

Multi-Energy Calibration: A Practical Method for Determination of Macro and Micro Nutrients in Meat by ICP OES

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The multi-energy calibration (MEC) was evaluated for the determination of Ca, Cu, Fe, K, Mg, Na, P, S, and Zn in meat samples by inductively coupled plasma optical spectrometry (ICP OES). This calibration method consists of using only two calibration standards and several atomic and ionic emission wavelengths with different sensitivities to determine the analyte concentration in the sample. Both calibration mixtures are prepared using the same amount of sample, which contributes to minimize matrix effects. The accuracy was evaluated using two certified reference materials, bovine liver (SRM 1577c) and bovine muscle (SRM 8414), with recoveries within 87-107% range. The method was applied for the determination of the analytes in meats of chicken, sheep loin, sheep carcass and bovine, and prove to be usable in samples with different characteristics.

Keywords: calibration strategies, multi-energy, matrix effect, ICP OES

Introduction

Given the high levels of meat consumption, the quantification of toxic and essential elements in this food is required to evaluate the quality and its nutritional value, in order to estimate its effects on human health.¹ The mineral content in meat varies, depending on factors such as diet, environmental conditions, cut and breed of the animal.²⁻⁴

Meat is a food rich in minerals such as Ca, Mg, Fe, P, and S, which are found at high levels, whereas other essential minerals, such as Cu, Mo, Se, Zn, and Co are present in trace amounts.⁵ In the literature, numerous studies have reported different analytical methods for the quantification of these elements. Most of them comprise the use of atomic spectroscopy techniques, as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical spectrometry (ICP OES), and graphite furnace and flame atomic absorption spectroscopy (GFAAS and FAAS).⁶⁻¹⁰ Sager *et al.*¹¹ quantified macro (Ca, K, Mg, Na, and P) and micro minerals (Al, Cr, Cu, Fe, Mn, Li, Mo, Ni, Pb, Rb, and Zn) in chicken meat using ICP OES and ICP-MS with indium as an internal standard. DjinoVIC-Stojanovic *et al.*¹² used the same analytical techniques and evaluated different internal standards, Li,

Bi, Ga, Ln, Tb, and Y for Zn and Mg determination in meat and meat products of the Serbian market.

As a general rule, when the analysis is performed by these spectroscopic techniques, external standard calibration is employed. Although it is relatively simple, important issues should be considered, such the similarity of the standard solutions with the sample matrix, to obtain reliable results and to reduce matrix effects, but achieving that matrix correspondence is not an easy task to perform. Internal standard calibration is one of the most commonly used strategies since it helps to minimize the matrix effects, reducing possible interferences.⁴ Another conventional method is the standard additions that gives precise results, but with an extended time of analysis and higher sample consumption.¹³

The multi-energy calibration (MEC), first described by Virgilio *et al.*,¹⁴ consists of measuring different signals of an analyte at various wavelengths. In this situation, the analyte concentration is kept constant, and the transition energies are measured for calibration. This method employs only two solutions: solution 1 (S1) which is composed of 50% (v v⁻¹) of sample and 50% (v v⁻¹) of standard solution containing the analytes, and solution 2 (S2), composed of 50% (v v⁻¹) of sample and 50% (v v⁻¹) of blank solution. For this method, the use of a 1:1 ratio is simpler; however, other dilution factors may be used. Then, various wavelengths are

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selected, and the solutions 1 and 2 are analyzed individually. This calibration strategy was applied to complex liquid samples such as green tea, cola, cough medicine, soy sauce and red wine for the determination of Mn, Cu, and Cr by ICP OES.¹⁴ Machado *et al.*¹⁵ used the MEC to determine the contaminants As, Ba, Cd, Cr, and Pb in inorganic fertilizer by microwave induced optical emission spectrometry (MIP OES). Babos *et al.*¹⁶ employed MEC for the determination of Ca, Cu, Fe, Mn and Zn in solid samples of bovine mineral supplements using laser-induced plasma atomic emission spectroscopy (LIBS).

The goal of this work is to investigate the applicability of the MEC as a potential calibration strategy for the quantification of Ca, Cu, Fe, K, Mg, Na, P, S and Zn in chicken, bovine and sheep meat samples by ICP OES after microwave-assisted digestion, considering the diversity of matrix characteristics of this kind of sample.

Experimental

Instrumentation

An ICP OES (Agilent Technologies, Model 5110, Synchronous Vertical Dual View, Mulgrave, Australia) was used for Ca, Cu, Fe, K, Mg, Na, P, S, and Zn determination. The ICP OES operational parameters are shown in Table 1. Argon with purity of 99.999% (White Martins-Praxair, Sartãozinho, SP, Brazil) was used for plasma generation, nebulization and as auxiliary gas. All samples were digested by microwave-assisted digestion in an Ethos 1 system (Milestone, Sorisole, Italy).

Reagents, standard solutions, and samples

All solutions were prepared using deionized water (resistivity > 18.2 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). The laboratory material used for the preparation of the solutions were washed with soap and distilled water, and then 24 h submerged in a 10% concentration (v v⁻¹) of HNO₃ cleaning solution and washed with deionized water before use. Nitric acid (Synth, Diadema, SP, Brazil) was previously purified using a subboiling acid distiller (Model BSB-939-IR, Distillacid, Berghof, Germany) and, together with 30% m m⁻¹ of H₂O₂ (Sigma Aldrich, Darmstadt, Germany), was used to digest the meat samples and the certified reference materials. Standard solutions were prepared by diluting a 1000 mg L⁻¹ stock solution of Ca, Cu, Fe, K, Mg, Na, P, S and Zn (Fluka, Buchs, St. Gallen, Switzerland) to obtain the analytical calibration solutions for the external standard calibration (EC), the internal standard calibration (IS),

Table 1. Instrumental parameters and operating conditions for analyte determinations by ICP OES

Instrumental parameter	Operating condition		
Radio frequency applied power / kW	1.2		
Plasma gas flow / (L min ⁻¹)	12.0		
Auxiliary gas flow / (L min ⁻¹)	1.0		
Nebulization gas flow / (L min ⁻¹)	0.7		
Peristaltic pump speed / rpm	12		
View	axial (Cu, Fe, P, S, Zn) and radial (Ca, K, Mg, Na)		
Stabilization time / s	15		
Integration time / s	3		
Nebulizer	concentric		
Nebulization chamber	cyclonic, double step		
Analyte	Wavelength / nm		
Ca	183.944; 315.887; 317.933; 318.127; 370.602; 373.690; 383.034; 386.409; 404.272; 407.865; 422.673; 430.253; 431.865; 443.496; 445.478; 612.222; 616.217 and 643.907		
	Cu	199.970; 217.895; 218.963; 219.227; 219.959; 222.778; 223.009; 224.427 and 224.700	
		Fe	234.350; 238.204; 239.563; 240.489; 258.588; 259.940; 260.709; 261.187; 261.382; 273.358; 370.792 and 373.13
			K
	Mg		
Na			
		P	177.434; 178.222; 178.703; 184.654; 185.057; 185.827; 185.878; 203.347; 213.547; 213.618; 214.914; 215.407; 253.561 and 255.326
			S
	Zn		
Y			

the standard additions (SA), and the MEC. Yttrium in the concentration of 5 mg L⁻¹ was used as an internal standard in the IS calibration. The range of calibration curves for EC was 0.5-50 mg L⁻¹ for each evaluated analyte.

Chicken, sheep loin, sheep carcass, and bovine meat samples were obtained in the local market (São Carlos, SP, Brazil). The method validation was performed by using the certified reference materials (CRM) bovine liver (SRM 1577c) and beef muscle (SRM 8414) (National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA).

Sample preparation

The meat samples were lyophilized (Model EC, MicroModulyo, New York, NY, USA), ground in a cryogenic mill (MA775, Marconi, Piracicaba, SP, Brazil), and homogenized. For the microwave digestion, approximately 100 mg of sample was weighed, and 3.0 mL of concentrated HNO₃, 5 mL of water, along with 2.0 mL of 30% (m m⁻¹) of H₂O₂ were added to the samples. The microwave heating program was applied in three steps: 15 min to reach 120 °C, 20 min to reach 180 °C and a standby time of 20 min at 180 °C (both at 1300 W power). After cooling to room temperature, the volumes were adjusted to 30 mL with deionized water.

MEC solutions

As previously mentioned, two solutions were prepared for MEC procedure. The selected ratio was 1:1, the solution 1 (S1) was composed by 50% (v v⁻¹) of digested meat sample and 50% (v v⁻¹) of standard solutions containing the analytes. In this case, the analyte concentrations in standard solution (C^{Standard}) were chosen by an earlier unpublished study. Solution 2 (S2) was composed of 50% (v v⁻¹) of digested meat sample and 50% (v v⁻¹) of the blank analytical solution.

Results and Discussion

The solutions for the construction of the calibration curve were prepared using a ratio of 1:1. The ratio was chosen to simplify the calculations of the analyte concentrations as well as to assume an intermediate concentration level between the sample and the standard. It should be emphasized that other ratios may be used, which will depend on the type of sample being analyzed. For example, samples with higher content of dissolved solids may require a higher dilution factor to improve the analytical response and not to clog in the nebulization system.¹⁴

The calibration curve was constructed considering the signals of S1 on the *x*-axis, while the S2 on the *y*-axis, thus generating a single point on the calibration curve. For each analyte, the wavelengths that had the highest sensitivity were selected, and the signals in each solution were measured. The first aspect related to the MEC is the easy detection of the emission lines that present spectral interferences. For this identification, it is only necessary to observe the points that stand outside the curve (linear model). During the calibration process, these lines are merely discarded.¹⁴⁻¹⁶

After the analysis of the wavelengths for each analyte, the emission lines were selected, resulting in 18 emission lines for Ca, 9 emission lines for Cu, 12 emission lines for Fe, 11 emission lines for K, 12 emission lines for Mg, 11 emission lines for Na, 14 emission lines for P, 12 emission lines for S, and 14 emission lines for Zn. Each selected emission line represents a point on the calibration curve, as was previously mentioned.

The obtained calibration curve for Cu in bovine liver (SRM 1577c) is shown in Figure 1.

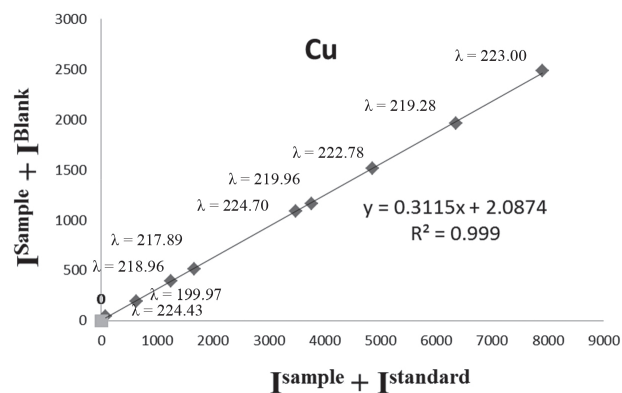


Figure 1. MEC curve used for the Cu determination by ICP OES in bovine liver (SRM 1577c).

According to Virgilio *et al.*,¹⁴ to choose the appropriate concentration of the standard, the signal ratio of the solutions S1 and S2 must be measured, and the desirable range should be between $10 \geq (S1 / S2) \geq 1.1$. This condition corresponds to an inclination between 0.1 and 0.9 and implies that the extremes would be avoided. The highlighted numbers presented in Table 2 represent the conditions used in all following MEC analyses. It should be noted that the slope in the Cu calibration curve for the CRM bovine muscle was around 0.01. The low amount of Cu in the CRM sample can explain this obtained low value, which was below the limit of detection (LOD) of the method, as confirmed further. The angular coefficients of the other evaluated analytes in the CRM 1577c (bovine liver) were between 0.19 and 0.39.

Table 2. MEC parameters of Ca, Cu, Fe, Mg, P, S, and Zn determination in meat certified reference materials by ICP OES

Analyte	Parameter	Bovine liver ^a / (mg L ⁻¹)			Bovine muscle ^b / (mg L ⁻¹)		
Ca	slope	0.310	0.474	0.674	0.319	0.471	0.677
	C ^{Std}	1	0.5	0.2	1	0.5	0.2
	C ^{analyte}	0.445	0.45	0.413	0.448	0.446	0.420
	C ^{certificated}		0.436			0.483	
Cu	slope	0.310	0.468	0.683	0.012	0.018	0.051
	C ^{Std}	2	1	0.4	2	1	0.4
	C ^{analyte}	0.883	0.879	0.861	< 0.01		
	C ^{certificated}		0.920			0.009	
Fe	slope	0.388	0.554	0.754	0.175	0.295	0.516
	C ^{Std}	1	0.50	0.20	1	0.5	0.2
	C ^{analyte}	0.635	0.500	0.200	0.212	0.209	0.210
	C ^{certificated}		0.660			0.237	
K	slope	0.286	0.355	0.571	0.337	0.501	0.715
	C ^{Std}	100	50	20	100	50	20
	C ^{analyte}	27.817	27.890	26.625	50.333	50.171	50.200
	C ^{certificated}		34.100			50.390	
Mg	slope	0.303	0.400	0.540	0.320	0.610	0.700
	C ^{Std}	5	2	1	5	2	1
	C ^{analyte}	2.174	1.333	1.174	2.353	3.128	2.333
	C ^{certificated}		2.060			3.200	
Na	slope	0.190	0.330	0.552	0.205	0.392	0.620
	C ^{Std}	30	15	6	20	10	4
	C ^{analyte}	7.037	7.395	7.400	6.684	6.440	6.527
	C ^{certificated}		6.778			7.000	
P	slope	0.289	0.443	0.660	0.215	0.349	0.574
	C ^{Std}	100	50	20	100	50	20
	C ^{analyte}	39.790	38.750	38.806	26.448	26.850	26.958
	C ^{certificated}		39.160			27.860	
S	slope	0.165	0.322	0.531	0.202	0.318	0.544
	C ^{Std}	100	50	20	100	50	20
	C ^{analyte}	19.799	23.727	22.633	24.908	23.362	23.86
	C ^{certificated}		24.960			26.5	
Zn	slope	0.217	0.355	0.564	0.186	0.31	0.551
	C ^{Std}	2	1	0.4	2	1	0.4
	C ^{analyte}	0.551	0.549	0.518	0.457	0.449	0.492
	C ^{certificated}		0.604			0.473	

^aSRM 1577c; ^bSRM 841. C^{Std}: analyte concentration in the standard solution; C^{analyte}: calculated sample concentration by using MEC (equation 2); C^{certificated}: CRM analyte concentration (100 mg of sample in 30 mL of digested final volume). The highlighted numbers represent the conditions used in all following MEC analyses.

Using the coefficient of the calibration curve (slope) and the analyte concentration added in S1 (C^{Std}), the analyte concentration (C^{analyte}) in the sample can be calculated according to the following equations:¹⁴

$$\text{Slope} = \frac{(C^{\text{analyte}})}{(C^{\text{analyte}} + C^{\text{Std}})} \quad (1)$$

Moreover, rearranging equation 1 as C^{Std} is known:

$$C^{\text{analyte}} = \frac{(\text{slope} \times C^{\text{Std}})}{(1 - \text{slope})} \quad (2)$$

Different concentrations were studied for each analyte in both reference materials (bovine liver and bovine muscle)

to evaluate how the concentration of the analyte (C^{analyte}) varies concerning the concentration of the standard solution (C^{Std}). The 50 mg L⁻¹ standard solution was used to calculate the analyte concentration of P in the sample. It should be noted that higher value was obtained with a solution of 20 mg L⁻¹. Otherwise, when the value was corrected to the mass fraction, the recovery was lower. According to the results shown in Table 2, it can be observed that the best results (highlighted concentrations) were obtained when C^{Std} was at least twice or equal to the analyte concentrations in the sample, as reported by Machado *et al.*¹⁵

The EC, IS, and SA calibration procedures were accomplished in a comparative study. To evaluate these calibrations, we calculated the recoveries of the analytes, that are shown in Table 3. The recovery intervals were obtained in the range of 73-98.6% for the EC, 87-108% for the IS, 86-115% for the SA and 87-107% for the MEC.

When the external calibration was applied, the Na accuracy presented unsatisfactory results. Na can be considered as a readily ionizable element (5.1 eV) and, according to the results, is remarkable that the high matrix effect needs to be compensated by the application of the IS or the SA calibration strategies. Also, the use of MEC for Na was more effective because it improves the accuracy compared to the other tested calibrations methods. In the same way, the use of MEC improved the accuracy of Ca, Mg, P, S, and Zn in the evaluated CRM.

Meat is as a complex organic matrix, and when digested, it presents dissolved carbon content that can provide spectral interferences, mainly for elements with the high energy of ionization. Besides, the presence of readily ionizable elements in the matrix such as Na, K, and Mg modifies the electrical density in the plasma, and consequently, the analyte signals can be suppressed. For this

reason, calibration strategies that employ matrix matching principles such as MEC are more appropriate to overcome such interference.

The MEC accuracy, estimated using the reference materials, are shown in Table 4. The analysis of variance (ANOVA) test statistical analysis was performed, and a significant difference was observed at 95% of confidence for Fe and Zn in the bovine liver. This difference can be given by the deviation in the determined value, increasing the uncertainty. For the other analytes in both reference materials, the *t* calculated was lower than the table to 95% confidence.

It is important to highlight that the MEC has the main advantage of simplicity in comparison to the classic calibration strategies. Since only two solutions are used, shorter preparation time is required. Likewise, it must be taken into account that applying MEC as a calibration strategy only one calibration curve needs to be prepared to calculate the slope of the line to determine the concentration of the analyte. For determining the most appropriate wavelength for calculating the concentration of the analytes, other classic calibration methods need one calibration curve for each wavelength. The MEC also has array matching capability, and therefore the matrix effects can be reduced. However, compared to the EC the measurement time of each sample is more extended because several wavelengths *per* analyte must be analyzed for both solutions, which can decrease the analytical frequency depending on the number of elements analyzed. Also, the MEC is prone to systematic errors during the preparation of the solutions, and the analyte must present multiple analytical lines to be able to apply this type of calibration strategy.

Table 3. Recovery of Ca, Cu, Fe, Mg, K, Na, P, S, and Zn in CRM using various calibration strategies. Mass fraction determined by ICP OES (n = 3)

Analyte	Bovine liver ^a / %				Bovine muscle ^b / %			
	EC	IS	SA	MEC	EC	IS	SA	MEC
Ca	98.6	108.0	104.4	100.2	79.5	91.3	94.1	95.2
Cu	97.1	89.4	129.2	95.9	< LOD	< LOD	< LOD	< LOD
Fe	92.1	93.2	98.48	95.6	84.0	88.0	93.7	94.2
Mg	82.2	84.2	93.8	97.2	82.9	87.3	87.0	98.4
K	92.4	91.3	96.1	101.9	85.4	89.2	86.1	98.0
Na	74.1	88.7	114.6	107.0	73.1	88.5	109.3	102.1
P	92.3	89.8	93.5	99.1	88.1	88.0	87.2	93.0
S	93.1	88.2	102.9	98.8	96.1	94.4	97.4	91.2
Zn	84.4	88.1	88.2	92.7	79.8	87.2	93.8	87.4

^aSRM 1577c; ^bSRM 8414. EC: external calibration; IS: internal standard; SA: standard addition; MEC: multi-energy calibration; LOD: limit of detection (Cu: 3 mg kg⁻¹).

Table 4. Ca, Cu, Fe, Mg, K, Na, P, S, and Zn mass fraction obtained in two CRM using MEC by ICP OES (concentration \pm standard deviation, n = 3)

Analyte	Bovine liver ^a		Bovine muscle ^b	
	Certificate	Determined	Certificate	Determined
Ca / (mg kg ⁻¹)	131 \pm 10	131 \pm 2	145 \pm 20	138 \pm 4
Cu / (mg kg ⁻¹)	275.2 \pm 4.6	264 \pm 53	2.84 \pm 0.45	< LOD
Fe / (mg kg ⁻¹)	197.94 \pm 0.65	189.3 \pm 2.3	71.2 \pm 9.2	66.8 \pm 1.3
Mg / (mg kg ⁻¹)	620 \pm 42	637 \pm 70	960 \pm 95	945 \pm 28
K / (% m m ⁻¹)	1.023 \pm 0.064	1.042 \pm 0.041	1.517 \pm 0.037	1.49 \pm 0.03
Na / (% m m ⁻¹)	0.2033 \pm 0.0064	0.218 \pm 0.002	0.210 \pm 0.008	0.196 \pm 0.004
P / (% m m ⁻¹)	1.175 \pm 0.027	1.164 \pm 0.020	0.836 \pm 0.045	0.78 \pm 0.03
S / (% m m ⁻¹)	0.749 \pm 0.034	0.74 \pm 0.03	0.795 \pm 0.041	0.725 \pm 0.021
Zn / (mg kg ⁻¹)	181.1 \pm 1	167.8 \pm 5.8	142 \pm 14	123 \pm 15

^aSRM 1577c; ^bSRM 8414. LOD: limit of detection (Cu: 3 mg kg⁻¹).

Limit of detection (LOD)

The LOD were determined according to preconized by the International Union of Pure and Applied Chemistry (IUPAC), as 3 times the equivalent concentration of blank (LOD = 3C_B). To calculate the LOD, we used the solution S1 as 25 mL of 1% HNO₃ plus 25 mL of 1 mg L⁻¹ analyte standard, and S2 as 25 mL of 1% HNO₃ solution (v v⁻¹) plus 25 mL of blank digestion solution, used as a sample. The blank concentration was then calculated using the MEC (n = 10). The LOD calculated were 0.02, 0.01, 0.001, 0.1, 0.002, 0.2, 0.05, 0.2, and 0.06 mg L⁻¹ for Ca, Cu, Fe, K, Mg, Na, P, S and Zn, respectively.

Expressing the results in mass fraction, the LODs for Ca, Cu, Fe, Mg, and Zn were found as 6, 3, 0.3, 0.7, and 19 mg kg⁻¹, respectively. For K, Na, P and S, the LODs were 0.0004, 0.0006, 0.0001, and 0.0006 g kg⁻¹, respectively. The limits of quantification (LOQ) were 19, 10, 1, 2, 58 mg kg⁻¹, and 0.001, 0.002, 0.0003 and 0.002 g kg⁻¹ for Ca, Cu, Fe, Mg, Zn, and K, Na, P and S, respectively.

The values obtained here are mostly comparable to those found in the literature concerning the determination of macro and micro minerals in meat. Sager *et al.*¹¹ determined

Ca, K, Mg, Na, P, Cu, Fe and Zn in chicken meat by ICP OES and obtained LOD of 0.01, 0.01, 0.002, 0.005 and 0.01 g kg⁻¹ for Ca, K, Mg, Na, and P, respectively. For Cu, Fe, and Zn, these values were found to be 0.20, 3.7 and 1.8 g kg⁻¹. Vieira *et al.*¹⁷ determined Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn in meat by ICP OES, with 2, 0.5, 1.5, 1.2, 0.4, 0.1, 5, 4, 4 and 1 mg kg⁻¹ of LOQ, respectively.

Cu and Zn were determined in sheep muscle by ICP OES with LOD of 0.0109 mg kg⁻¹ for Cu and 0.0357 mg kg⁻¹ for Zn, values lower than those found in the present work. This may have occurred due to the different way of LOD determination.¹⁸

Meat samples analysis

The MEC was applied to the nutrients determination of different types of meat samples, and the results are summarized in Table 5. The assessed samples had levels of Cu below the LOQ of the method (2.92 mg kg⁻¹).

Comparing the mass fraction of nutrients obtained in several types of meat with the results reported in the literature, it could be observed the similarity with the obtained results in the current work.^{2,4,12,17,19}

Table 5. Mass fraction of Ca, Cu, Fe, Mg, K, Na, P, S, and Zn in different types of meat using MEC (measurement \pm standard deviation, n = 3)

Analyte	Sample			
	Chicken	Sheep loin	Sheep carcass	Bovine
Ca / (mg kg ⁻¹)	165.9 \pm 1.5	215.04 \pm 0.70	18.067 \pm 1676	205 \pm 15
Cu / (mg kg ⁻¹)	< LOD	< LOD	< LOD	< LOD
Fe / (mg kg ⁻¹)	19.2 \pm 0.5	62 \pm 1	54 \pm 4	48 \pm 2
Mg / (mg kg ⁻¹)	899 \pm 16	888 \pm 9	1417 \pm 12	700 \pm 28
K / (% m m ⁻¹)	2.8 \pm 0.5	1.3 \pm 0.2	0.9 \pm 0.1	1.2 \pm 0.2
Na / (% m m ⁻¹)	0.29 \pm 0.05	0.29 \pm 0.03	0.42 \pm 0.07	0.35 \pm 0.02
P / (% m m ⁻¹)	0.80 \pm 0.01	0.81 \pm 0.02	3.4 \pm 0.2	0.60 \pm 0.03
S / (% m m ⁻¹)	0.71 \pm 0.01	0.88 \pm 0.03	0.37 \pm 0.06	0.53 \pm 0.02
Zn / (mg kg ⁻¹)	29.85 \pm 0.01	77 \pm 1	57 \pm 4	121 \pm 3

LOD: limit of detection (Cu: 3 mg kg⁻¹).

Conclusions

According to the obtained results, the MEC presents itself as a potential calibration strategy for the rapid and efficient quantification of macro and micro minerals in meat samples. This calibration strategy does not require modifications to the instrumentation nor the preparation of a wide range of standards. The recovery percentages were between 87 and 107% for the analyzed analytes. The results obtained did not present significant differences when compared to the traditional calibration procedures. Beyond being time-consuming compared to the external calibration and the requirement of multiple analytical lines of the analytes, MEC proved to be useful in complex samples, which requires matrix matching strategies to avoid analysis interference.

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