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

S. A. Bamford[1], I. Bogdanovic[2], M. Jaksic[2] Z. Medunic[2] D. Wegrzynek[1], E. Chinea-Cano[1], A. Markowicz[1]

[1] International Atomic Energy Agency, Agency's Laboratories Seibersdorf, Austria

[2] Ruder Boskovic Institute, Zagreb, Croatia

Correspondence to: **S.A.Bamford@iaea.org**

Abstract. Procedures for the quantitative analysis of thick samples by x-ray emission techniques, such as energy dispersive x-ray fluorescence (EDXRF) or particle induced x-ray emission (PIXE), approach differently the treatment of unknown composition of light elements (low Z analytes with $Z<10$) in the sample matrix (dark matrix). In PIXE analysis, simultaneous performance of Rutherford backscattering spectrometry (RBS) is today conventionally used to estimate the major matrix element composition needed in the fundamental parameter quantification procedure. Influence of the proton elastic scattering cross section database is discussed here in terms of typical samples analyzed by PIXE. It has been observed that in the case of plant-based samples (including biomonitors) where the major elements in the dark matrix are C, N and O, the existing proton elastic scattering database seems to be sufficiently reliable. Possibilities of RBS to also quantify hydrogen content, by difference, in these samples are also discussed. Optimization of the RBS technique was achieved through measurement and spectra simulation of samples with well-known composition (cellulose, Mylar, Kapton, graphite, and formvar). In addition, the scattering cross-section values used were chosen from Gurbich's experimental database at scatter angle of 165 degrees. for proton energies at 3 MeV. Validation of the RBS quantification method with the certified reference material Bowen's Kale gave satisfactory results for the elements H, C, and O. Samples of plant-based reference materials were subsequently analyzed and estimation of the "dark matrix" elemental composition by RBS technique, improved accuracy of the results from the EDXRF analysis

1. Introduction

In the quantitative analysis of thick samples by x-ray emission techniques, the fundamental parameter (FP) approach [1-3] to quantitative analysis is preferable. This can be attributed to the facts that FP method does not require large set of standards, is not limited to the range of concentration of the calibration standards, and standards must not necessarily have matching matrix and concentration levels as the samples to be analyzed. Nevertheless, FP method assumes homogeneity of sample, plain surface, negligible particle size effects, and complete definition of the sample matrix. Complete elemental characterization using EDXRF is not possible, but in the case of PIXE analysis simultaneous performance of Rutherford backscattering spectrometry (RBS) is today conventionally used to estimate the major element composition needed in the fundamental parameter quantification procedure. RBS can be used to quantify content of all elements (except hydrogen) in thick homogeneous samples [4]. However, if protons of several MeV are used, elastic cross sections differ from the Rutherford formula, and in such a case experimental cross sections have to be used. In the recent papers of Gurbich [5, 6, 7], database for C, O and Si have been systematically assessed. RBS simulations seem to be sufficiently reliable for samples of biological material where C, N and O dominate, as well as those with Si. However, in samples with significant amounts of Na, Al, K, Ca, insufficient database is still a problem.

2. Experimental

2.1 RBS and PIXE

The experimental set-up of the IAEA beam line at the Rudjer Boskovic Institute in Zagreb, Croatia consists of a universal scattering chamber equipped with Si(Li) detector for PIXE and surface barrier detector for RBS measurements. Setup is shown on *FIG 1*. Up to 16 samples can be mounted simultaneously at the sample changer wheel. To make charge measurement as good as possible, electron suppression electrode is added in front of the sample holder. As the preferable ion beams used for PIXE are 3 MeV protons, RBS measurements were also done using the same conditions. Beam current was kept at minimum of about 1 nA in the 5 mm diameter collimated beam. In such a case elemental loss due to beam heating is minimized. A silicon particle detector for RBS was positioned at the 165º in respect to the beam direction, while the Si(Li) detector for PIXE was at the 135º. Solid angles of both detectors were adjusted in a way to maintain similar count rates of both x-rays and backscattered particles.

By using 3 MeV protons, difficulties arise since the elastic scattering cross sections for protons from light target elements are as a rule non-Rutherford and they cannot be calculated from a simple analytical formula, as it is the case with conventional RBS using 1-2 MeV He ion beam. First, for appropriate quantitative analysis it is important to carefully select cross section data base for each element. Secondly, spectra simulation programs should be able to adequately include those cross sections into the simulation. For three elements, C, O and Si Gurbich [5, 6, 7] made extensive evaluation of non-Rutherford cross sections by compiling relevant experimental data, selecting reliable experimental points and calculating excitation functions in the framework of the optical model and the S-matrix theory. Free model parameters were adjusted by fit to the reliable experimental data. As a result excitation functions for different scattering angles and energies were calculated with reliability exceeding that of any individual measurement. Theoretical simulations of Gurbich for C, O and Si have been recently compared with new experimental measurements of Ramos et al. [8]. They have measured elastic cross sections for C, O, and Si at two different scattering angles, 140º and 178º in the energy range of 500 – 2500 KeV. The agreement between experimental data and theoretical simulations was good for all energies and both scattering angles for all three elements.

For other lighter elements, user can choose among existing individual experimental data. For N, as well as Al only one database is available for 165º scattering angle. For heavier elements like K or Ca which can be presented in percentage amounts in biological samples non-Rutherford cross section data base is either incomplete or not given at all. For those elements, elemental concentrations obtained from RBS simulations cannot provide reliable results and PIXE should be used for the quantification of those elements.

In SIMNRA program [9], used in our case for quantitative analysis of RBS spectra, all available experimental data for non-Rutherford cross sections are included and can be selected by the user. Data from Gurbich for C, O and Si are not included in the latest version of SIMNRA program (5.0) but can be downloaded from SIMNRA web site [10] for 165º scattering angle. For any other scattering angle the evaluated cross sections may be obtained by request from Gurbich. Gurbich data are also recommended by SIMNRA author to be selected as most reliable for quantitative RBS analysis [9].

2.2 **RBS and EDXRF**

The energy dispersive x-ray fluorescence spectrometer at the IAEA Laboratories used for this work comprises a tube-excited system in a secondary target (Mo) arrangement. It uses a Si(Li) detector with a resolution of 165 eV at 5.9 keV, and has a 10-position sample changer which is operated under vacuum. It has Canberra modules and the MCA used was a Genie2K. Pressed pellets of samples from IAEA cabbage and lichen reference materials were then analyzed using the QXAS software package. The quantitative methods employed for the determination of elemental concentrations are the Simple Quantitative (SQ) method, Emission-Transmission (ET) method, and the Full Fundamental Parameters'(FFP) method [11]. The a priori determined concentrations of the dark matrix elements using RBS were provided as an input in using the SQ and FFP methods.

3. Results and Discussions

In order to establish reliable procedure for determining sample matrix that can be later used as input for PIXE or XRF measurements of trace elements in biological materials, RBS spectra of samples (cellulose, Mylar, Kapton, graphite, formvar, etc.) with well known composition were collected. Spectra were analyzed by SIMNRA taking as input experimental conditions, collected charge and known sample composition. Instrument constant (per collected 1 μC charge) represents the product of the number of incident particles N multiplied by detector solid angle Ω, and was determined by making the best possible fit to the experimental data for each sample. This constant was measured in three different time periods and was found that it is not varying more than 5 % during 1-year period and was 4.77×10^{10} particles sr/1 μC. The constant (NΩ) tests also possible effect of incorrect current integration and dead time correction.

RBS spectra of certified reference materials (CRM): Cotton Cellulose (IAEA-V-9), Lichen (IAEA-336) and Bowen's Kale were also collected. As input for the analysis of these samples with SIMNRA, the determined instrument constant multiplied by collected charge was inserted. SIMNRA also require an initial guess of matrix composition ,and by varying light element composition to achieve best possible fit, matrix composition in three CRM was determined. In *FIG. 2*, the spectra of two samples with unknown (Kapton) and known composition are presented. Dots represent experimental points and full lines the simulated spectra. It is worth to mention that SIMNRA simulations of unknown samples are usually done by automatic fitting with program to reduce possible users` subjectivity in the evaluation process.

In case of biological materials where matrix consists mainly of C, N, O and H, SIMNRA simulation of RBS spectra can give us information about H content in the sample. If instrument constant is well known and charge collection is reliable, H can be added together with other matrix elements in the layer description. By making the best possible fit to the experimental data and normalizing concentrations to 100% H amount in the sample matrix can be estimated. As the typical reference materials used in PIXE and EDXRF analysis does not have certified light element content, a Bowen's Kale was the only reference material where information values for C, H and O and certified values for Ca and N can be found in the CRM data sheet. Results for matrix composition obtained by SIMNRA and values from CRM data sheet are given in Table 1. As can be seen from the table, results for Ca and N deviates by factor of two from certified values. This can be due to inadequate database for those two elements, or errors induced by low counting statistics at low concentration levels. The concentrations of light elements for the lichen and cotton cellulose samples were found to be quite similar. The elements identified were C, O and H with composition varying less than 5% in C and 8% in O from $C_6H_{10}O_5$ matrix.

In order to assess influence of reliable charge measurement on the results for hydrogen, RBS simulation for cotton cellulose sample was performed with different deviations of measured charge from the real value. Deviations in measured charge are influencing in two ways input parameters for analysis of PIXE spectra, first by changing total collected charge and second by changing sample matrix due to RBS spectrum fit. For XRF spectra deviation in measured charge is entering XRF spectra analysis only through change in sample matrix. The results obtained can be seen in Table 2. From Table 2 is visible that 10% change in collected charge will change trace element concentrations obtained by PIXE for not more than 7%.

Elemental analysis of samples from Lichen (IAEA-336), and Cabbage (IAEA-359) were then carried out using EDXRF technique with the predetermined dark matrix elements. In the Emission-Transmission (ET) method, absorption correction within a sample is experimentally measured for each sample matrix. However, in Simple Quantitative (SQ) method, the

absorption correction within a sample is calculated, and requires complete knowledge of the composition of matrix elements. Consequently, the Simple quantitative method is limited only to samples for which the matrix elements are known. The Full Fundamental Parameters (FFP) method also calculates the absorption correction by representing the matrix with two elements estimated from the scattered x-ray intensities. Hence, under normal circumstances, only the ET and FFP methods could have been used in the analysis of the unknown elements and their concentration values in the cabbage and lichen samples. However, with the a priori determination of the dark matrix elements, it was possible to use the SQ method taking as input (compound by difference) the composition of the matrix elements determined from RBS. Quantitative results for IAEA-336 Lichen obtained using FFP method are shown in Table 3. From the results it can be seen that the FFP method has the tendency to overestimate concentration for most elements when allowed to use its own estimated matrix elements. Nevertheless, when the a priori determined dark matrix elements are provided as an input to the FFP method, it improved the overall accuracy in the determination of elemental concentrations. As can be seen from Table 4, all the three quantitative methods produce comparable results for IAEA-359 Cabbage CRM when the predetermined dark matrix elements are used as inputs for the SQ and the FFP method.
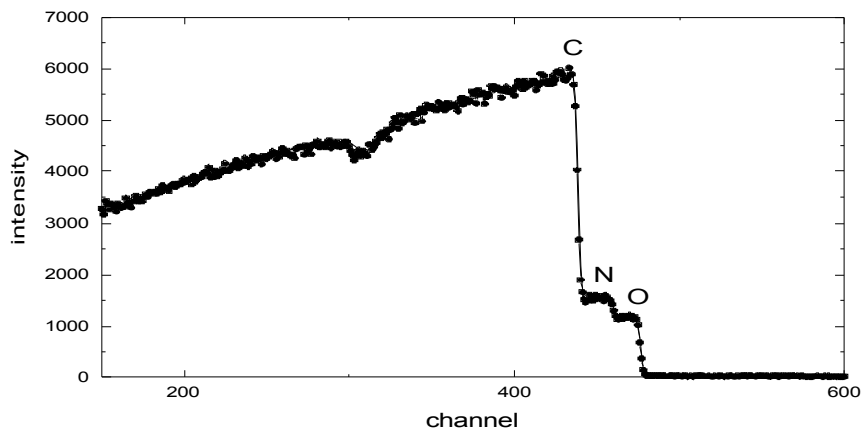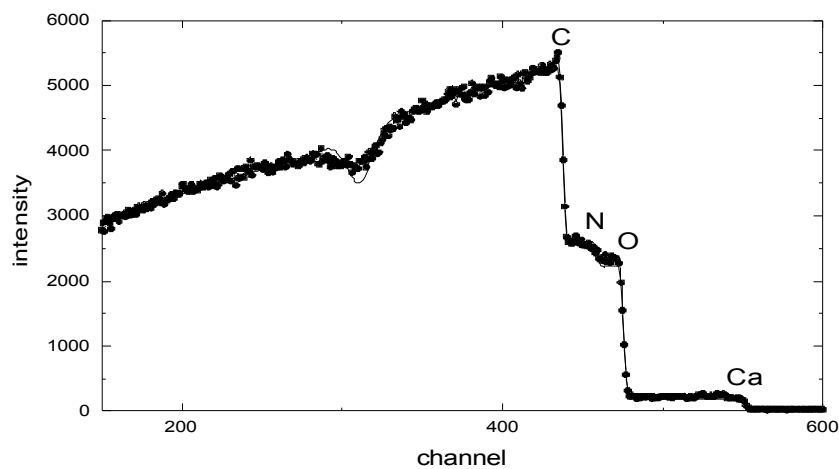

FIG. 2.1 RBS spectra for Kapton

FIG. 2.2 RBS spectra for Bowen's Kale samples

TABLE I. COMPARISON BETWEEN MATRIX COMPOSITION OBTAINED FROM SIMNRA AND CRM DATA SHEET VALUES FOR BOWEN'S KALE SAMPLE.

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

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

TABLE 3. QUANTITATIVE RESULTS FOR IAEA-336 OBTAINED USING FULL FUNDAMENTAL PARAMETERS (FFP) METHOD WITH A) MATRIX OBTAINED FROM RBS ($C_6H_{10}O_5$) 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)

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)

4. Conclusions

RBS is today conventionally used for estimating major element composition for fundamental parameter analysis by PIXE. In case of biological samples, database for proton elastically scattering from light elements are reliable enough to allow complete determination of sample matrix. By using set of well-known samples, instrument constant was determined. This constant was later taken as an input for matrix determination of unknown biological samples. It has shown how information about H content in the sample can be also extracted, although H is not detectable by RBS technique. It was found out from RBS analysis of three different plant-based samples that the major elements in the matrix of plant-based samples are quite close to the stochiometry $C_6H_{10}O_5$. Using this composition as an input value (compound by difference) in the quantitative packages available from the QXAS software, extended the usage of the SQ method to unknown plant-based samples, and improved accuracy in the results obtained using the FFP. The results obtained in the analysis of reference materials Lichen, IAEA-336 and Cabbage, IAEA-359 were in good agreement with the reference values for most elements.

5. References

1. HE, F., VAN ESPEN, P. Anal. Chem. 1991; **63**: 2237-2244.
2. WEGRZYNEK, D.,et al.,. X-ray Spectrom. 1993; **22**: 80-85.
3. HOLYNSKA, B., et al.,. Appl. Radiat. Isot. 1994; **45**: 409-413.
4. GRIME, G. W., Nucl. Instr. and Meth. 1996; **B 109/110**: 170
5. GURBICH, A, F., Nucl. Instr. And Meth. 1998; **B 136-138**: 60
6. GURBICH, A, F., Nucl. Instr. And Meth. 1997; **B 129**: 311
7. GURBICH, A, F., Nucl. Instr. And Meth. 1998; **B 145**: 578
8. RAMOS, A.R., et al.,, Nucl. Instr. And Meth. 2002; **B 190**: 95
9. MAYER, M., In *Technical Report IPP* 1997; **9/13**
10. http://www.rzg.mpg.de/~mam/

11. INTERNATIONAL ATOMIC ENERGY AGENCY, Manual, Quantitative X-ray Analysis System , Vienna (1996)