

VALIDATION OF γ SPECTROMETRY TECHNIQUE TO DETERMINE POTASSIUM IN FOODSTUFFS

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Introduction

The analytical method is based in the measure of the energetic γ -ray (1460.8 keV) emitted by ^{40}K when decays to gas ^{40}Ar by electron capture (EC) (11%).

¿Why validate the analytical method?

- In agreement with the international and national normative analytical methods need to be validated or revalidated: before their introduction into the routine use, whenever the original conditions do change.
- ¿Why Potassium?
- Among the trace elements in foodstuffs, K is one of the most important and it is a well-known essential element occurring all over the earth where reaches a relative abundance of 2.59% compared with the whole set of elements.
- Food potassium concentration widely varies, so its intake results quite dependent on diet; Reference Dietary Intake or Reference Daily Intake (RDI) for K varies between 1.56 g d^{-1} and 5.0 g d^{-1}

Aims

- Aim of this work is to validate the analytical method in determining potassium traces in foodstuffs by natural ^{40}K radiation. Results obtained were compared to those of the well-known Atomic Absorption Spectrometry technique.

Experimental

- Blank was calcium carbonate sigma ultra purity (potassium concentration lesser than 0.005 %). Standards were prepared spiking known amount of KCl (Reagent Grade) covering 5 levels of concentration from 0.3 to 6.0 %. To cover the requisite it was utilized the method described by Lavi and Alfassi by mixing always similar amounts of two solids. To clarify it we will use a numerical example. If we weigh 1 g of KCl, we add to it 1 g of CaCO_3 , and mixed obtaining the combined 2 g, and mixed thoroughly. The procedure of thorough mixing and adding similar amount of CaCO_3 to the mass of the mixture was repeated several times till we reach the final weight of mixture in which we are interested in.
- To know the quantity of KCl to reach required percentage of potassium without exceeding the total weight of sample necessary to have almost equal density, we use the next mathematical algorithm

Mathematic Algorithm for Calculate Weight of KCl

$$W_K = \left(\frac{\%K}{100} \right) * W_S$$

$$W_{KCl} * 2^n = W_S$$

$$W_{KCl} = \left(\frac{39 + 35.5}{39} \right) W_K$$

$$n = \frac{\log \left(\frac{W_S}{W_{KCl}} \right)}{\log 2}$$

Weight of KCl

%K req	W_{KCl} (g)	W_{KCl} corr(g)	n	n corr.	W_s	%K cal.
0.26	0.8443	1.5	6.8244	7	192	0.230
0.9	2.9226	3	5.8244	6	192	0.796
1.49	4.8386	5	5.0874	5	160	1.583
3.14	10.196	10	4.0874	4	160	3.336
5	16.237	11	3.9499	4	176	4.829
6	19.484	20	3.0874	3	160	6.375

Detection System



Parameters of method validation

- *Selectivity or specificity*
- *Linearity*
- *Range*
- *Precision*
- *Limit of Detection (LD), Limit of quantitation (LQ)*
- *Sensitivity*

Linearity

- *Linearity* is the ability of an analytical procedure to produce test result with are proportional to concentration (amount) of analyte, in this case K, in samples within a given concentration range. For this test it is required a linear relationship between the activity (analytical answer) with K concentration in the sample. So we have:

Linearity

$$A = \lambda N \quad \lambda = \frac{\ln 2}{t_{1/2}} \quad N = \frac{N_A * \%_K * W_S * P_{EC,A}}{100 * AW_K} \quad A = \frac{\#C}{T_L * \varepsilon}$$

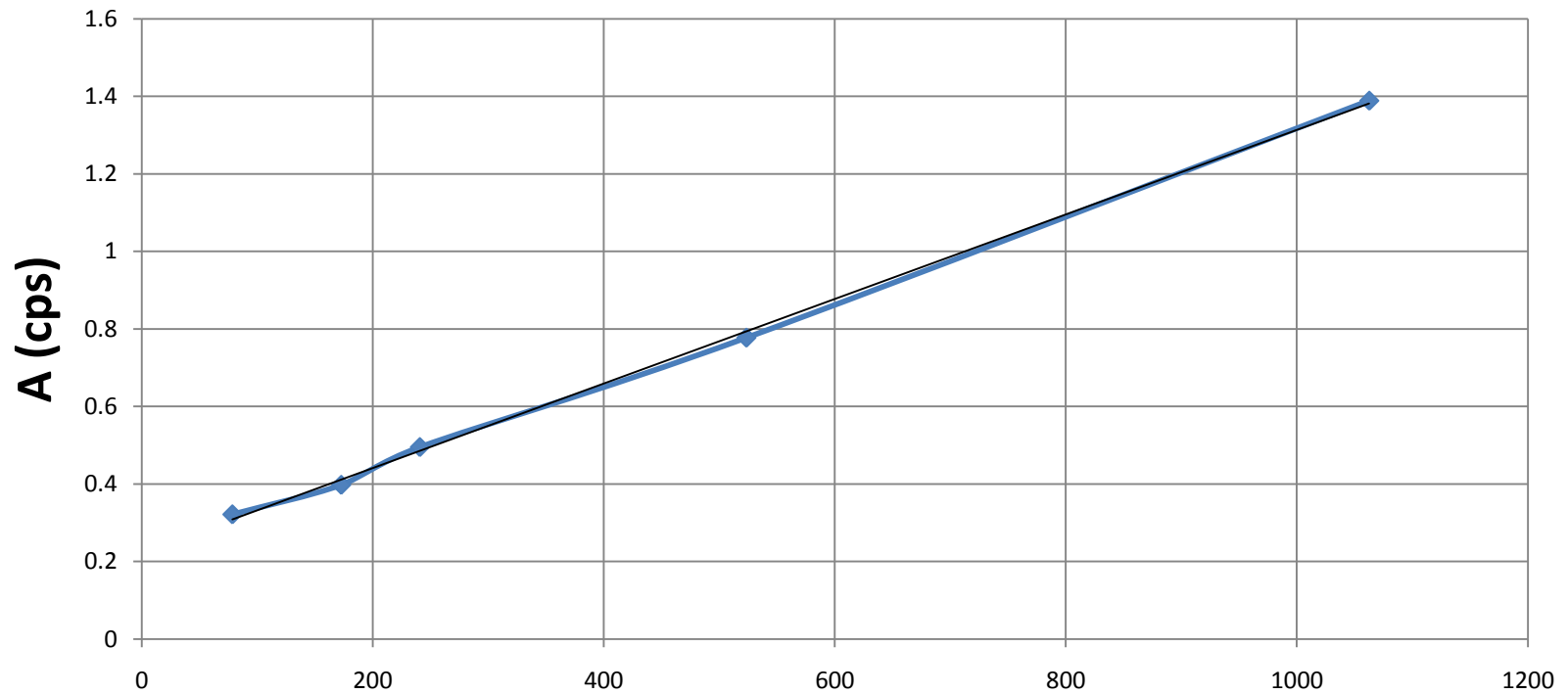
$$\frac{\#C}{T_L} = \frac{\ln 2 * N_A * P_{EC,A} * \varepsilon}{t_{1/2} * AW_K * 100 * 365 * 24 * 60 * 60} \%_K * W_S$$

$$y = \frac{\#C}{T_L} \quad m = \frac{\ln 2 * N_A * P_{EC,A} * \varepsilon}{t_{1/2} * AW_K * 100 * 365 * 24 * 60 * 60} \quad x = \%_K * W_S$$

Lineal regression (1). Analytical answer versus K concentration in mixture samples, counts per second.
First regression line data series

#C	RT (s)	LT (s)	DT(%)	W_m g	W_{m+CaCO_3} g	W_{s+m} g	#C/LT	%K*Ws	%K
27499	86400	85605.26	0.92	137.8	337.2	338.7	0.32	78.52	0.39
31184	86400	78470	9.18	137.6	327.8	331.1	0.39	172.75	0.89
39901	86400	80635.92	6.67	138	295	299.6	0.49	240.80	1.49
66907	86400	86092.54	0.36	137.6	294.1	304.1	0.77	523.49	3.14
112367	86400	80904.12	6.36	136.4	276.6	296.9	1.38	1062.68	6.62

Lineal Regression (1). Analytical answer versus K concentration in mixture samples, counts per second for the first data series



$$y = 0.0011x + 0.2224$$

$$R^2 = 0.999$$

%K*Ws

Summary Statistics of Regression Parameters

Lineal Equation

$$Y = 0.0011X + 0.22$$

m	0.00107	b	0.222
	0.00108		0.219
	0.00109		0.220
Average	0.00108		0.221

Precision

Concentration	Average	Std. Des.	VC
%	cps	cps	%
6.59	1.37	0.013	0.94
3.14	0.77	0.006	0.74
1.48	0.49	0.003	0.64
0.89	0.39	0.003	0.77
0.39	0.32	0.003	1.05

Accuracy GAMMA SPECTROMETRY

%K	%Kcal (1)	%K cal (2)	%Kcal (3)	%K average	%recovery
0.39	0.45	0.45	0.44	0.45	113.99
0.89	0.83	0.83	0.83	0.83	92.83
1.49	1.55	1.54	1.56	1.55	103.82
3.14	3.05	3.07	3.06	3.06	97.40
6.62	6.66	6.66	6.65	6.66	100.55
				AVERAGE	101.72
				STD.DEV	7.97
				VC	7.83

Confidence interval of (μ) of Recovery percentage

$$IC(\mu) = \bar{y} \pm t_{0.975, n-1} * \frac{S}{\sqrt{n}}$$

$$t_{0.975, (4)} = 0.776$$

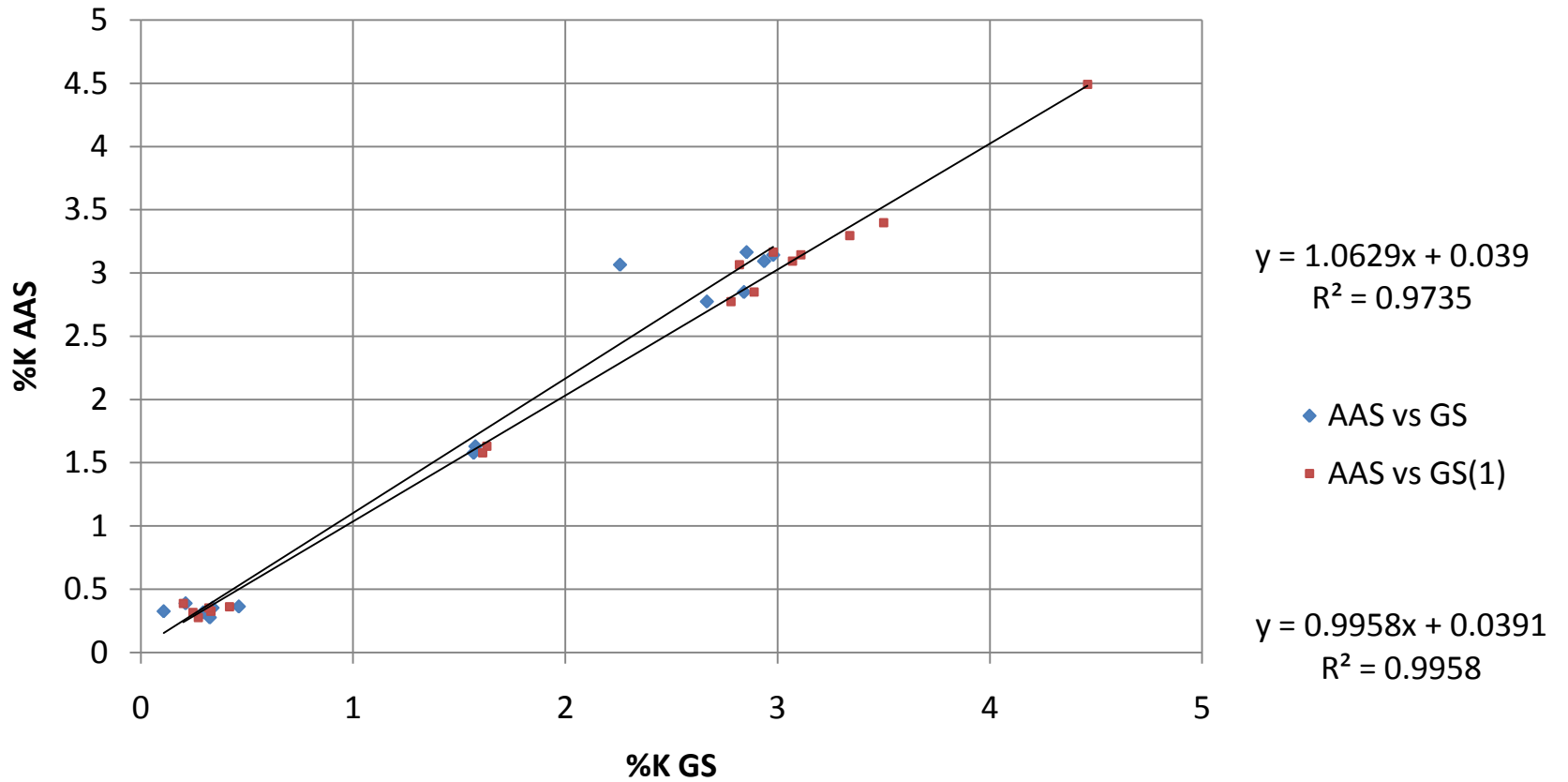
Accuracy. Percentage of recovery for AAS method

STD	Cert. Val %	Cal. Val. %	%recovery	(%recovery) ²
Std. Citrus leaves	1.82	1.6536	90.86	8255.02
Std. Wheat Flour	0.136	0.1362	100.15	10029.43
		ADDITION	191.00	18284.45

Sample	% de potasio		
	GammaS	GammaS (1)	AAS
Morita	2.94	3.07	3.09
Pasilla	2.85	2.98	3.16
Guajillo	2.98	3.11	3.14
Cuaresmeño	2.67	2.78	2.77
Poblano	2.84	2.89	2.85
Piquin	2.26	2.82	3.06
Peruano	1.58	1.63	1.63
Vaquita	1.56	1.61	1.58
masa (A)	0.32	0.271	0.27
Masa (B)	0.29	0.245	0.31
masa (C)	0.46	0.418	0.36
Masa (D)	0.11	0.33	0.32
Masa (E)	0.34	0.3203	0.35
Masa (F)	0.21	0.2	0.39
Tobacco 1	3.63	4.46	4.49
Tobacco 2	2.96	3.34	3.30
Tobacco 3	2.33	3.5	3.40

A comparison of uncertainties for AAS and Gama Spectrometry methods in this work and those previously reported

AAS vs GS and GS(1)



AAS - Gamma-spectrometry compared values and those previously reported

Mathematic algorithm to calculate uncertainty associated to regression line

$$U_{b,m} = \sqrt{S_m^2 + S_b^2}$$

$$U_{reg}^2 = \left(\frac{U_{m,b}}{y-b} \right)^2 + \left(\frac{S_m}{m} \right)^2$$

Sample	% potassium					
	GammaS	U	GammaS (1)	U	AAS	U
Morita	2.94	0.06	3.07	0.07	3.09	0.03
Pasilla	2.85	0.06	2.98	0.06	3.16	0.03
Guajillo	2.98	0.06	3.11	0.06	3.14	0.03
cuaresmeño	2.67	0.06	2.78	0.07	2.77	0.03
Poblano	2.84	0.07	2.89	0.08	2.85	0.03
Piquin	2.26	0.05	2.82	0.08	3.06	0.03
Peruano	1.58	0.04	1.63	0.03	1.63	0.02
Vaquita	1.57	0.04	1.61	0.04	1.58	0.02
masa (A)	0.33	0.04	0.271	0.06	0.28	0.003
Masa (B)	0.29	0.04	0.245	0.06	0.31	0.003
Masa (C)	0.46	0.04	0.418	0.06	0.36	0.003
Masa (D)	0.11	0.04	0.33	0.1	0.32	0.003
Masa (E)	0.34	0.04	0.3203	0.07	0.35	0.03
Masa (F)	0.21	0.04	0.2	0.05	0.39	0.004
Tobacco 1	3.63	0.14	4.46	0.2	4.49	0.04
Tobacco 2	2.96	0.15	3.34	0.18	3.30	0.03
Tobacco 3	2.33	0.14	3.5	0.17	3.40	0.03

A comparison of uncertainties for AAS and Gama Spectrometry methods in this work and those previously reported .

Limits of detection and quantitation

$$LD = \frac{3.3xS_{b_0}}{b_1}$$

$$LQ = \frac{10xS_{b_0}}{b_1}$$

	LD	LQ
%K	0.13	0.38
Bq/g	0.04	0.12

Sensitivity

- *Sensitivity* of the analytical method is calculated by linear-regression slope value; higher values mean higher sensitivity. Calculated slope value in Figure 1 do assigns about $0.0011 \text{ cps g}^{-1}$, so indicating that the method is not so sensitive because counting-time units are expressed in count per second as if total counting time were equivalent to a second. If counts were hour/day expressed since they were taken in a 24 h time period, the slope increase would give 4 cph g^{-1} and 94 cpd g^{-1} values, respectively, so indicating a more sensitive method. Graph in per-second counts has been chosen because activity is expressed in Bq.

Conclusions

- The analytical method for assessing potassium percentage in foodstuffs by gamma spectrometry, being based in an equation representing the independent variable (concentration) to a dependent variable, determines the parameters describing the straight line: slope, ordinate to origin, and lineal correlation coefficient.
- In this way we have been able to quantify the analyte contained in a sample having unknown concentration by applying the answer in the so-obtained straight-line equation.
- All evaluated parameters show that gamma- spectrometry method for determining potassium concentration is sensitive, specific, precise, acute and linear, covering an ample range of foodstuff reported concentrations. Preparing samples and performing experiments in any laboratory facility is not a complicated matter.