



USER'S GUIDE TO ROCKJOCK -- A PROGRAM FOR DETERMINING QUANTITATIVE MINERALOGY FROM POWDER X-RAY DIFFRACTION DATA

Open-File Report 03-78



U.S. Department of the Interior
U.S. Geological Survey

USER'S GUIDE TO ROCKJOCK -- A PROGRAM FOR
DETERMINING QUANTITATIVE MINERALOGY FROM POWDER
X-RAY DIFFRACTION DATA

By D. D. Eberl

U.S. Geological Survey
Open-File Report 03-78

Boulder, Colorado
2003

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, Secretary
U.S. GEOLOGICAL SURVEY
CHARLES G. GROAT, Director

Cover: Paul Nadeau, Jan Srodon and Dennis Eberl atop Corona Arch near Moab, Utah. Teresa Dudek is on top, but not in view. Photo by Krzysztof Mystkowski.

The use of trade, product or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

RTS-ID Number: R2-3055

Last revised May 20, 2008

Boulder, Colorado
2003

For additional information, write to:

Chief, Branch of Regional Research
U.S. Geological Survey
Box 25046, MS 418
Denver Federal Center
Denver, CO 80225;
or contact the author: ddeberl@usgs.gov

THE MOTIVE FOR METAPHOR

by Wallace Stevens

You like it under the trees in autumn,
Because everything is half dead.
The wind moves like a cripple among the leaves
And repeats words without meaning.

In the same way, you were happy in spring,
With the half colors of quarter-things,
The slightly brighter sky, the melting clouds,
The single bird, the obscure moon—

The obscure moon lighting an obscure world
Of things that would never be quite expressed,
Where you yourself were never quite yourself
And did not want nor have to be,

Desiring the exhilarations of changes:
The motive for metaphor, shrinking from
The weight of primary noon,
The A B C of being,

The ruddy temper, the hammer
Of red and blue, the hard sound—
Steel against intimation—the sharp flash,
The vital, arrogant, fatal, dominant X.

CONTENTS

“The Motive for Metaphor” by Wallace Stevens.....	iii
ABSTRACT.....	1
SUMMARY OF INSTRUCTIONS FOR A QUICK START.....	2
INTRODUCTION.....	3
COMPUTER REQUIREMENTS AND DISCLAIMER.....	4
HOW TO OBTAIN ROCKJOCK.....	5
INSTALLATION OF ROCKJOCK.....	5
Installation for Excel 2003.....	5
Installation for Excel 2007.....	8
Installation for Non-English Versions of Excel.....	9
ACKNOWLEDGMENTS.....	9
RUNNING ROCKJOCK.....	10
USING THE AUTOMATICK MODE.....	12
USING THE MANUAL MODE.....	13
SAMPLE PREPARATION AND ANALYSIS.....	14
ENTERING NEW STANDARDS INTO THE PROGRAM.....	15
MEASUREMENT ACCURACY.....	20
USEFUL TIPS.....	22
REFERENCES.....	26
APPENDIX 1: Input Sheet Inputs and Outputs.....	28
APPENDIX 2: Shifter Sheet Inputs and Outputs.....	33
APPENDIX 3: Full Pattern Sheet Inputs and Outputs.....	34
APPENDIX 4: Result Sheet Inputs and Outputs.....	36
APPENDIX 5: Standards Sheet Inputs.....	37
APPENDIX 6: Auto XRD Sheet Inputs.....	38
APPENDIX 7: Auto Results Sheet Outputs.....	39
APPENDIX 8: Auto Graph Sheet Inputs.....	40

APPENDIX 9: Resources for Quantitative Mineral Analysis.....	41
APPENDIX 10: Analysis of Reynolds Cup samples.....	43
How I Won the Reynolds Cup.....	46

TABLES

Table 1. Biases for 2002 Reynolds Cup samples run on different diffractometers (1, 2 and 3) analyzed using standards run on diffractometer 1 (Siemens D500). Results were calculated with an earlier version of RockJock.....	15
Table 2. Comparison between true values for artificial mixtures used in the 2002 Reynolds Cup quantitative analysis competition, and those calculated from XRD patterns using Option 2 in the RkJock5.xls program. Reynolds Cup samples prepared by Douglas McCarty. RockJock analyses are normalized to 100 %, and all minerals in the first column were entered into RockJock as present for all three samples. Combined biases are calculated using totals for 2:1 clays, rather than the individual 2:1 clays.....	42
Table 3. Comparison for 2004 Reynolds Cup samples. Reynolds Cup samples prepared by Reinhard Kleeberg. RockJock analyses are normalized to 100 %, and all minerals in the first column were entered into RockJock as present for all three samples. Combined biases are calculated using totals for plagioclase, kaolinite group and 2:1 clays rather than the individual minerals in these groups.....	43

FIGURES

Figure 1. Measurement error for kaolinite and quartz measured for samples containing fifty weight percent of these minerals.....	21
Figure 2. The Reynolds Cup trophy, awarded once every two years to the winner of an international quantitative mineral analysis competition (see http://www.dttg.ethz.ch/reynoldscup2004.html).....	44

USER'S GUIDE TO ROCKJOCK -- A PROGRAM FOR DETERMINING QUANTITATIVE MINERALOGY FROM POWDER X-RAY DIFFRACTION DATA

By **D. D. Eberl**

ABSTRACT

RockJock is a computer program that determines quantitative mineralogy in powdered samples by comparing the integrated X-ray diffraction (XRD) intensities of individual minerals in complex mixtures to the intensities of an internal standard. Analysis without an internal standard (standardless analysis) also is an option. This manual discusses how to prepare and X-ray samples and mineral standards for these types of analyses and describes the operation of the program. Carefully weighed samples containing an internal standard (zincite) are ground in a McCrone mill. Randomly oriented preparations then are X-rayed, and the X-ray data are entered into the RockJock program. Minerals likely to be present in the sample are chosen from a list of standards, and the calculation is begun. The program then automatically fits the sum of stored XRD patterns of pure standard minerals (the calculated pattern) to the measured pattern by varying the fraction of each mineral standard pattern, using the Solver function in Microsoft Excel to minimize a degree of fit parameter between the calculated and measured pattern. The calculation analyzes the pattern (usually 20 to 65 degrees two-theta) to find integrated intensities for the minerals. Integrated intensities for each mineral then are determined from the proportion of each mineral standard pattern required to give the best fit. These integrated intensities then are compared to the integrated intensity of the internal standard, and the weight percentages of the minerals are calculated. The results are presented as a list of minerals with their corresponding weight percent. To some extent, the quality of the analysis can be checked because each mineral is analyzed independently, and, therefore, the sum of the analysis should approach 100 percent. Also, the method has been shown to give good results with artificial mixtures. The program is easy to use, but does require an understanding of mineralogy, of X-ray diffraction practice, and an elementary knowledge of the Excel program.

SUMMARY INSTRUCTIONS FOR QUICK START

Below is a brief summary of instructions for using RockJock:

1. Very important: After copying RockJock onto your hard disk, and upon opening the program (for free expansion software see <http://www.stuffit.com>), first run the Solver option in the Full Pattern sheet. If necessary, turn on the Solver in the Visual Basic Editor. Then save the program. Macintosh users may need to follow the more detailed installation instructions beginning on page 5 of this manual, as will non-English language users. See the installation instructions section for adapting the program to run in Excel 2007.
2. Prepare samples for analysis by adding 0.111 g ZnO to 1.000 g sample. Grind the mixture in a McCrone mill for 5 minutes with 4 ml methanol. Dry the ground sample, sieve, mix well, side-pack the ground material into a holder to ensure random sample orientation, and then X-ray from 5 to 65 degrees two-theta using Cu K-alpha radiation, with 0.02 degree steps and a count time of 2 seconds per step.
3. Enter the X-ray diffraction (XRD) intensities for the sample into the Input sheet, column D, with the sample name in cell **D1**. To enter the data, use **COPY** and **PASTE**. Never use **CUT** and **PASTE**. When pasting, under the **EDIT** menu, choose **PASTE SPECIAL, VALUES**. Select the minerals likely to be present in the sample from the list in column G by entering a 1 (present) or a 0 (not present) in column H. Enter option 2 in cell **B21**, click the Start button, and wait and wait. The Stevens poem, which concerns quantitative analysis, is meant to be puzzled over while waiting. Weight percents of the selected minerals in the sample will appear in the Result sheet. For best results, replace mineral standards in the program (see Standards sheet) with ones that were run with your experimental setup, although adequate results may be realized from the present mineral standards even though you are using a different diffractometer. When using a different diffractometer it may be necessary to turn on the **Auto Background** correction in cell **B15** of the Input sheet by setting it to 1.

INTRODUCTION

A rock is composed of atoms that are arranged in variety of mineral structures. To characterize a rock, both the elemental composition and the mineralogy should be measured quantitatively. Sometimes the elemental composition is more important, as it would be, for example, in prospecting for gold. Sometimes mineralogy is more important, for example, if a rock contains swelling clay that is cracking building foundations. Often both measurements are needed, for example, in the case of a gold ore which contains a clay mineral that may impede the refining process.

The geochemical sciences have matured and prospered because they offer precise, accurate, and routine methods for determining quantitatively the elemental compositions of natural materials. Quantitative mineralogy by XRD, however, has lagged far behind the chemical methods, mainly because the quantitative analysis of clay minerals has proved to be a particularly difficult problem (Moore and Reynolds, 1997).

This report describes the RockJock computer program, and gives instructions on how to prepare and X-ray samples and standards for analysis by the program. RockJock offers a relatively simple and mostly automatic method for determining quantitatively the mineralogical composition of samples, including clay minerals, to within a few weight percent from powder X-ray diffraction data (see Appendix 10). The calculations are based on three previously published methods: (1) the matrix flushing technique of Chung (1974), in which integrated intensities of the unknown minerals are compared to that of an internal standard (in the case of RockJock, ZnO, zincite), thereby obviating the need for measuring the mass absorption coefficient for a sample; (2) the whole-pattern fitting routine of Smith and others (1987) for measuring integrated intensities by fitting the sum of pure mineral patterns to that of the measured XRD pattern; and (3) the quantitative method of Srodon and others (2001) for sample preparation, and for the method of measuring clay mineral content from non-basal reflections rather than from the more commonly used basal reflections.

RockJock is similar in its approach to the Microsoft Excel-based program FULLPAT (Chipera and Bish, 2002), except that the analysis procedure in RockJock is almost entirely

automatic. Also, RockJock finds the integrated intensity of the internal standard in an observed pattern by fitting the XRD pattern for the pure internal standard (ZnO) to the observed pattern in the same manner as it does for the other pure standard patterns. The library standards in FULLPAT contain the internal standard (Al_2O_3), and therefore, prior to analysis, these standards are normalized to an equal-internal standard basis so that the internal standard in each library pattern has the same integrated intensity as the internal standard in the observed pattern.

RockJock6 differs from previous versions of the RockJock program in that the program is compatible with Excel 2007 for the PC. In addition, features were added such as the ability to change the scale of mineral XRD patterns plotted in the Auto Graph sheet, and extended clay analysis has been eliminated. Excel 2008 for the Mac will not run RockJock because it does not contain the Solver.

COMPUTER REQUIREMENTS AND DISCLAIMER

RockJock will run under either Windows 98 (or higher versions), or Macintosh (System X) operating systems. Calculation times are long, so the fastest computer available (>1 GHz) should be employed. The Excel program has not been optimized to run on the Macintosh; therefore, a Windows system is preferred because it is faster. One calculation can take up to half an hour or more. The more minerals that are selected to be present, the slower the calculation. The calculation is slowed further if the AutoShift option is used. Use of RockJock requires installation of Microsoft Excel 2003 (or higher versions of Excel), including the Solver option (which may not be installed in a standard installation from the original Excel disk), and an elementary knowledge of how to use the Excel program. The program also can be run in Excel 2007 for the PC. In this report, the term “sheet” refers to a worksheet in Microsoft Excel. Cells, such as **B4**, designate column B and row 4. It may be necessary to use the English-language version of Excel (but see installation instructions below). RockJock works best on a computer having 100 megabytes or more of RAM. The program occupies about 50 megabytes of disk space.

Although this program has been used by the U. S. Geological Survey (USGS), no warranty, expressed or implied, is made by the USGS or the United States Government as to the accuracy and functioning of the program and related program material, nor shall the fact of distribution constitute any such warranty, and no responsibility is assumed by the USGS in connection herewith.

HOW TO OBTAIN ROCKJOCK

The latest version of the software described in this report can be obtained by anonymous ftp from the Internet address: <ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock>, by emailing the author at ddeberl@usgs.gov, or by writing D. D. Eberl, U.S. Geological Survey, Suite E-127, 3215 Marine Street, Boulder, Colorado, USA, 80303-1066. The RockJock folder at the ftp site can be opened by double clicking on the folder's name (RockJock), and the files downloaded by dragging them on to your hard disk. The useful files are RkJock6.xls, which is the quantitative analysis program; PkChopr.xls, which is the PeakChopper program that removes unwanted XRD peaks; and RockMan6.pdf, which is the most recent instruction manual for the RockJock program. Files can be decompressed using free software from: <http://www.stuffit.com>. Comments or concerns about RockJock should be directed to the author.

INSTALLATION OF ROCKJOCK

It can be tricky to install RockJock, so these instructions should be followed carefully when the program is run for the first time. These routines should only have to be done once, when the program is first installed on your computer, or if the program is installed on another computer from your computer.

Installation for Excel 2003

These instructions are for use with versions of Excel that predate Excel 2007, at which time Excel underwent a major format change. If the reader is using Excel 2007, then skip to the next section.

1. Copy the program and related files onto your hard disk by dragging them to your disk, or by double clicking on them at the ftp site. If the files are compressed with the .exe extension, they should decompress automatically under Windows when double clicked. Files with the .exe extension can be opened for the Macintosh if Aladdin expander software is used (see below). The latest version of expander software can be downloaded free from the web at: <http://www.stuffit.com>. After decompressing and opening the programs, more of the program can be viewed on the screen at one time by reducing the zoom size under the **View** menu.

2. After the program has been opened, go immediately to the Full Pattern sheet by clicking that tab near the bottom left of the screen. Under the Tools pull-down menu in this sheet, check to see that the Solver tool appears. If not, click the Add-ins option under the same menu and click the Solver option box. If the option does not install, then Solver has not been installed from the original Excel disk. Return to the original Excel disk and install the Solver (see the Help menu in Excel), and then repeat the steps above.

3. Next run the Solver once in the Full Pattern sheet by choosing the Solver from the **Tools** menu and by clicking the **Solve** button. If the following cells in the Solver are empty, then before starting the Solver fill them in as follows: **Set Target Cell** to **E1**; click the **Min.** button; set **By Changing Cells** to **E8**. This run will take a few minutes. If the **Maximum Time Limit** box appears, click **Stop** and then **OK**. If the Solver solution box appears, click **OK** to retain the Solver solution.

4. Return to the Input sheet by clicking on its tab at the bottom of the screen. Now it probably will be necessary to turn on the Solver in the Visual Basic Editor. To turn on the Solver, go to the **Tools** menu. Under **Tools**, choose **Macro**, then **Visual Basic Editor**. A new **Tools** menu will appear. Under this menu choose **References**. A box will appear named **Available References**. Click to check the **Solver** box in this box, and then go to paragraph 5 below. If the **References** option is dimmed so that it can not be chosen, then exit the Excel program (first exit the Visual Basic editor under the **File** menu and then exit Excel), and start again with step 2 above. It may be necessary the second time through to uninstall and then to reinstall the Solver (under the **Tools** menu in the Full Pattern sheet click **Add-Ins**, and uncheck

the Solver **Add-in** box, then repeat the procedure to recheck the Solver box). However, no Solver box may appear, or a checked box may appear that says MISSING:SOLVER.XLA. If so, click the **Browse** button. You now will have to look around to find the Solver box in order to check it to turn it on. In one version of Excel, twin boxes will appear. From the menus at the top of the boxes, it may be necessary to find **Microsoft Excel Files** in the **Show** menu and **Add-Ins** in the **From** menu (look in the Microsoft Office files under the Excel program and in Libraries). Make sure that **All File Types** are being shown, or especially those having the .xla extension. Choose **Add-Ins** in the left box, and open **Solver.xla** in the right box by double clicking. Click the **Enable Macros** button that appears. In a minute, SOLVER with a checked box should appear in the **Available References** box. Click the **OK** button. Under the **File** Menu, click **Close and Return to Microsoft Excel**.

5. If the Visual Basic editor is open, close it under the **File** menu. In the Input sheet, go to cell **AI239**, which will have a pink-colored font. This cell should show: =SOLVERSOLVE(TRUE). This macro statement can be seen at the top of the screen, in the formula bar beneath the **Tools** bar. If the equation cannot be seen, then under the **Tools** menu, click **Options**, and then under the **View** tab check the **Show formula bar** option. The **Status bar** and **Windows in Taskbar** options also should be checked. If cell **AI239** shows only =SOLVERSOLVE(TRUE), save the program and go to the next section in this report. However, especially for the Macintosh, there may be a long string of letters after the equal sign in this macro statement indicating the address of a hard disk. If this information is present, it must be removed from this and other cells before the program will run. To remove it, copy everything that comes between the equal sign and SOLVERSOLVE(TRUE) by highlighting it, and choosing **Copy** from the **Edit** menu. Click the red **X** in the Formula bar to return the cell value to its original state. Under the **Edit** menu, choose **Replace**. (In some systems it may be necessary to choose **Find** first, and then **Replace**.) Paste the copied material into the **Find What** box. Do not enter anything into the **Replace With** box. Click the **Replace All** button. Now the unwanted material has been removed from all cells in the program. Save the program, and you are ready to start to use it.

The program inputs and outputs are described in detail in Appendices 1 through 8 of this manual. Appendix 9 lists resources for quantitative analysis, and Appendix 10 gives RockJock analyses of the Reynolds Cup samples, samples which were used in international quantitative analysis competitions (Omotoso et al., 2006).

Installation for Excel 2007

The advantages of Excel 2007 are that it does not crash as frequently as Excel 2003, and that it can take advantage of the additional speed of multiprocessors. Excel 2008 for the Mac will not run RockJock because this version of Excel does not contain the Solver. The circuitous route for converting RockJock from Excel 2003 to Excel 2007 is as follows:

1. Open Excel 2007.
2. Under the **Office Button**, open RkJock6.xls.
3. Under the **Office Button**, **Save as, Excel Macro-Enabled Workbook**. The program is saved separately as RkJock6.xlms.
4. Under the **Office Button**, **Exit Excel**.
5. Open RkJock6.xlms.
6. Click the **Full pattern** tab at the bottom of the sheet.
7. Click the **Data** tab at the top of the sheet. In the **Analysis** section (far right top), click the **Solver** tool. If there is no Solver tool, then install the Solver by following the directions given in **Excel help**. Also install the **ToolPak Add-in** (without VBA).
8. After having clicked the **Solver** tool, when the **Solver** box appears, click **Close**.
9. Click the Input tab at the bottom left of the sheet.
10. Click the **Home** tab at the top left of the sheet.
11. In the Editing section (far right top), click **Find & Select**, then **Replace**. Next to **Find What:** enter **SOLVER**. Next to **Replace with:** enter **SOLVER** again.
12. Click **Replace All**. There should be 35 replacements. Close the box.
13. Under the **Office Button**, click **Save**.

Installation with Non-English versions of Excel

RockJock can run under non-English language versions of Excel if the user is willing to do some work. The Solver commands need to be modified in the Full Pattern sheet (Cells **C61:C71** and **D61:D63**), as follows. Go to the Full Pattern sheet. Click on cell **C61** to choose it. Under the Tools menu choose **Solver**. Make the following changes in the Solver box that appears on the screen: under **By Changing Cells**, erase the current entry and type **\$E\$7**; under **Subject to Constraints**, choose each entry and click **Delete** so that this box becomes empty. Next click on the **Options** button which is a part of the Solver box that is on the screen, and then click the **Save Model** button. Click **OK, OK**, and close the **Solver** box. Now cells **C61:C63** should contain the non-English language equivalent of the English entries. It may be necessary to separate the entries in Cell **C63** with slashes (/) rather than with commas or semicolons (, or ;), or maybe not. Now repeat the same procedure with cells **C65:C67**, **C69:C71**, and **D61:D63**. When finished, change the 9th entry in cell **D63** from 1 to 2 (...1,1,1... to ...1,2,1...). Save it, and, if the program runs, give thanks.

ACKNOWLEDGMENTS

The author thanks Alex Blum, Dan Kile, Cathy Rubin, and Howard Taylor for reviewing this manual. This program was partly developed under a Cooperative Research and Development Agreement (CRADA) between Texaco (now Chevron) and the USGS, and Douglas McCarty is thanked for his support and encouragement.

RUNNING ROCKJOCK

After saving the newly installed program, paste an XRD pattern (5 to 65 degrees two-theta with 0.02 steps and 2 seconds count time per step) for a sample into column D in the Input sheet. The intensities should start in cell **D2**, with the sample name in cell **D1**. For practice, use the French healing clay pattern that currently is in column D, or use the Reynolds Cup patterns that are stored in the Reynolds Cup sheet.

In order to use intensities from an X-ray diffraction system, the intensities must be converted into an Excel worksheet format. For instruments using Jade software, the X-ray files are converted into text files using Jade, and then the text files are opened using Microsoft Excel by choosing **Open** from the Excel **File** menu, and then by choosing the text file that is to be opened. The **Text Import Wizard** box then appears. Choose the **Delimited** option; click **Next**; choose the **Delimiter Space**; and then click **Finish**. The intensities, which should start at 5 degrees two-theta, now can be copied and pasted into RockJock.

Select whether the mineral is present or not by entering a **1** or a **0** into column H next to the mineral's name on the Input sheet. A limit of 40 minerals may be selected to analyze at one time. It also is possible to select how the mineral will be reported by changing the values in column J (for a non-clay enter **2**; for a clay enter **3**; or for no report enter **1**). Minerals also can be chosen to undergo AutoShift by entering a 1 in column I, as will be discussed below. Check on the Full Pattern sheet that cells **C6** to **C47** are set to zero. These cells shift the standard patterns in steps of 0.02 degrees two-theta, and can be set to zero automatically by entering **-1** in cell **B13** of the Input sheet, and by starting the program (enter the number for any option in cell **B21**, and click the **Start** button).

To analyze a single sample after having chosen the minerals present, set cells **B11**, **B13**, **B15** and **B17** to **0**, and **B21** to **2**. Press the **Start** button. The weight percents will appear automatically in the Result sheet at the end of the calculation. The total may differ from 100 percent by plus or minus 6 percent or more, because each mineral is analyzed separately, and there are small, unavoidable inaccuracies due to sample preparation (especially due to inhomogeneous mixing of zincite and sample) and to variability in the chemistry, orientation and

microstructure of the minerals. Weight percents for the earlier Reynolds Cup samples (stored in the Reynolds Cup sheet) may total to considerably more than 100% because they were prepared and X-rayed differently than the recommendations given here, and therefore do not perfectly fit the standards currently found in the program. However, accurate results are achieved for these samples by normalization to 100% (see Appendix 10).

After the calculation, check the graphs in the Full Pattern sheet to see the goodness of fit between the calculated and measured X-ray intensities. The red, calculated pattern should match the blue, measured pattern. If some peaks are not accounted for, more minerals may have to be chosen present in column H of the Input sheet, or the intensities of one or more of the standard XRD patterns may have to be shifted (discussed in the following paragraph). The two-theta angle for a peak can be found by pointing the mouse arrow to the peak maximum. The Common Lines sheet (Brown and Brindley, 1980) is helpful for identifying XRD peaks for common minerals. Calculations of Bragg's Law for converting two-theta angles into d-spacings, and vice versa, also can be found in this sheet.

Due to isomorphous substitutions, peak positions may vary for the same mineral between the standard mineral and the mineral in the sample. Peak positions for individual standard minerals can be shifted right or left by entering a plus or a minus whole number into the cells with the red zeros (in column C of the Full Pattern sheet), which are adjacent to the minerals to be adjusted. A minimum value for the degree of fit in cell **E1** of the Full Pattern sheet can be used as an indication of how far to shift the patterns. Once the peak positions have been adjusted, the program can be run again. This shift also can be accomplished automatically by entering a **1** in cell **B13**, and by indicating which minerals are to be shifted in column I of the Input sheet. Before running a new sample, be sure to check that all of the shift cells in the Full Pattern sheet (in column C) have been returned to zero (enter **-1** in cell **B13** in the Input sheet and start the program to return them to zero automatically).

X-ray patterns of artificial mixtures that were used in an international quantitative analysis competition, the Reynolds Cup, are included with the program (see the Reynolds Cup sheet in the program and Appendix 10 in this manual). The 2002 Reynolds Cup samples (RC-

AR1, RC-AR2, RC-AR3) require a peak shift of +12 for siderite, because this mineral has more Mg than does the program's standard. This shift can be done automatically by setting Input sheet cell **B13** to **1**, and cell **I24** to **1**.

USING THE AUTOMATIC MODE

RockJock can analyze a group of similar XRD patterns in one continuous run of the program, using a single set of mineral standards. Although analysis time for each pattern may be long, the program can run for about 9 hours (32,000 seconds, which is the maximum time allowed in the Solver, although sometimes it runs longer) without further input, at which time a **Continue** button that appears on the screen may have to be clicked to continue the analysis.

Enter the XRD patterns into the Auto XRD sheet in the columns that are indicated in this sheet. In the Input sheet, set cell **B11** to the number of XRD patterns to be analyzed; set the minerals present in column H; set cell **B21** to **2**; and click the **Start** button. At the end of the calculation, the results are saved automatically (see cell **L29** in the Input sheet), and the results themselves are in the Auto Results sheet. Graphs for the analysis of each sample can be studied in the Auto Graph sheet by entering the analysis number of the pattern (1, 2, 3, etc.) into cell **A2**. The analysis number of the patterns can be found in the top row of the Auto Results sheet. Individual patterns for standard minerals in the Auto Graph sheet can be enhanced for study by entering a value >1 into column M of this sheet.

The Auto Graph sheet can be copied and saved separately as a record of the analyses. To do this, click on the Auto Graph tab near the bottom of the screen to select this sheet. Under the **Edit** menu, select **Move or Copy Sheet**. Under **To Book** select **(new book)**, and check the **Create a Copy** box. Click the **OK** button. When the new worksheet is ready, under the **File** menu, choose **Save as**, and give the worksheet a name with an .xls extension (e.g., Yukon.xls). The Auto Results sheet also can be saved as a part of the new workbook in a similar manner.

USING THE MANUAL MODE

The Input sheet in RockJock can be used to find XRD peak positions, integrated peak intensities, and integral peak breadths. To do this, enter the XRD pattern into Column D in the Input sheet. Set the start angle, step size, and radiation wavelength in cells **B5**, **B7** and **B9**. Set cell **B21** either to **0** or to **1**, depending on whether the sample has a ZnO internal standard. Next set the angles in cells **C4** and **C6** to bracket the minimums of the peak to be measured. Set cells **C8** and **C10** to either **0** or **1**. If zeros are entered, the peak will be picked between the values entered into cells **C4** and **C6**. If ones are entered, the peak will be picked from minimum intensities on either side of the peak. Next set the background removal option in cell **C13**. Entering a **0** does not remove background, and this is the option selected automatically during quantitative analysis. Entering **1** or **2** causes the background to be picked from the minimum on the left or right side of the peak, respectively. Entering **3** causes the background to be picked from a line drawn between the minimums on the left and right sides of the peaks. Entering **4** causes the background to be selected from the pattern minimum (between 6 and 64 degrees two theta). After either **0** or **1** is entered into cell **B21** and the program is started, the manner in which the background was determined is drawn on the chart in the Input sheet. The results, which include the position of the peak's maximum intensity, the analytical range for the peak, the peak's maximum intensity, the positions of the peak's minimums, the peak's integrated intensity, and the peak's integral peak breadth, appear in column A.

SAMPLE PREPARATION AND ANALYSIS

Samples and standards should be prepared according to a method modified from that reported in Srodon and others (2001). It is important that these instructions be followed closely. A sample weight of 1.000 g is passed through a 400 to 500 μm sieve, mixed with 0.111 g of ZnO, and ground with about 4 ml of methanol in a McCrone micronizing mill (Appendix 9) for 5 minutes (use corundum or zirconium grinding elements). The mixture then is dried at about 85° C and sieved again two to three times to insure mixing. The sample plus zincite mixture usually can be passed through the sieve using a relatively stiff brush, but hard samples may have to be hand ground first. The mixture then is side packed into an XRD holder against frosted glass (obtained from Ward's Natural Science; Appendix 9) by tapping the holder on a hard surface. It is important that the ground, dried and sieved mixture be thoroughly mixed (separation of zincite occurs on drying), and that a representative sample of the sample plus zincite mixture be packed into the holder. Samples should be X-rayed from 5 to 65 degrees two-theta using Cu K-alpha radiation, with a step size of 0.02 degrees two theta, and a count time of two seconds per step when using a scintillation counter. Patterns that have been run using a radiation wavelength other than Cu K-alpha need to be converted into this radiation wavelength before being entered into the Input sheet. Such patterns can be converted by pasting them into column B in the Wavelength Conversion sheet in the RockJock program. Note that the converted pattern needs to span a minimum two-theta range from 5 to 65 degrees. Be sure that the Analysis ToolPak is installed in the Wavelength Conversion sheet, as is described in the sheet. This sheet also can be used to change the step size of a pattern from a smaller to a larger size.

Samples can be run without an internal zincite standard. For this standardless analysis, approximately 1 g samples are ground as described above without adding ZnO, and option 3 is entered into cell **B21** of the Input sheet. In addition, the Shifter sheet needs to be changed from shifts against ZnO to shifts against quartz (enter **3** in cell **B8** of the Shifter sheet), which will be present naturally in most samples, to no shift (enter **4** in cell **B8**), or to shifts against another position standard (enter the standard's XRD pattern into column J of the Shifter sheet, enter **5** in cell **B8**, and enter the two-theta angles that encompass the position standard peak in cells

B13:B14). Standardless analysis is normalized automatically to 100 percent. Therefore, there is no independent check as to whether or not all minerals present in the sample have been included in the analysis. Otherwise, the two types of analysis should give comparable results.

ENTERING NEW MINERAL STANDARDS INTO THE PROGRAM

The mineral standards that are now in the program have been run on a Siemens D-500 X-ray diffractometer with the following experimental setup for the X-ray beam: X-ray tube (Cu), 1 degree slit, soller slits, 1 degree slit, sample, 1 degree slit, no filter, 0.05 degree slit, graphite monochromator, 0.6 degree slit, scintillation detector. For the most accurate determinations, a replacement set of mineral standards (see below) should be developed by the user; however, mineral standards in the current program provide an immediate opportunity for practice and give adequate results for most purposes. Artificial mineral mixtures can be used to test the accuracy of the current mineral standards. It is important to test the automatic background correction when using the current program's mineral standards with XRD patterns from your instrument to see if this correction is necessary (set cell **B15** in the Input sheet to **1**; see below).

Table 1. Biases for 2002 Reynolds Cup samples run on different diffractometers (1, 2 and 3) analyzed using standards run on diffractometer 1 (Siemens D500). Results were calculated with an earlier version of RockJock.

Sample:	RC-AR1			RC-AR2			RC-AR3		
Diffractometer:	1	2	3	1	2	3	1	2	3
Bias:	6.8	7.8	13.7	9.6	15.0	13.9	13.3	11.8	26.6

Good results have been obtained thus far, based on limited data, by analyzing samples X-rayed on different machines using the Siemens-generated intensities for mineral standards that are currently stored in the program (table 1). The analyses reported in table 1 were run in a previous version of the RockJock program (RockJock.xls rather than the current RkJock6.xls). The best determinations were those that used standards that were X-rayed with the same instrument that

performed the measurement (Siemens D500; columns labeled “1” in table 1), yielding a total bias of 29.7 for the three samples. Diffractometers labeled 2 and 3 gave total biases of 34.6, and 54.2, respectively, indicating that, although it would be best to develop individualized standards, acceptable analyses may be made with the standard set that is presently in the program. Diffractometer 3 used a different type of detector (possibly defective) than that employed for diffractometers 1 and 2. It may be necessary to use a slit system that is similar to the experimental setup described in the first paragraph of this section.

If there are problems with background (for example, if the background from your instrument is different than the background for the stored standards), one can let the background be a part of the Solver solution by setting cell **B15** in the Input sheet to **1**. If your zincite pattern is subtly different from the stored pattern, artificial mixtures (e.g., 0.5 g each of kaolinite and quartz, plus 0.111 g ZnO) can be analyzed to test the zincite standard. If the RockJock values are consistently different from 100 percent, then the ZnO correction factor can be adjusted in the Result sheet, cell **N2**. For example, if you always have a total around 93% (46.5 % quartz + 46.5 % kaolinite) rather than 100 percent, then cell **N2** in the Result sheet can be set to 1.075 (e.g., $100/93 = 1.075$). A new zincite standard also can be entered into the program by pasting the two-theta justified zincite pattern into column **L** of the Full Pattern sheet, and by entering the integrated intensity for this pattern into cell **D3** of the Standards sheet. This intensity can be determined using the Input sheet, as is described below.

If new standards are to be developed:

1. First enter a pattern (5 to 65 degrees two-theta with 0.02 degree steps and 5 seconds count time per step) for pure ZnO (obtained from Fisher Scientific, Certified A.C.S., Dry Process; 1 g ground in a McCrone mill with 4 ml of methanol) into column **D** of the Input sheet, and plot it by entering **1** in cell **B21** and clicking the **Start** button. Next copy the modified pattern, which has automatically been smoothed (using a moving average of 3) and shifted with respect to the ZnO standard currently in the program, from cells **N2:N3002** in the Input sheet, and paste it into column **L** of the Full Pattern sheet (under the **Edit** menu, choose **Paste Special, Values**). Fill in zero cells at either end of the pattern with adjacent values. This pattern will

have been shifted automatically during plotting so that the XRD peaks have “true” positions when compared with published values (e.g., check that the 110 zincite reflection maximum is at 56.64 degrees two-theta for Cu K-alpha radiation). Use exactly this same ZnO chemical in all analyses.

2. Next determine the ZnO integrated intensity from 20 to 65 degrees two theta, as follows. Enter a position-corrected but not smoothed ZnO pattern into column D on the Input sheet (e.g., if necessary, shift the pattern manually), with intensities starting at 5 degrees two-theta in cell **D2**. Set cells **C4 = 20**, **C6 = 65**, and cells **C8**, **C10**, and **C13** to 0. Set cells **B11**, **B13**, **B15** and **B17** to **0** and cell **B21** to **1**, click the **Start** button, and record the integrated intensity (cell **A15** in the Input sheet). Enter this integrated intensity into the Standards sheet, cell, and save the program.

3. According to the instructions in Srodon and others (2001), two X-ray patterns (with at least 5 seconds count time per step) are prepared for each mineral standard, one for the pure mineral (about 1 g), and the other for a mixture of the pure mineral (0.400 g) with either a clay (0.400 g pure kaolinite) if the mineral is a non-clay, or with a non-clay (0.400 g pure quartz) if the mineral is a clay, plus the internal standard (0.200 g of ZnO). The mixture is ground in a McCrone mill for at least 5 minutes in 4 ml of methanol, except for pure clay standards, which may be ground for 20 minutes in 4 ml of hexane to ensure random orientation.

4. The pattern of the pure mineral needs to be justified in two-theta space with respect to the pattern that contains the ZnO internal standard. To do this, paste the XRD pattern for the ZnO-containing standard mineral into column D in the Input sheet. Enter **1** into cell **B21** and click the **Start** button. This operation will plot the XRD pattern shifted against the position of the ZnO internal standard. Choose a mineral XRD peak (not a ZnO peak, or the kaolinite or quartz additions), and determine its position by entering angles that are on either side of the peak into cells **C4** and **C6**. Push the **Start** button again. The two-theta peak position for this peak will appear in cell **A4**. Note this position. Now enter the X-ray intensities for the pure mineral into column D. Set cell **B21** to **0** and click the **Start** button. (The number 1 is not entered into this cell because the pure mineral does not have an internal ZnO standard against which to shift

the pattern.) The peak position for the pure mineral now appears in cell **A4**. This position should be the same as the angle noted for the ZnO-containing sample. If it is not the same, then manually shift the pattern of the pure mineral in a separate Excel worksheet by the number of steps necessary to make the peak position found for the pure mineral the same as that found for the ZnO-containing sample. Remove or insert intensities, having approximately the same value as adjacent intensities, at the top or bottom of the X-ray intensity data in order to have the shifted pattern vary from 5 to 65 degrees.

5. Next measure the integrated XRD intensities for the pure mineral, as was done for the ZnO pattern, and as is repeated here. Paste the shifted XRD pattern (see item 4 above) for the pure mineral into column D on the Input sheet. Set cells **C4**, **C6**, **C8**, **C10**, and **C13** to **20**, **65**, **0**, **0**, and **0**, respectively. Click the Start button, and record the integrated intensity (cell **A15**).

6. The manually shifted pattern for the pure mineral and the integrated intensities now must be entered into the Standards sheet. The smoothed, manually shifted pattern for the pure mineral standard first is copied from cells **N2:N3002** of the Input sheet. Click the tab for the Standards sheet. Enter the shifted XRD pattern for the pure standard mineral into the correct column, starting in column M. Note that the position of the mineral in the Standards table is keyed to the column of the mineral's pattern starting in column M. Enter the mineral name into column C, and the integrated intensity into column D. When the program is run, the name of the new standard will appear automatically in column G of the Input sheet.

7. Next measure the mineral intensity factor (MIF), which compares the integrated intensity of the mineral to that of the internal standard. MIF is defined as:

$$MIF = \frac{I_m(\%S)}{I_s(\%M)}, \quad (1)$$

where I_m and I_s are the integrated intensities of the mineral and the ZnO standard, respectively, and %S and %M are the weight percents of the ZnO standard (20 percent) and the mineral (usually 40 percent). The term MIF is defined the same as the reference intensity ratio (RIR) of earlier literature (Snyder and Bish, 1989); but the acronym MIF is preferred here because it is easier to pronounce, and because the standard for the MIF is zincite rather than corundum that

used for RIR. To measure the MIFs, set the “Present?” values in column H of the Input sheet to 1 for the mineral and for the material that the mineral is mixed with (a disordered kaolinite, such as KGa2, is mixed with a non-clay standard, and quartz is mixed with a clay standard). All other settings in column H should be zero, except for cell H73 which is set to 1 to account for corundum contamination during grinding. Set the values in column J as indicated at the tops of the column. The cell in column J should be set either to 2, in which case the mineral is to be reported as a non-clay, or to 3, in which case it is to be reported as a clay mineral. Cell **J73** for corundum should be set to 1 (no report). Do not use the AutoShift option. Set cell **C21** to **0.25** and cell **B21** to **2**. Click the **Start** button. When the calculation is complete, the MIF for the mineral analyses can be calculated, using equation 1, from the integrated intensities given in columns P in the Results sheet. However, the MIF solution also is presented automatically in column T in the Results sheet. Solve for kaolinite and quartz standards first, because these minerals are used in subsequent calculations. The MIF value now should be entered into column E in the Standards sheet in the appropriate cells. The MIFs can be checked by running the zincite-containing pattern again with the new MIFs in the standards table. Remember to set cell **C21** in the Input sheet to **0.25**, because a different zincite sample ratio is used to measure MIFs for mineral standards from that used to prepare normal samples (0.111).

Impure standards also can be used. If, for example, a clay standard contains a quartz impurity, the peaks for quartz in the “pure” pattern of the clay can be removed electronically using the PeakChopper program that accompanies the RockJock program. Its corrected X-ray pattern and integrated intensities from this pattern then are entered into the Standards sheet as described above. The ZnO + quartz spiked clay standard sample then is run as described above, again setting cell **C21** in the Input sheet to **0.25** for the ZnO/sample ratio used with the mineral standards [$0.25 = 0.2 \text{ g ZnO} / (0.4 \text{ g clay} + 0.4 \text{ g quartz})$]. After the calculation, the amount of quartz in the sample can be read in the Result sheet. For example, if the result of the calculation is 58 percent quartz, then the amount of quartz in the original clay sample was 8 percent (58 percent minus the 50 percent quartz added to the clay). In solving for the MIFs in equation 1, recall that the sample as made up contained only 40% of the standard. Thus, $\%M = 40 -$

$(40)(8)/50 = 33.6$, %S = 20, and I_m and I_s can be read in column P. Do not use the automatic solution found in column T in this case. MIFs for mineral standards that contain impurities also can be calculated automatically by filling in the red cells in **AK5** and **AK7** of the Results sheet. Other impurities can be handled in a similar manner. Be sure to return cell **C21** in the Input sheet to its original value [0.111 = g ZnO/(g sample) for a normal sample preparation] before running more samples.

MEASUREMENT ACCURACY

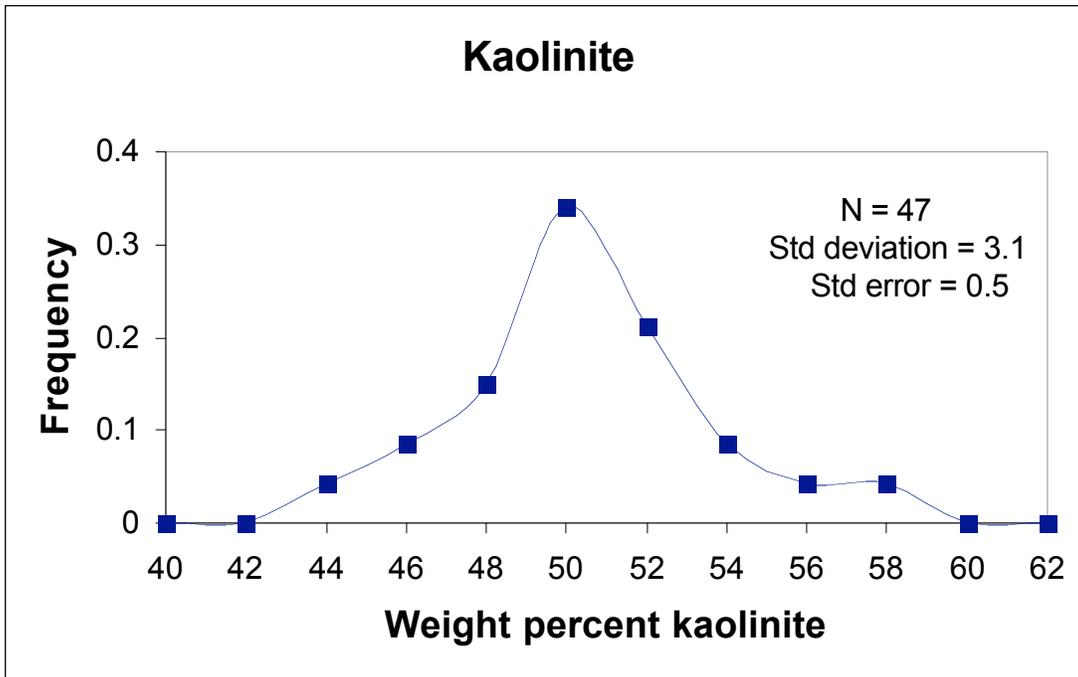
During the process of measuring MIFs for the RockJock program, many measurements were made of the weight percents of kaolinite (KGa2) and quartz mixed 50:50 with a range of other minerals. From these measurements, the standard deviation and standard error at 50 weight percent kaolinite or quartz was calculated (Figure 1). This calculation yields errors for kaolinite or quartz of approximately $\pm 6\%$ (1 standard deviation), or ± 3 weight percent at 50 weight percent of these minerals.

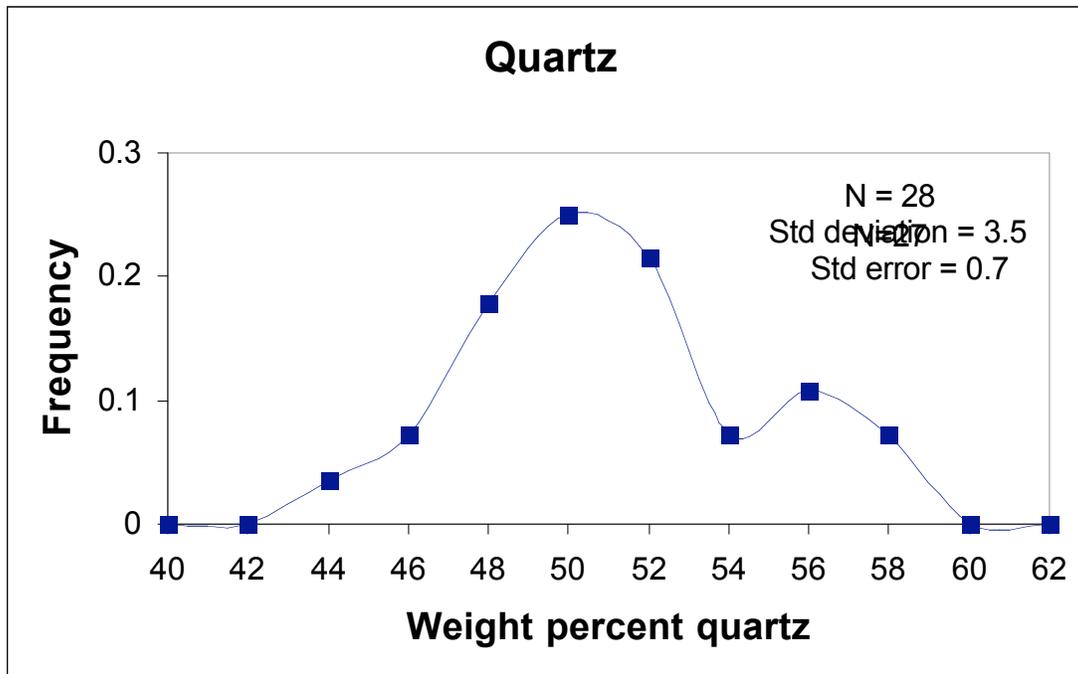
The accuracy of RockJock analyses also can be inferred from analyses of Reynolds Cup samples (Appendix 10). For the 2002 samples (Appendix 10, table 2 and the Reynolds Cup sheet), the combined bias for 3 samples is 35.9, and that for the 2004 samples (table 3) is 27.6, if the results are normalized to 100 % and if similar clays are combined into single categories, as was done during the judging of these contests. Bias is defined as the sum of the absolute difference in weight percents between the true values and the RockJock calculated values. As was mentioned previously, sample preparation, using instructions for a previous version of the program, was not ideal for the present program standards. A leading Rietveld analysis program, with the data reduced in a similar manner to the RockJock data, gives combined biases of more than 85 for each sample set.

The data in tables 2 and 3 also indicate that RockJock is very good at qualitative analysis. All of the phases contained in each contest were entered as being present in each analytical set. The only significant mistakes were in failing to detect 7.0 % ferruginous smectite in sample RC-

AR1 (table 2), and in giving sample RC2-3 3.2 % kaolinite when none was present (table 3). The Rietveld program was not as good at qualitative analysis.

Figure 1. Measurement error for kaolinite and quartz measured for samples containing 50 weight percent of these minerals.





USEFUL TIPS

To stop the calculation at any time, press the Escape (Esc) key. This key also can be pressed to study calculation progress during Solver solutions. To update the graphs during the Solver calculation, press the Esc key, and then click the Continue button that appears on the screen.

One aims for a degree of fit that is <0.100.

Pointing to a pattern in the graphs will bring up the mineral name associated with that pattern and the two-theta angle.

AutoShift works better for fewer minerals. Some phases which contain isomorphous substitutions may require AutoShift (e.g., illite), whereas others which are relatively pure (e.g., quartz) do not, although, for an unknown reason, quartz sometimes is shifted by one step. Such small shifts usually do not significantly affect the results of the calculation.

If a chart is selected on a sheet subsequent to the Input sheet, the program will not run, and a Macro error message will appear. To fix this problem, go to the sheet, click on any cell to unselect the chart, and start the program again.

It often is difficult to distinguish smectite from illite, so the weight percentages of these minerals could be added together when reported. Another technique has been developed (PVP surface area technique; Blum and Eberl, 2004) to distinguish between smectite and illite with the aid of RockJock and MudMaster calculations.

Fe-smectite is a common phase in sediments, but it can give a false-positive reading in RockJock. Be sure that your sample contains smectite before selecting this mineral by studying the low-angle region of the pattern. Treating oriented samples with ethylene glycol is especially helpful for uncovering the presence of smectite. Other patterns that do not have a well defined series of XRD peaks (e.g., volcanic ash, peat, etc.) also may give false positive readings.

Check the pattern's low angle region to see if minerals that have peaks in this region should be included in the analysis. Some of these minerals are: smectite (6 to 8 degrees two theta), illite and mica (8.8 degrees), chlorite (6.2 degrees), amphibole (10.5 degrees), gypsum (11.6 degrees), bassanite (14.8 degrees), alunite (17.9 degrees), etc. If these peaks are not found, then the mineral should not be included in the analysis, although the program often can solve this problem automatically.

If there is a question as to which feldspar is in a sample, select all of the feldspars the first time through, and then eliminate those that are less than 1 weight percent for the final calculation. The same strategy works, for example, with chlorite, smectite and illite.

Several different regions for analysis can be set in the Full Pattern sheet, cells **B4** through **B9**. This option is useful if a mineral has a distinctive peak outside the normal analysis range of 20 to 65 degrees. For example, gypsum has a strong peak at 11.6 degrees two-theta (Cu radiation). In this case, cells **B4** and **B5** have the normal values of 20 and 65, and cells **B6** and **B7** can be set to **11** and **12** to include this gypsum peak in the analysis. Low-angle clay peaks, especially those for illite and chlorite, generally are too variable to be useful in this type of approach. Likewise, some peaks, such as the most intense quartz peak at 26.64 degrees two theta, can be excluded from analysis by manipulating cells **B4** through **B9** in the Full Pattern sheet and cell **L37** in the Input sheet. For example, to exclude the strongest quartz peak, set cell **L38** in the Input sheet to **25**, and cells **B6:B7** in the Full Pattern sheet to **27** and **65**, respectively.

After an initial solution for a sample, the answer can sometimes be improved by shifting the mineral standards with respect to two-theta to minimize the degree of fit value in cell **E1** in the Full Pattern sheet. Standards can be shifted manually by entering positive or negative whole numbers into the appropriate cells in column C. The shifting also can be automated by entering a **1** into cell **B13** of the Input sheet, and by choosing the minerals to be shifted in column I of the Input sheet. Calculations that include automatic shifts are slower.

The 060 reflections for clay minerals generally shift towards smaller two-theta angles with increasing iron content. Similarly, the dominant dolomite peak shifts to smaller angles with increasing iron content. Increasing magnesium content causes the most intense calcite peak to shift towards larger angles.

If you develop your own standards, be sure to purchase a large quantity of ZnO, all from the same chemical lot, to use as a constant internal standard through the years.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) may be converted into bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) during grinding in alcohol. To prepare a gypsum standard, grind selenite crystals, which often do not convert in alcohol, or grind in water. To prepare a bassanite standard, heat gypsum to 150 C overnight. An equation for correcting gypsum weight percents for bassanite conversion during grinding is located in the Results sheet.

During sample preparation, after grinding in methanol and drying the sample, be sure to pass all of the sample mixture through the sieve several times before side packing it into the holders. This procedure insures that the ZnO internal standard, which may segregate during drying, is uniformly mixed with the sample.

Standardless analyses always sum to 100 percent, but this does not mean that these results are better than those run with an internal zincite standard. Both methods should give the same answer if all of the minerals present in a sample have been chosen to be present in the program.

A common reason for analyses $\gg 100\%$ is insufficient homogeneity in the analyzed mixture for the zincite internal standard. Also, preferred orientation of an abundant mineral in the sample can do the same.

Large amounts of pyrite will cause the Shifter to find the wrong peak if option 1 is used in the Shifter sheet. In this case, change cell **B8** in the Shifter sheet to option 2.

Enter corundum (McCrone) into every analysis to correct for contamination from grinding elements, but do not report it as a part of the analysis. This is done by entering 1's into cells **H73** and **J73** in the Input sheet.

Excel is not optimized to run on Macintosh system X, and therefore RockJock normally will run faster on a PC. Excel 2008 for the Mac can not run RockJock because this version of Excel does not contain the Solver.

The McCrone grinding vials can be prevented from leaking by cutting a Viton rubber disk to fit inside the upper screw cap.

When entering data always use **COPY** and **PASTE**. Never use **CUT** and **PASTE**. The latter command may change references in related cells. When pasting, under the **EDIT** menu, choose **PASTE SPECIAL, VALUES**. This routine insures that only the numbers are pasted, and not equations in the copied cells.

The program sometimes crashes, especially when run under the Xp system. It rarely or never crashes during a calculation, but too often crashes when the contents of a cell are changed after a calculation. If this happens, do not try to recover the program, because a cell that directs the Solver has been corrupted. When the crash alert appears on the screen, uncheck the box that says **Recover my work and restart Excel**, and click the **Don't Send** button. Then restart the program. If you mistakenly forget to uncheck the box, then simultaneously type the **CONTROL-ALT-DELETE** keys to interrupt the saving process, click **Task Manager, Applications, End Task, End Now, Don't Send**, then exit Excel, and restart the RkJock6.xls program. Excel 2006 may crash in this manner every time when run in the Xp system, and, therefore, it saves time and serenity simply to exit Excel after a calculation and restart the program. Excel 2007 does not crash often.

It would be good to experiment with the Auto Background correction (enter **1** in cell **B15** of the Input sheet) to see if this option is necessary to use with your experimental setup.

If you use the standards that are currently in the program, run artificial mixtures to check that RockJock is giving good answers for your experimental setup.

For Mac users, it may be necessary to close all Excel worksheets except RockJock to get the program to run.

The Solver fits the measured pattern with the standard patterns from 19 to 65 degrees two theta. However, for historical reasons, the when standards are entered into the program their integrated intensities are measured from 20 to 65 degrees two theta.

The Sample Chem sheet has been added recently to calculate an approximate chemistry for a sample from its quantitative mineralogy. Directions for its use are located in the sheet itself.

REFERENCES

- Blum, A.E. and Eberl, D.D., 2003, Measurement of clay surface area by polyvinylpyrrolidone (PVP) sorption: A new method for quantifying illite and smectite abundance: Unpublished written communication.
- Brown, G. and Brindley, G.W., 1980, X-ray diffraction procedures for clay mineral identification, *chap. 5* of Brindley, G.W. and Brown, G., eds., *Crystal structures of clay minerals and their X-ray identification*: Mineralogical Society, London, p. 305-359.
- Chipera, S.J. and Bish, D.L., 2002, FULLPAT: a full pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns: *Journal of Applied Crystallography*, v. 35, p. 744-749.
- Chung, F.H., 1974, Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix flushing method for quantitative multicomponent analysis: *Journal of Applied Crystallography*, v. 7, p. 519-525.
- McCarty, D.K., 2002, Quantitative mineral analysis of clay-bearing mixtures: The “Reynolds Cup” contest. *Committee on Powder Diffraction Newsletter*, 27, June 2002, p. 12-16, <http://www.iucr.org/iucr-top/comm/cpd/Newsletters>.
- Moore, D.M. and Reynolds, R.C., Jr., 1997, *X-ray diffraction and the identification and analysis of clay minerals*: Oxford, Oxford University Press, 378 p.
- Omotoso, O., McCarty, D. K., Hillier, S., and Kleeberg, R., 2006, Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds Cup contest: *Clays and Clay Minerals*, v. 54, p. 748-760.
- Smith, D.K., Johnson, G.G., Jr., Scheible, W., Wims, A.M., Johnson, J.L., and Ullmann, G., 1987, Quantitative X-ray powder diffraction method using the full diffraction pattern: *Powder Diffraction*, v. 2, p. 73-77.
- Snyder, R.L. and Bish, D.L., 1989, Quantitative analysis, *in*, Bish, D.L. and Post, J.E., eds., *Modern powder diffraction*: Mineralogical Society of America *Reviews in Mineralogy*, v. 20, p. 101-144.

Srodon, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., and Eberl, D.D., 2001, Quantitative X-ray diffraction analysis of clay-bearing rocks from random preparations: *Clays and Clay Minerals*, v. 49, p. 514-528.

APPENDIX 1: INPUT SHEET INPUTS AND OUTPUTS

Summary of inputs for the Input sheet.

<u>Input</u>	<u>Cell</u>	<u>Value</u>	<u>Comments</u>
Sample name and XRD intensities	D1 and following	Name and intensities	Enter sample name in cell D1, and sample XRD intensities in cells D2 through D3002.
Sample name	B3	None	<u>Do not enter a name.</u> Name is entered automatically from cell D1 when program is run.
Starting angle for X-ray intensities	B5	Usually 5 degrees	Should be 5 degrees or smaller for quantitative analysis.
Step size	B7	0.02	Must use 0.02 for quantitative analysis unless all of the standards are changed to a different step size.
Radiation wavelength	B9	1.5418	Program is currently set up for Cu K-alpha radiation. Some changes in the program will have to be made to use other wavelengths.
Auto analysis?	B11	0 or positive whole number	Enter the number of patterns that were entered into the Auto XRD sheet. A zero leads to analysis of the single pattern that was entered into column D of the Input sheet.

AutoShift standard patterns?	B13	-1 = set all to zero; 0 = keep present shifts; 1 = shift	Shifts the standard patterns with respect to two-theta during the Solver solution to account for isomorphous substitutions, etc. Slows the calculation.
Auto background correction?	B15	1 = yes	Causes the background to be a part of the Solver solution. Enter 1 if the samples are run on different instrument than standards or to correct for Fe fluorescence.
Collect results or reset defaults	B17	0, 1 or 2	0 turns this feature off. 1 pastes results from Full Pattern sheet into Results sheet. 2 returns inputs to default values.
Type of analysis	B21	0 through 3	Performs the type of action indicated on the Input sheet in cells B20 and B21. 0 = plots sample XRD pattern with no shift; 1 = plots pattern with shift against internal standard (position standard is set in Shifter sheet, usually ZnO); 2 = Full pattern analysis; 3 = Standardless analysis.
Start angle	C4	Angle	Starting angle for manual peak analysis
End angle	C6	Angle >C4	Ending angle for manual peak analysis.
Auto pick left background?	C8	0 = no; 1 = yes	If 1, finds minimum on left side of peak. Otherwise the value used is that entered in cell C4.

Auto pick right background?	C10	0 = no; 1 = yes	If 1, finds minimum on right side of peak. Otherwise, the value used is that entered in cell C6.
Background correction type	C13	0 through 4	Removes background according to description in cells B11 and B12
Solver convergence	C18	1 to 3	Specifies value at which Solver will be satisfied that it has found a solution in comparing the calculated to the measured XRD pattern.
ZnO/sample ratio	C21	Wt ZnO/wt sample	Normally 0.111 (0.111g ZnO/1g std), but use 0.25 for standards [for standards, wt.ZnO/(wt standard + wt kao or qtz) = 0.6g/(1.2g + 1.2g)].
Watch calculation?	L25	1 = yes	Turns on screen during calculation. Slows calculation.
Smooth Power	L27	Enter whole number	Smooths measured XRD pattern, with larger number causing more smoothing. Enter 1.
Auto save after auto analysis?	L29	Enter 0, 1, or 2.	Saves program and results after analysis run. Enter 2.
Number of iterations for AutoShift	L31	Enter whole number.	Causes the calculation to iterate the number of times entered when solving for shifts. Enter 1.
Progressive AutoShift?	L33	Enter 0 or 1	If 1 is entered, shifts are not erased after each auto analysis sample. Enter 0.
Print each result?	L35	1 = yes	Causes each result during auto analysis to be printed. Enter 0.

Starting and ending	L37	Enter 20 and	Indicates what part of the pattern should be analyzed during full pattern analysis.
two theta for full	&	65	
pattern analysis.	L38		

Summary of outputs for Input sheet.

<u>Output</u>	<u>Cell</u>	<u>Value</u>	<u>Comments</u>
Position of XRD peak maximum	A4 and A5	Gives two-theta value and d-spacing of chosen peak	Peak is chosen as the maximum intensity between the two-theta values entered into cells C4 and C6.
Analysis range	A7 and A8	Chosen two-theta values for peak analysis	Gives the analysis range chosen for the peak in cells C4 and C6.
Maximum intensity of peak	A10	Intensity	Gives maximum intensity of chosen XRD peak.
Angles for tail minimums	A12 and A13	2-theta for left and right sides of peak	If cells C8 and C10 = 1, then the two theta values are the minimum values for the peak. Otherwise, they are the values entered into cells C4 and C6.
Integrated intensity	A15	Integrated peak intensity	Integrated intensity between angles given in cells A12 and A13.
Integral peak breadth	A17	Integrated/max intensity	Peak intensities are integrated between two-theta values found in cells A12 and A13.

APPENDIX 2: SHIFTER SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Choose internal two-theta position standard	B8	Enter 1 through 5, depending on the position standard chosen.	Normally use 56 and 57 degrees to find top of 110 ZnO peak. Sometimes the sample will interfere with this peak (especially true for pyrite standard), in which case, the 103 ZnO peak should be used. Quartz or no shift should be used for standardless analysis.
Set angles	B13 & B14	6 to 64 degrees	Sets angles for alternative position standard that was entered into column J. Such a standard can be taken from the patterns in the Standards sheet.
Steps for shifting sample	B16	Positive or negative whole number	This cell automatically adjusts when program is run. However, the pattern also can be shifted manually by entering a positive or negative whole number into this cell, and turning off shifter.

APPENDIX 3: FULL PATTERN SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Choose two-theta regions for Solver analysis	B4 to B9	Usually 20-65 degrees.	By changing cells B6 to B9, other two-theta regions also can be entered into the analysis. For example, low-angle peaks can be included in the analysis, or certain peaks can be excluded, in cooperation with cells M30:M35 of the Input sheet.
Shift standard patterns	C8 to C47	Positive or negative whole number	Shifts standard patterns with respect to two-theta. After initial Solver solution, shift patterns manually using these cells to minimize the degree of fit value in cell E1. Then run the program again. Cells C6 and C7 shift the measured pattern and the ZnO pattern, respectively, and, therefore, always should be set to 0.
Standard pattern factors	E7 to E47	Decimal	These cells are varied automatically during the Solver solution, and are multiplied by the intensities of the stored standard XRD patterns. But they also can be manipulated manually to change the proportions of the standard patterns in the graphs.
Bragg's Law	D50 to D59	Enter d-spacing or two-theta	To calculate XRD peak positions or spacings.

Solver model C60: Solver Controls Solver settings for Full Pattern and shift
 C71; setup analyses, respectively.
 D60:
 D63

APPENDIX 4: RESULT SHEET INPUTS AND OUTPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Calculation time	A1 to A6	Time and date	Gives calculation time.
Weight percent minerals, shifts, and type of analysis	Cols. A to D	Weight percents, steps shifted, and option run	The weight percent total should be approximately 100 percent. Normalized values also are presented.
Warnings	Col G	Normally hidden text	Warns about non-standard settings in the program.
Weight percents from full pattern analysis	Col. J	Percents	
ZnO sample ratio	P1	Normally 0.111	(Weight ZnO)/(weight sample). This value is set in cell C21 of the Input sheet.
ZnO correction factor	N2	Set to 1.	Method for normalizing results when using different sources of ZnO (see manual).
Corrected ZnO/sample ratio	P2	Equals O2 x Q1	It is an output, so do not change it.
Automatic calculation of MIFs	Cols. T and AK	Calculates MIFs for standards	Standards need to be prepared correctly. See standards section in this manual. AK is for impure standards.

APPENDIX 5: STANDARDS SHEET INPUTS

<u>Input or Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Standards table	Col D to Col G	Enter information for standards	Enter information about the standards, as is described in this manual, including sample name, integrated intensities for Full Pattern (20-65 degrees), MIFs, and sample descriptions.
Intensities for pure standards	Start in Col M	XRD intensities for standards	Start at 5 degrees and use 0.02 degree steps. Do not remove background. Note that column in which intensities are entered is related to position in Standards table (see above). Standards need to be shifted to their true two-theta value with respect to the 110 zincite peak.

APPENDIX 6: AUTO XRD SHEET INPUTS

<u>Input</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Intensities for samples to be analyzed in series of analyses.	Start in Col C	XRD intensities	Start at 5 degrees and use 0.02 degree steps. Put the sample name in the first row, followed by intensities. Set value of cell B11 in the Input sheet to the number of patterns to be analyzed that are contained in the Auto XRD sheet.

APPENDIX 7: AUTO RESULTS SHEET OUTPUTS

<u>Output</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Time for calculation	A1 to A6	Time and dates	Gives starting and ending times, and dates for automatic calculation.
Results of Auto calculation	Start in Col C	Weight percents	Pattern number in row 1 is used to identify result in Auto Graph sheet. Results are completely erased if new Auto calculation is started. Look farther down in sheet for normalized weight percents and shifts.

APPENDIX 8: AUTO GRAPH SHEET INPUTS

<u>Input</u>	<u>Cells</u>	<u>Value</u>	<u>Comments</u>
Pattern number	A2	Whole number	Entering pattern number produces graphs and weight percents for each auto analysis. Pattern number corresponds with number for result shown in Auto Results sheet. This page can be saved separately, as is described in the 'Using the Automatic Mode' section of the instruction manual.
Multiplier	Col. M	Number = or > 1	Multiplies standard pattern by the value entered. Good for identifying trace phases.

APPENDIX 9: RESOURCES FOR QUANTITATIVE MINERAL ANALYSIS

Sources of standard minerals:

Source Clay Minerals Repository
Purdue University
1150 LILY Hall
West Lafayette, IN 47907-1150 USA
Voice: (765) 494 4258 FAX: (765) 496 2926
E-mail: sourceclays@purdue.edu
Web: <http://cms.lanl.gov> (follow links to Source Clays Project)

Ward's Natural Science
5100 West Henrietta Road
P.O. Box 92912
Rochester, NY 14692-9012 USA
Voice: 1-800-962-2660 FAX: 716-334-6174
International calls: 716-334-6174
Web: http://www.wardsci.com/online_catalog/

Excalibur Mineral Corp.
1000 North Division Street
Peekskill, NY 10566 USA
Phone: (914) 739-1134
Email: info@excaliburmineral.com

Trinity Mineral Company
John Veevaert
P.O. Box 2182 Weaverville, California 96093-2182 USA
Phone: (530) 623-2040; (888)-689-8402 (Toll Free)
Email: john@trinityminerals.com

David Shannon Minerals
6649 East Rustic Drive
Mesa, Arizona 85215 USA
Phone: (480) 985-0557.

Mineralogical Research Co.
15840 East Alta Vista Way
San Jose, California 95127-1737 USA
Phone: (408) 923-6800

McCrone Micronising Mill:

McCrone Associates
850 Pasquinelli Drive
Westmont, IL 60559 USA
Voice: 800-622-8122; Fax: 630-887-7764
Web: <http://www.mccrone.com/mac/home2.html>

Jade XRD search-match software:

Materials Data
1224 Concannon Blvd.
Livermore, CA 94550 USA
Voice: 925-449-1084; FAX: 925-373-1659
Web: <http://www.materialsdata.com>

Information concerning the Solver:

Frontline Systems Incorporated
Voice: 775-831-0300
Web site: <http://www.solver.com>

Microsoft Excel:

Web site: <http://www.microsoft.com/office/excel/default.asp>

APPENDIX 10: ANALYSES OF REYNOLDS CUP SAMPLES

Table 2. Comparison between true values for artificial mixtures used in the 2002 Reynolds Cup quantitative analysis competition, and those calculated from XRD patterns using Option 2 in the RkJock5.xls program. Reynolds Cup samples prepared by Douglas McCarty. RockJock analyses are normalized to 100 %, and all minerals in the first column were entered into RockJock as present for all three samples. Combined biases are calculated using totals for 2:1 clays, rather than the individual 2:1 clays.

Sample:	RC-AR1		RC-AR2		RC-AR3	
	TRUE	RkJock5	TRUE	RkJock5	TRUE	RkJock5
Quartz	20.0	20.4	40.0	40.4	15.0	15.6
Microcline	9.0	9.2	11.0	10.6	2.0	2.7
Albite	7.0	9.1	9.0	11.5	2.0	2.8
Calcite	5.0	6.0	3.0	3.2	17.0	20.1
Dolomite	3.0	3.2	2.0	2.0	5.0	4.8
Siderite (shift of +12)	3.0	2.4	2.0	1.6	5.0	4.2
Halite	3.0	2.6	2.0	0.6	2.0	1.5
Pyrite	2.0	1.5	3.0	2.1	2.0	1.2
Gypsum	0.0	0.1	0.0	0.1	5.0	1.8
Barite	2.0	2.4	2.0	2.2	2.0	2.4
Kaolinite	9.0	9.7	7.0	7.0	10.0	8.9
Total 2:1 clays	32.0	26.4	15.0	13.8	33.0	33.6
Fe-smectite	7.0	0.0	6.0	4.1	5.0	3.9
Illite 1M	25.0	26.4	9.0	9.7	28.0	29.7
Chlorite	5.0	7.0	4.0	4.8	0.0	0.4
Total	100.0	100.0	100.0	100.0	100.0	100.0
Detailed bias	–	17.0	–	9.9	–	15.4
COMBINED BIAS	–	14.2	–	8.5	–	13.2

Table 3. Comparison for 2004 Reynolds Cup samples. Reynolds Cup samples prepared by Reinhard Kleeberg. RockJock analyses are normalized to 100 %, and all minerals in the first column were entered into RockJock as present for all three samples. Combined biases are calculated using totals for plagioclase, kaolinite group and 2:1 clays rather than the individual minerals in these groups.

Sample:	RC2-1		RC2-2		RC2-3	
Mineral	TRUE	RkJock5	TRUE	RkJock5	TRUE	RkJock5
Quartz	24.8	23.7	45.7	44.1	14.7	13.3
K-feldspar	8.5	10.2	9.2	9.0	2.1	1.8
Plagioclase group	6.5	6.4	10.7	13.1	2.9	4.1
albite	6.5	6.0	4.0	4.3	0.0	0.0
oligoclase	0.0	0.0	6.7	3.3	2.9	2.4
andesine	0.0	0.3	0.0	5.4	0.0	1.7
Calcite	5.0	5.0	0.0	0.0	18.6	19.5
Dolomite	2.0	2.0	0.0	0.1	6.0	6.0
Magnesite	0.0	0.0	0.0	0.0	4.9	4.5
Halite	0.0	0.0	0.0	0.0	1.5	1.0
Pyrite	2.5	1.9	0.0	0.1	0.0	0.0
Anhydrite	0.0	0.0	0.0	0.0	14.6	14.0
Hematite	0.0	0.0	2.5	1.9	0.0	0.0
Anatase	0.1	0.0	1.5	0.2	0.0	0.0
Rutile	0.0	0.0	1.5	1.7	0.0	0.0
Kaolinite group	16.0	17.2	15.4	17.0	0.0	3.2
kaolinite	16.0	17.2	9.9	12.6	0.0	3.2
dickite	0.0	0.0	5.5	4.4	0.0	0.0
Total 2:1 clays	30.1	30.8	10.5	11.1	25.1	23.3
illite 1Mt	10.5	10.9	5.5	4.0	0.0	2.5
I/S mixed layer	10.1	8.8	0.0	3.3	0.0	5.4
montmorillonite	9.5	9.4	0.0	0.0	8.0	2.4
muscovite + illite 2M1	0.0	1.7	5.0	3.8	17.1	13.0
Chlorite	4.5	3.0	3.0	1.7	9.6	9.4
Total	100	100	100	100	100	100
Detailed bias	–	10.5	–	24.3	–	27.4
COMBINED BIAS	–	7.1	–	9.9	–	10.6

Figure 2. The Reynolds Cup trophy, awarded once every two years to the winner of an international quantitative mineral analysis competition (see <http://www.dttg.ethz.ch/reynoldscup2004.html>).



Abstract submitted to the 2002 meeting of The Clay Minerals Society:

HOW I WON THE REYNOLDS CUP*

The Clay Doctor, Dept. of Earth, Wind, Fire and Water Sciences, Clayhead University, 9-10 Big Fat Hen Road, Rockland, BA 00002

I suddenly became interested in minerals at a very young age, when other children began to throw rocks at me. Rocks that contained clay hurt less; so I began to wonder how much kaolinite was in this one, how much galena in that. My father bought me my first X-ray diffractometer when I was 10, and there was no turning back. While other children were reading *Tales from the Crypt Comics*, and later *Hustler Magazine*, I was reading the *X-ray Powder Diffraction Card Files*, memorizing d-spacings. So when Dr. Douglas McCarty from ChevronTexaco sent me the three unknowns that contained mixtures of pure mineral separates, I was ready to analyze them quantitatively.

I analyzed the samples as follows. They came in the mail in an Airborne Express pouch. I opened the pouch with a dry-wall knife that is kept in the second drawer from the top in the X-ray lab. It is the type that has a retractable blade. Then I removed the bottles from the package, and analyzed them.

I am so undeserving of this honor, but I am happy to have become the first winner of the Reynolds Cup. I would like to thank my parents, my music teacher, and the little gal who let me make a left turn into the parking lot this morning. I especially thank Dr. McCarty for mistakenly sending me the answers along with the bottles, which saved a lot of analysis time. I realize that in accepting this award I will be responsible for helping to organize the next competition. Also, I understand that the Cup is not permanently mine, but that it will circulate to the next winner. Therefore, in some ways, the Reynolds Cup is similar to the Stanley Cup, except for the hockey. Now I kiss the Cup, raise it above my head, and run around the meeting room yelling, wrapped in a flag.

In the (unlikely) event that I do not win, I will relinquish this time at the podium to the real winners so that they can explain how they won the Reynolds Cup.

*Note: The Clay Doctor was later disqualified for failing a random drug test.