Multimineral determination in petfood matrices using WDXRF

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Good Food, Good Life

Introduction:

With a simple sample preparation (grinding + pelletizing) allied to rapid measurement, X-ray fluorescence is a good candidate for implementation near the production lines of food industry.
Today, EDXRF and WDXRF (low power = 50 W max) are successfully used for the quantification of several analytes in milk powders and processed cereals, constituting an useful tool for process quality control.

Objective:

In this study, we investigated the potentiality of WDXRF system for analysing 10 elements: Na, Mg, P, Cl, K, Ca, Mn, Fe, Cu and Zn in petfood.

Samples:

Coming from European markets, various manufacturers, cat and dog foods, varied recipes and raw materials.
Split in 2 sets: calibration (18 samples) and validation (40 samples)

All concentrations expressed in mg/100g.

Methods:

Reference values determined in duplicates using in–house validated procedures: by ICP-AES for all minerals and by potentiometry for chloride.

WDXRF
3 pellets / sample
pellets: 6 grams, Ø 32 mm, 2 to 4 tonnes of pressure.
540 seconds total time of analysis, including background counting. All elements analysed with 40kV – 5mA.

ARL™ OPTIM'X WDXRF

Element Channel	Counting time	Crystal	Detector
Na Ka 1,2	80	AX06	FPC
Mg Ka 1,2	80	AX06	FPC
Ca Ka 1,2	14	LiF 200	FPC
P Ka 1,2	20	InSb	FPC
K Ka 1,2	14	LiF 200	FPC
Cl Ka 1,2	20	InSb	FPC
Fe Ka 1,2	40	LiF 200	FPC
Cu Ka 1,2	60	LiF 200	SC
Zn Ka 1,2	14	LiF 200	SC
Rh Ka Compton	10	LiF 200	SC

Evaluation of the XRF method using robust statistics by comparison of WDXRF data with reference methods ones.

Reference method value (ICP-AES or potentiometry)	y_i
WDXRF value	$\hat{y}_i$
Number of samples	N
Difference	$d_i = \hat{y}_i - y_i$
Robust standard deviation of repeatability (from triplicates)	$\mathrm{SD_{rob}}(r) = 1.2011 \times Med_{i=1\,\mathrm{to}\,n}\{\mathrm{SD}_i\}$
Bias	$\overline{d} = \frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)}{n}$
Standard error of calibration	$SEC = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{n-1}}$
Difference standard deviation	$SD(d) = \sqrt{\frac{\sum_{i=1}^{n}(d_i - \overline{d})^2}{n-1}}$
Standard error of prediction	$SEP = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{n}}$

Calibration results:

Element	Min	Max	R^2	n	SEC
Na	221	841	0.907	17	49
Mg	48.5	134.0	0.873	15	7.5
P	406	1620	0.945	17	78
Cl	322	1340	0.997	17	18
K	325	864	0.974	17	22
Ca	641	1820	0.912	17	84
Mn	2.18	6.86	0.912	17	0.45
Fe	11.30	29.00	0.916	17	1.37
Cu	1.10	2.30	0.932	17	0.08
Zn	8.82	30.00	0.994	18	0.47

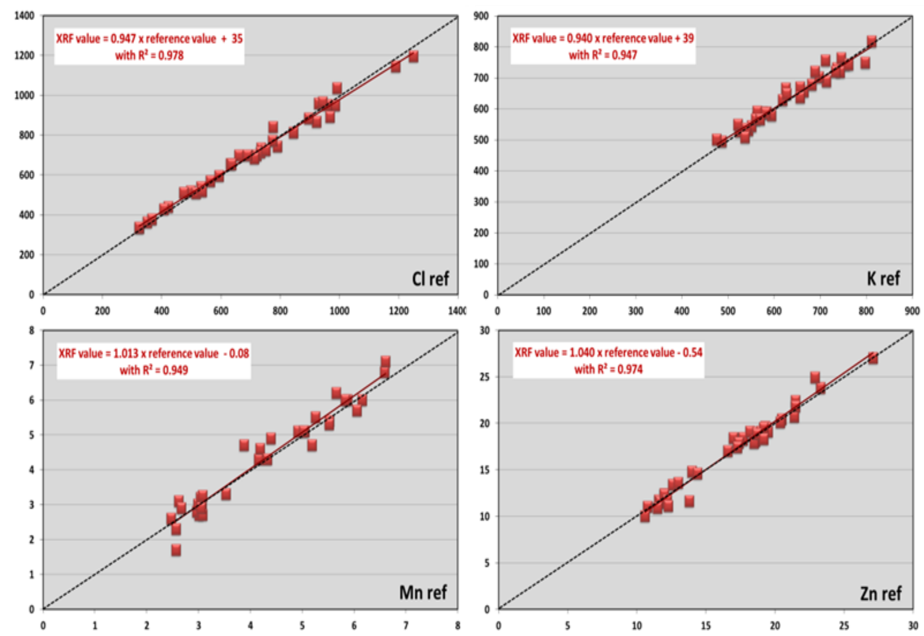
Validation results:

All samples were considered when fitting within the calibration ranges.

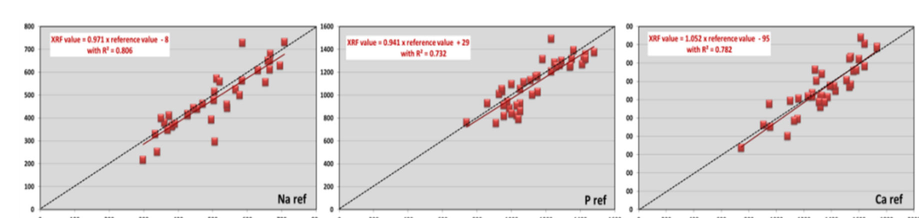
Element	R^2	n	Bias	Bias = 0 Y/N	A	B	SD(d)	SEP	SD(r)	SD(u)
Na	0.806	37	-19	Y	0.971	-8	45	62	5	45
Mg	0.637	34	-5.9	Y	0.677	30.3	15.2	14.4	1.4	15.3
P	0.732	40	-36	Y	0.941	29	118	111	13	119
Cl	0.978	36	3	Y	0.947	35	33	32	4	33
K	0.947	35	2	Y	0.940	39	22	21	4	22
Ca	0.782	38	-38	Y	1.052	-95	145	133	30	148
Mn	0.949	34	-0.04	Y	1.013	-0.08	0.31	0.31	0.14	0.34
Fe	0.719	37	-0.17	Y	0.787	3.76	2.17	2.45	0.42	2.21
Cu	0.501	38	0.10	N	0.715	0.62	0.155	0.21	0.07	0.17
Zn	0.974	40	0.15	Y	1.040	-0.541	0.60	0.72	0.16	0.62

$$SD(u) = \sqrt{SD(d)^2 + SD(r)^2}$$

Cl, K, Mn and Zn: excellent results (correlation and performance indicators)



Na, P and Ca: average results
(good correlation but weak performance indicators)



Mg, Fe and Cu: poor results
(poor correlation and weak performance indicators)

Conclusion:

Compared to classical validation results for milk powders, those obtained with petfood are not fully satisfactory.
Further investigations will be needed to identify the reasons of these weak performance indicators: diversity of processes, production sites, recipes and therefore raw materials, as well as potential heterogeneity and possible occurrence of residual cartilage.

Reference: Wavelength dispersive X-ray fluorescence measurements on organic matrices: application to milk-based products.
L. Perring and D. Andrey : X-Ray Spectrometry, 2004, 33, 128-135

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