A Remotely-Controlled, Semi-Automatic Target System for Rutherford Backscattering Spectrometry and Elastic Recoil Detection Analyses of Polymeric Membrane Samples

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Abstract: A new target system for Rutherford backscattering spectrometry and elastic recoil detection analysis is described which enables remotely controlled, semi-automatic analysis of multiple organic polymer samples without exceeding damaging incident beam fluences. Control of fluence at a given beam current is achieved using two stepper motors to move a thin aluminum disc loaded with polymer samples both radially and azimuthally across the beam. Flexible beam spot locations and sample irradiation times are remotely controlled in two steps via two custom LabVIEW™ programs. In the first step, a digital image of the target disc is converted into precise radial and azimuthal coordinates for each mounted polymer sample. In the second step, the motors implement the user-directed sample irradiation and fluence. Schematics of the target system hardware, a block diagram of interactions between the target system components, a description of routine procedures, and illustrative data taken with a 2-MeV \(^4\)He\(^{2+}\) analysis beam are provided.

Key Words: Rutherford backscattering spectrometry, elastic recoil detection, membranes, thin film composite, reverse osmosis, nanofiltration
1. Introduction

Rutherford backscattering spectrometry (RBS) has recently been used as an analytical technique to study the physico-chemical properties of the active layers of thin-film composite membranes for water purification [1-9]. Thin-film composite membranes used in applications such as reverse osmosis and nanofiltration consist of an ultrathin (∼50−200 nm) organic active layer that lies on top of an intermediate polysulfone support (∼30 μm) backed by a polyester fabric (∼200 μm) [10, 11]. The performance of such thin-film composite membranes, in terms of water permeation and contaminant rejection, is mostly determined by their active layer [10, 11]. As a result, the development of new improved membranes significantly benefits from studying the physico-chemical properties of the active layers and their interactions with water and contaminants. The recently published [1-6, 8] membrane characterization procedures that use RBS for sample analysis take advantage of the ability of RBS to resolve the active layer from their significantly thicker polysulfone and polyester supports [2, 5, 12].

During RBS analyses, a high-energy ion beam (e.g., 2-MeV $^4$He$^+$ [2, 5]) is used to irradiate the target sample, and the spectrum resulting from the backscattered ions is analyzed to obtain the elemental composition of the irradiated sample with nanometer depth resolution [2, 5, 12]. Unfortunately, beam irradiation of organic polymers results in polymer degradation [13-17] with a corresponding emission of beam-generated small molecules [13, 14] that leads to a changing elemental composition of the irradiated sample as a function of beam ion fluence [13-15, 17]. Studies [13, 16, 17] of polymer degradation upon beam irradiation have shown, however, that induced changes in the elemental composition of irradiated samples can be neglected below
fluence thresholds that depend on the polymer analyzed. Among the materials relevant to the structure of thin-film composite membranes, polysulfone has shown the lowest fluence threshold value at $3 \times 10^{14}$ ions/cm$^2$ using a 2-MeV $^4$He$^+$ ion beam [17].

For RBS to be useful in the study of the properties of the active layers of thin-film composite membranes [1-9], the beam ion fluence is maintained below the threshold values where changes in the elemental composition of the sample analyzed would be detected. Given that the elements (i.e., H, C, O, N, S) that make up thin-film composite membranes have relatively small scattering cross sections (0-342 mb/sr) [12], the only possible strategy to avoid exceeding fluence threshold values, while obtaining enough counts to quantify accurately the sample elemental composition, is to scan a relatively large area (e.g., a few square centimeters) with the analysis beam. One achieves this either by analyzing multiple points of the membrane sample or by continuously scanning the ion beam over the sample [2-8]. Such scanning patterns have been achieved by continual manual positioning of scattering target stages, a technique which is highly impractical for analysis of multiple samples. Active layers of thin-film composite membranes can also be studied after isolating the active layer on a solid surface by peeling off the polyester backing and dissolving the polysulfone support using organic solvents [18-21]. Isolated active layers are generally relatively small (i.e., a few square centimeters) and irregular in shape, and therefore, the RBS analysis of isolated active layers requires both irregular scanning patterns and millimeter-accurate positioning of the beam over the sample to stay within the sample boundaries.
Thus, an innovative target system is needed to implement practical analysis of multiple organic membrane samples while satisfying the fluence threshold, sample location, and scanning pattern requirements described above. Accordingly, the objective of this work was to design, fabricate and test a scattering target system for RBS analysis, and the sister technique of elastic recoil detection (ERD) analysis, with the following capabilities: (i) remote control; (ii) irradiation of samples according to regular and irregular scanning patterns defined by the user; (iii) positioning of beam on target with millimeter-scale accuracy; and (iv) accommodation of multiple samples of any shape on the sample holder.

2. Accelerator and Scattering Chamber

The new RBS/ERD target system utilizes systems associated with the tandem electrostatic accelerator at the Triangle Universities Nuclear Laboratory (TUNL). Existing hardware at TUNL includes a duoplasmatron ion source equipped with a sodium charge-exchange canal used to produce a 30-keV $^4\text{He}^-$ ion beam which is injected into the accelerator. After initial acceleration to the electrostatic accelerator terminal at 0.67 keV, the $^4\text{He}^-$ beam is stripped of its electrons in a thin carbon foil inside the terminal, and then further accelerated. The emerging 2-MeV $^4\text{He}^{2+}$ beam is momentum selected by deflection (52 degrees) through an analyzing magnet, focused, and transported 15 meters to a multipurpose, aluminum scattering chamber. The chamber is cylindrical in shape with internal diameter and depth of 59.7 cm and 26.0 cm, respectively. The beam enters the chamber through entrance slits of adjustable aperture that typically define a square 3-mm × 3-mm beam cross section. The beam spot on target is located 6.4 cm above a bottom plate that holds several detectors of scattered or recoil particles emerging
from the polymer film being used as a target. This bottom plate can be rotated while under
vacuum around the vertical axis of the chamber to set the desired detector angles. Signals from
the detectors are first sent through pre-amplifiers at the scattering chamber before being sent to
the accelerator control room for further processing and digitization.

3. RBS/ERD Target System

The new RBS/ERD target system consisting of a target rod, static stage, dynamic stage, and
target wheel is shown in Figure 1. The target rod secures and locates the rest of the target system
precisely inside the scattering chamber and allows for rotation of the system around the central
vertical axis of the chamber. The static stage houses a stepper motor that controls vertical
movement of the dynamic stage along two precisely located steel rods. The target wheel is
attached to a second stepper motor on the dynamic stage which controls its azimuthal motion.
The two stepper motors thus move the target wheel vertically and rotate it around its central axis.
The target system is controlled via two custom LabVIEW™ programs. One program,
WheelScan, combines a digital picture of a loaded target wheel with input from the user to
establish the movement patterns of the two stepper motors. A second program, MotorLord, then
uses data generated by WheelScan to control the two stepper motors, thus implementing desired
movements of the target wheel. Figure 2 illustrates the interaction between the hardware,
software and user of the target system. Detailed information about all system components is
included in the following sections.

Insert Figure 1. Size suggestion: 1.5 column
3.1. Hardware

3.1.1. Sample Holder Target Rod

The nickel-plated brass target rod supporting the sample holder system slides vertically and rotates easily while maintaining a secure vacuum seal with the scattering chamber lid. The positioning handle of the target rod has azimuthal fiducial marks in 5 degree increments to indicate the angle of incidence of the beam with respect to the normal of the target wheel. The positioning handle is also pinned to a frame atop the scattering chamber to support the weight of the sample holder system and align the vertical axis of the rod with the horizontal beam axis. Using an optical transit, the horizontal rotation axis of the target wheel was confirmed to intersect both the axis of the beam and the vertical axis of the rod through the center of the scattering chamber to within 0.5 mm.

3.1.2. Target Wheel

The aluminum target wheel, having 15.9-cm outer diameter and 0.8-mm thickness, is designed to be lightweight and to hold as many membrane samples as possible while fitting within the scattering chamber. The 1.59-cm inner diameter of the target wheel fits snugly over a Delrin® hub to define its axial location while providing electrical insulation from the rest of the sample holder apparatus. Four calibration holes, 0.5 mm in diameter, positioned in a 110-mm × 110-mm
square grid centered on the axis of the wheel are used as reference points to define the exact position of membrane samples as described in Section 3.2.1. Additionally, the target wheel has an engraved 3.18-cm diameter circle centered on the wheel axis and an engraved chord whose closest point is located 7.6 cm from the center of the target wheel. Samples must lie within these engraved boundaries as the vertical scanning range of the wheel is limited by the size of the scattering chamber. The Delrin® hub at the center of the wheel can easily be detached from and re-attached to the sample holder, allowing for sample loading and removal. Membrane samples may be secured to the wheel by double-sided conductive tape, which inhibits charge build-up and conducts heat to the wheel when beam strikes the membranes, or alternatively by using two perpendicular diametrical arrays of small threaded holes in the wheel to clamp samples in place.

3.1.3. Lower Stages

Two stages, one static and one dynamic, which are attached to the bottom of the target rod house, separate identical vacuum-rated stepper motors (NEMA 11 bipolar vacuum-rated stepper motor, Lin Engineering, Morgan Hill, CA, USA). The motor on the static stage controls the vertical motion of the target wheel, while that mounted on the dynamic stage controls its azimuthal rotation.

The shaft of the vertical motor is coupled directly to an Acme threaded rod (0.375-inch diameter, 16 pitch) and the corresponding threaded insert is attached to the dynamic stage. Motion of the dynamic stage is guided by two steel rods, 6.3 mm in diameter, which fit into linear Teflon® bushings. The stepper motor normally has 200 full steps per revolution (1.8 deg/step); however,
a motor driver/controller circuit (TMCM-310/SG, Trinamic Motion Control GmbH & Co. KG, Hamburg, Germany) is used to microstep the motor eight times per full step resulting in more precise control of the motion with 1,600 microsteps per revolution (0.225 deg/microstep). A microswitch attached to the static stage indicates when the dynamic stage reaches its uppermost point, giving the motor driver/controller a reference point for positioning the vertical motor. As long as power to the motor driver/controller circuit is maintained, the driver/controller tracks the number of microsteps from the reference point allowing for accurate vertical positioning of the wheel.

The azimuthal motor drive shaft attaches to the Delrin® hub of the target wheel via a custom keyed, shouldered shaft extension. The Delrin® hub is pressed onto the shaft extension and snugly against the shoulder for precise positioning of the target wheel within the scattering chamber. The rotary stepper motor has 200 full steps per revolution but is micro-stepped 64 times per full step resulting in 12,800 microsteps per revolution (0.0281 deg/step) allowing for very precise azimuthal rotation of the target wheel. The azimuthal motor also has a small rear drive shaft where an absolute magnetic encoder (MAE3 Absolute Magnetic Kit Encoder, US Digital, Vancouver, WA) is attached to enable highly accurate tracking of the azimuthal position of the target wheel. The encoder outputs a digital clock signal of 250 Hz whose variable duty cycle is correlated to the azimuthal position of the drive shaft. The pulse width of the signal has 12-bit precision giving the encoder a resolution of 4,096 distinct duty cycles per revolution.

A graphite brush housed in Delrin® is attached to the dynamic stage of the target system. This brush is spring loaded to make good sliding contact against the insulated target wheel during
A wire connected to the brush carries current outside of the scattering chamber for remote beam current integration and monitoring.

Electronics outside the scattering chamber power the stepper motors, the absolute position encoder, and the motor driver/controller. Electronic connections to the two stepper motors, absolute encoder, and microswitch from the external power supplies and motor driver/controller are established via a 25 pin D-subminiature (DB-25) vacuum feedthrough in the scattering chamber wall.

3.2. Software

National Instruments LabVIEW™ and Vision Development Module programs are used to control the target system. Two LabVIEW™ virtual instruments called WheelScan and MotorLord are used to control the beam irradiation of samples on the target wheel as described in the following sections.

3.2.1. WheelScan

The first virtual instrument, WheelScan, determines the coordinate positions of the membrane samples on the target wheel and the method and pattern for beam irradiation of each sample. The primary input to WheelScan is a digital photograph of the target wheel loaded with membrane samples, taken with the engraved target wheel chord oriented approximately horizontally and located in the upper third of the picture. When WheelScan is executed, it
prompts the user to specify the width of the expected square beam spot in millimeters as well as the expected incident angle. The user then selects the digital photograph of the loaded target wheel and identifies the location of the four calibration holes on the wheel image by clicking on them. Since the physical locations of the calibration holes on the wheel are precisely known, WheelScan uses their pixel locations on the digital wheel image to determine the physical dimension of an image pixel. WheelScan then converts locations in the image, specified by pixel coordinates, into physical locations on the wheel itself, specified by polar coordinates (mm, radians) with the origin at the center of the target wheel.

The user then specifies the number of individual samples to be analyzed, and designates the scanning mode to be used for each sample by selecting between point, discrete rastering and continuous rastering. For point samples, the user selects a single coordinate where the beam will be focused for the duration of the exposure of the sample. Point samples are used for calibration of RBS/ERD energy spectra, and should be samples that are not damaged by prolonged beam exposure. For discretely- or continuously-rastered samples, the user employs a polygon tool to draw on the digital wheel image a closed outline of the area to be analyzed. Using the specified beam width, WheelScan decomposes the specified polygon area into a series of adjacent arcs that define the beam irradiation pattern. For each arc, both the start and end angles and the radial displacement are saved by the software. If the sample is to be discretely rastered, WheelScan decomposes each arc into a series of discrete points that are spaced far enough apart to avoid overlapping beam spots. After defining all samples, the user assigns a name to the file in which WheelScan stores the data that define the raster patterns of all samples in the wheel. The generated file is then ready to be used by the second virtual instrument, MotorLord.
3.2.2. MotorLord

The second virtual instrument, MotorLord, uses the data created by WheelScan to control the two stepper motors on the target system and data acquisition from the RBS/ERD detector(s). LabVIEW™ interfaces with the microswitch in the target stage and the electronics that comprise the RBS/ERD data acquisition system (DAQ) via a small USB DAQ (USB NI-6009, National Instruments, Austin, TX, USA) that handles digital, transistor-transistor logic input and output. LabVIEW™ communicates with the motor driver/controller using a TCP connection established via an Ethernet-to-RS232 converter (ESL 1 port RS-232 DB9, Lava Computer MFG Inc., Toronto, Canada). The output signal from the absolute magnetic encoder is input into a microcontroller (PIC18F4520, Microchip Technology Inc., Chandler, AZ) with a 20 MHz crystal which calculates the duty cycle of the system. The microcontroller communicates with LabVIEW™ via RS232 through a TTL-to-RS232 level converter (MAX232, Maxim Integrated Products Inc., Sunnyvale, CA).

When MotorLord is executed, the user loads the file generated using WheelScan which contains the raster patterns of the samples to be analyzed. MotorLord then sends digital inhibit signals to the analog-to-digital converter (ADC) and scalar of the RBS/ERD data acquisition system. The software then instructs the vertical motor to move the dynamic stage upward until the microswitch is tripped, establishing the zero reference position for the motor; this procedure recurs between analysis of any separate samples to assure continued precision. As described above, MotorLord also reads the duty cycle of the absolute magnetic encoder which provides the
position of the rotary motor. Once the wheel position is properly set to user-chosen locations, the beam current is tuned to the desired value, as needed, by the accelerator operator. Once tuning of the beam current is complete, the user selects the sample to analyze. For a point sample, MotorLord instructs the two motors to move to the corresponding polar coordinates and enables the DAQ, beginning data collection. The user can stop data collection at any time by clicking on a command button.

For discretely-rastered samples, the user inputs the number of points to be analyzed and the time each point is to be irradiated. MotorLord then instructs first the rotary and then the vertical motors to move to their respective initial sample coordinates. Once at the target coordinate, MotorLord enables data collection. After the specified irradiation time has been reached, MotorLord inhibits data collection, moves the motors so the beam hits the next point on the sample and re-enables data collection. This process continues until all specified points on the sample have been irradiated.

For continuously-rastered samples, MotorLord prompts the user to input the desired raster speed (mm/s) and analyzes the raster pattern to determine a starting angle 0.1 radians outside the raster area. MotorLord then moves the rotary motor to this starting angle and the vertical motor to the starting radial position of the innermost arc. Next, the software instructs the rotary motor to move to the beginning point of the current arc, enables data collection, and instructs the motor to move at the user-specified speed towards the end angle of the arc. Once there, the rotary motor is returned to the start of the arc and data collection is inhibited before the motor is returned to
the starting angle. MotorLord then instructs the vertical motor to move to the radial position of the next arc and the process is repeated until all the arcs have been rastered.

The user has the option to pause or abort RBS/ERD analysis at any point during a sample run. Once all the desired samples have been analyzed, the user ends execution of MotorLord.

4. Results

Figure 3 shows RBS spectra of the ESPA3 reverse osmosis membrane (circles) and its polysulfone support (triangles) (Hydranautics, Oceanside, CA). To facilitate spectra comparison, counts for the polysulfone support have been normalized so that the sulfur plateau matches that of the ESPA3 membrane. The inset in the figure depicts the thin-film composite structure of the ESPA3 membrane and indicates that the active layer is made of polyamide; such structure with a polyamide active layer is the most common structure of reverse osmosis and nanofiltration membranes [2, 6, 10]. The polysulfone support lacks the top polyamide layer and is made up of only the polyester backing and the polysulfone layer.

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The RBS spectra were obtained using the new target system and a 2-MeV $^4\text{He}^{2+}$ analysis beam collimated to a square shape of $3\text{ mm} \times 3\text{ mm}$. The membrane samples (i.e., $2.5\text{-cm} \times 5.0\text{-cm}$ coupons) were attached to the target wheel using double-sided conductive tape, and the ion fluence was always maintained below $3\times10^{14} \text{ ions/cm}^2$ to prevent damage of the polymer
material [17]. The experiments were performed using incident, exit and scattering angles of 22.5°, 42.5° and 160°, respectively, and a sample-detector distance of 75 mm. A collimator with a 6-mm wide rectangular aperture was used in front of the detector. The depth of RBS analysis for the experimental settings used is <5 µm [12] which is much lower than the thickness (~30 µm) of the polysulfone layer. As a result, the polyester backing does not contribute to the spectra.

While the data in Figure 3 come from experiments performed using RBS geometry and continuously-rastered samples, we also verified the correct performance of the system for ERD geometries, and point and discretely-rastered samples (data not shown). The choice of scanning mode did not affect the data collected, i.e., different scanning modes with the same geometry and fluence generated statistically indistinguishable spectra. Additionally, all scanning modes with RBS geometry resulted in RBS spectra of the membranes analyzed consistent with what is expected from the literature [1-8]; the spectra in Figure 3 are examples of such typical spectra. No ERD spectra have been reported in the literature for RO and NF membranes. The study of such spectra will be the subject of subsequent work.

The signal in an RBS spectrum is the result of backscattering events of the projectile ions (4He²⁺) upon collision with atoms in the sample that have a larger mass than the projectile ions [12]. As a result, the spectra in Figure 3 for the ESPA3 polyamide membrane and the polysulfone support contain peaks and plateaus indicative of the presence of only carbon, nitrogen, oxygen, sulfur and chlorine, but not of hydrogen [2, 6]. Also, as depicted in Figure 3, the ESPA3 membrane has a nitrogen peak while the polysulfone support does not. The nitrogen peak is the result of
$^4\text{He}^{2+}$ scattering from the top polyamide active layer in the ESPA3 membrane [2, 5]. Additionally, since the helium beam loses energy as it travels through the membrane [12] and the top polyamide layer in the ESPA3 membrane does not contain sulfur, the onset of the sulfur signal appears at lower energies in the spectrum of the ESPA3 membrane [2, 5]. Using the theoretical hydrogen-to-carbon ratios of 0.667 and 0.815 for the elemental compositions of polyamide and polysulfone [2, 5, 10, 22], respectively, the commercial software SIMNRA [23] was used to simulate the spectra in Figure 3 (see solid lines). Elemental compositions of C$_{0.50}$H$_{0.41}$O$_{0.07}$S$_{0.02}$ and C$_{0.49}$H$_{0.33}$O$_{0.08}$N$_{0.08}$Cl$_{0.01}$ were obtained for the polysulfone support and the ESPA3 reverse osmosis membrane, respectively. The thickness of the polyamide active layer was estimated at 100 nm assuming a polyamide density of 1.24 g/cm$^3$ [7, 21]. All results are consistent with previously published results [7].

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References


**User Input:**
- Digital Image of Target Wheel
- Raster Speed and Sample Number

**LabView VI WheelScan**
- Raster Pattern Data

**LabView VI MotorLord**
- Enable/Inhibit Signal

**PIC 18F4520 Microcontroller**
- Target Wheel Azimuthal Position

**Rotary Motor**
- Encoder Signal

**TMCM 310/SG Motor Driver/Controller**
- Target Wheel Vertical Position

**User Input:**
- Digital Image of Target Wheel
- Beam Width, Beam Angle, Number of Samples, Type of Sample, Sample Boundaries

**RBS/ERD Data Acquisition System**
- Micro-switch
Polyamide active layer $\approx 100 \text{ nm}$

Polysulfone support $\approx 30 \mu\text{m}$

Polyester backing $\approx 300 \mu\text{m}$

Normalized counts

Energy (KeV)

$C$ 12

$N$ 14

$O$ 16

$S$ 32

$Cl$ 35

ESPA3 support

ESPA3