

WDXRF AS A TOOL FOR ASSESSING HOMOGENEITY IN FOOD MATRICES



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ABSTRACT

Certified Reference Materials (CRM) are tools that provide reliability, ensure the validity of the results and allow establishing metrological traceability of measurements [1], especially in food, where the variety of matrices and analytes complicates its availability. The National Metrology Institute of Colombia (INM) has produced CRMs of elements in food matrixes and has assessed their homogeneity using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), obtaining relative uncertainties of around 3.5%. Recognizing of the importance of achieving lower uncertainties, the INM has also used WDXRF to evaluate homogeneity in three batches of matrix reference materials —wheat flour, rice flour, and tilapia flour— obtaining relative uncertainties due to homogeneity lower than those reported with ICP-MS (around 1%). These results highlight the advantages of the WDXRF, offers a promising alternative for assessing the homogeneity of matrix CRM batches and supports the development of new uses for technics that usually are used to measure inorganic matrices.

INTRODUCTION

In food measurements, where matrices are complex and analytes may be heterogeneously distributed, the evaluation of homogeneity becomes even more critical. The ISO 33405:2024 standard provides guidelines for assessing homogeneity and stability [2], emphasizing the use of precise and selective methods.

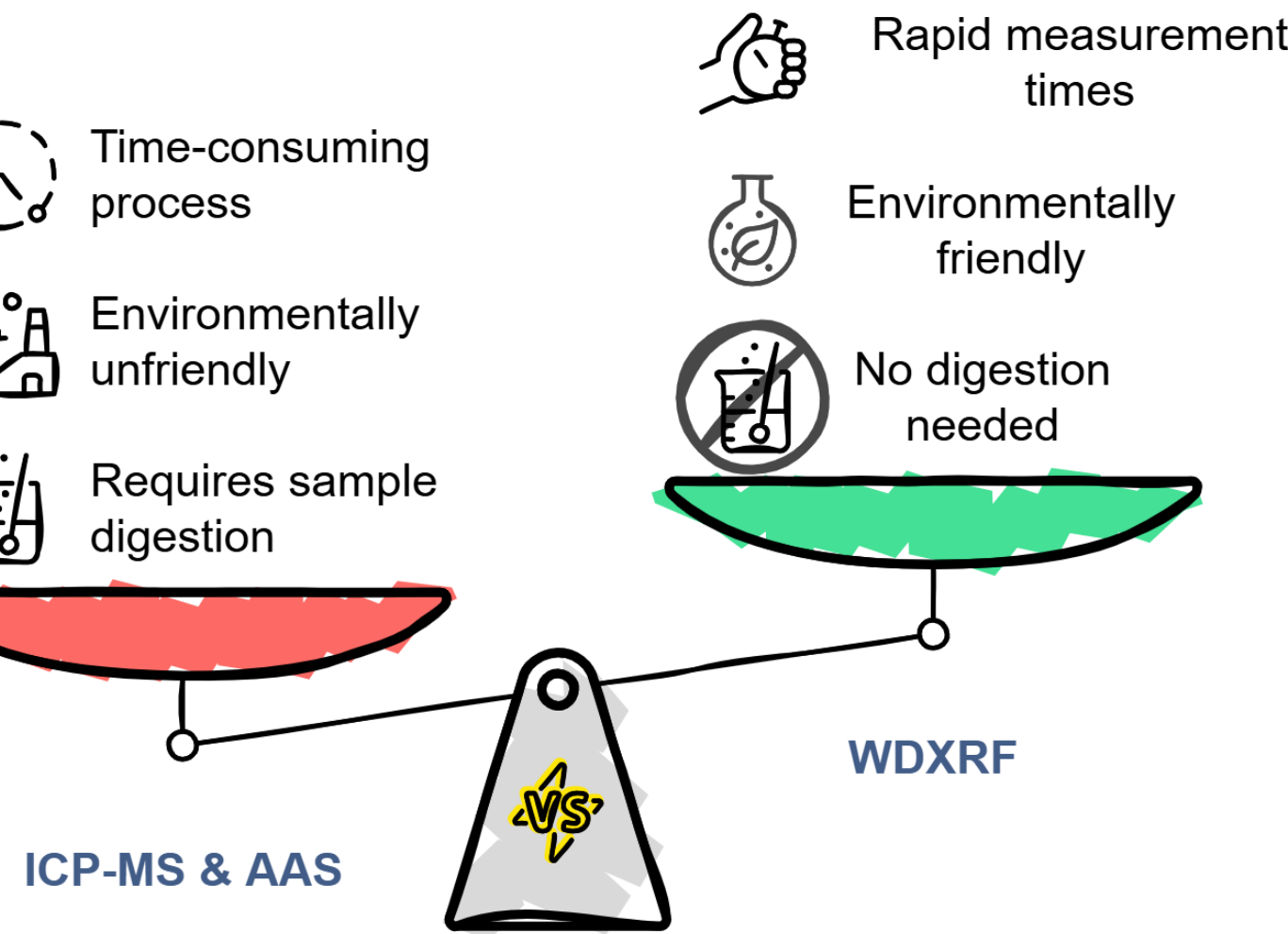
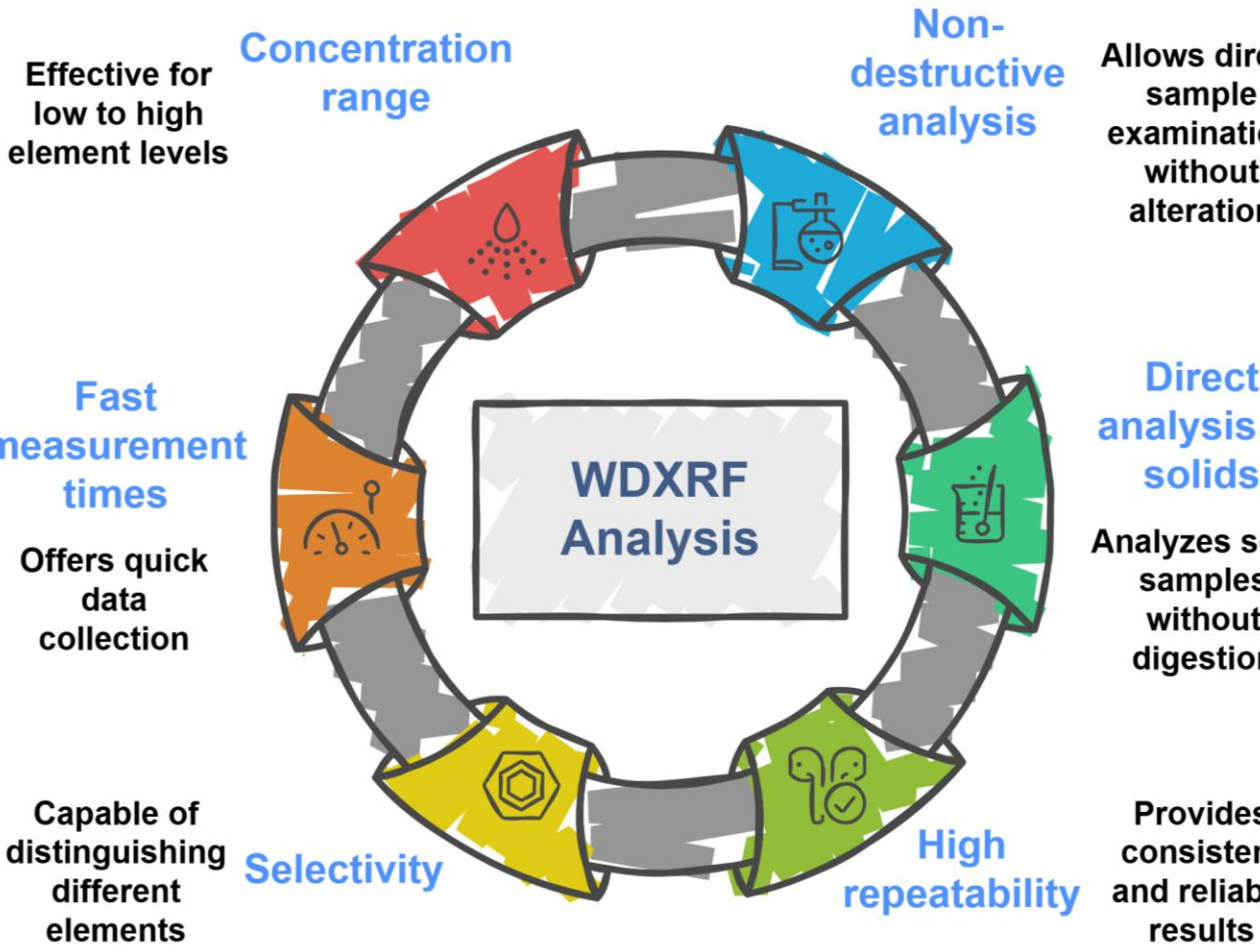
The homogeneity of a reference material batch affects the uncertainty of the certified value. Proper assessment of homogeneity is essential in CRM production. The uncertainty associated with a certified value can be expressed as:

$$u_{MRC} = \sqrt{u_{hom}^2 + u_{lts}^2 + u_{char}^2}$$

Were, u_{hom} is the uncertainty by homogeneity, u_{lts} is the uncertainty by stability and u_{char} is the uncertainty by characterization. The total uncertainty is expressed according to the GUM [3].

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and **Atomic Absorption Spectrometry (AAS)** have traditionally been used to assess the homogeneity of Certified Reference Materials (CRM) in matrices.

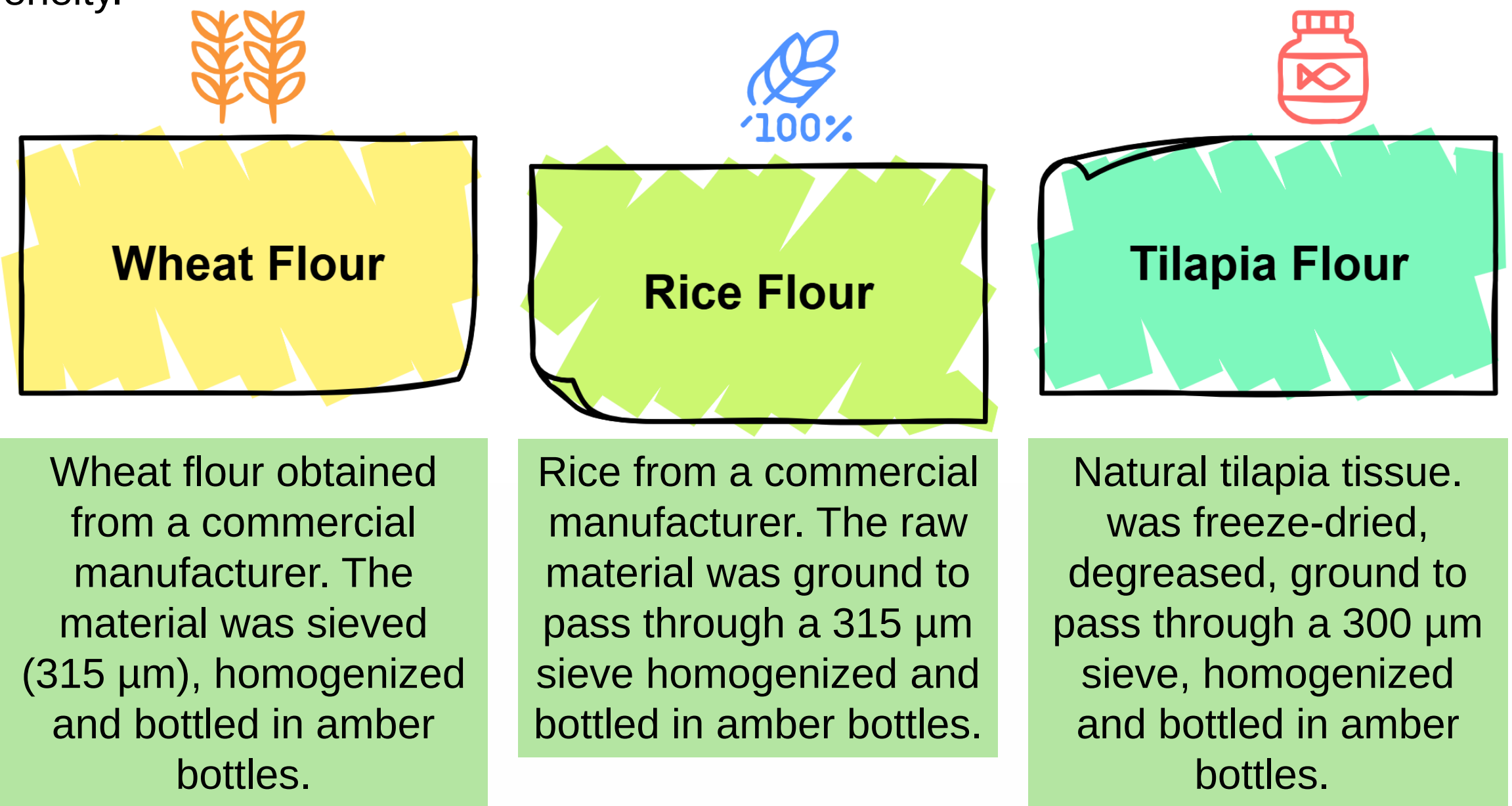
The INM has utilized Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to assess the homogeneity of CRMs, achieving relative uncertainties of approximately 3.5%. However, recognizing the need for improved precision, the INM also employed WDXRF to evaluate the homogeneity of three specific batches of matrix reference materials: wheat flour, rice flour, and tilapia flour.



Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF) is a non-destructive analytical technique that allows direct analysis of solid samples without the need for digestion [4].

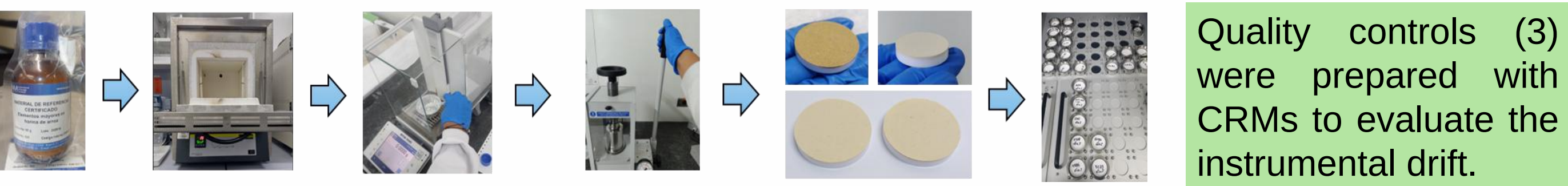
MRC PRODUCTION IN FOOD

In the INM, WDXRF is used to assess the homogeneity of three batches of reference materials: wheat flour, rice flour, and tilapia flour, with the aim of achieving lower uncertainties due to material heterogeneity.



METHODOLOGY FOR PREPARATION AND MEASUREMENT BY WDXRF

The samples were selected by stratified random sampling [2], taking 10% of the batch. From each bottle, 3 independent replicates were prepared, which were dried at 90 °C for 2 h and subsequently pressed in a Specac Atlas 25T hydraulic press at pressing time from 40 s to 120 s at a load of 20 t.



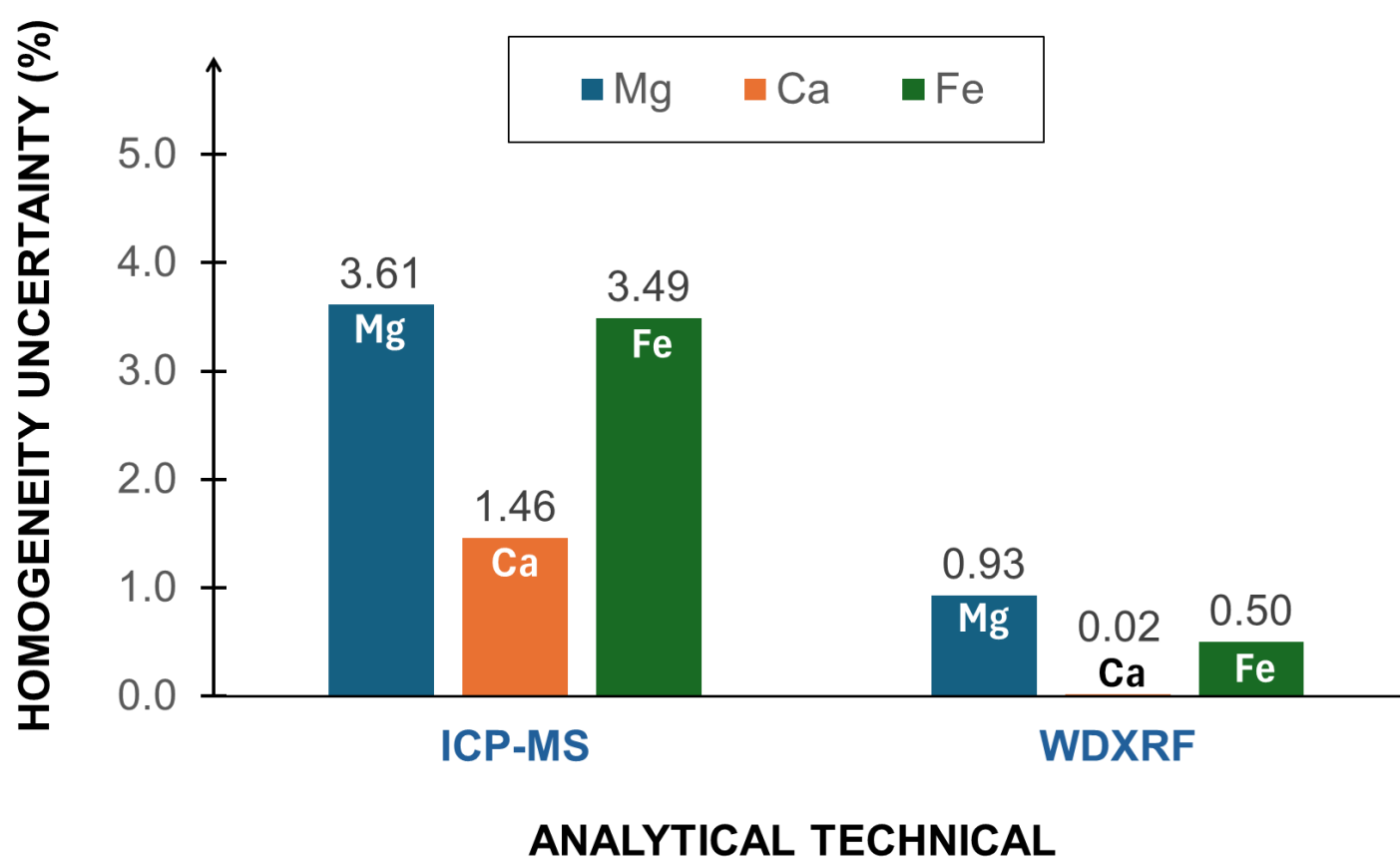
Four instrumental replicates for each RM pellet were measured under repeatability conditions, using a Bruker AXS S8 Tiger X-Ray Fluorescence Spectrometer. The specifications of the method parameters used in WDXRF are presented below:



Z	Line name	Energy (keV)	Current (mA)	Voltage (kV)	Crystal	Peak ($^{\circ}$ 2 θ)	Collimator	Detector
20	Ca K α_1 -HS-Min	3.6918	60	50	LiF200	113.111	0.46	Flow
16	S K α_1 -HS-Min	2.3079	100	30	PET	75.776	0.46	Flow
15	P K α_1 -HS-Min	2.0137	100	30	PET	89.408	0.46	Flow
30	Zn K α_1 -HR-Min	8.6392	50	60	LiF200	41.834	0.23	Scintillation
29	Cu K α_1 -HR-Min	8.0481	50	60	LiF200	45	0.23	Scintillation
12	Mg K α_1 -HS-Min	1.2533	100	30	XS-55	20.297	0.46	Flow
26	Fe K α_1 -HS-Min	6.4041	50	60	LiF200	57.555	0.46	Scintillation
19	K K α_1 -HS-Min	3.3139	60	50	LiF200	136.678	0.46	Flow

RESULTS

Homogeneity studies conducted on wheat flour using ICP-MS show higher homogeneity uncertainties compared to those obtained using WDXRF: for example, for the element Mg, the relative uncertainty (u_{hom}) decreased from 3.61 % using ICP-MS to 0.93 % using WDXRF. This behavior is also observed for other elements.

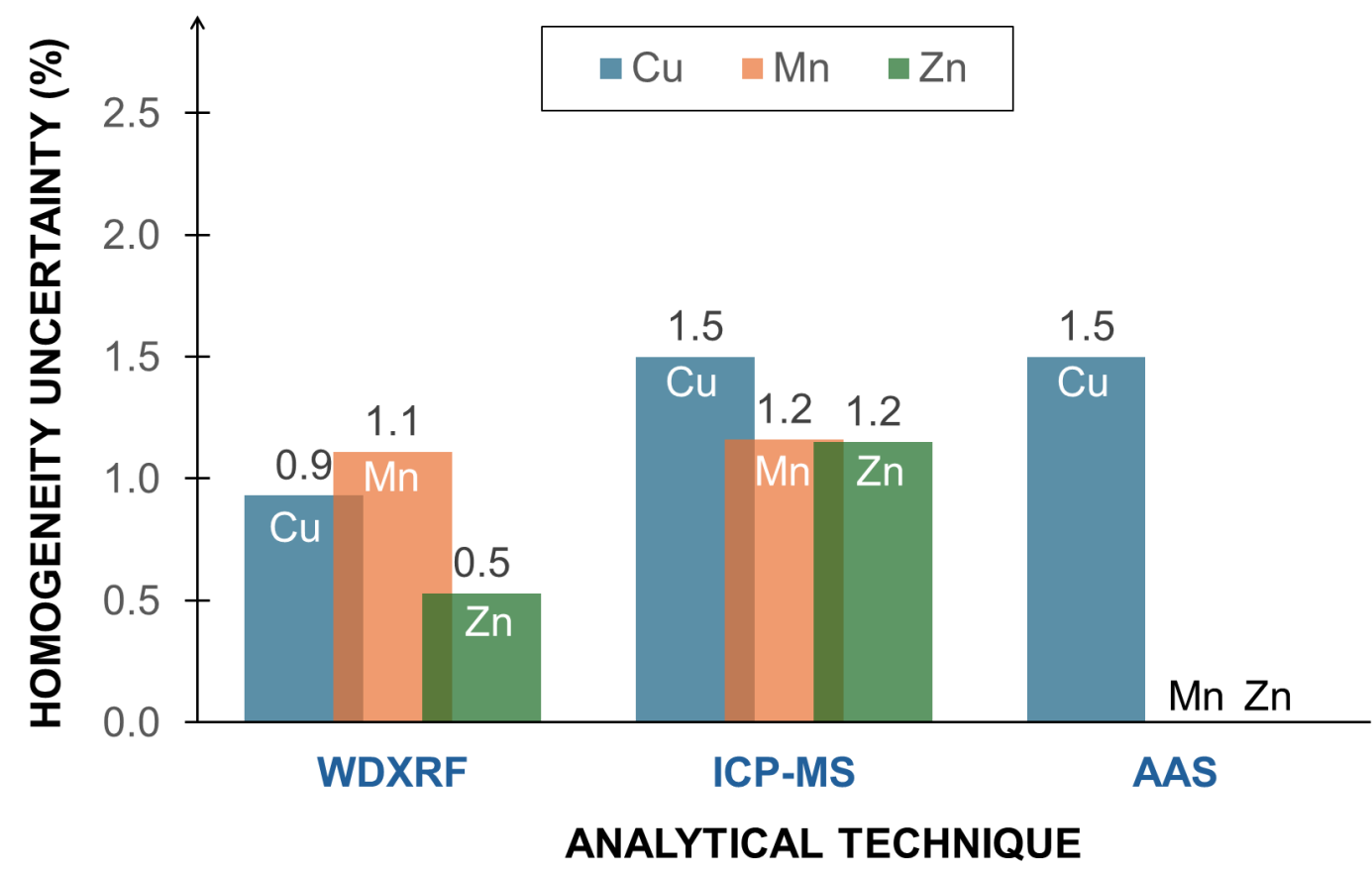


The use of WDXRF for homogeneity assessment in food reference materials (RM) such as wheat flour, rice flour, and tilapia flour showed relative u_{hom} values ranging from 0.93% to 4.18% for magnesium (Mg) and from 0.05% to 1.07% for iron (Fe). These values are comparable to or even lower than those obtained with traditional techniques such as ICP-MS.

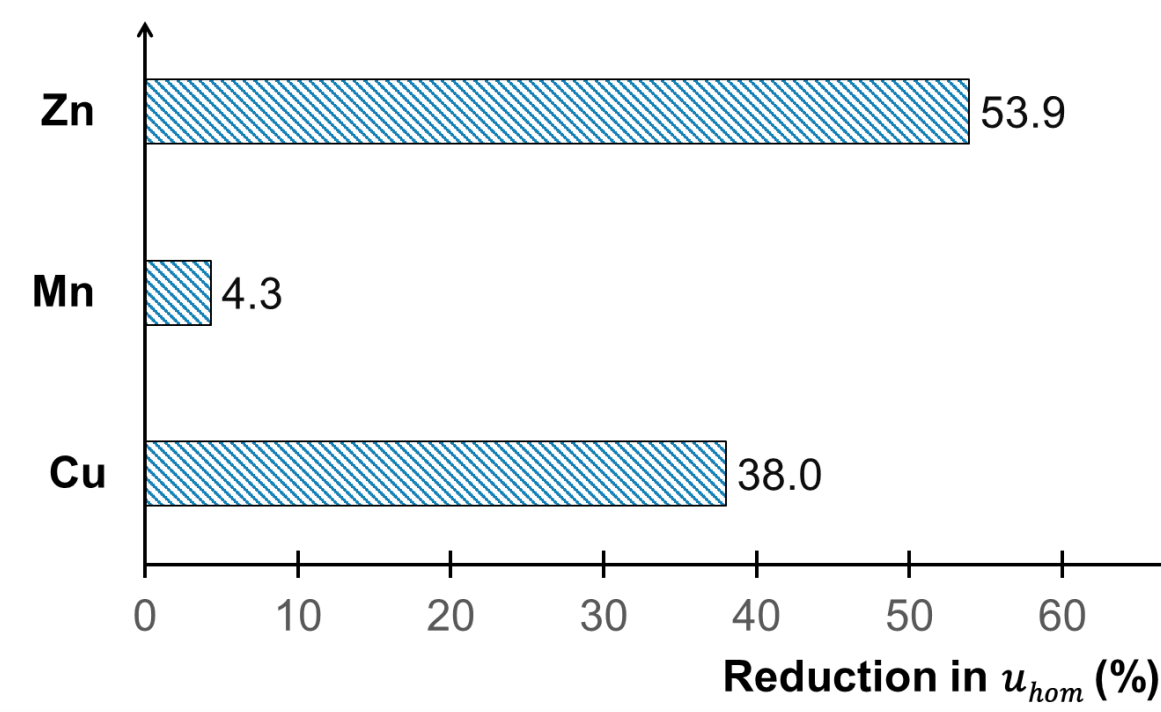
For the assessment of homogeneity, in addition to the guidelines of ISO 33405:2024, the homogeneity of variances, data normality, and the presence of outliers (Grubbs test) were also assessed. The DerSimonian and Laird statistical estimator was also used.

Analyte	Relative uncertainty of homogeneity (u_{hom})		
	RM wheat flour (%)	RM rice flour (%)	RM tilapia flour (%)
Mg	0.93	2.56	4.18
P	0.19	2.34	1.12
S	0.03	0.95	0.32
K	0.21	1.72	0.02
Ca	0.02	2.23	0.13
Fe	0.50	1.07	0.05

Other food reference materials (RM) offered by the Joint Research Center include *IRM-804 Rice Flour*, which presents homogeneity studies for elements such as Cu, Mn, and Zn using techniques like inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) [5]. A reference material of the same matrix is *INM-027-1 Rice Flour*, where WDXRF was used to determine homogeneity.



Reduction in Homogeneity Uncertainty for Rice Flour RMs



This confirms that the WDXRF technique, compared to ICP-MS and AAS techniques, can be much more suitable for homogeneity assessment.

CONCLUSION

WDXRF is a valuable analytical technique for assessing homogeneity and candidate reference materials (RM), especially in the food sector. Its ability to perform rapid, non-destructive measurements on solid samples makes it a complementary tool to more sensitive techniques such as ICP-MS and even AAS.

The integration of WDXRF into RM certification processes can enhance the efficiency of homogeneity studies by enabling faster statistical estimations, using the statistical approach proposed in ISO 33405:2024 for variance analysis.

REFERENCES

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