Na, S and Mg through ICP-OES was performed according to the guidelines described by the UNI EN ISO 15151:2020. For both milk and cheese, 0.50 g of sample was weighed in a 50-mL plastic tube. Samples were added with 0.5 mL of H_2O_2, 0.125 mL of a 1000 mg/L iridium standard solution and 10 mL of 65% HNO_3. To start the mineralisation process, samples were placed in a hot block plate and heated at 115°C for 2 h. Samples were cooled and Milli-Q water was added up to a final volume of 50 mL. Mineralised milk and cheese samples were filtered into 10-mL plastic tubes to prevent obstructions of ICP-OES suction line.

Instrument settings, chemical parameters and physical conditions used for the ICP-OES analyses were selected according to the recommendations provided by the instrument manufacturer (Table 1). Standard solutions were freshly prepared and mineral quantifications (including Ca, K, P, Na, S and Mg) were obtained with 5-point calibration curves (i.e. 0, 1, 5, 10, 20 and 50 mg/L). All calibration curves exhibited a coefficient of determination (R^2) >0.99. The calibration of the ICP-OES apparatus was checked before the analysis of each batch of samples through a standard solution used for initial calibration verification (ICV). The ICV solution was prepared as a mixture of the standard solutions used for instrument calibration by appropriate dilution in ultrapure water. All standard solutions were acidified with 2% HNO_3, and iridium was added as internal standard in the same concentration used for milk and cheese samples (2.5 mg/L). Wavelengths used to quantify each of the mineral elements are reported in Table 2.

ED-XRF analysis

Energy-dispersive X-ray fluorescence analysis was performed in the laboratory of Eurolab S.r.l. directly on milk and cheese samples, without any previous treatment,

Table 1 Parameter settings of the inductively coupled plasma optical emission spectrometer for detection and quantification of mineral elements in milk and cheese.

Parameter	Settings
Power	1.400 W
Cool gas flow rate	12 L/min
Auxiliary gas flow rate	1.0 L/min
Nebuliser flow rate	1.0 L/min
Sample aspiration rate	2.5 mL/min
Spray chamber	Schott
Plasma torch	Quartz, 1.8-mm injector tube
Technical replicates	3

Table 2 Wavelengths used by the inductively coupled plasma optical emission spectrometer for detection and quantification of mineral elements in milk and cheese.

Minerals	Wavelengths (nm)
Calcium	396.85
Potassium	177.50
Phosphorus	279.55
Sodium	589.59
Sulphur	766.49
Magnesium	180.78

through Spectro Xepos 5C ED-XRF (Ametek, Kleve, Germany). Samples were weighed (5 g) and placed in ED-XRF plastic cups specifically designed for instrument autosampler. Prior to each analysis, all data relating to the sample were provided to the instrument (i.e. the type of matrix and the exact weight), and the type of analysis method to be used was selected according to whether it was milk or cheese. This is an important step as the accuracy of the ED-XRF technique depends on the uniformity and quantity of material that the X-rays have to pass through. The instrument took 20 min to run each sample. For each mineral, results of the ED-XRF analysis were available as normalised impulses (NI).

Statistical analysis

Energy-dispersive X-ray fluorescence calculations were made using the following formula, based on Lucas–Tooth quantification, implemented in the Spectro software:

$$c_i = K_0 + K_1 * I_i + \sum_j a_j * I_i I_j + \sum_k a_k * I_i I_k^2 + \sum_m a_m I_i^2 I_m$$

where i = observed element, c_i = concentration of the element i, K_0 = offset of the calibration, K_1 = slope of the calibration, I_i = fluorescence intensity of the element i, a_x = empirically calculated corrections.

Pearson's correlation coefficients (r) between concentrations of milk minerals determined through ICP-OES technique were estimated using the PROC CORR of the SAS software (SAS Institute Inc., Cary, NC, USA). The same procedure was adopted to calculate r between the concentrations of cheese minerals.

The calibration of the ED-XRF instrument was carried out on a subset of 50 individual milk samples as a regression model between the concentration of each element measured through ICP-OES and NI produced by ED-XRF analyses. In particular, samples included in the calibration subset were chosen to cover the greatest observed variability of Ca, K, P, Na, S and Mg in milk. Therefore, within the milk matrix, a total of 6 subsets were available for the calibration of each mineral element. The validation of the method was performed on the entire data set (n = 205) as a regression model between mineral elements measured by ICP-OES versus mineral elements predicted through ED-XRF using calibration models previously obtained. The same procedure was adopted for the calibration of the ED-XRF instrument in the case of cheese samples. In particular, 25 of 63 samples were selected in order to cover the greatest observed variability of Ca, K, P, Na, S and Mg in cheese. Again, the calibration was performed as a regression model between the concentration of each element measured through ICP-OES and NI provided by ED-XRF. Within the cheese matrix, a total of 6 subsets were set for the calibration of each mineral element. Also in this case, the validation of the ED-XRF technique was performed on the entire data set (n = 63) using calibration models previously developed. The accuracy of the ED-XRF technique in quantifying each mineral element was expressed through the coefficient of determination in calibration for milk (R^2_{Cm}) and cheese (R^2_{Cc}) and through the coefficient of determination in validation for milk (R^2_{Vm}) and cheese (R^2_{Vc}).

RESULTS AND DISCUSSION

Descriptive statistics and Pearson's correlations

Table 3 summarises the descriptive statistics of mineral content in individual raw milk samples. Potassium showed the greatest concentration, averaging 1612.90 mg/kg, followed by Ca, P, Na, S and Mg, averaging 1541.35, 930.00, 485.37, 290.65 and 79.43 mg/kg, respectively. These values substantially agree with the results reported by Zamberlin *et al*. (2012) and Toffanin *et al*. (2015). Calcium, K and P exhibited a similar and relatively low coefficient of variation (CV) in the range of 11.02% to 11.56%. The greatest variability was observed for *S*, which exhibited a CV of 76.47%. Pearson's correlations calculated for mineral elements in individual raw milk samples are reported in Table 4 (above diagonal). The strongest correlations were

observed between Ca and Mg ($r = 0.63$; $P < 0.001$), Ca and P ($r = 0.62$; $P < 0.001$), and K and P ($r = 0.61$; $P < 0.001$). Moderate-to-low correlations were calculated between P and Mg ($r = 0.56$: $P < 0.001$), K and Mg ($r = 0.46$; $P < 0.001$), Ca and K ($r = 0.44$; $P < 0.001$), Na and Mg ($r = 0.35$; $P < 0.01$), and Ca and Na ($r = 0.17$; $P < 0.01$). All the remaining correlations did not statistically differ from zero ($P > 0.05$).

Among cheese mineral elements, Na and Mg were the most and the least abundant, averaging 8965.02 and 415.35 mg/kg, respectively (Table 3). In fact, NaCl is added during the brining phase, as it acts as a preservative by inhibiting the growth of undesirable bacteria (Ash and Wilbey 2010). In addition, Na has a role in the activity of proteolytic and lipolytic enzymes, which in turn influence cheese texture and flavour. With the only exception of S, cheese mineral elements showed greater variability than their milk counterparts, with CV from 15.60% for Ca to 52.84% for Na. This is likely due to the greater variability of cheese samples, which indeed comprised different kinds of cheese products from various geographical regions. The milk samples were instead collected on a single farm from animals of the same breed. Pearson's correlation coefficients calculated for mineral elements in cheese samples (Table 4, below diagonal) ranged from moderate negative association between Na and K ($r = -0.44$; $P < 0.001$) to strong positive association between S and Ca ($r = 0.66$; $P < 0.001$).

Table 3 Descriptive statistics of mineral elements in milk ($n = 205$) and cheese ($n = 63$) determined through inductively coupled plasma optical emission spectrometry.

Trait	Mean	SD	CV (%)	Minimum	Maximum
Milk minerals (mg/kg)					
Calcium	1541.35	178.17	11.56	1093.00	1896.00
Potassium	1612.90	177.67	11.02	1173.00	2161.00
Phosphorus	930.00	105.65	11.36	663.00	1225.00
Sodium	485.37	84.31	17.37	297.00	874.10
Sulphur	290.65	222.25	76.47	162.20	2477.00
Magnesium	79.43	18.11	22.80	41.54	131.90
Cheese minerals (mg/kg)					
Calcium	8606.79	1342.68	15.60	4701.00	11,091.00
Potassium	966.43	163.60	16.93	617.80	1363.00
Phosphorus	6363.17	1450.33	22.79	2539.00	8778.00
Sodium	8965.02	4737.29	52.84	2366.00	24,088.50
Sulphur	1663.75	321.74	19.34	887.10	2963.00
Magnesium	415.35	101.91	24.53	125.70	595.60

SD, standard deviation; CV, coefficient of variation.

Calibration and validation of milk mineral elements

Figure 1 depicts the calibration scatter plots of ED-XRF normalised impulses *versus* measured content of Ca, K, P, Na, S and Mg in milk. To calibrate the ED-XRF instrument and to develop the calibration models, we selected a subset of 50 individual milk samples. For each mineral, calibration models were developed as a regression model between the concentration measured through ICP-OES and normalised impulses of the ED-XRF tool. The greatest accuracies were obtained for S ($R^2_{Cm} = 0.45$) and K ($R^2_{Cm} = 0.35$). Even lower R^2 was obtained for Ca, Na, P and Mg ($R^2_{Cm} = 0.27$).

Validation scatter plots of predicted *versus* measured content of Ca, K, P, Na, S and Mg in milk are shown in Figure 2. The validation was performed on the entire data set ($n = 205$) using calibration models previously obtained. Results demonstrate the difficulty of ED-XRF to accurately predict the concentration of minerals in the milk matrix. The greatest accuracy was obtained for K ($R^2_{Vm} = 0.39$), P ($R^2_{Vm} = 0.38$) and Ca ($R^2_{Vm} = 0.27$). This phase also confirms the low sensitivity of the ED-XRF instrument to determine the concentration of Mg ($R^2_{Vm} = 0.02$) and Na ($R^2_{Vm} = 0.05$) probably due to their low atomic weight making them difficult to be directly quantified using this technology (Perring and Andrey 2003).

Our results suggest that the quantification of milk minerals through ED-XRF requires sample lyophilisation to reduce the moisture content of the untreated matrix and to cope with water noise, which is likely affecting the accuracy of the results (Perring and Andrey 2003). Also, the prediction of milk minerals through MIRS technology entails a similar

Table 4 Pearson's correlation coefficients[a] between milk (above diagonal) and cheese (below diagonal) mineral elements determined through inductively coupled plasma optical emission spectrometry.

Trait	Calcium	Potassium	Phosphorus	Sodium	Sulphur	Magnesium
Calcium	–	0.44***	0.62***	0.17**	−0.02	0.63***
Potassium	0.29*	–	0.61***	−0.01	−0.01	0.46***
Phosphorus	0.57***	0.06	–	0.08	0.07	0.56***
Sodium	−0.20	−0.44**	0.12	–	0.04	0.35**
Sulphur	0.66***	0.22	0.56***	−0.16	–	0.06
Magnesium	0.26	0.02	0.32*	0.54***	0.13	–

[a]Statistical significance is given as: *$P < 0.05$; **$P < 0.01$; ***$P < 0.001$.

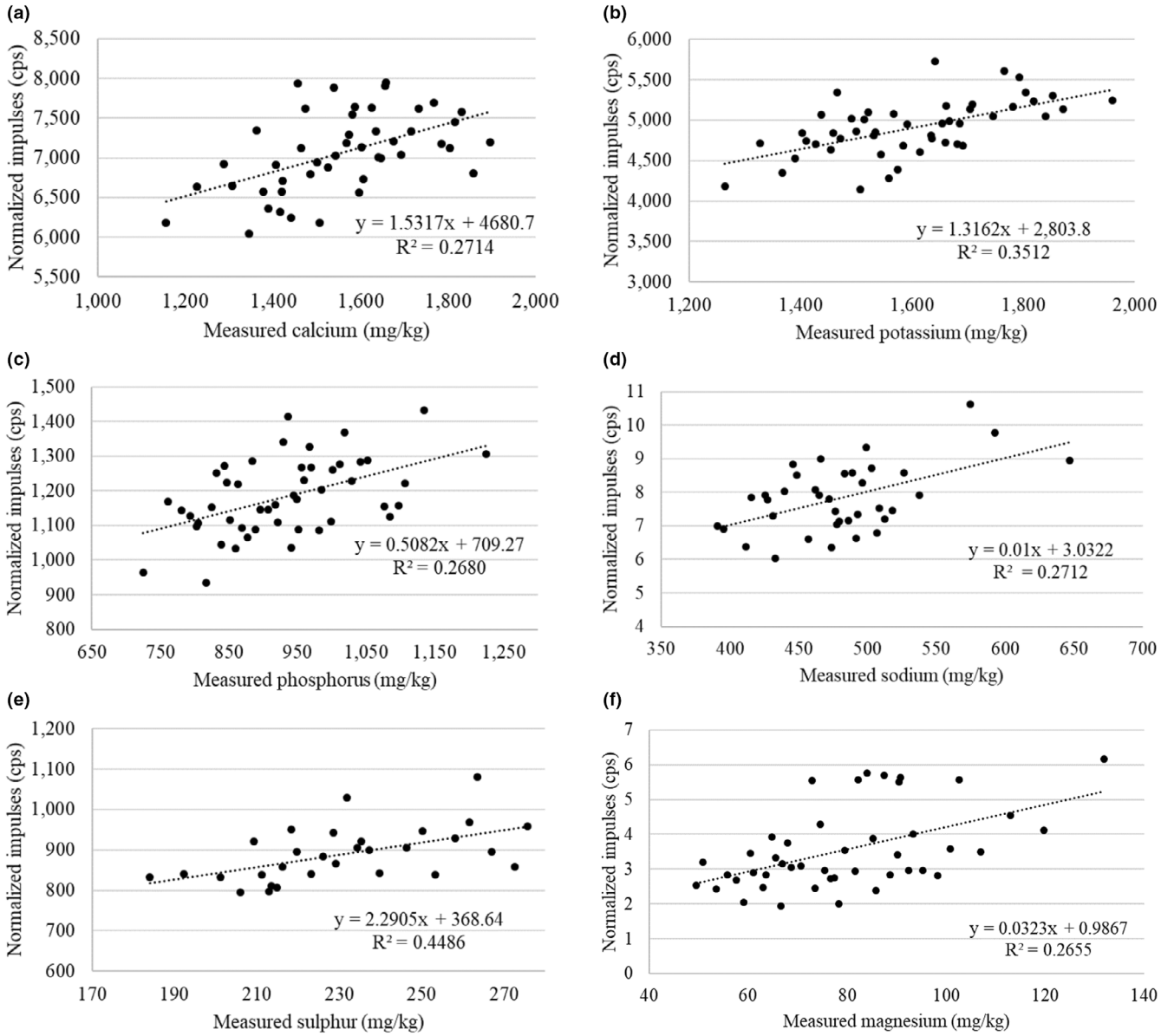

Figure 1 Calibration scatter plots of energy-dispersive X-ray fluorescence normalised impulses (*y*-axis) *versus* measured content (mg/kg) of calcium (a), potassium (b), phosphorus (c), sodium (d), sulphur (e) and magnesium (f) in milk (*x*-axis).

approach, which is applied '*a posteriori*' on spectral data by eliminating wavelengths associated with high noise level related to water absorption (Hewavitharana and van Brakel 1997). By coupling this procedure to the PLS regression and the uninformative variable elimination, Visentin *et al*. (2016) obtained R^2 in validation of 0.67, 0.69, 0.65, 0.40 and 0.68 for Ca, K, Mg, Na and P, respectively.

Calibration and validation of cheese mineral elements

Figure 3 depicts the calibration scatter plots of ED-XRF normalised impulses *versus* measured content of Ca, K, P, Na, S and Mg in cheese. For the calibration, 25 of 63 samples were selected to cover the greatest variability of Ca, K, P, Na, S and Mg. The greatest accuracy was obtained for K (R^2_{Cc} = 0.80), P (R^2_{Cc} = 0.79), Ca (R^2_{Cc} = 0.75) and S (R^2_{Cc} = 0.70). As with the milk matrix, lower R^2 were obtained for Na (R^2_{Cc} = 0.26) and Mg (R^2_{Cc} = 0.23) likely due to both their modest quantities in the cheese matrix and their low atomic weight, which make them more subjected to low signal-to-noise ratio.

Validation scatter plots of predicted *versus* measured content of Ca, K, P, Na, S and Mg in cheese are shown in

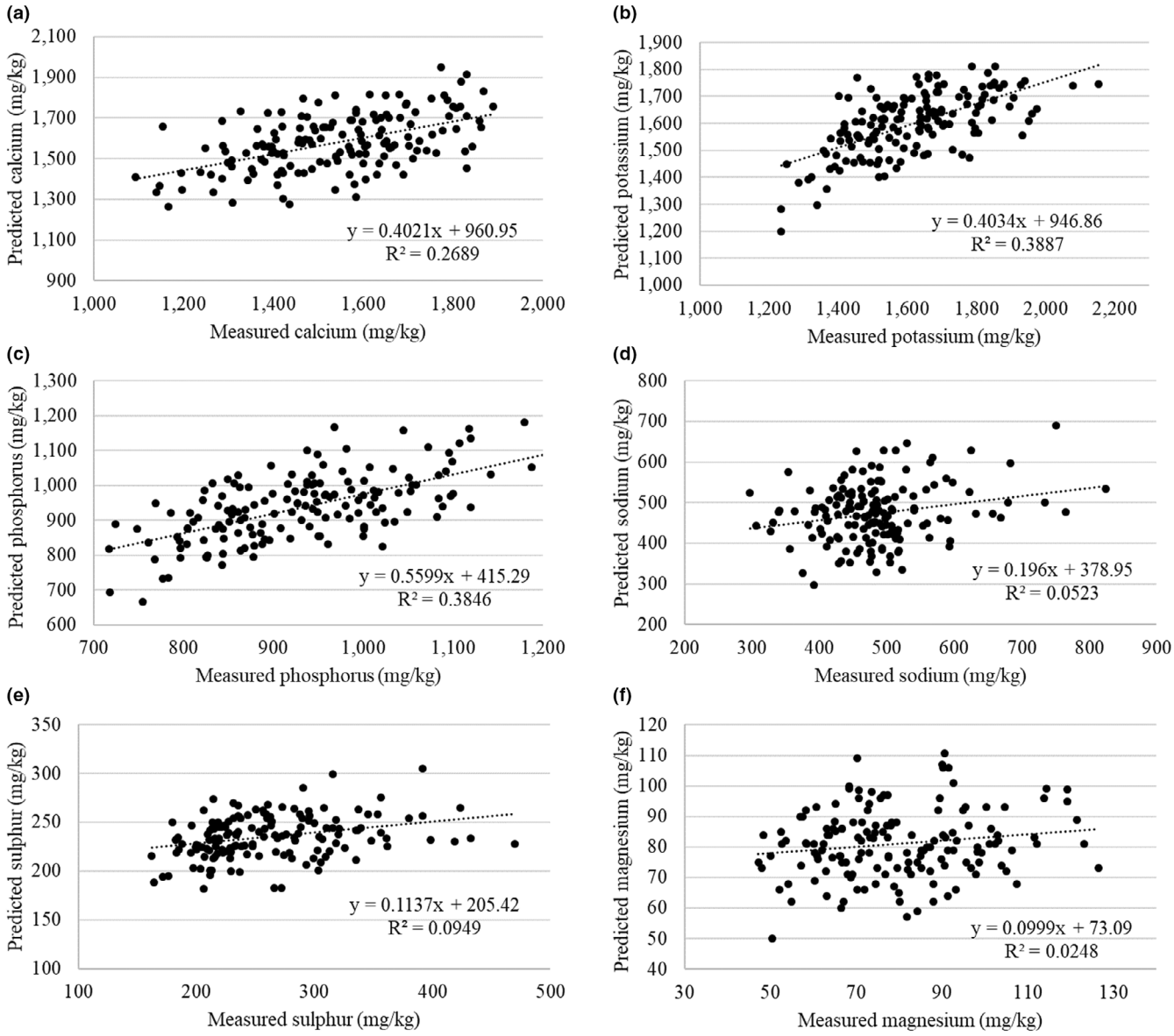

Figure 2 Validation scatter plots of predicted (*y*-axis) *versus* measured (*x*-axis) content (mg/kg) of calcium (a), potassium (b), phosphorus (c), sodium (d), sulphur (e) and magnesium (f) in milk.

Figure 4. The validation was performed on the entire data set ($n = 63$) using calibration models previously obtained. Results demonstrate a better capacity of the ED-XRF technique to correctly predict the concentration of the different minerals in the cheese matrix. The greatest accuracy was obtained for Ca ($R^2_{Vc} = 0.75$), K ($R^2_{Vc} = 0.60$), S ($R^2_{Vc} = 0.46$) and P ($R^2_{Vc} = 0.43$). Comparable results were obtained by Manuelian *et al*. (2017), who assessed the effectiveness of near-infrared reflectance and near-infrared transmittance spectroscopy models to predict the major mineral composition of different cheeses. The same authors reported coefficients of determination in external validation ranging from 0.75 for P to 0.25 for K. In our study, lower accuracies were obtained for the quantification of Mg ($R^2_{Vc} = 0.30$) and Na ($R^2_{Vc} = 0.26$) in cheese, confirming results previously reported for milk samples.

CONCLUSIONS

The present study evaluated the effectiveness of the ED-XRF technique for the quantification of minerals in milk and cheese samples, avoiding preliminary preparatory

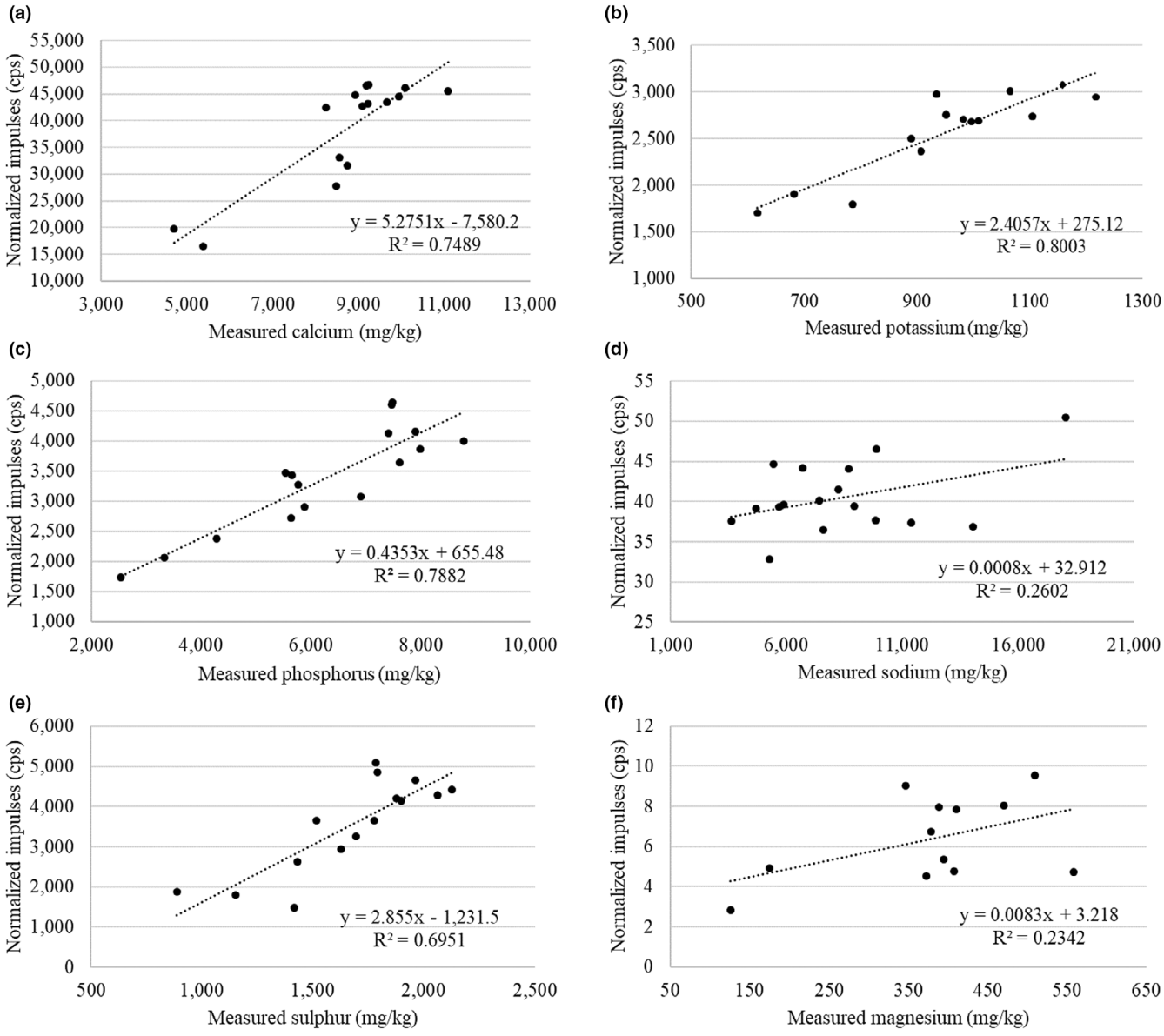

Figure 3 Calibration scatter plots of energy-dispersive X-ray fluorescence normalised impulses (*y*-axis) *versus* measured content (mg/kg) of calcium (a), potassium (b), phosphorus (c), sodium (d), sulphur (e) and magnesium (f) in cheese (*x*-axis).

treatments. Results highlight that the ED-XRF technique does not provide satisfactory results for Na and Mg, likely due to the limited sensitivity of the instrument and to water noise. Better results were obtained for the cheese matrix, where water content is lower, and minerals are present in greater concentrations and with greater variability. Indeed, Ca and K exhibited R^2_{Vc} of 0.75 and 0.60, respectively. The results of the present study are significant even for those elements characterised by a low prediction accuracy, as they offer perspectives for the dairy industry in order to choose the best analytical option. In conclusion, lyophilisation is still recommended to exclude water interference and to obtain homogeneous samples, even if this practice entails time-demanding preparation of samples prior to the analytical phase.

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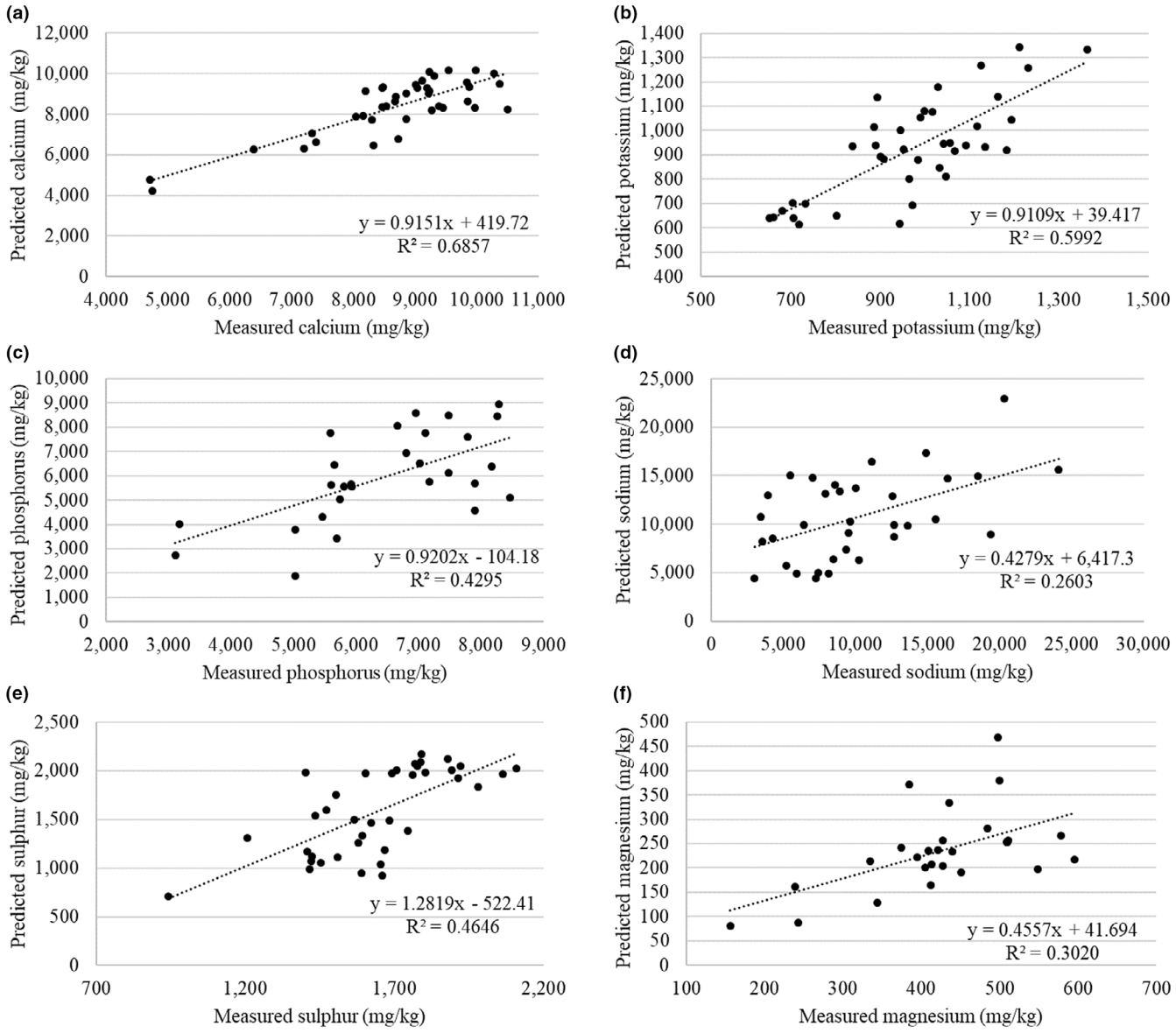

Figure 4 Validation scatter plots of predicted (*y*-axis) *versus* measured (*x*-axis) content (mg/kg) of calcium (a), potassium (b), phosphorus (c), sodium (d), sulphur (e) and magnesium (f) in cheese.

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AUTHOR CONTRIBUTIONS

Elena Visentin: Data curation; formal analysis; investigation; methodology; software; validation; writing – original draft; writing – review and editing. **Giovanni Niero:** Conceptualization; investigation; supervision; writing – review and editing. **Martino Cassandro:** Conceptualization; funding acquisition; project administration; supervision; validation; writing – review and editing. **Mauro Penasa:** Conceptualization; investigation; project administration; resources; supervision; writing – review and editing. **Massimo De Marchi:** Conceptualization; funding acquisition; project administration; resources; supervision; writing – review and editing.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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