Optimization of RBS Analysis as an Input for Quantification in X-ray Emission Techniques

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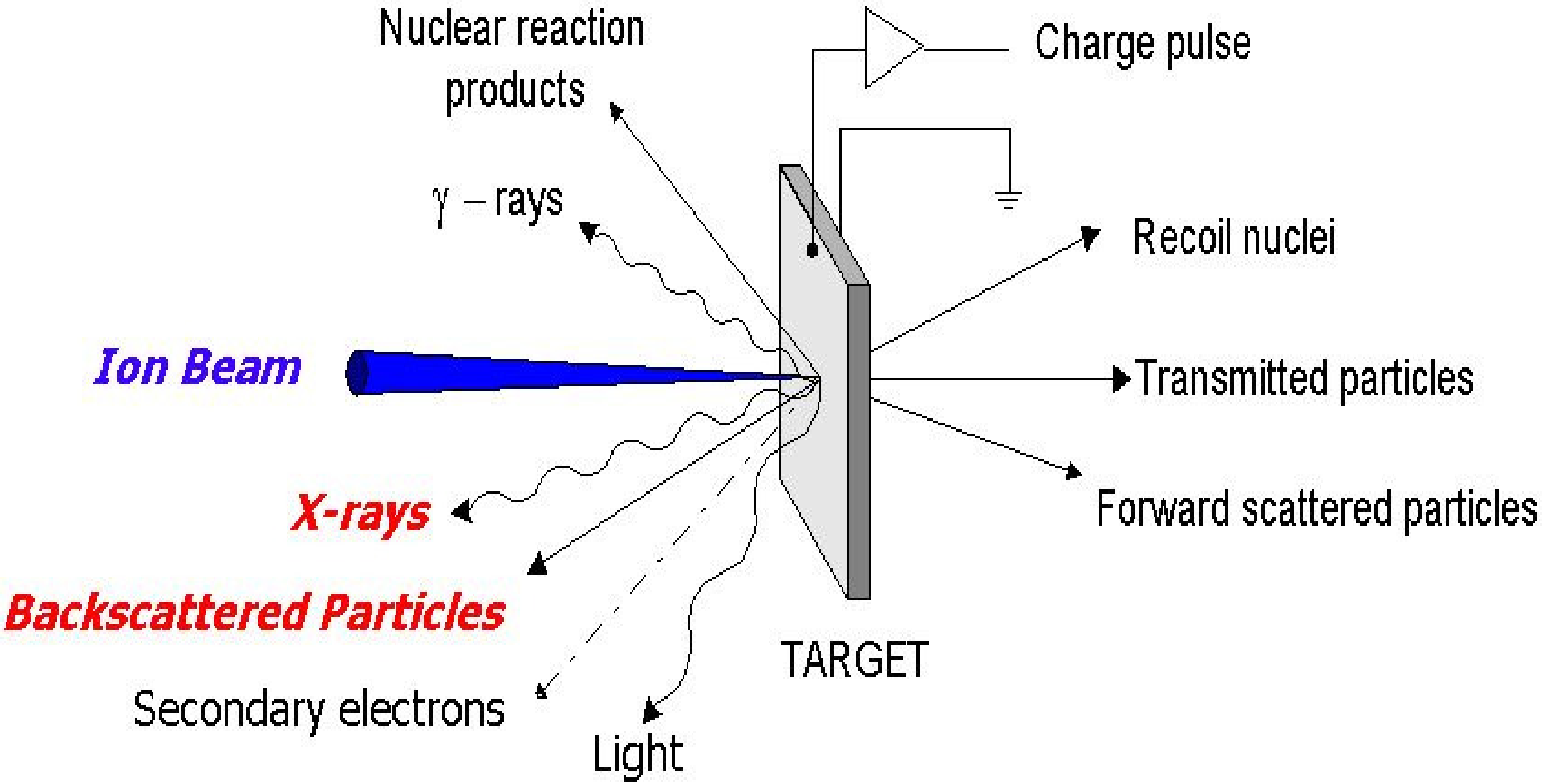
Outline

- Fundamental parameters’ approach to quantification
- Experimental set-ups
    - ***RBS*** and ***PIXE***
    - ***RBS*** and ***EDXRF***
- Measurements and Results
- Conclusions

The Fundamental Parameters'(FP) approach

- Advantages
  - minimizes number of calibration standards required (one single-element standard may be sufficient for quantitative analysis)
  - standards need not have matching matrix and concentration level as the samples to be analyzed
  - Quantification method is applicable to different sample matrices and different sample thickness
- Major disadvantage
  - Complete knowledge of sample matrix is required (sum of the mass fraction of the measurable elements = 1). Hence, best suited for steel, alloys or samples with well-defined matrix
    - » What about dark matrix elements ?

Interaction of ions with matter: RBS and PIXE



IAEA PIXE/RBS BEAM LINE

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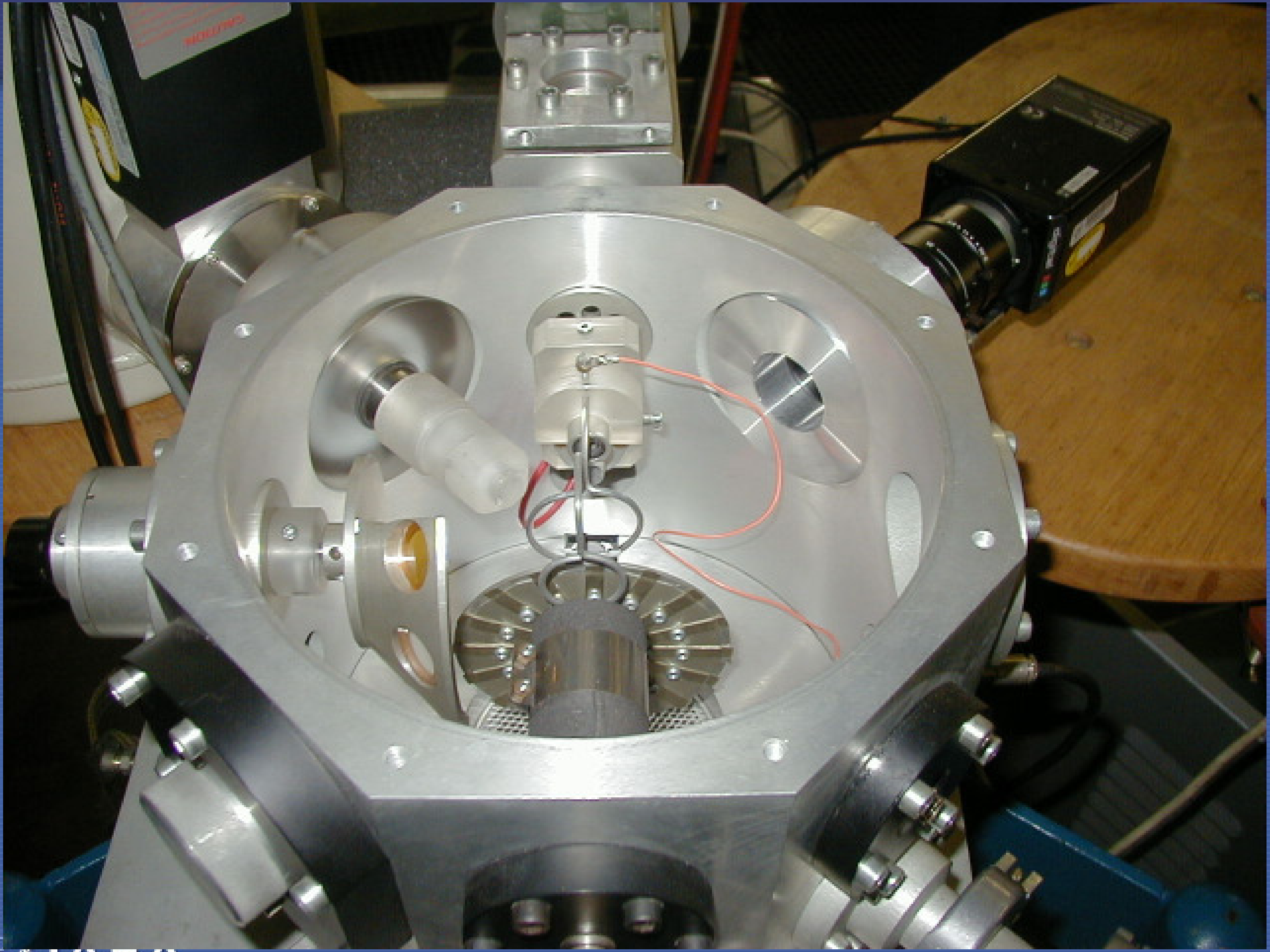
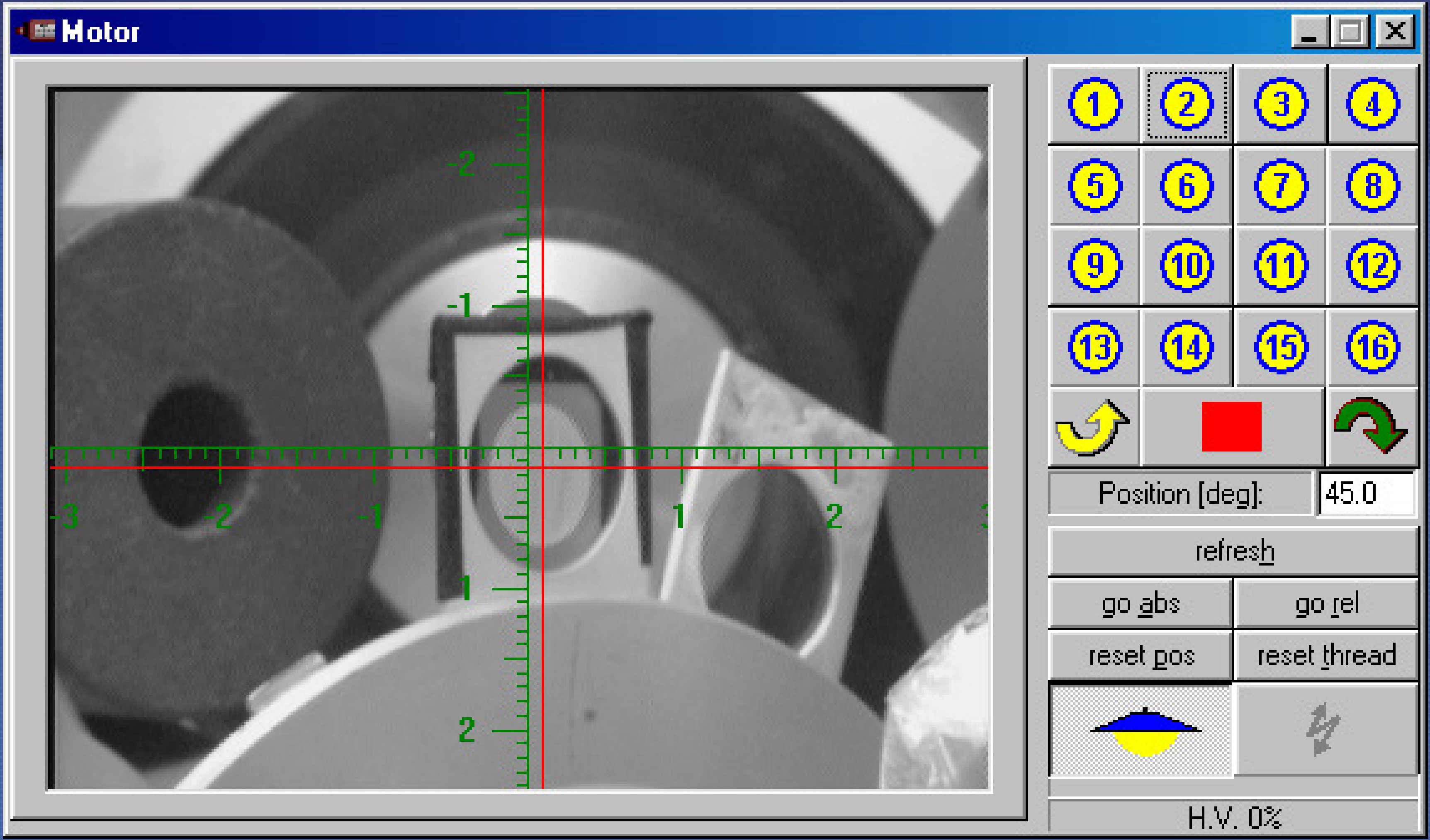
3 MeV protons; Si particle det. for RBS at 165°; Si(Li) det. for PIXE at 135°

Sample chamber





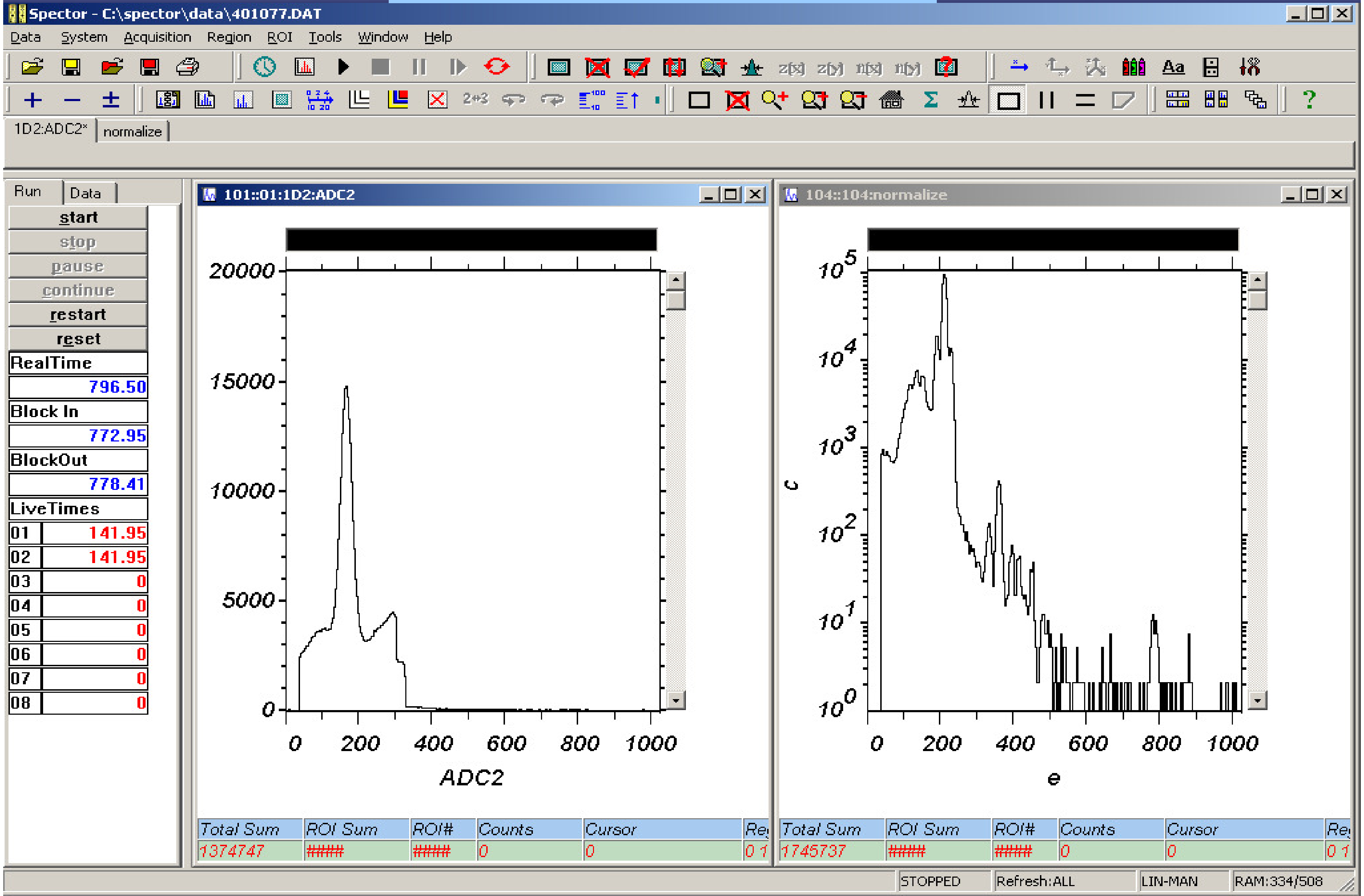
Position [deg]: 45.0

H.V. 0%

Sample position allocation: (remote motor,video,light,and bias control)

16 positions separated by 22.5º ;   fine step movements of 0.9º/step; possibility of resetting *(0º) at any position;* ***detector HV bias*** *(ON/OFF)*

SPECTOR (PIXE/RBS)



RealTime	
	796.50
Block In	
	772.95
BlockOut	
	778.41
LiveTimes	
01	141.95
02	141.95
03	0
04	0
05	0
06	0
07	0
08	0

Total Sum	ROI Sum	ROI#	Counts	Cursor	Re
1374747	#####	#####	0	0	0 1

Total Sum	ROI Sum	ROI#	Counts	Cursor	Re
1745737	#####	#####	0	0	0 1

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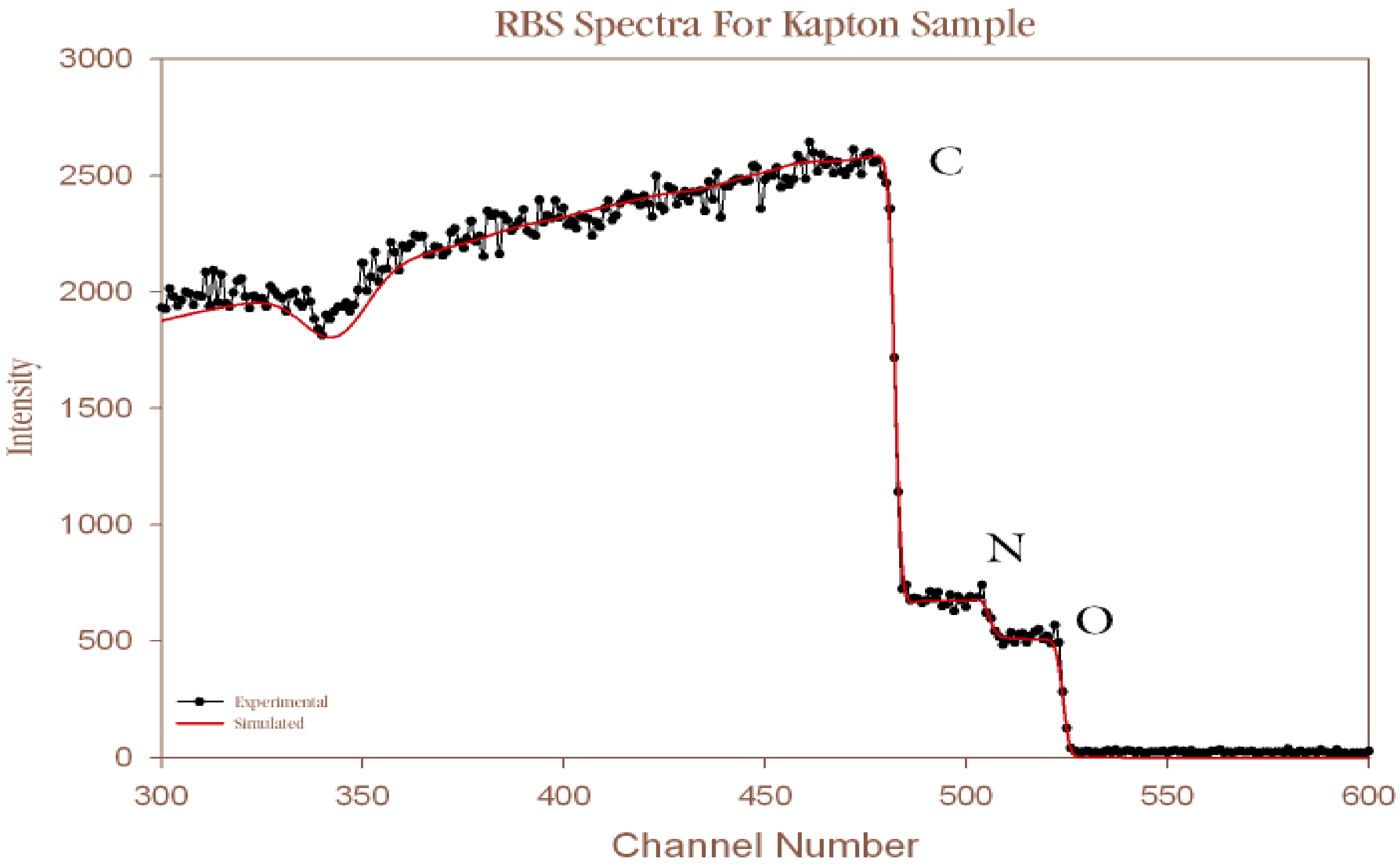
RBS and proton scattering cross-section database

- RBS determination of light elements (Z<10) in thick samples (sample matrix estimation)

- For 3 MeV p^+, x-sections are non-Rutherford, cannot be calculated from a simple analytical formula, and only few database for 165º scattering angle exist.
  - *N (at 165º): Lambert & Durand*
  - *C, O, Si (at 165º): Gurbich –experimental data*

- Gurbich's database was therefore downloaded into the SIMNRA program used for simulation and quantitative analysis of RBS spectra obtained



RBS spectra also collected for Cellulose, Mylar, Graphite, and Formvar samples

RBS and SIMNRA

- RBS Instrumentation Constant, $C_q = N\ \Omega$

  where N= number of particles that correspond to 1µC charge

  Ω= particle detector solid angle

- Ω is difficult to measure directly so is determined from the experimental measurement of Cq using samples with known composition
- C_q was measured in three different time periods and found to be 4.77×10^{10} particles.sr with maximum variation of 5%. C_q also tests possible effect of incorrect current integration and dead time correction
- Assessment of the database for C, N, O, and Si using CRMs (Bowen's Kale sample and IAEA-V9 Cotton Cellulose) and the determined value for C_q

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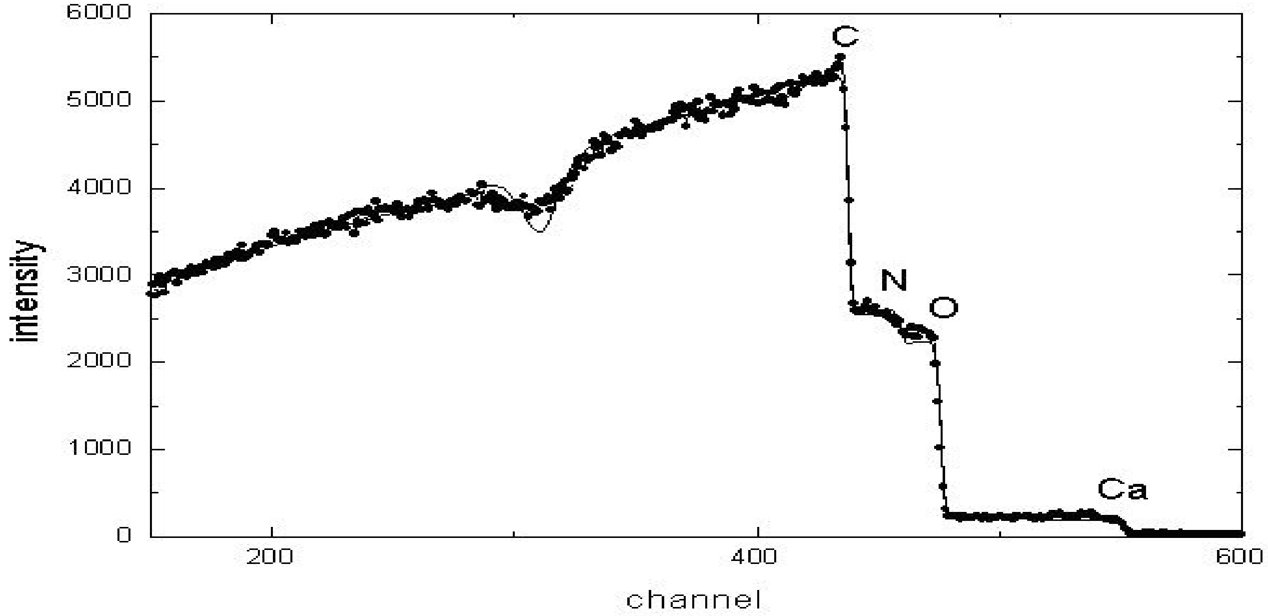


RBS spectra for Bowen's Kale sample

Table 1. Comparison between matrix composition obtained from SIMNRA and CRM data sheet values for Bowen's kale sample. (N) – not certified, (C) - certified

Element	SIMNRA (wt %)	CRM data sheet (wt %)
H	5.7	5.7 (N)
C	42.5	45 (N)
N	7	4.3 (C)
O	35	39 (N)
Ca	9	4 (C)

Influence of charge and matrix variations

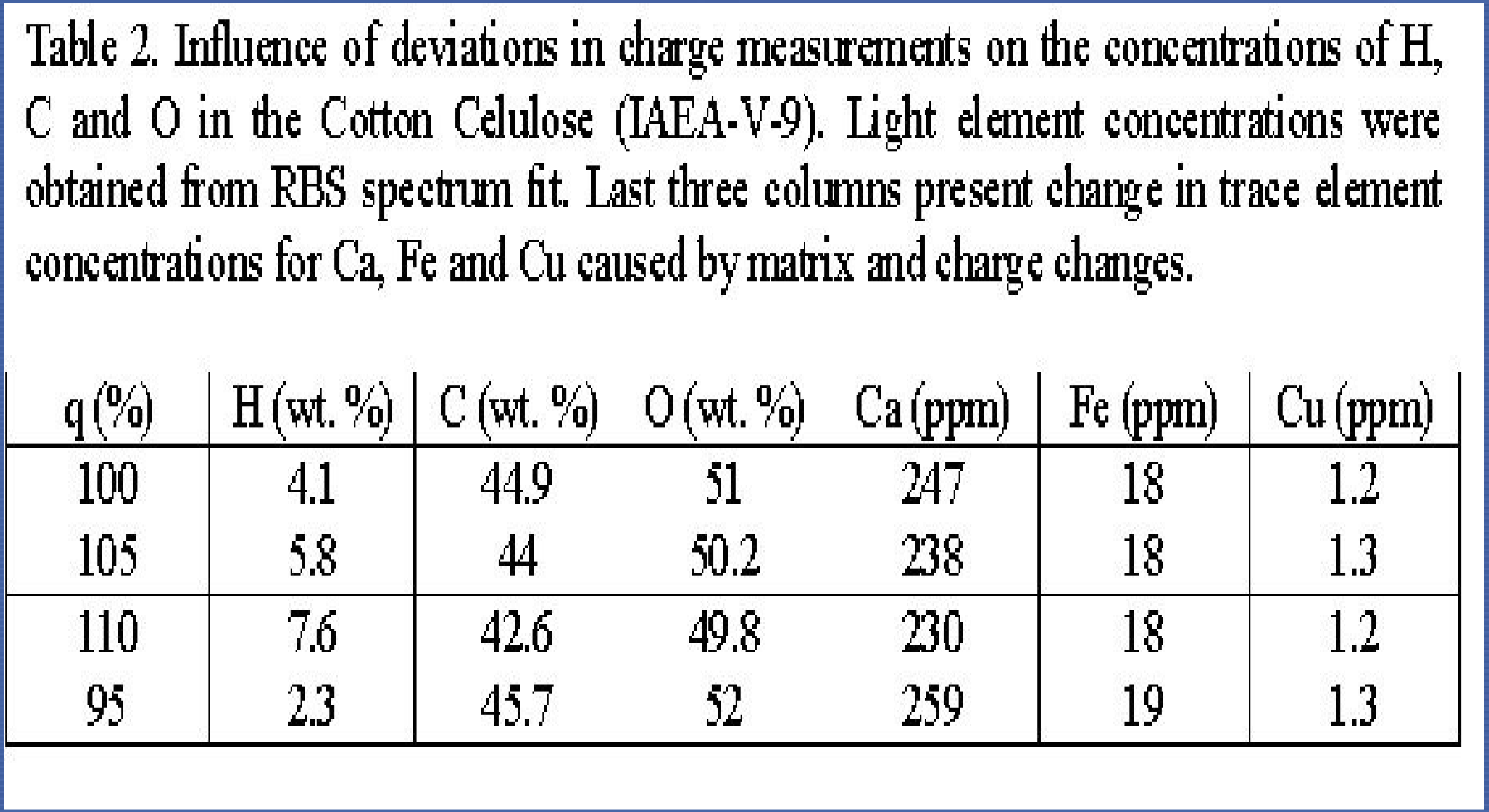
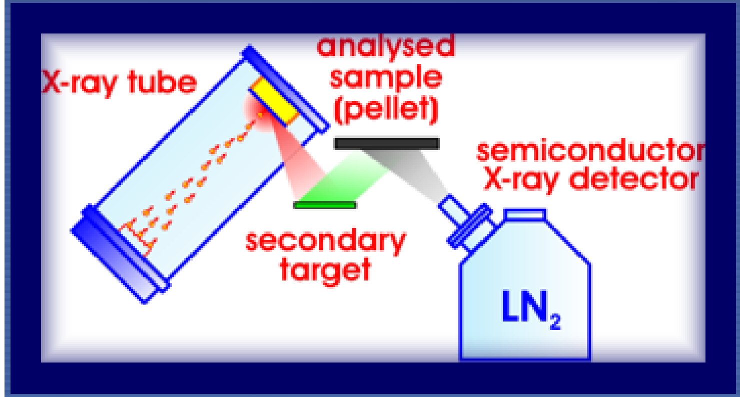


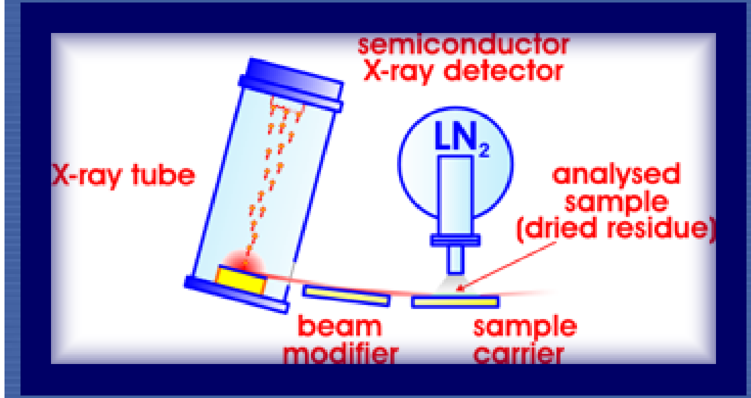
Table 2. Influence of deviations in charge measurements on the concentrations of H, C and O in the Cotton Celulose (IAEA-V-9). Light element concentrations were obtained from RBS spectrum fit. Last three columns present change in trace element concentrations for Ca, Fe and Cu caused by matrix and charge changes.

q (%)	H (wt. %)	C (wt. %)	O (wt. %)	Ca (ppm)	Fe (ppm)	Cu (ppm)
100	4.1	44.9	51	247	18	1.2
105	5.8	44	50.2	238	18	1.3
110	7.6	42.6	49.8	230	18	1.2
95	2.3	45.7	52	259	19	1.3

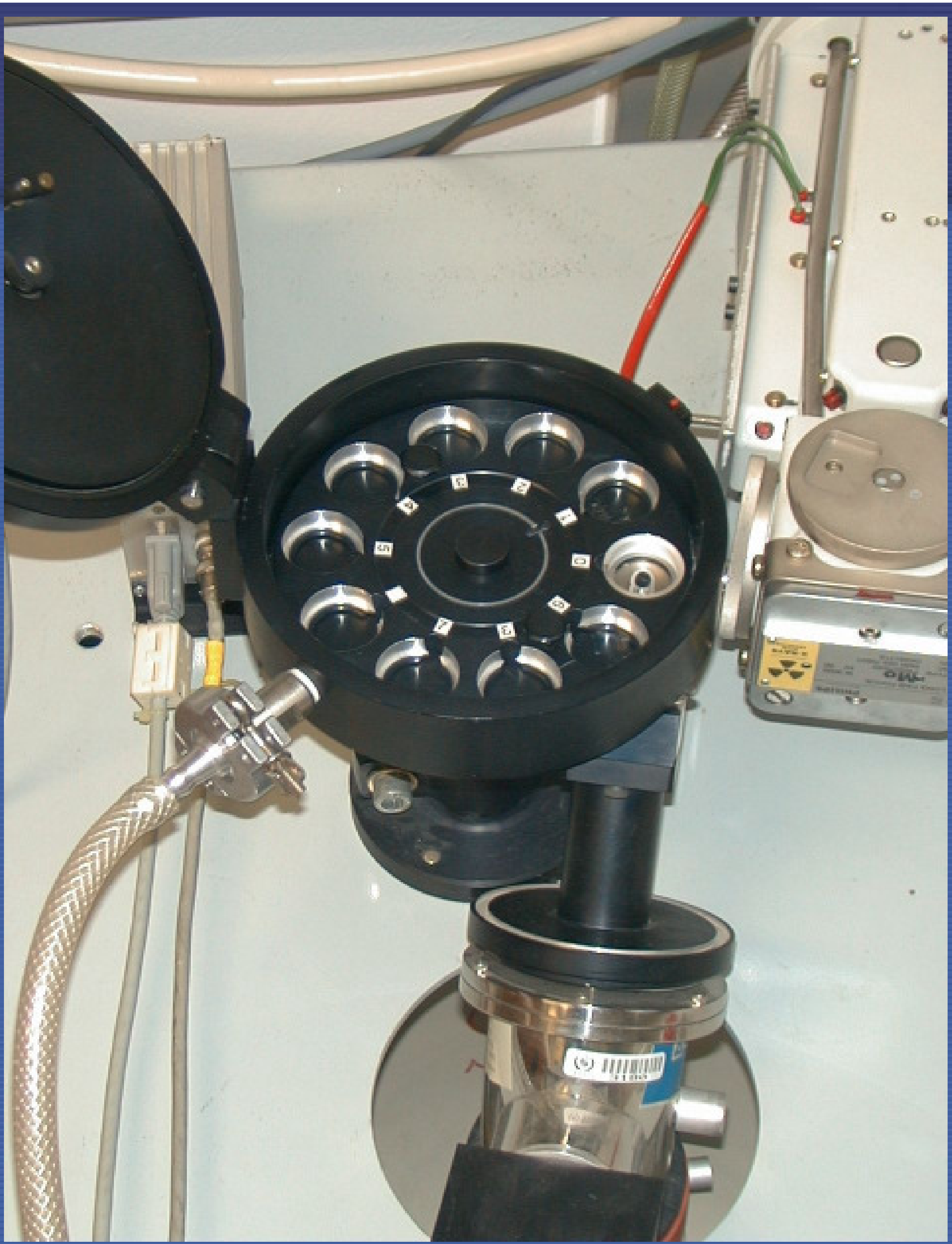
RBS and EDXRF



EDXRF sec. target spectrometer



TXRF spectrometer



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RBS and EDXRF : IAEA-336 (lichen)

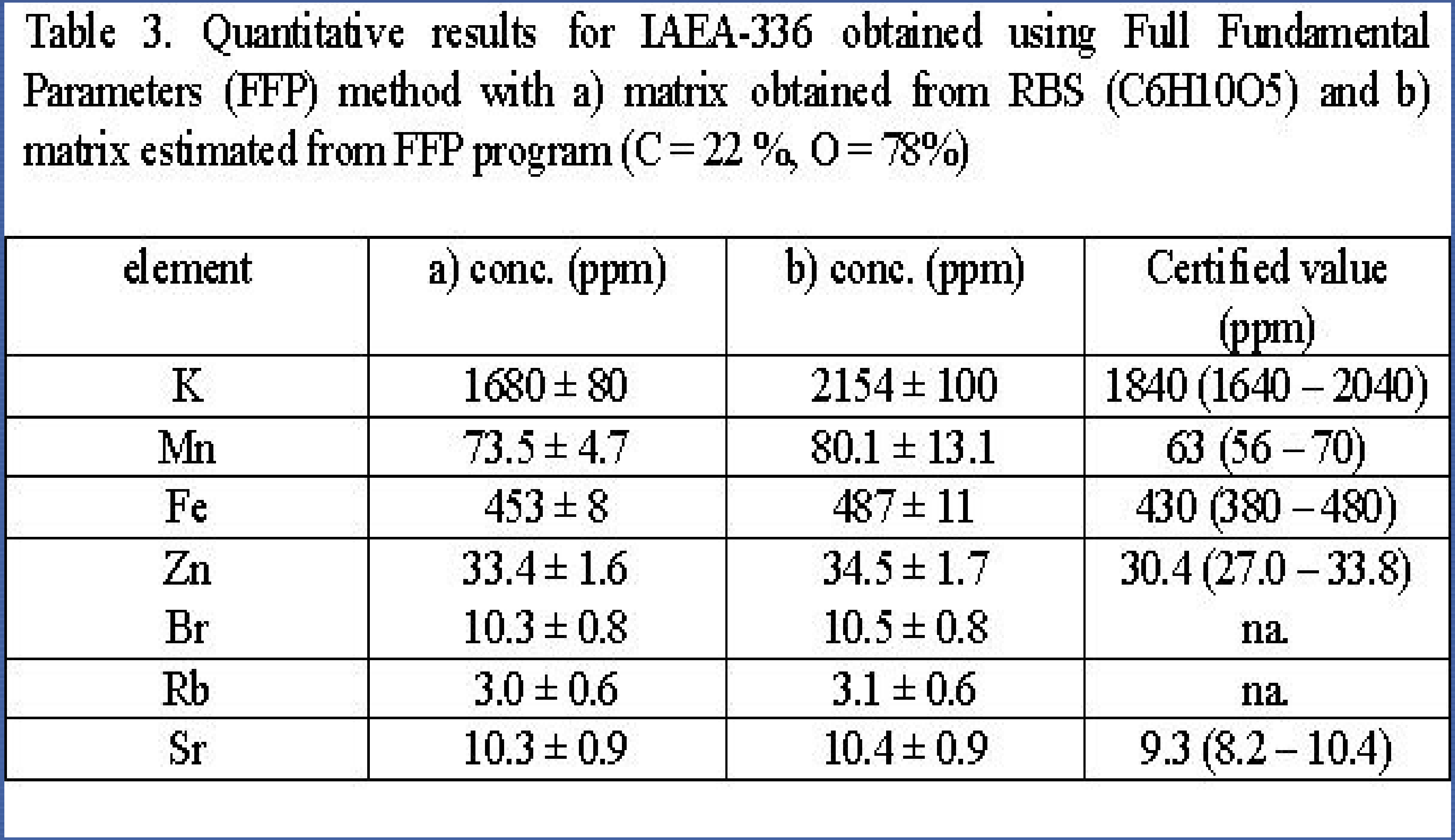

Table 3. Quantitative results for IAEA-336 obtained using Full Fundamental Parameters (FFP) method with a) matrix obtained from RBS (C6H10O5) and b) matrix estimated from FFP program (C = 22 %, O = 78%)

element	a) conc. (ppm)	b) conc. (ppm)	Certified value (ppm)
K	1680 ± 80	2154 ± 100	1840 (1640 – 2040)
Mn	73.5 ± 4.7	80.1 ± 13.1	63 (56 – 70)
Fe	453 ± 8	487 ± 11	430 (380 – 480)
Zn	33.4 ± 1.6	34.5 ± 1.7	30.4 (27.0 – 33.8)
Br	10.3 ± 0.8	10.5 ± 0.8	na.
Rb	3.0 ± 0.6	3.1 ± 0.6	na.
Sr	10.3 ± 0.9	10.4 ± 0.9	9.3 (8.2 – 10.4)

RBS and EDXRF : IAEA-359 (Cabbage)

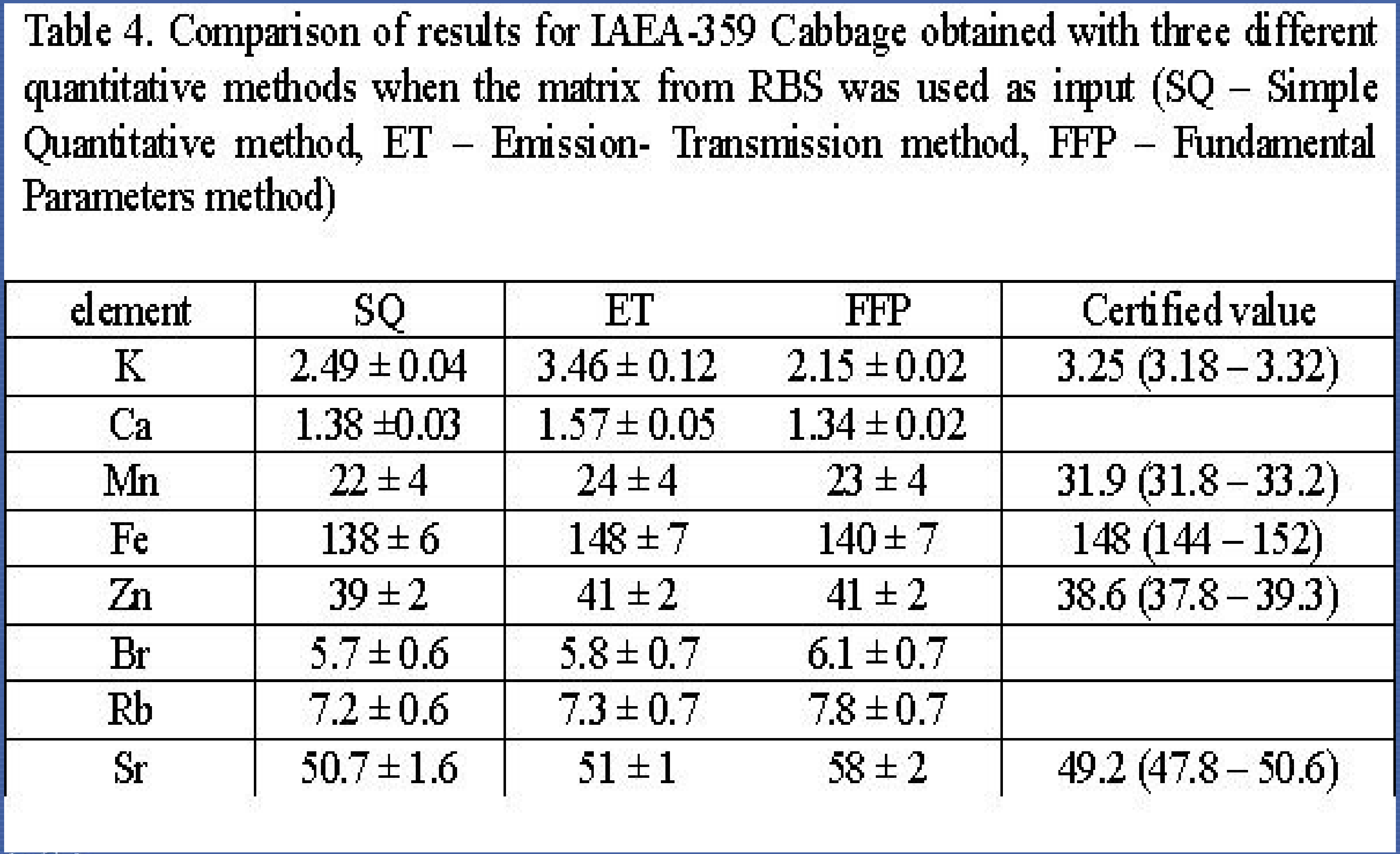

Table 4. Comparison of results for IAEA-359 Cabbage obtained with three different quantitative methods when the matrix from RBS was used as input (SQ – Simple Quantitative method, ET – Emission- Transmission method, FFP – Fundamental Parameters method)

element	SQ	ET	FFP	Certified value
K	2.49 ± 0.04	3.46 ± 0.12	2.15 ± 0.02	3.25 (3.18 – 3.32)
Ca	1.38 ±0.03	1.57 ± 0.05	1.34 ± 0.02	
Mn	22 ± 4	24 ± 4	23 ± 4	31.9 (31.8 – 33.2)
Fe	138 ± 6	148 ± 7	140 ± 7	148 (144 – 152)
Zn	39 ± 2	41 ± 2	41 ± 2	38.6 (37.8 – 39.3)
Br	5.7 ± 0.6	5.8 ± 0.7	6.1 ± 0.7	
Rb	7.2 ± 0.6	7.3 ± 0.7	7.8 ± 0.7	
Sr	50.7 ± 1.6	51 ± 1	58 ± 2	49.2 (47.8 – 50.6)

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Conclusions

- Establishment of a reliable and well calibrated routine RBS measurement system using the SIMNRA program

- Assessment of existing database on proton scattering cross-section for C, N, O, Si
- The potential of using this procedure for the determination of H (by difference- normalization to 100%) in the dark matrix

- A proiri determination of matrix element concentration by RBS and subsequent utilization in X-ray emission analytical methods (PIXE and EDXRF)

- Specific advantage in the analysis of plant-based materials

- Extension and improvement in accuracy of quantitative methods in the QXAS program for EDXRF analysis