

# STUDY OF WHEAT SPECIMENS BY ISOTOPE-EXCITED X-RAY FLUORESCENCE ANALYSIS

D. HEGEDÜS, J. SOLYMOŠI, N. VAJDA, P. ZAGYVAI, L. GY. NAGY,  
K. LÁSZLÓ and F. GAÁL\*

Department for Applied Chemistry,  
Technical University, H-1521 Budapest

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## Summary

Six different wheat specimens were studied by isotope-excited x-ray fluorescence analysis.  $^{125}\text{I}$  and  $^{55}\text{Fe}$  ring sources were used for excitation; x-ray radiation was measured with a cooled Si(Li) detector. Some of the results were checked by neutron activation analysis. The air-dry wheat samples were milled in a ball mill; the tablets for measurements were prepared with boric acid additive. The accuracy of the results was 5–9%.

## Introduction

The chemical composition of natural foods is complex: besides the major constituents C, H, O and N they contain numerous elements in larger or lesser amounts. Some elements are indispensable for life, others are toxic. The biological role of many elements is little known or unknown as yet. In the diagnosis and therapy of certain diseases it may be of importance for the physician to know the elemental composition of the patient's diet. For the above reasons, reliable tables listing the elemental composition of foods are of great importance [1].

Accurate knowledge of elemental composition is also significant for plant breeders and growers as well as for stock-breeders, since the presence or absence of certain elements largely affects crop results and the quality of agricultural products [2, 3, 4].

Established methods are at disposal to analyse the major constituents of foods. However, analysis of other elements, particularly those present in microconcentrations poses numerous problems. Some authors who have developed analytical techniques for such purposes use dry or wet incineration

\* Institut za Hémiju PMF Novi Sad, Yugoslavia

in sample preparation to concentrate the elements [5]. Both incineration techniques are very delicate operations involving non-desirable losses and contamination.

We chose milling of the dry wheat specimens in agate mills and tableting of the milled product to prepare samples.

### X-ray fluorescence analysis

This analytical technique is well known in the literature. K and L electron shells of the atoms in the sample being analysed are excited with charged particles or with electromagnetic radiation from an x-ray tube or from radioisotopes. The excited state ceases within  $10^{-15}$  s, accompanied by the emission of the characteristic x-radiation of the excited atoms. The energy levels of the characteristic x-ray spectra of elements increase monotonously with their atomic number (Fig. 1). In the figure the excitation energy ranges of some practicable isotope ring sources are also represented. In the energy-dispersive technique, the characteristic x-radiation is analysed with a cooled semiconductor Si(Li) detector.

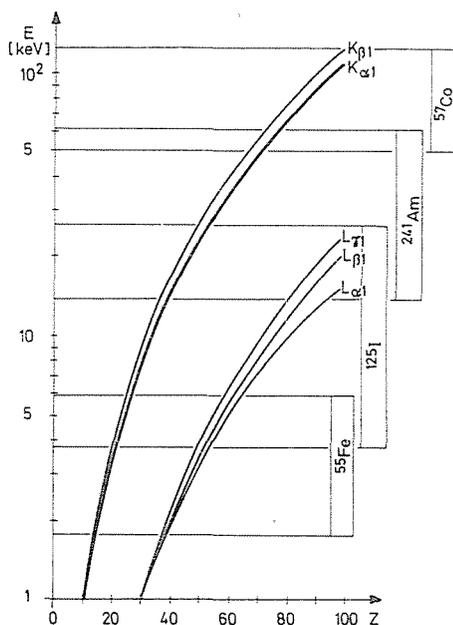


Fig. 1. Energy vs. atomic number of K $_{\alpha, \beta}$  and L $_{\alpha, \beta, \gamma}$  x-ray spectra and excitation ranges of ring sources

The energy levels of the characteristic x-radiation indicate the qualitative composition of the sample. The intensities  $I_i$  of the individual lines are proportional to the amounts  $m_i$  of the emitting elements:

$$I_i = I_0 \cdot G \cdot \varepsilon_{E_i} \cdot K_i \cdot m_i$$

where  $I_0$  is the intensity of the exciting radiation,  $G$  is the geometrical factor of the apparatus,  $\varepsilon_{E_i}$  is the detection efficiency of the characteristic radiation with energy  $E_i$ , and  $K_i$  is the fluorescent efficiency. If conditions of measurement are properly selected,  $I_i$  is directly proportional (through  $m_i$ ) to  $C_i$ , the concentration of the element in question [6, 7].

## Experimental

### *Preparation of samples*

The air-dry wheat specimens were milled for identical periods in an agate ball mill at unchanged setting of the mill. The product was then pressed to tablets with boric acid as additive (diam. 10.0 mm, mass 0.3000 g, boric acid content 40%; tableting pressure 7.8 MPa, time 30 s).

### *Conditions of measurement*

The measuring apparatus used was an energy-dispersive x-ray fluorescence analyser constructed by the Nuclear Research Institute of the Hungarian Academy of Science in Debrecen and operated at the Department for Applied Chemistry of the Technical University Budapest (Figs 2 and 3). The exciting isotopes applied were  $^{55}\text{Fe}$  and  $^{125}\text{I}$  ring sources characterized by the following data:

Radioisotope	Half-life, years	Disintegration	Utilizable radiation keV	Photons per disintegration	Activity GBq
$^{55}\text{Fe}$	2.7	electron capture	5.9 (Mn K)	28.5	0.2
$^{125}\text{I}$	0.164	electron capture	27.4 31.1 (Te K) 35.5	138	0.8

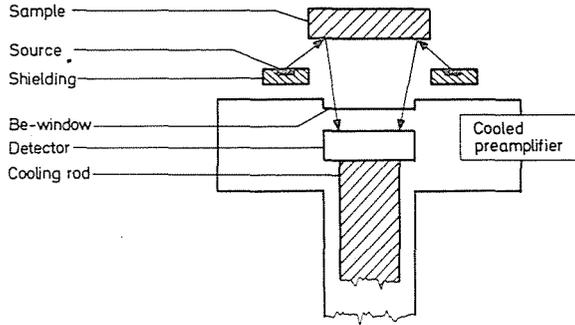


Fig. 2. Arrangement of source, sample and detector in the energy-dispersive x-ray fluorescence spectrometer

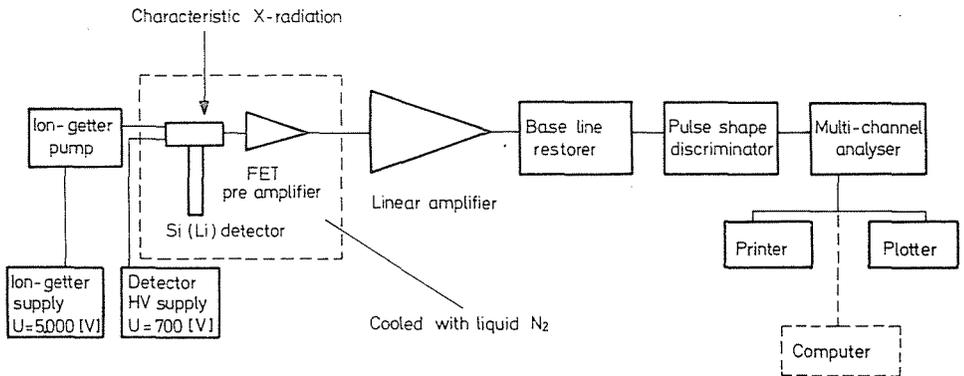


Fig. 3. Diagram of the energy-dispersive x-ray fluorescence analyzing apparatus in operation at the Department for Applied Chemistry of the Technical University Budapest

Experimental conditions of neutron activation for checking results:

Sample mass: 100 mg

Comparator sample: 100 mg  $\text{KHCO}_3$

Blank: polyethylene

Cladding of sample: polyethylene film

Irradiation: Training Reactor of the Technical University Budapest

Thermal neutron flux:  $2 \cdot 10^{11}$  n/cm<sup>2</sup> s

Irradiation time: 4 hrs

Cooling time: 0–3 hrs

Measuring system: Ge(Li) cooled semiconductor detector 4 k ICA-70 analyzer

Measurement time: 1000 s

On-line data processing with a HP 9825A minicomputer:

- peak finding
- energy calibration
- computation of area below peak
- qualitative analysis utilizing an in-built spectrum library
- quantitative analysis by  $\text{KHCO}_3$  monitoring

### Results and discussion

Qualitative and quantitative analysis was based on the x-ray fluorescent spectra of the individual samples (Figs 4 and 5). Quantitative analysis was performed by the element-addition technique. To determine the concentration of the element  $i$  we added the element  $i$  in increasing concentrations to identical-mass samples. From the data pairs  $I_i - c_i$  we calculated the concentration  $c_{ix}$  of the sample by linear regression (Fig. 6).

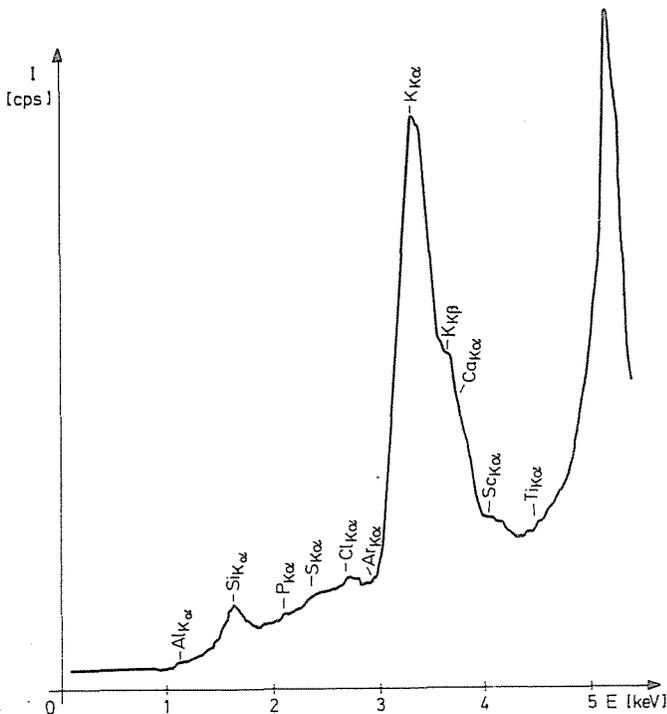


Fig. 4. X-ray spectrum of wheat specimen No. 3. Excitation source:  $^{55}\text{Fe}$ ; shielding: Pb

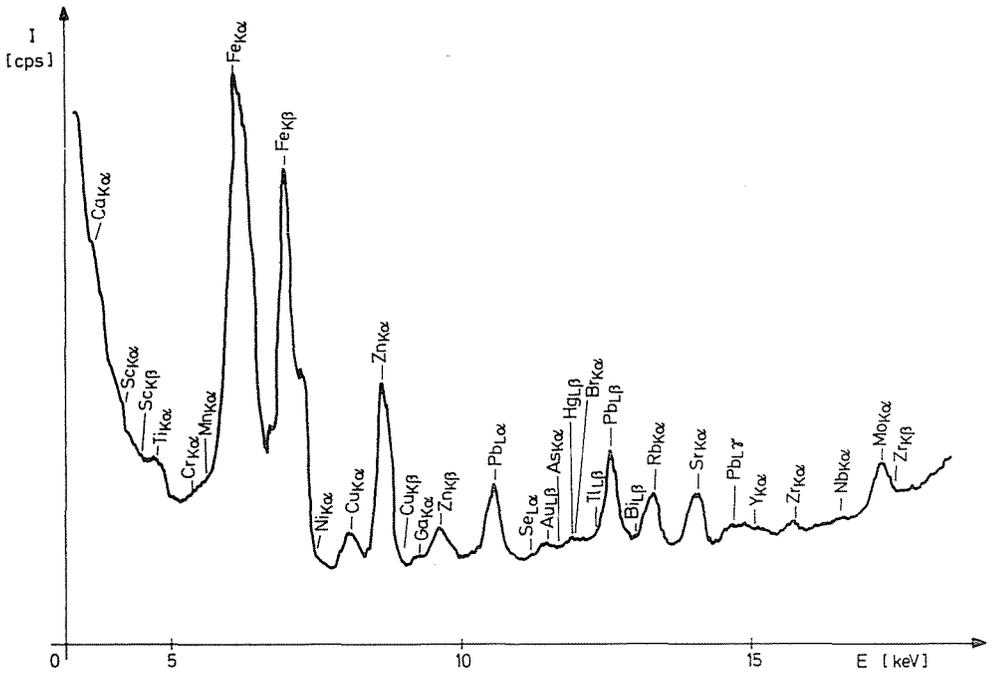


Fig. 5. X-ray spectrum of wheat specimen No. 3. Excitation source:  $^{125}I$ , shielding: Pb

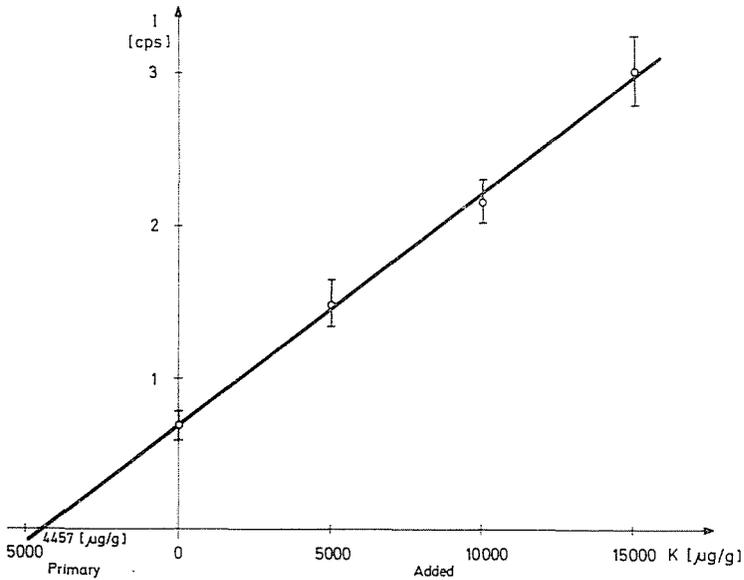


Fig. 6. Potassium content of wheat specimen No. 2 determined by the addition technique

The relationships between the measured intensity of the x-ray spectral line  $I_i$  and the concentration of the element  $C_i$  is

$$C_i = KI_iMS.$$

The relationship indicates four factors affecting measurement of  $C_i$ :

1. The factor  $K$  depends on the construction and operating conditions of the spectrometer. It changes from instrument to instrument even within the same type. For a given instrument,  $K$  is constant, if the instrument is operated at constant conditions, including ambient temperature. Since the value of  $K$  depends on many conditions, it is impossible to calculate its accurate value. In practice it is determined by calibration.

2. The intensity  $I$  is the net intensity measured above the background; it depends on the stability of the apparatus and on counting statistics.

3.  $M$  accounts for the inter-element effect, it includes primary and secondary absorption effects and third-element effects. These effects lead to systematic errors in the determination of the true intensity. Hence accuracy of the calculated  $C$  values depends directly on the extent to which one succeeds in minimizing or correcting  $M$ .

4.  $S$  accounts for the heterogeneity of the sample. Inhomogeneities commensurable with the penetration depth of the x-ray will affect the measurement of  $I$ . The effect of  $S$  is reduced or eliminated by appropriate sample preparation [8].

It follows from the above that however conscientious measurements of  $K$  and  $I$  will yield well-reproducible results, but — in extreme cases — concentration estimates will be incorrect, unless intereffects between elements are eliminated or at least reduced to a negligible extent.

The element-addition technique eliminates intereffects, and therefore yields accurate and reproducible results. Intereffects between elements in the milled wheat matrix are, as a matter of fact, minimized by the low atomic numbers of the major constituents H, C, N and O. X-ray-active constituents are present in low concentrations with the exception of potassium; this element, however, is present in close to equal amounts in the various specimens. Intereffects between elements are further reduced by the additive boric acid being present in amounts of 40%.

The results of analysis are listed in Table 1. The accuracy of the data is between 5 and 9%. Concentration data for K and Mn were checked by neutron activation analysis; the results agreed with those of x-ray fluorescence analysis within the experimental error. The data listed for Na in the table were obtained by neutron activation analysis, with a reproducibility within 30%.

The average concentrations of some elements found for the six wheat specimens, and — for comparison — their average concentrations in five other

**Table 1**  
Microelement concentrations in wheat specimens  
( $\mu\text{g/g}$ )

No.	Excitation source															
	$^{55}\text{Fe}$					$^{125}\text{I}$										
	Na*	K	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Se	Rb	Sr	Y	Zr	Mo
1	63	3640		33	101			13	56.7			6	5		0.9	0.4
2	67	4460	27	27	117			17	71.4		1.2	7	6		0.3	0.5
3	77	4370		32	62			7	28.9	0.5		2	3	0.3	0.3	0.1
4	43	2490		66	140			12	70.3	0.8		7	6		1.1	0.2
5	31	3860	17	43	106	1.4	1.6	12	56.7	0.8	0.9	6	6		0.9	0.4
6	20	3900	12	35	84			9	55.5			5	6		0.9	0.6
Average	50.2	3786.7		39.3	101.7			11.7	56.6			5.5	5.3		0.7	0.4
Average	**			39	95			15	56.6			6.3				

\* Data obtained by neutron activation analysis

\*\* Averages calculated from [5]

wheat varieties, calculated from the data obtained by Török and Szőkefalvi-Nagy [5] are listed at the bottom of Table 1. Agreement is astonishingly good.

It should finally be summed up that our method, eliminating incineration, is fully suitable for elemental analysis of wheat specimens, which — as stated in the introduction — is of great interest for many specialists. Particularly reliable analytical methods and sample preparation techniques are needed to determine the concentrations of microelements. Energy-dispersive x-ray fluorescence analysis for cereals has an accuracy better than 9%, its sensitivity is around 1  $\mu\text{g/g}$ . Milling in an agate mill and tableting with boric acid as additive is very well suited: errors due to losses and contamination occurring due to incineration are eliminated. For routine analyses, efficiency of the x-ray fluorescence method can be increased and experimental error can be reduced to some per cents by computerized matrix correction.

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Dr. Dezső HEGEDÜS  
Dr. József SOLYMOSI  
Nóra VAJDA  
Dr. Péter ZAGYVAI  
Prof. Dr. Lajos György NAGY  
Krisztina LÁSZLÓ  
Ferenc GAÁL

H-1521 Budapest

Institut za Hémiju PMF Novi Sad,  
Yugoslavia