A MANUAL FOR A LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS) FOR LIGHT STABLE ISOTOPES—VERSION 7.0

U.S. GEOLOGICAL SURVEY

Open-File Report 98-284
Revision of Open-File Report 97-812

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By Tyler B. Coplen

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Reston, Virginia

1998

U.S. DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director

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A MANUAL FOR A LABORATORY INFORMATION MANAGEMENT SYSTEM (LIMS) FOR LIGHT STABLE ISOTOPES— VERSION 7.0

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ABSTRACT

The reliability and accuracy of isotopic data can be improved by utilizing database software to (i) store information about samples, (ii) store the results of mass spectrometric isotope-ratio analyses of samples, (iii) calculate analytical results using standardized algorithms stored in a database, (iv) normalize stable isotopic data to international scales using isotopic reference materials, and (v) generate multi-sheet paper templates for convenient sample loading of automated mass-spectrometer sample preparation manifolds. Such a database program is presented herein. Major benefits of this system include (i) an increase in laboratory efficiency, (ii) reduction in the use of paper, (iii) reduction in workload due to the elimination or reduction of retyping of data by laboratory personnel, and (iv) decreased errors in data reported to sample submitters. Such a database provides a complete record of when and how often laboratory reference materials have been analyzed and provides a record of what correction factors have been used through time. It provides an audit trail for stable isotope laboratories.

Since the original publication of the manual for LIMS for Light Stable Isotopes, the isotopes ^{3}H, ^{3}He, and ^{14}C, and the chlorofluorocarbons (CFCs), CFC-11, CFC-12, and CFC-113, have been added to this program.

Information on downloading this report and downloading code and databases is provided at the Internet address: http://water.usgs.gov/software/geochemical.html, or from the author at the E-mail address: tbcoplen@usgs.gov.

INTRODUCTION

Over the past two decades, the laboratory of the Isotope Fractionation Project of the Water Resources Division of the U.S. Geological Survey in Reston, Virginia, has analyzed water and solid samples for the determination of stable hydrogen, carbon, nitrogen, oxygen, and sulfur isotope ratios for numerous individuals. In order to track these samples, we have developed a laboratory information management system (LIMS) based on the relational database program Microsoft Access[1]. This manual discusses this database program and is an update of Coplen (1997). This database program now includes the isotopes ^3H, ^3He, and ^{14}C, and the chlorofluorocarbons (CFC): CFC-11, CFC-12, and CFC-113. ^3H users are directed especially to pay particular attention to the section on ^3H beginning on page 106. ^{14}C users should pay particular attention to the section on ^{14}C beginning on page 105. CFC users should pay particular attention to the section on CFCs beginning on page 107.

Access is available as one of the applications in Microsoft Office Professional. Access allows storage of more data than can be stored in spreadsheet programs. An Access database can be larger than 100 MB. Because LIMS is a relational database application, data are stored in separate tables in such a way as to eliminate or minimize repeating of data.

LIMS for Light Stable Isotopes has proven useful in laboratories that (i) receive samples for isotopic analysis from numerous individuals, and (ii) perform at least a few thousand isotopic analyses per year. Users who do not meet at least one, and likely both these criteria, will probably not find worthwhile the investment in time that it takes to learn and fully apply LIMS for Light Stable Isotopes.

Experience has shown that approximately one week is required to become reasonably acquainted with LIMS for Light Stable Isotopes and set it up for operation in a laboratory. The user should plan one day for the tutorial (see page 20) and three to four days to set up a new database and begin importing isotopic analyses from mass spectrometers in the laboratory. Although this may seem like a large investment in time, current users report that the rewards in increased productivity and better organization in a laboratory far outweigh this setup cost.

LIMS for Light Stable Isotopes can store information about samples and analytical results for the following isotope ratios, isotopes, and CFCs:

$^2H/^1H$	$^{11}B/^{10}B$	$^{18}O/^{16}O$	$^{37}Cl/^{35}Cl$	$^{129}Xe/^{132}Xe$
^3H	$^{13}C/^{12}C$	$^{21}Ne/^{20}Ne$	$^{38}Ar/^{36}Ar$	$^{136}Xe/^{132}Xe$
^3He	^{14}C	$^{22}Ne/^{20}Ne$	$^{40}Ar/^{36}Ar$	CFC-11
^4He	$^{15}N/^{14}N$	$^{30}Si/^{28}Si$	$^{83}Kr/^{84}Kr$	CFC-12
$^7Li/^6Li$	$^{17}O/^{16}O$	$^{34}S/^{32}S$	$^{86}Kr/^{84}Kr$	CFC-113

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[1] The use of trade, brand or product names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Two versions of LIMS for Light Stable Isotopes are available. LIMS for Light Stable Isotopes version 7.0 operates on the Microsoft Windows 95 or Windows NT 4.0 (or higher) platforms under Access 97. LIMS for Light Stable Isotopes version 1.4, runs on the Microsoft Windows 3.1 or the Windows for Workgroups 3.11 platform under Microsoft Access 2.0. The two versions of LIMS for Light Stable Isotopes are nearly identical. This report discusses version 7.0, but version 1.4 users can use this manual also. Where important differences occur, they are discussed herein.

Hardware Requirements

LIMS for Light Stable Isotopes 7.0 requires an IBM compatible computer. A 486, Pentium, or Pentium Pro computer with 16 MB of memory is satisfactory; however, a 32-MB Pentium is recommended. A speed of at least 66 MHz is needed, but 200 or 233 MHz is desirable to minimize delays while Access runs some queries. Although a 15-inch monitor can be used, a 17-inch monitor will be easier to use because small fonts are used on some of the forms. Although a 640 x 480 pixel video driver and video adaptor card may display text at its largest size, a screen resolution of 800 x 600 pixels works satisfactorily with 17-inch monitors, and a screen resolution of 1024 x 768 pixels works satisfactorily with 21-inch monitors. A mouse is required.

A Hewlett Packard LaserJet III printer was used to generate the reports in this report. If a different printer is employed, **the user should confirm that the fonts available are sufficiently small that no information is omitted from the user's reports**.

Software Requirements

LIMS for Light Stable Isotopes 7.0 (abbreviated LIMS from here on) runs under Microsoft Access 97 and requires Microsoft Windows 95 or NT 4.0 (or higher). LIMS will not function properly with Access 95. Access 97 is one of the applications in the Microsoft Office Professional suite. Installation of Microsoft Excel 97 is also required. (Note that installation of Excel 5.0 is useful, but not required for LIMS 1.4 users.)

The complete LIMS application or only the most recent code file can be downloaded from the Internet (http://water.usgs.gov/software/geochemical.html). Additionally, LIMS can be supplied by the author (E-mail: tbcoplen@usgs.gov) on eight 1.44 MB diskettes (version 1.4 can be supplied with only five diskettes—the code file is much smaller). Diskettes for LIMS for Light Stable Isotopes 7.0 consist of:

Program Files (4 diskettes)	To be installed on the user's computer
New Database	For the user's laboratory database. To be installed after completing the tutorial.
Example Database	Installed with program files in the selected folder.
Excel 5.0 Template for Creating Sample Projects	For use by those submitting samples to user's laboratory.
Example Import Formats	Contains ten files with isotopic analyses that can be imported into the LIMS example database.

Installation Instructions

As is done for many database applications, LIMS is divided into two database files. One is the code (Lm7code.mdb) and the other is the backend database (LM4DATA.mdb, Lm7data.mdb, or similar) where all of the user's isotopic data reside. The location of these two files on the user's computer is unimportant—they can reside in separate folders or in the same folder on the user's hard drive (or on another computer on the user's network). LIMS runs on a single computer or on computers networked together using Microsoft Windows for Workgroups or Microsoft Windows NT 4.0 (or higher).

Installation on a single computer from the Internet

The installation on a single computer is as follows:

1. Install Microsoft Access 97 on your computer (from Microsoft Office Professional 97 if desired) if not already installed. Two optional components must be installed when Access 97 is installed:

    i. Database Drivers option under Data Access components, and

    ii. Microsoft Graph under Office Tools.

2. Install Microsoft Excel 97 on your computer (from Microsoft Office Professional 97 if desired) if not already installed.

3. Decide upon the directory (and subdirectory) that will contain LIMS and create it. In the author's laboratory C:\Share\Limsdata is used.

4. Download the file, Lims7.exe, from http://water.usgs.gov/software/geochemical.html and move

it to the directory (and subdirectory) decided upon in the step above.

5. Lims7.exe is a self-extracting compacted file that can create five subdirectories and populate them with files. Expand Lims7.exe by clicking the **Start** button, clicking **RUN**, and then typing the following into the command line:

> **[drive]:\ [root directory] \ [sub directories chosen in step 3] \ lims7.exe -d**

For example, the author would type:

> **C:\Share\Limsdata\lims7.exe -d**

Five subdirectories should be created and populated with files. All of these files are backups of the original files. The user should make copies of them as requested below.

6. Copy the file Lm7code.mdb in the subdirectory "\code" to the directory (and subdirectory) decided upon in step 3 above.

7. Copy the files in the subdirectory "\expl-db" to a diskette and label it "LIMS for Light Stable Isotopes 7.0—Example Database."

8. Copy the files in the subdirectory "\imp-fmts" to a diskette and label it "LIMS for Light Stable Isotopes 7.0—Example Import Formats."

9. Copy the file in the subdirectory "\new-db" to a diskette and label it "LIMS for Light Stable Isotopes 7.0—New Database."

10. Copy the files in the subdirectory "\xls-tpl" to a diskette and label it "LIMS for Light Stable Isotopes 7.0—Excel 5.0 Template for Creating Sample Projects."

11. Copy the file Lm7datae.mdb from the subdirectory "\expl-db" to the directory (and subdirectory) decided upon in step 3 above.

This completes the installation on a single computer. Multiple copies of the LIMS 7.0 code can be installed on a network, allowing more than one person to use your backend database at a time. See the instructions on page 7.

After the features of LIMS have been explored using the example database (see page 20), a new database (found on the LIMS New Database diskette, created above) can be installed (see page 79). Be sure to delete the example database (or change its name or move it to another folder) to force LIMS to query the user for the location of the new database.

Installation on a single computer from diskettes

The installation on a single computer is as follows:

1. Install Access 97 (from Microsoft Office 97 Professional if desired) if not already installed. Two optional components must be installed when Access 97 is installed:

    a. Database Drivers option under the Data Access components, and

    b. Microsoft Graph under Office Tools.

2. Install Excel 97 if not already installed.

3. Decide upon the name of the folder that will hold the backend database (the primary reservoir of the user's data). In the author's laboratory this folder is C:\SHARE\LIMSDATA.

4. Insert the diskette labelled "LIMS for Light Stable Isotopes 7.0 Program Files Setup - Disk 1" into the computer.

5. Click **Start**.

6. Click **Run**.

7. Click **Browse** and locate "setup.exe" on the diskette.

8. Click **Open** and follow the installation instructions. When asked for the folder in which to locate LIMS, use that identified in step 3. The program will be installed. The installation program will prompt the user for each of the four program setup diskettes in turn.

9. Add "LIMS 7.0" to the **Start** button menu if desired. The instructions can be found by selecting Help, searching for "Start menu" and then for "adding programs to" under the Start menu. For Windows NT 4.0 the instructions are:

    a. Click **Start** and then point to **Settings**.

    b. Click **Taskbar**, and then click the **Start Menu Programs** tab.

    c. Click **Add**, then click **Browse**.

    d. Locate the program you want to add, and then double-click it.

    e. Click **Next**, and then double-click the menu on which you want the program to appear.

f. Type the name that you want to see on the menu (LIMS 7.0, for example), and then click **Finish**.

g. If Windows NT 4.0 prompts you to choose an icon, click one, and then click **Finish**.

This completes the installation on a single computer. Multiple copies of the LIMS 7.0 code can be installed on a network, allowing more than one person to use your backend database at a time. See the instructions below.

After the features of LIMS have been explored using the example database (see page 20), a new database (found on the LIMS New Database diskette) can be installed (see page 79). Be sure to delete the example database (or change its name or move it to another folder) to force LIMS to query the user for the location of the new database.

Installation on a network

Multiple copies of the LIMS code can be installed computers on a network, allowing more than one person to use the backend database at a time. The installation is as follows:

1. First install LIMS on the computer on which the backend database will reside using either the Internet or diskette installation instructions above.

2. Share the folder that serves as the location of the backend database using Microsoft Explorer by right clicking the mouse (clicking the right-hand mouse button for right handed people) when the cursor is on the folder to be shared. Select sharing and enter a Share Name of your choice. In the author's laboratory "LIMSDATA" is used.

3. Copy the LIMS program code file, Lm7code.mdb, to each computer on your network as desired.

Then, for each computer that contains Lm7code.mdb, do the following:

4. Install Access 97 (from Microsoft Office 97 Professional if desired) if not already installed. Two optional components must be installed when Access 97 is installed:

    a. Database Drivers option under the Data Access components, and

    b. Microsoft Graph under Office Tools.

5. Install Excel 97 if not already installed.

6. Open Microsoft Access.

7. Find Lm7code.mdb on this computer and open it.

8. Follow the installation instructions. LIMS will be unable to find the backend database and will prompt the user to find it. Click on the Network Neighborhood icon and find the backend database in the directory shared in step 2 above. Once the paper size has been selected, click the **Exit** button.

9. Add "LIMS 7.0" to the **Start** button menu if desired as shown above.

This completes the installation.

After the features of LIMS have been explored using the example database (see page 20), a new database (found on the LIMS New Database diskette) can be installed (see page 79). Be sure to delete the example database (or change its name or move it to another folder) to force LIMS to query the user for the location of the new database.

Installation of version 1.4 from the Internet

The installation for LIMS 1.4 (the version for Microsoft Windows 3.1 and Microsoft Windows for Workgroups) on a single computer are given below (for instructions on installing LIMS 1.4 on a network, contact the author):

1. Install Microsoft Access 2.0 on your computer (from Microsoft Office Professional if desired) if not already installed.

2. Decide upon the directory (and subdirectory) that will contain LIMS 1.4 and create it. In the author's laboratory C:\Share\Limsdata is used.

3. Download the file, LIMS4.EXE, from http://water.usgs.gov/software/geochemical.html, and move it to the directory (and subdirectory) decided upon in the step above.

4. LIMS4.EXE is a self-extracting compacted file that can create five subdirectories and populate them with files. Expand LIMS4.EXE by selecting "Run," from the Windows Program Manager, and then typing the following into the command line:

    [drive]:\ [root directory] \ [sub directories chosen in step 2] \ lims4.exe -d

    For example, the author would type:

    C:\Share\Limsdata\lims4.exe –d

Five subdirectories should be created and populated with files. All of these files are backups of the original files. The user should make copies of them as requested below.

5. Copy the file LM4CODE.MDB in the subdirectory "\CODE" to the directory (and subdirectory) decided upon in step 2 above.

6. Copy the files in the subdirectory "\EXPL-DB" to a diskette and label it "LIMS for Light Stable Isotopes 1.4—Example Database."

7. Copy the files in the subdirectory "\IMP-FMTS" to a diskette and label it "LIMS for Light Stable Isotopes 1.4—Example Import Formats."

8. Copy the file in the subdirectory "\NEW-DB" to a diskette and label it "LIMS for Light Stable Isotopes 1.4—New Database."

9. Copy the files in the subdirectory "\XLS-TPL" to a diskette and label it "LIMS for Light Stable Isotopes 1.4—Excel 5.0 Template for Creating Sample Projects."

10. Copy the file LM4DATAE.MDB from the subdirectory "\EXPL-DB" to the directory (and subdirectory) decided upon in step 2 above.

11. Register Microsoft Graph by running the file GRAPH5.EXE using the Run command from the Windows Program Manager. It will indicate that it can only be run from within another program. To locate GRAPH5.EXE it may be easiest to use the command Browse.

This completes the installation. The user will probably find it useful to add a shortcut icon to one of the program groups in Microsoft Windows (see the Microsoft Windows manual for instructions). In this manner, the user can double click on this icon, Access 2 will open, and LIMS will open automatically. You are now ready to begin the tutorial on page 20.

Installation of version 1.4 from diskettes

The Microsoft Windows version of LIMS (version 1.4) is smaller. The code is provided in compressed form on a single diskette. The installation for LIMS 1.4 on a single computer are given below (for instructions on installing LIMS 1.4 on a network, contact the author):

1. Install Access 2.0 (from Microsoft Office Professional if desired) if not already installed.

2. Decide upon the directory (and subdirectory if desired) that will contain LIMS and create it. C:\SHARE\LIMSDATA is used in the author's laboratory.

3. Copy LM4DATAE.mdb from the diskette labelled "Example Database" to the directory or subdirectory created in step 2.

4. Copy LM4CODE.EXE from the diskette labelled "Program File Setup - Disk 1" to the directory or subdirectory created in step 2.

5. Extract the code file by running LM4CODE.EXE using the Run command from the Windows Program Manager.

6. Register Microsoft Graph by running the file GRAPH5.EXE using the Run command from the Windows Program Manager. It will indicate that it can only be run from within another program. To locate GRAPH5.EXE it may be easiest to use the command Browse.

This completes the installation. The user will probably find it useful to add a shortcut icon to one of the program groups in Microsoft Windows (see the Microsoft Windows manual for instructions). In this manner, the user can double click on this icon, Access 2 will open, and LIMS will open automatically.

Instructions for Removing LIMS for Light Stable Isotopes 7.0 (Uninstallation)

If LIMS was installed from the Internet, the user can open Microsoft Explorer and delete the following:

1. Subdirectories "\code", "\imp-fmts", "\new-db", "\xls-tpl", and "\expl-db".

2. Files Lm7code.mdb, Lm7datae.mdb, Lm7data.mdb, Limsdata.log, Lm7prefs.mdb, Import.log, Lims_err.log.

If LIMS was installed from diskettes:

1. Insert the diskette labelled "LIMS for Light Stable Isotopes 7.0 Program Files Setup - Disk 1" into the computer.

2. Click **Start**.

3. Click **Run**.

4. Click **Browse** and locate "setup.exe" on the diskette.

5. Click **Open** and the LIMS installation program will check for installed component.

6. Click **Uninstall** and follow the instructions.

CONCEPTS

Most isotope laboratories can accept a variety of sample types. These sample types are called **media** in LIMS terminology and represent the type of material or compounds analyzed. The current list of media appears in table 1. There may be slight variations between table 1 and some versions of LIMS because media are added occasionally.

When samples are delivered to a laboratory, they normally are sent with a document listing the samples and describing the analyses to be performed. In LIMS, this document is called the **sample submission document**. Before the samples can be analyzed, the samples must be logged in to LIMS. This activity is commonly called "logging in samples."

The date on the sample submission document is the **submission date** and is a key for storing the samples in LIMS. A group of samples **of a single medium** comprises a **project** in LIMS. Suppose a group of organic sludge samples for C and N isotopic analysis and water samples for δ^2H and $\delta^{18}O$ determination is submitted by Howard Q. Johnson. These samples must be logged in as two separate projects with media numbers of 1 and 26 (see table 1). Note that the sample medium is the medium of the samples that arrives at the laboratory, not media that might be prepared during the sample preparation in the laboratory. Thus, coal samples submitted for $\delta^{34}S$ analysis might be converted to $BaSO_4$ or Ag_2S during sample preparation, but they would be logged in as medium 28 (C- and S-bearing material) or as medium 69 (other S-bearing material) and not as medium 72 (sulfate mineral) or medium 66 (sulfide mineral). Note that users are free to delete and add media in LIMS as necessary for their specific laboratory use. If a coal sample is to be analyzed for δ^2H, $\delta^{13}C$, and $\delta^{34}S$, then it must be logged in twice. The reason for this is discussed below.

When samples arrive at the laboratory, each sample must have a unique identifier by which the sample submitter distinguishes his (her) samples. In LIMS this is called the **Sample ID** or the **Field ID**. When samples are logged into LIMS, LIMS will assign an alphabetic **Prefix** and an integer, separated by a hyphen, to each sample. This is called the **Our Lab ID** in LIMS, and it is the unique identifier by which LIMS knows each sample. Examples are N-3345, W-332, and R-10. The prefix is determined by the medium. Possible prefixes are listed in table 2. Consider sample prefixes as "cabinets" in which samples are stored. Water samples (for δ^2H and $\delta^{18}O$ analysis) are stored in the "W" cabinet and thus have the prefix W. Carbonates are stored in the "C" cabinet, and so on. Samples analyzed primarily for nitrogen and sulfur isotopic composition are given the prefixes N and S, respectively. The prefix R is commonly used for gaseous reference samples, but one may choose samples with other prefixes for use as reference samples. Lastly, the prefix J is user definable. It is not used for any media. Originally it was thought that it would be used for reference samples identified by Julian date, thus, the letter *J*. In a laboratory analyzing primarily extraterrestrial samples, the prefix J could be used for various extraterrestrial media analyzed by the laboratory. Using this system samples are kept in numeric order and they are easy to locate in cabinets, saving laboratory personnel time.

Table 1. Media codes used in LIMS version 7.0.

Media Code	Prefix	Description
1	W	water (H & O)
2	C	Calcite
3	C	Dolomite
4	C	DIC
5	G	gaseous carbon dioxide
6	G	gaseous hydrogen
8	R	gaseous carbon dioxide reference
10	R	gaseous hydrogen reference
12	R	gaseous nitrogen reference
14	R	gaseous sulfur dioxide reference
16	R	gaseous oxygen reference
20	G	methane (H & C)
21	G	coal (H & C)
22	G	oil (H & C)
23	G	cellulose (H & C)
24	G	other H-bearing material
25	G	organic C
26	G	C- and N-bearing material
27	G	C- and O-bearing material
28	G	C- and S-bearing material
29	G	C- and Cl-bearing material
30	G	other C-bearing material
31	C	Aragonite
45	C	other carbonate
46	G	Graphite
50	N	pure nitrogen gas
52	N	N-bearing solid (salts, rock, etc)
53	N	organic N
55	N	water (dissolved nitrate)
56	N	water (dissolved ammonium)
58	N	other N- & O-bearing materials
59	N	other N-bearing material
60	N	nitrous oxide
64	S	water (dissolved sulfate)
65	S	water (dissolved sulfide)
66	S	sulfide mineral
69	S	other S-bearing material
70	S	gaseous sulfur dioxide
71	S	elemental sulfur
72	S	sulfate mineral
79	G	gaseous oxygen (analyzed as CO2)
80	G	gaseous oxygen (analyzed as O2 for 17O & 18O)
81	G	quartz (O & Si)
82	G	silicate rocks (O & Si)
89	G	other O-bearing material

Table 1. Media codes used in LIMS version 7.0 (contd).

Media Code	Prefix	Description
103	R	Li reference material
104	G	water (dissolved Li)
106	G	phosphate mineral
107	G	Li (in silicates)
109	G	other Li-bearing material
113	R	B reference material
114	G	water (dissolved B)
115	G	B (in evaporites)
118	G	B (in rock)
119	G	other B-bearing material
123	R	gaseous silicon tetrachloride reference
125	G	elemental silicon
126	G	Silicate
129	G	other Si-bearing material
133	R	gaseous methyl chloride reference
134	G	water (dissolved Cl)
139	G	other Cl-bearing material

The samples in a project will comprise a **range of samples**. Thus, the water samples submitted by Howard Q. Johnson above might comprise the project whose samples range from W-3321 through W-3355.

Once samples have been logged into LIMS and been given an Our Lab ID, they can be analyzed for isotopic composition. Samples cannot be analyzed prior to logging them in to LIMS because the Our Lab ID needs to be entered in the sample ID field of the mass spectrometer analysis. In addition to regular submitters, it is useful to have some additional submitters, such as "Reference" and "Test." Test and Reference have both submitted samples in the example database discussed below and are included in the table of customers in this database.

Table 2. List of sample prefixes used in LIMS version 7.0.

Prefix	Description
C	Carbonate samples
G	General samples
J	User defined
N	Samples submitted primarily for N isotopic analysis
R	Gaseous reference samples
S	Samples submitted primarily for S isotopic analysis
W	Water samples

Samples may be analyzed for a variety of isotopes, isotope ratios, and CFCs (see Table 3).

Table 3. List of isotopes, isotope ratios, and CFCs that can be selected in LIMS version 7.0.

Code	Description
2	$^{2}H/^{1}H$
3	$^{13}C/^{12}C$
5	$^{15}N/^{14}N$
6	$^{34}S/^{32}S$
7	$^{17}O/^{16}O$
8	$^{18}O/^{16}O$
10	$^{7}Li/^{6}Li$
11	$^{11}B/^{10}B$
12	$^{30}Si/^{28}Si$
13	$^{37}Cl/^{35}Cl$
14	^{14}C
15	^{3}H
16	^{3}He
17	^{4}He
18	$^{38}Ar/^{36}Ar$
20	$^{40}Ar/^{36}Ar$
21	$^{21}Ne/^{20}Ne$
22	$^{22}Ne/^{20}Ne$
23	$^{83}Kr/^{84}Kr$
24	$^{86}Kr/^{84}Kr$
25	$^{129}Xe/^{132}Xe$
26	$^{136}Xe/^{132}Xe$
27	CFC-11
28	CFC-12
29	CFC-113

Samples are prepared for isotopic analysis using set methods or **procedures**. Table 4 lists the procedures (this list may differ slightly in some versions of LIMS) that can be selected. Procedures can be edited, added, and deleted (see page 93) except that procedures that are currently used in other tables in the database should not be deleted. The codes between 100 and 199 are miscellaneous codes for a variety of purposes. Thus, ion gauge readings of the sample and standard (161 and 162) can be stored. Concentrations of C, N, and S from elemental analyzers can be stored (codes 189, 190, and 191). Codes 200 to 299 are for $\delta^{2}H$ procedures, codes 300 to 399 are for $\delta^{13}C$ procedures, *etc.* The abbreviations "DI" and "CF" are dual inlet and continuous flow.

Table 4. List of sample preparation procedures used in LIMS version 7.0.

Code	Description
0	N/A
100	m/z = 2 ion beam (sample)
101	m/z = 2 ion beam (standard)
102	m/z = 3 ion beam (sample)
103	m/z = 3 ion beam (standard)
104	m/z = 4 ion beam (sample)
105	m/z = 4 ion beam (standard)
106	m/z = 12 ion beam (sample)
107	m/z = 12 ion beam (standard)
108	m/z = 13 ion beam (sample)
109	m/z = 13 ion beam (standard)
110	m/z = 14 ion beam (sample)
111	m/z = 14 ion beam (standard)
112	m/z = 15 ion beam (sample)
113	m/z = 15 ion beam (standard)
114	m/z = 16 ion beam (sample)
115	m/z = 16 ion beam (standard)
116	m/z = 17 ion beam (sample)
117	m/z = 17 ion beam (standard)
118	m/z = 18 ion beam (sample)
119	m/z = 18 ion beam (standard)
120	m/z = 20 ion beam (sample)
121	m/z = 20 ion beam (standard)
122	m/z = 22 ion beam (sample)
123	m/z = 22 ion beam (standard)
124	m/z = 28 ion beam (sample)
125	m/z = 28 ion beam (standard)
126	m/z = 29 ion beam (sample)
127	m/z = 29 ion beam (standard)
128	m/z = 30 ion beam (sample)
129	m/z = 30 ion beam (standard)
130	m/z = 32 ion beam (sample)
131	m/z = 32 ion beam (standard)
132	m/z = 33 ion beam (sample)
133	m/z = 33 ion beam (standard)
134	m/z = 34 ion beam (sample)
135	m/z = 34 ion beam (standard)
136	m/z = 36 ion beam (sample)
137	m/z = 36 ion beam (standard)
138	m/z = 40 ion beam (sample)

Table 4. List of sample preparation procedures used in LIMS version 7.0 (contd).

Code	Description
139	m/z = 40 ion beam (standard)
140	m/z = 44 ion beam (sample)
141	m/z = 44 ion beam (standard)
142	m/z = 45 ion beam (sample)
143	m/z = 45 ion beam (standard)
144	m/z = 46 ion beam (sample)
145	m/z = 46 ion beam (standard)
146	m/z = 47 ion beam (sample)
147	m/z = 47 ion beam (standard)
148	m/z = 50 ion beam (sample)
149	m/z = 50 ion beam (standard)
150	m/z = 52 ion beam (sample)
151	m/z = 52 ion beam (standard)
152	m/z = 64 ion beam (sample)
153	m/z = 64 ion beam (standard)
154	m/z = 66 ion beam (sample)
155	m/z = 66 ion beam (standard)
160	Contamination
161	Ion gauge (sample)
162	Ion gauge (standard)
163	Major ion beam (sample)
164	Major ion beam (standard)
165	Yield
187	H concentration
188	O concentration
189	C concentration
190	N concentration
191	S concentration
192	δ^2H received unexpectedly
193	δ^{13}C received unexpectedly
195	δ^{15}N received unexpectedly
196	δ^{34}S received unexpectedly
197	δ^{17}O received unexpectedly
198	δ^{18}O received unexpectedly
200	DI, δ^2H, (medium 6 & 10)
201	DI, 2 mL, 30 deg., Pt equil., δ^2H, (medium 1)
210	DI, Zn reduction, δ^2H, (medium 1)
220	DI, U reduction, δ^2H, (medium 1)
225	DI, combus. & U reduction, δ^2H, (media 20, 21, 22, 23, & 24)
300	DI, Gaseous carbon dioxide. δ^{13}C, (media 5 & 8)

Table 4. List of sample preparation procedures used in LIMS version 7.0 (contd).

Code	Description
303	DI, Filtered, δ^{13}C, (medium 4)δ
312	DI, 100% phosphoric acid, δ^{13}C, (medium 2, 3, 31, & 45)
340	DI, CH4 combus. to CO2 δ^{13}C (medium 20)
352	DI, Qtz sealed tube, 800 deg, δ^{13}C, (media 21, 22, 23, 25, 26, 27, 29, 30, & 46)
354	CF, CO2 gas, δ^{13}C, (medium 8)
355	CF, GCC, δ^{13}C, (media 25, 26, 27, 29, & 30)
356	CF, EA, δ^{13}C, (media 21, 22, 23, 25, 26, 27, 28, 29, 30, & 46)
500	DI, Gaseous nitrogen, δ^{15}N, (media 12 & 50)
510	DI, Total N, solid sample, combust, δ^{15}N, (medium 52)
515	DI, Organic sample, combust, δ^{15}N, (medium 53)
520	DI, Diss. nitrate, FD1 (add KOH to pH > 9), FD2, δ^{15}N, (medium 55)
522	DI, Diss. ammonium, FD1 (add H2SO4 to pH < 3), δ^{15}N, (medium 56)
580	DI, δ^{15}N, (medium 26)
580	DI, δ^{15}N, (medium 58)
580	DI, δ^{15}N, (medium 59)
582	CF, N2O, δ^{15}N, (medium 60)
583	CF, GCC, δ^{15}N, (medium 26)
583	CF, GCC, δ^{15}N, (medium 59)
584	CF, EA, δ^{15}N, (medium 26)
584	CF, EA, δ^{15}N, (medium 52)
584	CF, EA, δ^{15}N, (medium 53)
584	CF, EA, δ^{15}N, (medium 59)
600	DI, Delta, δ^{34}S, (medium 14)
600	DI, Delta, δ^{34}S, (medium 28)
600	DI, Delta, δ^{34}S, (medium 64)
600	DI, Delta, δ^{34}S, (medium 65)
600	DI, Delta, δ^{34}S, (medium 66)
600	DI, Delta, δ^{34}S, (medium 69)
600	DI, Delta, δ^{34}S, (medium 70)
600	DI, Delta, δ^{34}S, (medium 71)
600	DI, Delta, δ^{34}S, (medium 72)
662	CF, EA, δ^{34}S, (medium 28)
662	CF, EA, δ^{34}S, (medium 64)
662	CF, EA, δ^{34}S, (medium 65)
662	CF, EA, δ^{34}S, (medium 66)
662	CF, EA, δ^{34}S, (medium 69)
662	CF, EA, δ^{34}S, (medium 71)
662	CF, EA, δ^{34}S, (medium 72)
688	CF, pure SO2, δ^{34}S, (medium 14)

Table 4. List of sample preparation procedures used in LIMS version 7.0 (contd).

Code	Description
700	DI, $\delta^{17}O$ of ref. or working std O2, (medium 16)
780	DI, $\delta^{17}O$ of gaseous O2, (meduim 80)
800	DI, 2 mL equilibration $\delta^{18}O$, (medium 1)
809	DI, Guanidine H2O, $\delta^{18}O$, (medium 1)
810	DI, $\delta^{18}O$, (media 5, 8, 27, 64, 79, & 89)
820	DI, 25 deg., 100% phosphoric acid, $\delta^{18}O$, (media 2, 3, 31, & 45)
821	DI, 50 deg., 100% phosphoric acid, $\delta^{18}O$, (media 2, 3, 31, & 45)
850	DI, SO2, $\delta^{18}O$, (media 14, 70, & 72)
859	DI, User definable oxygen-isotope fractionation, $\delta^{18}O$, (media 2, 3, & 31)
860	DI, BrF5, $\delta^{18}O$, (media 81 & 82)
878	DI, $\delta^{18}O$ on O2 gas converted to CO2, (media 16 & 80)
879	CF, $\delta^{18}O$ on O2 gas converted to CO2, (media 16 & 80)
880	DI, $\delta^{18}O$ on O2 gas as O2, (media 16 & 80)
881	CF, $\delta^{18}O$ on O2 gas as O2, (media 16 & 80)
883	CF, convt. to O_2 for analysis, $\delta^{18}O$, (media 27, 58, 81, 82, & 89)
884	CF, convt. to CO_2 for analysis, $\delta^{18}O$, (media 27, 58, 79, 81, 82, & 89)
886	CF, pure CO2, $\delta^{18}O$, (media 5 & 8)
887	CF, N2O, $\delta^{18}O$, (medium 60)
888	CF, pure SO2, $\delta^{18}O$, (media 14 & 70)
890	DI, N-bearing material, $\delta^{18}O$, (media 55 & 58)
1030	$\delta^{7}Li$, (medium 103)
1040	$\delta^{7}Li$, (medium 104)
1060	$\delta^{7}Li$, (medium 106)
1070	$\delta^{7}Li$, (medium 107)
1090	$\delta^{7}Li$, (medium 109)
1130	$\delta^{11}B$, (medium 113)
1140	$\delta^{11}B$, (medium 114)
1150	$\delta^{11}B$, (medium 115)
1180	$\delta^{11}B$, (medium 118)
1190	$\delta^{11}B$, (medium 119)
1230	DI, $\delta^{30}Si$, (medium 123)
1240	DI, BrF5 $\delta^{30}Si$ (media 81, 82, 125, 126, & 129)
1320	DI, $\delta^{37}Cl$, (medium 29)
1330	DI, $\delta^{37}Cl$, (media 133 & 139)
1340	DI, diss. Cl, $\delta^{37}Cl$, (medium 134)

When samples are analyzed for isotopic composition, LIMS requires that each mass

spectrometric isotopic analysis have a unique integer value, known in LIMS as the **analysis number**. This is required for its relational database structure. In the case that a mass spectrometer measures two isotopic ratios simultaneously, such as $\delta^{13}C$ and $\delta^{18}O$ on CO_2 with a mass spectrometer having three Faraday-cup collectors, both isotope-ratio analyses can be stored with the same integer analysis number. For compound specific continuous flow isotopic analyses, δ values from as many as 999 peaks can be stored for each analysis number.

Because the majority of the samples analyzed by the author's laboratory have been either water or carbonate samples, each sample has normally required two isotopic analyses: δ^2H and $\delta^{18}O$ for water samples and $\delta^{13}C$ and $\delta^{18}O$ for carbonates, for example. Thus, the LIMS Table of Samples has been designed to store and present conveniently two types of isotopic analyses for a medium. Usually, the analysis of the element with the lower mass is the low analysis (or low procedure) and the other is the high analysis (or high procedure). One consequence of this scheme is that occasionally one may want to analyze a sample for three isotopic ratios (C, N, and S, for example). There are two possible solutions to this problem. One is to save the third isotopic ratio using a procedure code between 100 and 199. As many as 100 parameters can be stored for each analysis using these special procedure codes. For an example of the use of these codes, see page 57. Alternatively, the user might log in the sample twice. For example, one might use medium 26 (C- & N-bearing material) and medium 69 (other S-bearing material). If this is not acceptable, the user can modify the existing structure of LIMS and can add more fields to the Table of Samples and to the samples form. LIMS is reasonably flexible and can be modified by users. Users can add new media codes and procedure codes (see page 85), or delete existing ones.

Once samples have been analyzed, the isotopic analyses are imported into LIMS. The isotopic results are "corrected" using isotopic reference materials analyzed with the samples. The isotopic results are then saved in the table that contains the sample information. This activity is called "storing data." Once all the samples in a project have been analyzed and the isotopic results have been stored, the project is reported. This is commonly called "reporting results." The next section is a tutorial that describes these activities in more detail.

EXAMPLE DATABASE

Introduction

The tutorial that follows uses an example database to help the reader to familiarize himself or herself with the various forms and reports in LIMS, and it will illustrate where and how various types of data are stored in LIMS. To use the example database, the installation of LIMS must have been completed (see page 6). If another database has been installed, you will need to temporarily change its name to force LIMS to query the user for the file specifier of the example database. Start LIMS by selecting LIMS 7.0 from the Start button menu or run Access 97 and open the file Lm7code.mdb.

The figures and text in this tutorial apply to the U.S. English regional settings for Microsoft Windows. If another regional setting is used, reports and input will correspond to that setting. Thus, for Sweden a date-time would be entered as 1996-09-30 16:32 and a depth of three and one-half meters would be entered as 3,5. If LIMS indicates that an entry error has been made and that the entry needs to be a numeric value, the user should check to be sure that the correct decimal separator (comma versus decimal point) is being entered.

WARNING. The reports shown in this tutorial were printed using a Hewlett Packard LaserJet III printer. Some printers will not support the same fonts as the HP LaserJet III. If the user's printer employs a font with wider characters, some characters may be omitted from LIMS reports. The user should compare closely the printer output of Figs. 7, 11, 20, 22, 23, and 25 to ensure that no characters have been omitted. In the event that characters have been omitted, the user should contact the author (e-mail tbcoplen@usgs.gov).

If LIMS has been used previously and a new database has been installed (either Lm7data.mdb or LM4DATA.mdb), the user should record any preferences or tokens that have been saved in the configuration table because they will be changed during this tutorial. After the tutorial is completed and the new database is reinstalled, the user can edit these preferences and tokens to their values prior to execution of the tutorial.

When one opens LIMS for the first time, the code module will be unable intentionally to locate the backend database. A message similar to the following will appear:

Welcome to LIMS for Light Stable Isotopes. Please find the database for your samples and analyses. For the tutorial it is Lm7datae.mdb.

The user should click **OK**. The file dialog form will appear and the user should locate the backend database. For this tutorial this is the file Lm7datae.mdb and is found in the folder in which the LIMS code module, Lm7code.mdb, is found. (For LIMS 1.4 users, the backend database for this tutorial is the file LM4DATAE.mdb). LIMS should then require a minute or so to complete linking to tables in the backend database.

Once the code module connects with the tables in the backend database, a message similar to the following may appear:

A previous LIMS preferences file has been found. LIMS will replaces the preferences and tokens in this new version of LIMS with those saved by the previous version of LIMS.

If this message does appear, click **Cancel** to begin a new tutorial session.

The following message will appear if a paper format for the printer has not been selected:

Welcome to LIMS for Light Stable Isotopes.

You need to select either U.S. or European A4 size paper for reports. This can be changed at a later date. LIMS will default to U.S. standard paper.

Choose no to use A4 paper for printing.

Click **Yes** or **No** as appropriate for your printer.

The LIMS Main Menu is now shown on the screen. Click **Special Features** and LIMS will prompt the user for the password. Enter the password supplied, and the Special Features subform will open on the Main Menu (Fig. 1). The functions of the buttons on the Main Menu are summarized below.

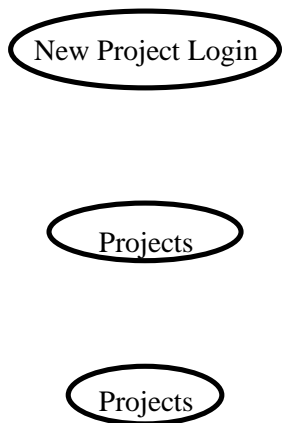|	
Projects	Opens the Search Projects form and allows the user to locate a project (group of samples).
New Project Login	Login samples to be analyzed.
Import New Project	Login samples to be analyzed using the Excel diskette provided by the sample submitter.
Samples & Analyses	Open the sample form with the desired sample, and open the analysis form if the sample has been analyzed.
Print Sample Range	Prints a range of samples such as between C-4444 and C-4449.
Import Analyses	Import isotopic analyses from a diskette written to by a mass spectrometer.
Print Templates	Edit the list of samples to be analyzed and print a multi-sheet template for laying out the samples for organized isotopic analysis.
Add or Change Analyses	Add or Edit mass spectrometric isotopic analyses.
Correction Factors and Normalization Equations	Allows the user to adjust ("correct") the isotopic data to account for drift in the working standard, *etc.*
Normalization Equation Ranges	Allows the user to view and print out the equations for the corrections made in the step above.
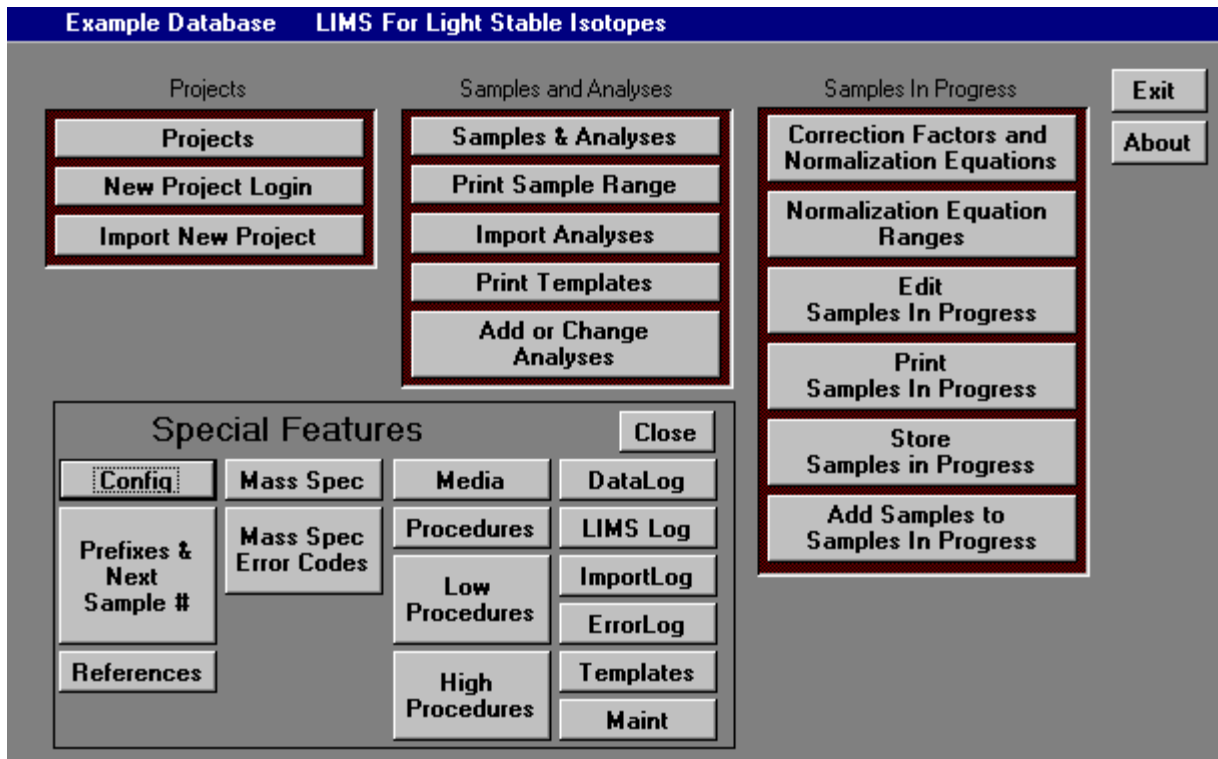
Fig. 1. LIMS Main Menu.

Edit Samples In Progress	Allows the user to view isotopic analyses of samples just analyzed and to ignore analyses of samples in the calculation of their final δ value.
Print Samples In Progress	Print the isotopic analyses of samples recently analyzed, calculating final δ values where possible.
Store Samples In Progress	Once the user is satisfied with the final δ value of a sample, the δ value is saved in the Table of Samples.
Add Samples to Samples In Progress	Reevaluate the isotopic analysis that went into determining the final δ value of a sample.
Exit	Exit LIMS and close Access 97.
About	Information about LIMS for Light Stable Isotopes.
Config	Edit the preferences, parameters, and tokens in LIMS.
Prefixes & Next Sample # References	Edit the integers of the Our Lab ID numbers assigned during login of samples. Add, edit, or delete laboratory reference materials.
Mass Spec	Install, edit, or delete a mass spectrometer.
Mass Spec Error Codes	Add, edit, or delete mass spectrometric error codes.
Media	Add, edit, or delete media.
Procedures	Add, edit, or delete procedure codes.
Low Procedures	Add, edit, or delete low procedure codes.
High Procedures	Add, edit, or delete high procedure codes.
Data log	Future use.
LIMS Log	Review certain LIMS' activities.
Import Log	Summary of importing activities.
Error Log	A log of LIMS errors.
Templates	Add, edit, or delete the instructions for creating a multi-sheet paper template used for laying out samples to be analyzed as a group (such as in a carousel).

The tasks necessary to login samples, analyze samples, and report isotopic results are shown in Figs. 2 and 3. This tutorial takes the reader through these tasks. In Figs. 2 and 3, tasks are shown on the right and the applicable Main Menu (Fig. 1) button to execute the task is shown on the left. For the readers' convenience, Figs. 2 and 3 are also shown (in the printed documentation only—not on the Internet download version) on the last page of this manual as a foldout page. The user should now turn to this page and open it out so that it can be viewed as the reader trudges through this tutorial. Click **Close** to close the **Special Features** subform.

Use This Button on Main Menu of LIMS for Light Stable
Isotopes to Execute TheseTasks

**TASKS TO LOGIN
SAMPLES**

(1)	Samples received

New Project Login

(2)	Log in samples to add them to the **Table Of Samples**

Projects

(3)	Print labels

Projects

(4) Add samples to **Table Of Samples To Be Analyzed**

(5)	Label sample containers

(6)	Put samples into cabinets for storage until analyzed
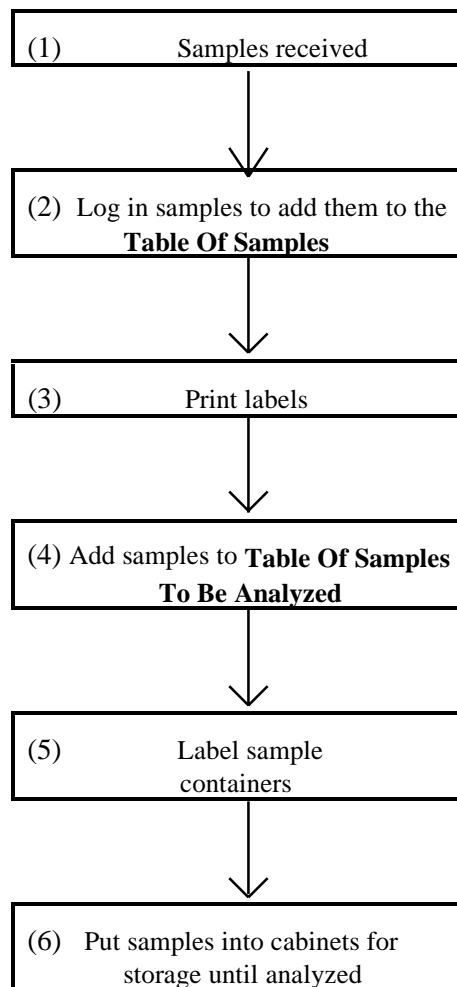
Fig. 2. Login sample tasks.

**TASKS TO ANALYZE AND REPORT
SAMPLES**

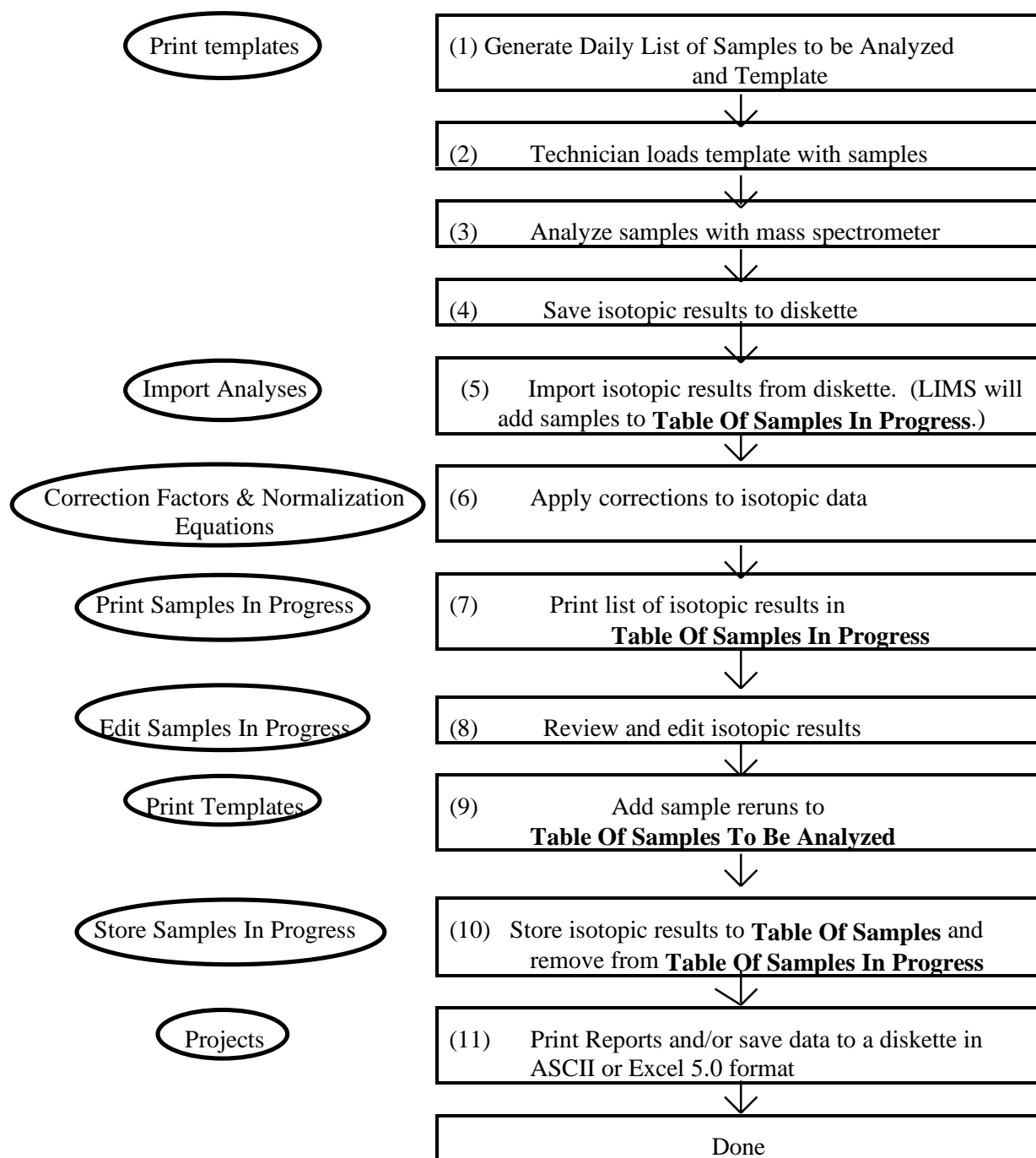|	
(Print templates)	**(1)** Generate Daily List of Samples to be Analyzed and Template
	↓
	(2) Technician loads template with samples
	↓
	(3) Analyze samples with mass spectrometer
	↓
	(4) Save isotopic results to diskette
	↓
(Import Analyses)	**(5)** Import isotopic results from diskette. (LIMS will add samples to **Table Of Samples In Progress**.)
	↓
(Correction Factors & Normalization Equations)	**(6)** Apply corrections to isotopic data
	↓
(Print Samples In Progress)	**(7)** Print list of isotopic results in **Table Of Samples In Progress**
	↓
(Edit Samples In Progress)	**(8)** Review and edit isotopic results
	↓
(Print Templates)	**(9)** Add sample reruns to **Table Of Samples To Be Analyzed**
	↓
(Store Samples In Progress)	**(10)** Store isotopic results to **Table Of Samples** and remove from **Table Of Samples In Progress**
	↓
(Projects)	**(11)** Print Reports and/or save data to a diskette in ASCII or Excel 5.0 format
	↓
	Done

Fig. 3. Tasks to analyze and report data.

Login New Samples Form

When samples are delivered to a laboratory, they normally are sent with a document listing the samples and describing the analyses to be performed. In LIMS this is called the sample submission document. The date on this document is the submission date and is a key for storing projects, a group of samples of the same medium, in LIMS. Suppose a box of organic sludge samples from Howard Q. Johnson has arrived in the laboratory for isotopic analysis.

Click **New Project Login** on the Main Menu to open the **Login New Samples** form (Fig. 4). The **Login New Samples** form allows the user to enter basic information about a project, such as the date, sample submitter, Sample ID's, country, and other information. When the **Login New Samples** form opens, the country combo box is set to the default country selected in the **LIMS For Light Stable Isotopes Configuration** form (see page 86 for instructions), which one accesses by clicking **Special Features** on the Main Menu. After completing the LIMS tutorial and installing a new database, the user will want to change the default country to his or her own country.

Enter the date on the sample submission letter. If U.S. regional settings are in effect, the user would enter June 6, 1995 or 6/6/95 and press the Enter key. For Swedish regional settings, the user would enter 1995-06-06. Select Johnson as the customer from the **Customer** combo (combination) box by clicking on the down arrow on the right side of the control to open it. Then select Johnson by clicking the mouse on Johnson. Select 26 as the medium (C- & N-bearing material). Set the Country to Canada. Set the State/Province to 002--> British Columbia. For the Project Purpose or Title enter Weller Toxics Study. For Location put Victoria, B.C. Howard Johnson submitted 18 samples with Sample ID's of

Yta-01 through Yta-10

and

Yta-12 through Yta-19

that we want to add as a range. Click on **Add Range**. Since we will be omitting one Yta value, it will be easier if we add 19 lines and delete 1. Enter Yta-01 in the **From** box. Press **Enter**. Enter Yta-19 in the **to** box. Press **Enter** and the message similar to the following appears.

You have chosen to add 19 rows. Is this correct?

Click **Yes**. Now one needs to delete Yta-11. Using the vertical scroll control, bring Yta-11 into view. Click on the gray area at the far left of the screen in the row Yta-11. This row should be selected (blackened). Press the Delete key on the keyboard (or click the right mouse key and select Cut). A message similar to the following should appear:

You are about to delete 1 record(s).

Fig. 4. Login New Samples form.

If you click Yes, you won't be able to undo this Delete operation. Are you sure you want to delete these records?

Select Yes and save the project by clicking **Save**. A message similar to the following

> **Create project record**
> **6/6/95 Johnson, Howard Q**
> **G-13 to G-30**

appears. Select **OK**. The project has now been added to the database and the second task in Fig. 2 is completed.

A comment about the values entered in the Add Range form above is useful. The user might be tempted to enter Yta-1 (instead of Yta-01) and Yta-19. If these values are entered, LIMS responds with the message

> **Invalid Range**

because LIMS is unable to determine correct sample IDs. (This problem may be attacked in a future version of LIMS.)

In any one project, Sample IDs must be unique. If one adds two samples with identical Sample IDs, a message similar to the following appears.

> **The changes you requested to the table were not successful because they would create duplicate values in the index, primary key, or relationship. Change the data in the field or fields that contain duplicate data, remove the index, or redefine the index to permit duplicate entries and try again.**

This is Microsoft Access' way of informing the user that one of the Sample IDs will need to be changed to continue.

<u>**Import New Project Button**</u>

The second way to add a project to LIMS is by importing **sample headings** (the information about each sample such as collection date, latitude, *etc.)* and project information previously stored on a diskette as an Excel 5 spreadsheet by the sample submitter—use the diskette labelled Excel 5.0 Template for Creating Sample Projects (see page 81) and click **Import New Project** on the Main Menu (but don't do it now). This method has the great advantage that the sample submitter enters all of the Sample IDs; thus, laboratory personnel do not need to retype any of them. Any mistakes are the responsibility of the sample submitter!

Search for a Project Form

Now is a good time to print a project report and to print adhesive-backed labels for the samples just entered (the third task in Fig. 2). These tasks are performed from the **Projects** form.

Click **Projects** on the Main Menu. The **Search** for a project form (Fig. 5) should open. In the subform (the light area on the form), the entry

5/15/96   Reference G-12   Acetanilide for GCC tests

or similar is highlighted. The first column contains the submission date of the project, the second is the last name of the sample submitter, the third is the range of samples in the project, the fourth is the project title or purpose, and the fifth is the location. One can use the vertical scroll bar or the up and down arrow keys to move to another project. Note that there are about 36 projects in the database. Several projects contain only a single sample. The first twenty or so projects have been found useful in the author's laboratory. These include:

1.   Several test or "garbage" samples for testing, such as W-1, C-1, *etc*,
2.   C-3, G-3, N-3, and S-3 are defined to be a blank (with no boat) for an elemental analyzer,
3.   C-4, G-4, N-4, and S-4 are defined to be an empty boat for an elemental analyzer, and
4.   R-1 through R-5 are defined to be continuous flow reference gases, H_2, N_2, *etc.*

To open a project either double-click it, the user would click on the project to select it and depress the **Enter** key or click **Find** (but don't do it yet).

One can limit searches by using the search tools on this form. Suppose one only wants to see the samples submitted by Johnson. From the **Name** combo box select Johnson. Click **Search**. Only the five Johnson projects should be displayed. One can limit searches with multiple criteria. Suppose one only wants to see Johnson's prefix G samples. From the **Prefix** combo box select "G--> General" and then click **Search**. Two projects are shown. If only one project had been displayed, LIMS would have opened the project.

Project Form

Select the project "6/6/95 Johnson" and double-click on it to open the **Project** form (see Fig. 6). On the **Project** form those text boxes which cannot be edited are shown with a darker background. If one wants to edit an entry, one must first click **Edit**. This feature is used throughout LIMS to prevent workers from accidently changing data. The following describes the buttons on the Project form:

List displays all the projects in the database.

Fig. 5. Search for project form.

Fig. 6. Project form.

The four navigation buttons, **|<, <, >,** and **>|,** allow one to go to the first, the previous, the next, and the last project, respectively. The navigation buttons work the same way on other forms in LIMS. When the current project is the last project, > and >| are grayed out to indicate that they are disabled.

Delete allows one to delete a project (and all the samples in that project). Thus, one could delete the Johnson project entered (but do not do it). A password may be required to delete a project. Use the password sent with the diskettes.

Delta Plot loads Microsoft Graph and displays a δ^2H versus δ^{18}O plot of samples in the project (unless Microsoft Graph has not been loaded, and then one needs to add this component from the Microsoft Office 97 Professional installation media). This button is enabled only for medium 1, water samples, and is demonstrated later in this tutorial.

Results allows one to save (i) project δ values in ASCII format to a diskette or (ii) data from an entire project to a diskette in Excel 5.0 format. The latter is a useful feature because sample submitters occasionally need all of the sample information (latitude, longitude, *etc.*, including δ values) in an Excel spreadsheet. This button provides LIMS with that functionality.

Import transfers data from an Excel 5.0 spreadsheet to the Table of Samples (see page 81). Two unpopulated (empty) spreadsheet templates are provided on the diskette labelled Excel 5.0 Template for Creating Sample Projects (see page 81). They are useful when someone does not have all of the required sample information when samples are submitted. For example, latitudes and longitudes are sometimes provided after samples have been submitted. Using a populated spreadsheet, data can be added to the database without retyping by laboratory personnel (see page 81).

Print Report prints a report containing the δ values of all samples in the selected project.

Print Labels and **Print Small Labels** print two sizes of labels, 30 or 80 labels per page of U.S. standard 8.5-inch by 11-inch label stock, or 21 or 84 labels per page on A4 stock, respectively. The Avery stock numbers for 30 and 80 labels per page are 5260 and 5267, respectively. These label are also available in colors. A4 stock with 21 labels per page is available from Ryman (stock number P21). Avery (stock number L7656) provides 84 labels per A4 page.

The user should now click **Print Report** to print a report containing the δ values of all samples in the project (Fig. 7). Since the project has just been logged in and no samples have yet been analyzed, no isotopic results are shown on the report. The user should compare his or her printer output with that in Fig. 7 to ensure that no characters have been omitted.

Click **Print Small Labels**. LIMS will ask if one wants to print labels for every sample in the project. The user has the possibility to print a single label or labels for a range of samples. Select **Yes** to print a label for every sample in the project. LIMS will query the user for the number of labels for each sample. Enter 3 and click **OK** or press the **Enter** key on the keyboard. The printer should print a page of

Medium: 26 --> G [C & N] C- and N-bearing material
Purpose: Weller Toxics Study

Location: Victoria, B.C.

Sample ID:	Collection Date	Our Lab ID	δ^{13}C VPDB(‰) Value	Comment	δ^{15}N AIR(‰) Value	Comment
Yta-01		G-13				
Yta-02		G-14				
Yta-03		G-15				
Yta-04		G-16				
Yta-05		G-17				
Yta-06		G-18				
Yta-07		G-19				
Yta-08		G-20				
Yta-09		G-21				
Yta-10		G-22				
Yta-12		G-23				
Yta-13		G-24				
Yta-14		G-25				
Yta-15		G-26				
Yta-16		G-27				
Yta-17		G-28				
Yta-18		G-29				
Yta-19		G-30				

Fig. 7. Example of project report after being logged in. No δ values are
shown because no isotopic analyses have been performed on these samples.

56 labels (Fig. 8). The user should compare his or her printer output with that in Fig. 8 to ensure that no characters have been omitted. Had the user loaded adhesive label stock in the printer, adhesive labels for samples would have been printed. This completes the third task in Fig. 2.

Sample Form

The user should add some geographic information to some of the Johnson sludge samples. Click **Samples** on the **Project** form to open the **Sample** form (Fig. 9). The **Sample** form shows the first sample in the project (G-13). (One can also open the **Sample** form by clicking **Samples & Analyses** on the Main Menu.) Click **List** and select G-17. Alternatively, the navigation buttons can be used to move through samples in a project.

On the **Sample** form, there are eight fields that one can set with one's own user defined captions (see page 85). They are:

Sample ID	User Def Caption 5
User Def Caption 2	User Def Caption 6
User Def Caption 3	Caption 7
User Def Caption 4	Other Info

(Note that there are no periods in any of the above captions. A period is not allowed in a field name (see page 85 for all disallowed characters.) Perhaps a user is analyzing urine from diabetic patients. One of the fields could be defined as "Days After Dose" (see page 85).

In case samples are for repay, the Project Account field may be useful.

There are over 200 "countries" on the **Country** combo control. They can be updated by editing the underlying table of countries. States, provinces, or administrative districts are listed for some countries.

One can use as many of the fields on the **Sample** form as are desired. If only a few fields will ever be used, one could easily modify the code and make unused labels and text boxes invisible. If this is done, one may also want to make the same changes to the **Range of Samples** report.

On the **Sample** form, one can see blocks identified as Low Analysis and as High Analysis. These will contain the low and high δ values discussed on page 19 once the sample has been analyzed.

A Comment is available for both the low and high analysis. The user might use these to indicate the standard deviation of the analyses, to indicate a sample bottle has broken, *etc.*

Clicking **Analyses** opens the **Analysis** form with analyses of the sample. Since this project has just been logged in, no isotopic analyses yet exist. Try it.

G-13	G-13	G-13	G-14
Yta-01	Yta-01	Yta-01	Yta-02
G-14	G-14	G-15	G-15
Yta-02	Yta-02	Yta-03	Yta-03
G-15	G-16	G-16	G-16
Yta-03	Yta-04	Yta-04	Yta-04
G-17	G-17	G-17	G-18
Yta-05	Yta-05	Yta-05	Yta-06
G-18	G-18	G-19	G-19
Yta-06	Yta-06	Yta-07	Yta-07
G-19	G-20	G-20	G-20
Yta-07	Yta-08	Yta-08	Yta-08
G-21	G-21	G-21	G-22
Yta-09	Yta-09	Yta-09	Yta-10
G-22	G-22	G-23	G-23
Yta-10	Yta-10	Yta-12	Yta-12
G-23	G-24	G-24	G-24
Yta-12	Yta-13	Yta-13	Yta-13
G-25	G-25	G-25	G-26
Yta-14	Yta-14	Yta-14	Yta-15
G-26	G-26	G-27	G-27
Yta-15	Yta-15	Yta-16	Yta-16
G-27	G-28	G-28	G-28
Yta-16	Yta-17	Yta-17	Yta-17
G-29	G-29	G-29	G-30
Yta-18	Yta-18	Yta-18	Yta-19
G-30	G-30		
Yta-19	Yta-19		

Fig. 8. Example of a small labels report.

Sample

| List | ◄ | ◄ | 13 | ► | ►| | Edit | Analyses | Print Project | Copy | Close | Johnson, 6/6/95 |

Our Lab ID: `G-13`
Medium: `26 --> G [C & N] C- and N-bea`
Last Edit: `7/2/98 11:44:00 AM`

Low Analysis 13C
Procedure: [　　　　　　　]
Comment: [　　　　　　　]
Delta: [　　　　　　　]

High Analysis 15N
Procedure: [　　　　　　　]
Comment: [　　　　　　　]
Delta: [　　　　　　　]

Decimal Degrees
Lat: [　　　] Long: [　　　]
Accuracy: [　　　　　　　]

Meters
Elevation: [　　　]
Top: [　　　]
Bottom: [　　　]

Sample ID: `Yta-01`
User Def Caption 2: [　　　　　　　]
User Def Caption 3: [　　　　　　　]
User Def Caption 4: [　　　　　　　]

User Def Caption 5: [　　　　　　　]
User Def Caption 6: [　　　　　　　]
State/Province: `002 --> BC, BRITISH COLUMBIA`
Country: `CA --> Canada`
Caption 7: [　　　　　　　]
Project Acct: [　　　　　　　]
Collection Date: [　　　　　　　]
End Collection Date: [　　　　　　　]

Phone Number: [　　　　　　　]

Other Info: [　　　　　　　]

Fig. 9. Sample form.

Print Project will print a report identical to the report generated by clicking **Print Project** on the **Project** form (Fig. 7).

Edit enables editing of the information in the light colored text boxes (those not grayed out).

The latitude and longitude of many samples are important. One can enter or display data in either degrees-minutes-seconds (DMS) format (*e.g.*, 1214512) or in decimal degrees format (*e.g.*, 121.75333). The symbols ∘, ', and " are not accepted for data entry. One can set the display default to either **Decimal Degrees** or **DMS** using a software switch on the **LIMS For Light Stable Isotopes Configuration** form (see page 86).

The user needs to enter the latitude and longitude of sample G-17. If necessary, click **Decimal Degrees** to toggle the format to **DMS**. Click **Edit**. Click the **Lat** text box and enter 483807 for the latitude. Press **Enter**. Enter -1233015 for the longitude (the minus sign is for the Western Hemisphere). Press **Enter**. The accuracy of the latitude and longitude can be selected if desired.

The elevations and depths of some samples are important. One can use meters or feet and set the default [for samples imported where the submitter has not specified meters or feet on his Excel 5.0 template (see page 81)] using a software switch on the **LIMS For Light Stable Isotopes Configuration** form (see page 86).

Sample G-17 came from a site with an elevation of 142 meters. If the length units are **Feet**, click to change it to **Meters** if necessary. Click the **Elevation** text box and enter the elevation of 142. Press **Enter**. The depth to the top of the perforated interval is 3.5 m. Enter 3.5 in **Top** and press **Enter**. The depth to the bottom of the perforated interval is 4 m. Enter 4 in **Bottom** and press **Enter**.

Both a collection date/time and ending date/time are available. The ending date/time is useful for rain samples.

The collection date/time of sample G-17 is February 2, 1995 11:30 a.m. Click the **Collection Date** text box. Enter 2/2/95 11:30 as the collection date and time.

Click **Save** to save the information entered thus far.

The **Copy** button can be used to copy sample information to another sample. It is useful in the event a user has submitted samples with more than one medium from the same location. Often water samples are submitted for δ^2H and δ^{18}O analysis along with samples for δ^{34}S analysis. The **Copy** button is used to copy the headings entered for W samples to the S samples.

Suppose the sulfate mineral sample, S-6, was collected from the same location as sample G-17 (Yta-05). The user needs to copy the location information of G-17 to S-6. Click **Copy**. Several fields will be highlighted and LIMS will inform the user:

This command will copy the highlighted information to another sample. Use this command very carefully!

Click **OK**. If prompted, enter the password. Enter S-6 by selecting the **Prefix** S and entering 6 into the **Sample #** text box. Click **Copy**. LIMS will advise the user:

The Sample ID of the sample selected is BaSO4.

Click **OK** and the highlighted fields are copied to sample S-6 as will be shown below.

Click **Close** to return to the **Project** form.

Add Samples To Be Analyzed Form

LIMS can populate a multi-sheet template with samples for isotopic analysis. One first needs to add the samples to the Table of Samples To Be Analyzed.

Click **Templates** on the **Project** form (Fig. 5) to add samples to this table. The **Add Samples To Be Analyzed** form should open (Fig. 10). (The user should not confuse the **Add Samples To Be Analyzed** form with the **Samples To Be Analyzed** form. The latter is opened by clicking on **Print Templates** on the Main Menu and is discussed later in this tutorial.) The information used to set the default entries on the **Add Samples To Be Analyzed** form is obtained from template configuration tables. These are edited by clicking on **Special Features** on the Main Menu and then selecting **Templates** (but don't do it now).

Only the template "EA for C & N" is available for medium 26 (C- & N-bearing material), so it is automatically loaded into the **Template** combo box by LIMS. The **From** and **To** values that define the sample range are set to 13 and 30. The user can edit them. The default number of repeat analyses is 1; thus, samples will only be put on the template once. The user can increase this value if needed. Leave it at 1. The default low procedure code is 356 (CF, EA, Delta 13C), so this value is entered into the low procedure combo box by LIMS. Two other low procedure codes (352 and 355) are valid for medium 26 and can be selected by the user. Likewise, the user may accept the default high procedure code of 584 (CF, EA, Delta 15N) or choose one of the other values in the high procedure combo box. Select the **Front of the queue** toggle button to add these samples to the top of the Table of Samples To Be Analyzed. Click **Add** to add the samples to the Table of Samples To Be Analyzed. LIMS will respond with a message box indicating that the repeats have been added. This completes the fourth task in Fig. 2.

If one wants to delete all the samples of a project from the Table of Samples To Be Analyzed, one would click **Delete** (but don't do it). Click **OK**. Close the **Project** form.

Fig. 10. Add Samples To Be Analyzed form.

The user can now confirm that information was copied from sample G-17 to sample S-6. Click **Samples & Analyses**. Click the **Prefix** S, enter 6, and click **Find**. The **Sample** form opens showing sample S-6. Note that data was copied from G-17. Click **Close**.

Print Sample Range Form

Clicking **Print Sample Range** prints information from the Table of Samples for a range of samples. Try printing the range W-41 to W-42. The Access report generated is shown in Fig. 11. The user should compare his or her printer output with that in Fig. 11 to ensure that no characters have been omitted.

Printing a Template and the Samples To Be Analyzed Form

After sample projects are created in LIMS, one can add the samples to the Table of Samples To Be Analyzed [(as the user did above (page 38)] in order to load them in turn on a multi-sheet template that LIMS can generate. Additionally, LIMS can save the sample headings on a diskette and these headings are available to the mass spectrometer data acquisition and control program. If the computer controlling the mass spectrometer can read these sample headings from the diskette, then the headings need not be typed into the mass spectrometer computer by the operator. If a user's computer software is not able to read these sample headings, the user may want to contact the mass spectrometer manufacturer and "encourage" the manufacturer to provide software that can read these headings since this is a significant time saver.

On the Main Menu click **Print Templates** to open the **Samples To Be Analyzed** form (Fig. 12). Click **List** and select the template "EA for C & N." "EA for C & N" is the C and N elemental analyzer template. One can see that there are 18 samples waiting to be analyzed by the elemental analyzer for $\delta^{13}C$ and $\delta^{15}N$. The sample list shows the low and (or) high procedure code(s) and the number of repeats remaining. The number of repeats is the number of times that a sample needs to appear on a template. When generating a template, LIMS takes samples from the top of the list. **Each time a sample is taken, the number of repeats is decremented by one**.

One can edit the list of samples by adding samples, deleting samples, editing the sample number and prefix of a sample, and changing the number of repeats. **A sample can appear more than once**. We will first add a sample to the list. Click on the last record of the subform marked by an asterisk in the left column. LIMS immediately fills in the default number of repeats, the low procedure code, and the high procedure code, 1, 356, and 584, respectively. For an experiment, try to enter W-1 as the sample. Enter W as the prefix and 1 as the sample. When the user attempts to update the record by clicking another record on the subform, the message

This record is not compatible with the EA for C & N. Perhaps the medium is of an incorrect type or the sample does not exist.

Fig. 11. Example of Print Sample Range report.

Fig. 12. Samples To Be Analyzed Form for the EA for C and N.

Click **OK**. Enter G for the prefix and 17 for the sample.

To cancel an entry, press the Escape key on the keyboard, but don't do it now.

To locate a sample quickly, one can use **Find**. Click **Find** and the **Search** form appears. Click **Prefix** G, enter 17 in **Sample** text box, and click **Find**. The cursor will locate the **first** G-17.

Move G-13 to the bottom of the queue. Move the focus to sample G-13 by clicking on the cell containing 13. Then click on the down arrow button. G-13 will be moved to the bottom of the queue. Next, move it to the top of the queue. Click on the cell containing 13. Click on the up arrow button. G-13 should be moved to the top of the queue. One will notice that it is quicker to move samples to the end of the queue that to move them to the top of the queue.

The user may also move a group of records to the top or bottom of the queue. (Unfortunately, this feature does not work in LIMS 1.4). This is done by selecting a group of records and then clicking the up or down arrow button. For example, to move the records G-19 through G-28 to the bottom of the queue, click on the cell containing 19, hold the Shift key down and click on the cell containing 28, release the Shift key, and click the down arrow button. LIMS will display the message:

Samples G-19 through G-28 will be moved to the bottom of the queue.

Click **Cancel** since we do not want to move them now.

Once the number of repeats reaches zero, the user commonly deletes the sample by selecting it with the mouse and pressing the keyboard Delete key. A range of sample can be deleted by first selecting the range of samples to be deleted (drag the mouse along the left edge of the list box) and then by pressing the Delete key on the keyboard. Clicking the **Delete** button on the form allows one to delete a single sample, the sample that has the focus. One can also use **Delete** on the **Add Samples To Be Analyzed** form (see page 38) to delete all the samples from the selected project.

Click on the last record, G-17. Click **Delete**. The sample just added has been deleted.

The user should now generate a multi-sheet template and diskette for the EA for C & N template. Click **New Template**. LIMS will advise the user of the number of samples waiting to be analyzed (18 in this case). Click **OK**. LIMS populates the template with samples and reference samples according to the specifications of the template. To populate the template, LIMS performs the following steps:

1. LIMS determines if any ports are to be empty according to the user's template configuration specifications and makes these ports empty. If a port is not working properly due to improper operation of a valve or solenoid, that port may be set to "Empty" by editing the template configuration (select **Special Features** and then **Templates**).

2. LIMS examines the user's template configuration specifications and places fixed reference

samples in any ports so specified. For example, the user may want the second port to always have a reference sample in it.

3. LIMS determines how many floating reference samples (if any) are to be placed in each bank (manifold) of the preparation device and places them in ports using a random number generation routine. A floating reference sample is a reference sample that is randomly interspersed among a group of samples.

4. LIMS fills in the remaining ports with samples taken from the Table of Samples To Be Analyzed. If LIMS reaches the bottom of the list and still needs more samples to complete population of the template, LIMS begins again selecting samples from the top of the queue, choosing samples that have repeats greater than zero. Thus, a sample can appear more than once on a template. If LIMS exhausts samples from the Table of Samples To Be Analyzed, LIMS fills the remaining ports with a sample so designated on the **Template Configuration** form (see page 97). This often is W-1, or an equivalent "test" sample.

Creating a new template format and editing an existing template format is discussed beginning on page 97.

After the template is generated, LIMS will display the message

You can add Aliquot IDs if desired. You cannot edit any other field.

Click **OK**. Typically, the aliquot ID of each sample would be printed on the isotopic analysis sheet by the mass spectrometer, assuming that the vendor's software can import the information saved to a file on a diskette by LIMS.

Click **Print**. When requested by LIMS, insert a blank diskette into the computer and click **OK**. The following actions now take place:

1. A list of samples is printed (Fig. 13). This list helps the analyst locate the samples.

2. A multi-sheet template is printed (Fig. 14a–14e),

3. Sample headings are saved on the diskette for use by the mass spectrometer, and

4. A backup of the Table of Samples To Be Analyzed is made.

5. The number of repeats for each sample shown on the template is decremented by one.

LIMS will inform the user that the oldest backup has been replaced successfully. Click **OK**.

EA for C N Samples To Be Analyzed

Port	Sample #	Amount
00	G-4	_____
01	G-5	_____
02	G-13	_____
03	G-14	_____
04	G-15	_____
05	G-16	_____
06	G-17	_____
07	G-18	_____
08	G-19	_____
09	G-20	_____
10	G-21	_____
11	G-22	_____
12	G-23	_____
13	G-24	_____
14	G-25	_____
15	G-26	_____
16	G-27	_____
17	G-28	_____
18	G-29	_____
19	G-30	_____
20	G-3	_____
21	G-3	_____
22	G-3	_____
23	G-3	_____
24	G-3	_____
25	G-3	_____
26	G-3	_____
27	G-3	_____
28	G-3	_____
29	G-3	_____
30	G-3	_____
31	G-3	_____
32	G-3	_____
33	G-5	_____
34	G-3	_____
35	G-3	_____
36	G-3	_____
35	G-3	_____
38	G-3	_____
39	G-3	_____

Port	Sample #	Amount
40	G-5	_____
41	G-3	_____
42	G-3	_____
43	G-3	_____
44	G-3	_____
45	G-3	_____
46	G-3	_____
47	G-3	_____
48	G-3	_____
49	G-3	_____

Fig. 13. Example of List of Samples To Be Analyzed for the EA for C & N template.

45/G-3	46/G-3	47/G-3
30/G-3	31/G-3	32/G-3
15/G-26	16/G-27	17/G-28
00/G-4	01/G-5	02/G-13

Page 1

Fig. 14a. Page 1 of multi-sheet template (EA for C & N) for an elemental analyzer.

48/G-3	49/G-3	
33/G-5	34/G-3	35/G-3
18/G-29	19/G-30	20/G-3
03/G-14	04/G-15	05/G-16

Page 2

Fig. 14b. Page 2 of multi-sheet template (EA for C & N) for an elemental analyzer.

36/G-3	37/G-3	38/G-3
21/G-3	22/G-3	23/G-3
06/G-17	07/G-18	08/G-19

Fig. 14c. Page 3 of multi-sheet template (EA for C & N) for an elemental analyzer.

39/G-3	40/G-5	41/G-3
24/G-3	25/G-3	26/G-3
09/G-20	10/G-21	11/G-22

Page 4

Fig. 14d. Page 4 of multi-sheet template (EA for C & N) for an elemental analyzer.

42/G-3	43/G-3	44/G-3
27/G-3	28/G-3	29/G-3
12/G-23	13/G-24	14/G-25

Fig. 14e. Page 5 of multi-sheet template (EA for C & N) for an elemental analyzer.

Note that the last approximately 30 positions on your template are populated with G-3 (see Fig. 13), an empty sample on the elemental analyzer carousel (see page 29). Also, because a random number generator is used to position the three floating reference samples (G-5), the user's template will be slightly different than the one shown in Figs. 13 and 14a–14e.

The last multi-sheet template is saved in case the printer malfunctions. If you need to print it again, click **Last Template** on the **Samples To Be Analyzed** form.

Clicking **Make Backup** creates a backup of the Table of Samples to Be Analyzed shown on the **Samples To Be Analyzed** form (Fig. 12). To restore a previous backup, click **Retrieve Backup** and select the day and time of the backup to be restored. The last nine backups are retained by LIMS.

Close the **Samples To Be Analyzed** form. This completes the first task in Fig. 3. The technician would now load the template with samples and analyze them (tasks 2 and 3 on Fig. 3).

Analysis Form

The tutorial will digress briefly to discuss the **Analysis** form which is used to show the isotopic analysis of a sample that has been analyzed. To open the **Analysis** form, it is first necessary to open the **Sample** form. The easiest way to open the **Sample** form (Fig. 9) is to click **Samples and Analyses** on the Main Menu. Click **Samples and Analyses**. The W is already selected, so enter 8 and press **Enter**. The sample form should open. The **Analysis** form is opened by clicking **Analyses** on the **Sample** form. Click **Analyses** and a message indicates that there are no analyses for sample W-8. This is correct since the Comment text box indicates that the sample was broken (this is a real sample and it was broken). Move to sample W-9 by clicking **List** or the navigation buttons. Click **Analyses** and the **Analysis** form opens (Fig. 15).

Analysis D-117229 is visible. To view other analyses, select them by clicking **List**. There are two δ^{18}O analyses from the DuPont mass spectrometer and two δ^2H analyses from the VG mass spectrometer. To edit an analysis, click **Edit** and the **Edit Analysis** form opens. One may need to enter the password.

Close the **Analysis** form and the **Sample** form to return to the Main Menu.

Add or Change Analyses Form

Assume the Johnson sludge samples have now been analyzed along with numerous other samples. The user needs to add these isotopic analyses to LIMS. Isotopic analyses are added in either of two ways, they are entered using the keyboard or they are imported from a file created by the mass spectrometer software. First enter isotopic data using the keyboard.

Fig. 15. Analysis form.

Enter the missing mass spectrometer analysis information as follows. Click **Add or Change Analyses**. The **Add or Change Analyses** form should appear (Fig. 16). From the Mass Spec combo (combination) box, select V-->VG in 5B131. When the hourglass cursor disappears, W has been selected as the sample prefix. Note that only three prefixes are shown for this mass spectrometer (G, R, and W) because it can only analyze hydrogen isotopic ratios. [The Table of Media (table 1) shows that there are no media with prefixes C, J, N, or S for hydrogen isotopic analysis.] Above the **Mass Spec** combo box is **Range of Mass Spec Analyses for List** option group. This only applies to the **List** button, which is used below. Generally, the user will want to accept the default of the last 1,000 analyses because selecting all analyses may require a query of the database that takes more than a minute in the case of large databases.

The analysis number of the missing analysis is 128329. Click **New Analysis**. LIMS determines that the next analysis number should be 128329 and LIMS inserts this value in the **Analysis #** text box. By chance it is exactly the analysis that is missing, so press **Enter** and the focus (cursor) moves to the **Aliquot ID** text box. Users often identify the aliquot of the sample analyzed with A, B, etc. This 20 character field can be used as one chooses. It will not be used now, so press **Enter**. The cursor should move to the **Standard** text box.

Enter 24 for the working standard. The integers 1 to 366 are normally used in the author's laboratory for identification of working standards (the day of the year in which it was loaded). One can force error checking for the integers 1 to 366 using one of the switches on the **LIMS For Light Stable Isotopes Configuration** form (page 86).

Enter 31 for the port number. Port numbers can be up to six characters long. Integer port numbers between 0 and 99 are used in the author's laboratory. One can ensure that users enter only integer port numbers between 0 and 99 by enabling a software switch (page 86).

Enter March 1, 1997 6:24 PM (or 18:24) for the date/time analyzed. The date/time format may be different depending upon the Window's date and time default settings of the user's computer.

The cursor should move to the **Comment** text box. This 32-character field can be used to store text for each analysis, as one chooses. It is not used now, so press **Enter**. The cursor moves to the **Prefix W**. Accept this prefix and press **Enter**. The cursor moves to the **Sample** text box.

The sample number of the missing analysis is W-6, so enter 6 and press **Enter**. LIMS will now search the database for information about sample W-6 and it will fill in the following information:

Sample submitter (owner)	Reference
Submission date	Jan. 5, 1995
Sample ID	Light Lab Ref
Media	01 for water

Fig. 16. Add or Change Analyses form.

The cursor should be in the **Isotope** combo box. Select 2H from the **Isotope** combo box if it is not already selected and press **Enter**. The cursor moves to the **Procedure** combo box and procedure 201 is selected because it is the default low procedure code for the medium water (see page 94).

Enter -389.86 for the δ value and press **Enter**.

The mass spectrometer error code is 0 (no error), so press **Enter**. The error code is similar to the Micromass "Run Code." The focus should move to **Save**. Click **Save** or press **Enter** to save this analysis.

Next the user should select "P --> My Delta Plus" from the **Mass Spec** combo box. Note that LIMS now makes the **Peak Number** text box visible because the Delta Plus has continuous flow capabilities. Click **List** and the analyses, peaks, and procedure codes for the last 1000 analyses of the Delta Plus are shown. Additionally, the date and time of analysis, Aliquot ID, port ID, Our Lab ID, Standard, and δ value are shown. Click on P-110 and this analysis is loaded into the form.

The function of the buttons on this form is similar to those on other forms and is described below:

Edit enables the user to edit the isotopic analysis (and peak number if shown). Most fields can be edited. LIMS will perform data validation whenever possible. Thus, LIMS would not allow the user to change the Our Lab ID of a sample on the VG mass spectrometer from W-1 to S-1 because the VG mass spectrometer is not able to analyze sulfur isotopic ratios.

New Peak enables the user to enter a new peak to an existing mass spectrometric analysis.

New Procedure enables the user to enter a new procedure code. LIMS will constrain the isotope and procedure codes to those that are valid for the medium of the sample and the capabilities of the mass spectrometer, that is, the isotopes it can analyze.

Delete enables the user to delete an analysis and peak number.

Next the user will enter isotopic data from files saved by mass spectrometers, so click **Close** to close the **Add or Change Analyses** form.

Import Analyses Button

The **Import Analyses** button on the Main Menu is used to import isotopic analyses from a file on a diskette that has been saved by a mass spectrometer. In addition to the LIMS default format, LIMS can import isotopic analyses from analysis files created by Analytical Precision, Europa Scientific, Finnigan MAT, and Micromass mass spectrometers. The format for each manufacturer is discussed is some detail beginning on page 109. LIMS cannot import all formats of all manufacturers. In particular, importing of Micromass continuous flow isotopic results is not yet available because there are a variety of formats

rather than a unique format.

When any sample analysis is imported, the Our Lab ID and the isotope (see table 3) is appended to the Table of Samples In Progress unless it already is present in this table. Typically the user will "apply a correction to" the δ values (discussed below) and store the final δ value in the Table of Samples so that final reports of results can be generated. When the final δ value is stored in the Table of Samples, the sample is deleted from the Table of Samples In Progress because the user no longer needs it there.

LIMS Default Import Format

The LIMS default import format for isotopic analyses is a Microsoft Access 2.0 .mdb database file (see page 109). Next import isotopic results in the LIMS default format. Insert the LIMS Example Database diskette into the computer. Click **Import Analyses**. When prompted to select a mass spectrometer, select "D --> DuPont." Note that the Import Format combo box is set to "LIMS Default" because this is the only choice for the DuPont mass spectrometer. [It is the only choice because the import format in the mass spectrometer configuration table (page 91) for the DuPont mass spectrometer has been set to "LIMS Default." Had it been left blank, LIMS would have prompted the user to select the import format from the list of import formats.] Click **OK** and the file dialog form opens and displays the .mdb files on the diskette. The DuPont mass spectrometer generated the file LmImpDef.mdb, so select it and click **Select**. The status form should open. The form is updated after each line of data in the file of isotopic results is processed. Six analyses should be imported and LIMS should advise the user that D-117457 through D-117462 have been imported. Click **OK**. If one were to import LmImpDef.mdb again, one would see that the status form would process 6 lines and that there would be 6 duplicate records.

Analytical Precision Import Format

Software from Analytical Precision saves isotopic results in an Access 2.0 database file (see page 111 for the format). Next import isotopic results from an Analytical Precision file. Click **Import Analyses**. Select "A --> My AP" from the mass spectrometer combo box. Click **OK** and the file dialog form will show all of the .mdb files on the diskette. Select the file AP_Imp.mdb and click **Select**. Thirteen records should be imported, A-1318 through A-1323. To view these analyses, click **Add or Change Analyses**. Select mass spectrometer "A --> My AP", and click **List**. Note that for the first analysis, A-1318, both $\delta^{13}C$ and $\delta^{18}O$ values have been imported (procedure code 300 is the $\delta^{13}C$ analysis and procedure code 810 is the $\delta^{18}O$ analysis). The user will note that analyses A-1318 through A-1322 are for gaseous CO_2 samples from a mass spectrometer test (samples G-7 through G-11). Analysis 1323 is an elemental analyzer analysis of sample G-1 and has two peaks, the first is N_2 and its $\delta^{15}N$ value is +0.33; the second is CO_2 and its $\delta^{13}C$ value is -24.35. Note that a value of -1.58 is listed for procedure code 198 of peak 2. Procedure code 198 is $\delta^{18}O$ received unexpectedly. The Analytical Precision mass spectrometer saved the $\delta^{18}O$ value of the CO_2 sample on the diskette. But LIMS knows that the medium

of sample G-1 is 26, C- and N-bearing material. Thus, LIMS knows that this medium has no oxygen in it (as far as LIMS is concerned). When LIMS imported the $\delta^{18}O$ value, the only way LIMS could store it was as procedure code 198. Click **Close** to close the **Add or Change Analyses** form.

Europa Scientific Import Format

Software from Europa Scientific has for several years saved isotopic results in an ASCII .prn file. An example, Europa.prn, is provided on the Example Import Files diskette. In March 1997 a new format was adopted (see discussion on page 112). The new format is an ASCII text file (.txt) given the name Mercury.txt. Import a Europa Scientific file. Click **Import Analyses**. Choose "U --> My Europa." The Europa Scientific import format is automatically selected. Click **OK**. The file dialog form should open showing the .txt files on the Example Database diskette. Choose Mercury.txt. Click **Select**. The status form should show that 7 lines have been processed and 7 analyses imported. LIMS will advise the user that analyses U-25 through U-30 have been imported. One can view these analyses as done above by clicking **Add or Change Analyses**. Select "U --> My Europa" for the mass spectrometer and click **List**. One can see that U-25 through U-29 are $\delta^{15}N$ elemental analyzer analyses—the procedure code is 584. U-30 shows 2 peaks from a nitrogen isotope GC combustion analysis (a compound specific isotopic analysis of sample G-1). Select U-25 and click **Close**.

Finnigan MAT Import Format

Introduction.

Finnigan MAT isotopic results need to be saved in a Lotus (.wks) format using ISODAT at the Finnigan mass spectrometer computer. See page 112 for details on creating a .wks file that is compatible with LIMS.

When Finnigan ISODAT analyses are imported, the unique integer that LIMS uses for the analysis number is the Finnigan mass spectrometer Spec No. This number must be unique. **Therefore, if a user needs to replace a computer or hard disk, the Spec No must be set during installation to the next unique integer.** For example, if the last Spec No. of the last analysis before the computer failed was 33115, the replacement computer must be installed with a Spec No. of 33116.

The format for Finnigan dual inlet, GC combustion (GCC), and EA (elemental analyzer) files are different. They are discussed in detail beginning on page 113. Each will be imported in turn by the user.

Dual Inlet.

Click **Import Analyses**. Select "F --> My 251" from the mass spectrometer combo box. "Finnigan ISODAT" is automatically displayed in the **Import Format** combo box. Click **OK**. The file dialog form will open and display all of the .wks files on the diskette. Select Finn_di.wks. The status form should open and three lines will be processed—this may take a few minutes. Note that 24 records have been added to LIMS. Three $\delta^{15}N$ values and 21 other values should have been imported. These

include sample and standard major ion beam voltages, ion gauge values for the standard and sample, and voltages of some interfering masses of the sample. One can examine these analyses as follows. Click **Add or Change Analyses**. Click "F --> My 251" and click **List**. The first line shows a $\delta^{15}N$ value (procedure code 580) of 0.73 of N-40 for analysis F-18206. In addition the $\delta^{15}N$ value, LIMS has imported seven other values. Specifically, the following procedure codes have been imported for each of the three analyses:

    124 m/z = 28 ion beam (sample)
    138 m/z = 40 ion beam (sample)
    140 m/z = 44 ion beam (sample)
    161 Ion gauge (sample)
    162 Ion gauge (standard)
    163 Major ion beam (sample)
    164 Major ion beam (standard)

Values for all of these parameters have been saved in LIMS. Select procedure code 161 of analysis F-18206. A value of 2.9617180824 has been saved in LIMS for ion gauge reading of the sample. Click **Close**.

    Importing Finnigan isotopic data is not always straightforward. Sometimes the column heading of the data one wishes to import is not what one expects. Examine the format of the data just imported. Open Excel. Open A:\Finn_di.wks. One will see that isotopic results start in row 6 and that each row contains all the isotopic results for a given analysis number (Finnigan's "spec no."). In this file the $\delta^{15}N$ values are given in the column with the heading "d-29/28."

GCC.

    Click **Import Analyses**. Select "P --> My Delta Plus" from the mass spectrometer combo box. "Finnigan ISODAT" is automatically displayed in the **Import Format** combo box. Click **OK**. The file dialog form will open and display all of the .wks files on the diskette. Double click F_GCCCO2.wks. LIMS will display the message (if LIMS doesn't show this message, see the note below):

    Finnigan GCC analyses found. For the reference sample IDs, LIMS will use:

    R-2 for the CO_2 reference gas

    (These can be changed using the configuration form. To change, click Cancel and click Special Features on the main menu.)

This message indicates that R-2 will be substituted for the Our Lab ID of the reference gas (standard). Click **OK**. LIMS will open the **Status** form, will import the $\delta^{13}C$ and $\delta^{18}O$ values, and advise the user that three analyses (P-515 through P-517) and 42 records have been imported. Delta values for 7 peaks

of each analysis have been imported (3 analyses $\times$ 7 peaks $\times$ 2 δ values per peak = 42 records). Page 116 discusses several factors that need to be considered to import Finnigan GCC analyses.

EA.

    The user needs to import the isotopic data for Mr. Johnson's samples from Victoria, B.C. Click **Import Analyses**. Select My Delta Plus and click **OK**. Select Finn_EA.wks and click **Select**. LIMS will advise the user that elemental analyzer analyses have been found and that R-2 will be used for the CO_2 reference and R-3 for the N_2 reference. Click **OK**. LIMS will import analyses P-620 through P-659 (160 records). For each elemental analyzer analysis of a C- and N-bearing substance, ISODAT provides two peaks and two isotopic analyses. The first analysis is of N_2 gas (peak 1 is the N_2 reference and peak 2 is the sample), and the subsequent analysis is of CO_2 gas (peak 1 is the sample and peak 2 is the CO_2 reference). If the user checks analyses P-620 and P-621 by clicking **Add or Change Analyses**, selecting "P--> My Delta Plus" from the Mass Spec combo box, and clicking **List**, the user will find that both $\delta^{13}C$ and $\delta^{18}O$ analyses have been imported. LIMS has correctly identified the N_2 reference gas as R-3 and assigned it a $\delta^{15}N$ value of -4.13‰ (procedure code 500) and identified the CO_2 reference gas as R-2 and assigned it a $\delta^{13}C$ value of -41.22, both obtained from the table of references. LIMS has retained the asterisks from the ISODAT .wks file identifying the references. Note that both peaks 1 and 2 have N and C concentration values listed for them (the values listed for procedure codes 190 and 189, respectively). This completes the fifth task in Fig. 3.

    LIMS can also import Finnigan $\delta^{34}S$ elemental analyzer analyses. Page 116 discusses several factors that are important in importing Finnigan elemental analyzer analyses.

    Click analysis P-100 and click **Close** to close the **Add or Change Analyses** form.

<p align="center">Micromass Import Format</p>

    Micromass uses comma separated variable (csv) text files that can be imported into spreadsheet programs. The format of dual inlet files for various gases is relatively similar according to Micromass; however, the format for continuous flow samples has varied often. According to Tim Brockwell, providing a stable format for continuous flow measurements has not been given a high priority. Therefore, currently LIMS does not import Micromass continuous flow analyses.

    Next import some $\delta^{18}O$ values of water from a dual inlet Micromass file. Click **Import Analyses**. Select "M --> My Micromass" from the mass spectrometer combo box and "Micromass" will be loaded into the **Import Format** combo box. Click **OK** and the file dialog form will show all of the .csv files on the diskette. Select the file Mm_o18w.csv and click **Select**. LIMS will inform the user that there are no Micromass analyses in the database and will suggest a default value of 1 for the first analysis number. Because Micromass does not maintain an integer analysis number, incremented sequentially for each analysis, Micromass users are forced to generate and maintain such analysis numbers themselves. The

user should accept the default of 1 and click **OK**. Five lines are processed and 30 records are imported (Analyses M-1 through M-5). Thus, results of 6 procedures have been stored for each analysis (line in the file). In addition to importing $\delta^{18}O$ values, LIMS has imported the following procedure codes:

     161 Ion gauge (sample)
     162 Ion gauge (standard)
     163 Major ion beam (sample)
     164 Major ion beam (standard)
     193 Delta 13C received unexpectedly

The user can open the **Add or Change Analyses** form and verify this. (Select "M --> My Micromass" for the mass spectrometer, and click **List**. The code 193 appears for each analysis because water samples (medium 1) were analyzed, and LIMS knows that water samples have only H and O in them—no C. But the mass spectrometer analyzed CO_2 samples and saved both $\delta^{13}C$ and $\delta^{18}O$ values. Thus, LIMS imports $\delta^{13}C$ values and stores them as procedure 193. Note that Micromass' "Run Serial Number," if available, is stored in the comment field, for example for analysis M-5 as "RSN = 2572." Close the **Add or Change Analyses** form.

LIMS For Light Stable Isotopes Configuration Form

Suppose one does not want to import ion gauge readings or major ion beam voltages. The user needs to set a software flag to disable importing of these values. Click **Special Features**. Enter the password if requested. Click **Config**. The **LIMS For Light Stable Isotopes Configuration** form will open (Fig. 17). This form allows users to (i) edit eight alternative field (column) names of the Table of Samples, (ii) edit the labels "top" and "bottom" on the samples form (and the range of samples report), (iii) change the color of many of the forms in LIMS, (iv) set software switches, and (v) edit the value of various tokens used in the software.

Click **List**. Select "STORE_INTERF_MASSES" and click it. Click **Edit**. Change the entry in the **Value** text box from -1 to 0 (zero, not the letter oh). Click **Save**. Click **List**. Click "STORE_MAJOR_VOLTAGES." Click **Edit**. Change the entry in the **Value** text box from -1 to 0. Click **Save**. Click **List**. Click "STORE_EA_CONCENTRATIONS." Click **Edit**. Change the entry in the **Value** text box from -1 to 0. Click **Save**. Click **List**. Click "STORE_ION_GAUGES." Click **Edit**. Change the entry in the **Value** text box from -1 to 0. Click **Save**. Click **List**. Click "STORE_UNEXPECTED_PROCEDURES." Click **Edit**. Change the entry in the **Value** text box from -1 to 0. Click **Save**. Click **Close**. Click **Close** on the **Special Features** subform. Now interfering masses, major ion beam voltages, elemental analyzer concentrations, ion gauge readings, and unexpected procedures will not be imported. This will prevent LIMS from importing unneeded information and will aid in keeping the user's database smaller. As a consequence, queries will run more quickly and LIMS will respond more quickly. Users will need to set to -1 any of these parameters they need to store. An extensive discussion of the **LIMS For Light Stable Isotopes Configuration** form starts on page 85.

Fig. 17. LIMS For Light Stable Isotopes Configuration form.

Correction Factors and Normalization Equations Form

The δ values imported into the table of analyses in LIMS are called penultimate delta values, that is, the delta value before the last. To calculate the final delta value, one uses the equation

$$\text{Final delta} = a \times \text{Penultimate Delta} \; + \; b$$

where the coefficients a and b are determined by analyzing reference materials with known δ values (see Coplen, 1988, for a discussion of normalization). The coefficient b takes into account drift of the working standard, etc. The coefficient a takes into account contraction of the δ scale by one's mass spectrometer or variation in the H_3^+ contribution to the $m/z = 3$ ion beam when analyzing hydrogen. In the case of $\delta^{34}S$, the user could employ it to take into account the difference between the SF_6- and SO_2-based sulfur-isotope scales.

Click **Correction Factors and Normalization Equations**. The **Analyses and Normalization Equations** form opens (Fig. 18) allowing one to choose a mass spectrometer and isotope to view. Start with ^{18}O for water samples on the Dupont by selecting "D (DuPont) for 18O (water)" from the **Correction Factor List** combo box. The **Analyses from** and **to** text boxes are automatically filled with the last 501 analyses. Click **Query** to display the list of all DuPont analyses in the database between D-116962 and D-117462.

The mass spectrometric analysis number in the first column increases downward and consists of the single letter prefix of the mass spectrometer and the integer analysis number. The peak number is given in the second column. The value of the peak number will be 1 for all dual inlet analyses. It can range between 1 and 999 for continuous flow compound specific GC combustion isotopic analyses. The time and date occupy the third column. The sample analyzed (Our Lab ID) is given in the fourth column, and port and working standard ID are given in the fifth and sixth columns. The coefficients a and b, separated by a comma, are given in the seventh column. Currently many b values are null. The last column contains range markers. A range marker shows a range of analyses (such as 117446 through 117456) and the coefficients a and b that are applicable to the analyses in that range. The "pd" stands for penultimate δ value. Thus, the last range marker on screen,

117446 - 117456; 1.00000*pd-0.47

indicates that the final delta value of each analysis **of a water sample** in the range D-117446 to D-117456 is calculated by multiplying the penultimate δ value by 1.00000 and subtracting 0.47. The range marker is shown at the bottom of a range of analyses, that is on the last analysis (D-117456). One can move from analysis to analysis by use of the vertical scroll bar on the right side of the form. Note that **all** of the DuPont analyses are shown, not just the $\delta^{18}O$ analyses. Because DuPont for ^{18}O (water) was selected from the Correction Factor List, one can only put range markers on $\delta^{18}O$ analyses of water samples. Each $\delta^{18}O$ analysis of a water sample is indicated by an asterisk (*) after the Our Lab ID in the fourth column.

Fig. 18. Analyses and Normalization Equations form.

Unmark is used to delete a range marker. Click on the range marker "117409 - 117445; 1.00000*pd-0.55" at analysis D-117445. Note that the next range marker which is at D-117456 covers the range 117446 - 117456. Click **Unmark**. The range marker on D-117445 is removed and the range of the range marker at D-117456 is updated to 117409 - 117456.

One creates a range marker in two ways. The first to be discussed is highlighting an analysis and then double-clicking on it. The user should Select "D (DuPont) for 13C" from the **Correction Factor List** combo box. The **Analyses from** and **to** text boxes are automatically filled with the last 501 analyses. All of the DuPont isotopic analyses need to be evaluated so replace 116962 in the **Analyses from** text box by 1. Click **Query** to display the list of analyses. The working standard was changed on Feb. 22, 1995—the standard changed from 362 to 53 (at analysis D-117334). Therefore, the user will put the first range marker at the last $\delta^{13}C$ analysis before the working standard was changed, that is at D-117332. The user should move to this analysis and click it. The user should press the **Enter** key or double-click on analysis D-117332 to create a range marker. In a few seconds, the **Normalization Equation Coefficients** form should appear (Fig. 19).

The **Normalization Equation Coefficients** form is used to calculate the coefficients a and b from the isotopic analysis of reference materials interspersed with the samples. The coefficient a, the expansion factor, is labelled **Exp. Coef**, and b, the additive correction factor, is labelled **Add. Corr**. (see Fig. 19). All of the $\delta^{13}C$ reference materials analyzed between D-000001 and D-117332 are shown in the subform in red font. D-116957 is the first analysis. One can use the vertical scroll bar to scroll through the analyses. In this example, we have 23 analyses. The sample number (Our Lab ID) is shown in the first column and the mass spectrometer analysis number is in the second. The peak number is appended to the analysis number as a decimal. For example, peak number 14 of analysis number 123456 would be P-123456.014. If the peak number is 1 (which it is for all dual inlet analyses, and it is here), **the ".001" is not shown**. **This feature is adopted for most of the forms and reports in LIMS**. The working standard ID appears in the third column, the port number in the fourth, the mass spectrometer error code in the fifth (typically not used by most vendors, so it is 0), the penultimate delta in the sixth, the final delta for the analysis in the seventh, and an Ignore check box in the eighth column. Note that LIMS may use -999 as a default delta value to indicate a null value. Analysis D-117195 was evidently lost, and the mass spectrometer error code indicates that the sample was too small. The DuPont mass spectrometer then provided the value of -999 as the penultimate delta value and set the Ignore check box to True. Because of unknown difficulties with a sample, the DuPont mass spectrometer analyzed the sample three times (D-116957 through D-116959) and automatically ignored the first two analyses. At this point, the user should peruse the analyses and ignore any additional analyses that should not be included in the determination of the coefficients a and b. The mean is 2.04 and the standard deviation is 0.02. Thus, there is no statistically valid reason for eliminating any of these analyses. The value following the **Reference** combo box is 1.89 per mill [note that LIMS uses the ISO spelling of ‰, (ISO, 1992)]. This is the "true" value of this reference material that LIMS obtained from the table of references (see page 89 for instructions on adding, editing, and deleting δ values of references). Because the mean value is 2.04, the difference is -0.15. This value appears in text box labelled Proposed Add. Corr (Proposed Additive Correction Factor) and is the proposed value of the coefficient b. The value of a is 1.0000, in the box above. There is only one reference material, C-5. Because it takes at least two points to determine the coefficients of a straight line, one cannot determine another value for a, and the existing proposed value

Fig. 19. Normalization Equation Coefficients form.

of 1.00000 is retained. Calculation of an expansion coefficient different than 1.00000 is demonstrated in an example below with hydrogen isotopic data on page 68. To accept the factor of -0.15 and apply it to analyses D-000001 though D-117332, click the large arrow button between the labels Accepted and Proposed. The δ^{13}C values in on the underlying form are automatically updated and the range marker

1 - 117332; 1.00000*pd-0.15

appears in column seven of the **Analyses and Normalization Equations** form (one can grab the top of the **Analyses and Normalization Equations** form with the mouse and move it down to view the underlying form). The proposed values have been copied to the text boxes below the label **Accepted**. This is an easy way to apply correction factors to a large quantity of data quickly. It potentially eliminates errors that commonly can occur when correcting data "by hand."

If one wants to apply a different value for the additive correction factor than is shown (proposed), one only needs to delete the proposed value and enter the preferred value. Clicking the large arrow key applies the new preferred value and updates the isotopic data in the selected range. If one wants to apply a value for the expansion coefficient other than 1.00000 (the proposed value), one needs to deselect the **Force Exp. Coef. to 1.00000** check box and replace the proposed value by the new value. Clicking the large arrow key applies the values in the "Proposed" column and updates the isotopic data in the selected range.

The user should now click **Print** to obtain a permanent record of this determination of normalization coefficients (see Fig. 20). The user should compare his or her printer output with that in Fig. 20 to ensure that no characters have been omitted.

Click **Close** and move to analysis D-117461, the last δ^{13}C analysis in the list. Double-click on it. A correction factor of -0.17 should be shown. Apply it by clicking the large arrow button and close the form. The correction factors for all of the δ^{13}C data in the database have now been completed.

To calculate correction factors (normalization coefficients) for the δ^{18}O values of the carbonates, select "D (DuPont) for 18O (other than water)" from the **Correction Factor List** combo box and press **Enter**. Replace the current value of 116962 in the **Analyses from** test box with 1. Click **Query** to show the DuPont analyses again. This time the asterisks denote δ^{18}O analyses (other than water). Water is treated separately because the coefficients a and b are sometimes different than for non-water samples. Double-click on D-117333. The standard deviation is 0.05 so accept the existing isotopic results. Click the large arrow button and the additive correction factor of -1.25 is applied to the analyses in the selected range. Close the **Normalization Equation Coefficients** form. The range marker

1 - 117333; 1.00000*pd-1.25

is shown in column eight of the **Analyses and Normalization Equations** form. Move to D-117462

Expansion Coefficient: 1.00000
   Correction Factor: -0.15

Date	Analysis #	Port	Proc. Code	Error Messages	Penultimate Delta	Ignore
C-5						
1/6/95 9:32:32 AM	D-116957	77	312	10 --> Ignore	+1.84	Ignore
1/6/95 9:50:46 AM	D-116958	77	312	10 --> Duplicate	+2.03	Ignore
1/6/95 10:18:04 AM	D-116959	77	312		+2.04	
1/7/95 12:14:18 AM	D-116993	84	312		+2.04	
1/7/95 3:07:16 AM	D-117003	89	312		+2.04	
1/8/95 1:39:18 PM	D-117011	73	312		+2.02	
1/9/95 8:13:36 PM	D-117023	75	312		+2.05	
1/9/95 10:29:59 PM	D-117031	84	312		+2.05	
1/11/95 12:33:03 AM	D-117053	75	312		+2.03	
1/11/95 4:33:47 AM	D-117067	83	312		+2.04	
1/12/95 7:12:21 AM	D-117089	74	312		+2.04	
2/10/95 11:46:37 AM	D-117107	83	312		+2.03	
2/13/95 6:19:52 PM	D-117121	74	312		+2.01	
2/13/95 8:38:46 PM	D-117129	78	312		+2.04	
2/15/95 2:27:56 AM	D-117154	76	312		+2.04	
2/15/95 9:24:37 AM	D-117178	89	312		+2.03	
2/15/95 3:36:28 PM	D-117182	71	312		+2.03	
2/16/95 7:20:38 AM	D-117195	71	312	03 --> Too Small or	-999.00	Ignore
2/17/95 3:45:41 PM	D-117251	89	312		+2.06	
2/18/95 8:44:25 PM	D-117263	83	312		+2.01	
2/20/95 6:19:34 PM	D-117328	74	312		+2.01	
2/21/95 8:45:39 PM	D-117330	77	312		+2.04	
2/21/95 10:30:02 PM	D-117332	81	312		+2.06	
					+2.04 ± 0.02	

Computed value of C-5 relative to VPDB: 1.89 per mill
Value should be (from reference table): 1.89 per mill

Fig. 20. Example of Normalization Equations Coefficients report.

and double-click. The proposed additive correction factor is -1.32. Accept it (click the arrow button) and close the **Normalization Equation Coefficients** form. The δ^{13}C and δ^{18}O correction factors for carbonates in the database (also for G samples if there were any for δ^{13}C and δ^{18}O) are completed.

LIMS allows one to take into account expansion or contraction of the δ scale. As an example, calculate the normalization coefficients and allow the expansion coefficient to differ from 1.00000. From the **Analyses and Normalization Equations** form select "V (VG in 5B131) for 2H" and click **Query**. The correction factors (normalization equation coefficients) have been calculated for all but the last 21 analyses. Thus, one only needs to determine correction factors for these 21 analyses. Since these analyses extend over less than 1/4 day, one can treat them as one range. Double-click on V-128329. When the **Normalization Equation Coefficients** form opens, click the **Reference** combo box and select W-5. The proposed values of the expansion coefficient and additive correction factor are 1.00000 and 8.03. Accept these values and click on the arrow button to update the underlying form. Now click the option button **Show All References** from the References option group. The analyses of W-6 are now added to the subform. Their Final Deltas are about -382. The true value, -395.1, can be found by clicking the **Reference** combo box to open it. What has happened is that the mass spectrometer has "misbehaved" and the H_3^+ value has increased significantly. One needs to normalize the isotopic data over this range and one can do this by clicking **Force Exp. Coef. to 1.00000** check box in order to uncheck it. The message

Will determine best fitting normalization equation coefficients.

appears. Click **OK** or press **Return**. The Proposed and Accepted Expansion Coefficient and Additive Correction Factor have changed to 1.03879 and 10.42. The Final Delta values for the two W-6 samples should have changed to -395.63 and -394.56, appropriate for a true value of -395.1.

To determine the best fitting coefficients, the option button **Show All References** must be selected. If one has three or more reference materials in the range of analyses, analyses of all three will appear in the subform and will be used to calculate the best fitting coefficients unless one has checked the Ignore box for one or more of them. Given analyses for three materials, analyses for any one can be eliminated by ignoring all of its analyses (checking the **Ignore** check box of each of its analyses). Close the **Normalization Equation Coefficients** form.

The second method to create a range marker is to use **Mark**. In the event that there are no analyses of reference samples in the range to be marked, the **Mark** button is the only method to create a range marker. The user will first be prompted for the expansion coefficient and then for the additive correction factor. The user should select "F (My 251) for 15N" from the **Correction Factor List** combo box. Click **Query**. Click (do not double-click) on analysis F-18208 to select it unless it is already selected. Click **Mark**. Use 1.00000 for the expansion coefficient. Enter -0.28 for the additive correction factor. The range marker

1 - 18208; 1.00000*pd-0.28

has been created.

View/Edit opens the **Normalization Equation Coefficients** form using the range marker affecting a particular analysis unless there are no reference samples in that range. In that case, LIMS displays the message:

No reference samples found in the correction range selected.

Note that the highlighted selector bar need not be on a range marker, and the current analysis remains highlighted rather than moving the highlighting to a range marker. If the highlighted analysis does not have an asterisk, the user will be advised that they need to move to an analysis that matches that selected in the **Correction Factor List** combo box, that is, one that does have an asterisk in column 4.

Now do the correction factors for Mr. Johnson's samples from Victoria, B.C. Select "P (My Delta Plus) for ^{13}C." Click **Query**. Note the asterisks in column 6. ISODAT uses these to indicate that this is a standard. Do not confuse these asterisks with the ones in column 4 which indicate that the isotope of an analysis is identical to that selected in the **Correction Factor List** combo box. Double click on peak 2 of P-659. From the **Reference** combo box choose G-5, which is the reference material that was analyzed in the elemental analyzer with Mr Johnson's samples. The standard deviation is 0.01, so accept the proposed additive correction factor of -0.27 and click the arrow button. This completes the δ^{13}C corrections; click **Close**. Repeat for My Delta Plus for δ^{15}N. Select "P (My Delta Plus) for 15N." Click **Query**. Double click on the last δ^{15}N analysis, that is, the last one with an asterisk in column 4 (peak 2 of P-658). After the **Normalization Equation Coefficients** form opens, select G-5 from the **Reference** combo box. The additive correction factor is -0.13 and the standard deviation is 0.06 so accept these coefficients and click on the large arrow button. Click **Close**. This completes task 6 in Fig. 3.

Close the **Analyses and Normalization Equations** form.

Print Samples in Progress Form

When mass spectrometer analyses are added to the Analyses table in LIMS, they are also automatically added to the Table of Samples In Progress. When the user is satisfied with the δ value of a sample (assuming that the sample may require replicate analysis), the final δ value is "stored," saving its δ value in the Table of Samples. When a δ value of a sample is stored, that sample is removed from the Table of Samples In Progress.

As an example, print the δ^{13}C results for the samples C-5 through C-7. Click **Print Samples in Progress** and the **Print Samples in Progress** form should open (Fig. 21). Select C for the Prefix. The Isotope combo box is automatically updated and opened displaying ^{13}C and ^{18}O as possible selections. Select ^{13}C. Enter 5 and 7 in the **From** and **to** boxes, respectively. Click **Print**. LIMS displays the message
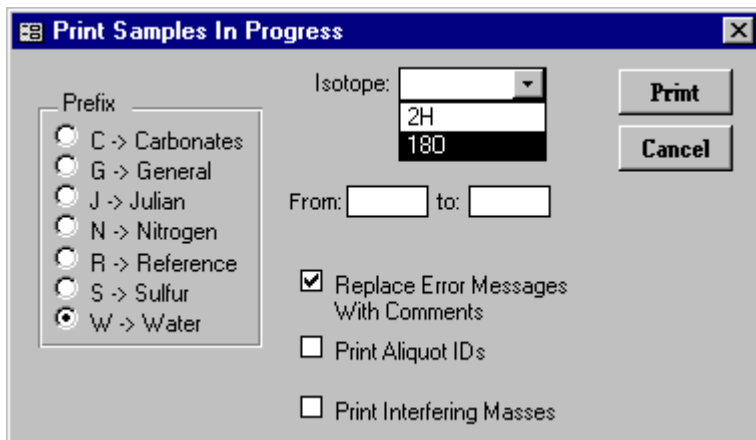
Fig. 21. Print Samples In Progress form.

Do you really want to print all of the analyses of reference sample C-5?

This message appears in order to allow the user to modify the selection to minimize wasting of paper. Click **Yes**. A Samples In Progress report is printed for the selected range (Fig. 22). The user should compare his or her printer output with that in Fig. 22 to ensure that no characters have been omitted. Note that analyses D-116957, D-116958, and D-117195 are ignored for sample C-5 (note large **X** in right column of Fig. 22). LIMS calculates a mean $\delta^{13}C$ value, 1.89, and two standard deviations. The first is labelled Std Dev 1 and includes all of the analyses. The second, Std Dev 2, is calculated after the farthest outlier is eliminated. Means for both standard deviations are determined and the one that appears as the Final Delta is the one associated with the Std Dev in bold font. Users might look at the existing code that is enabled when the software switch, Reston Features (page 86), is enabled. This algorithm in LIMS can be modified to suit the user's own needs.

Aliquot IDs and (or) interfering mass values can be printed (assuming they exist in the database). Click **Print Samples In Progress** on the Main Menu. Select the Prefix N. Select ^{15}N for the Isotope. Check the **Print Aliquot ID's** and the **Print Interfering Masses** check boxes. The **Replace Error Messages With Comments** check box should already be checked. Enter 41 in the **From** text box. Click **Print**. The report printed (Fig. 23) shows values of m/z = 28, 40, and 44 for this sample. The user should compare his or her printer output with that in Fig. 23 to ensure that no characters have been omitted. Ion gauge values for the sample and standard are shown, and values for the major ion beam electrometer outputs of the sample and standard are shown.

Click **Print Samples In Progress**, select **Prefix** G, select ^{13}C for the **Isotope**, enter a sample range of 13 to 30, and click **Print**. This will print the $\delta^{13}C$ analyses of Mr. Johnson's samples. Repeat for $\delta^{15}N$. This completes the seventh task in Fig. 3.

Edit Samples In Progress Form

Edit Samples In Progress is used to edit the analyses that determine the Final δ value. Click **Edit Samples In Progress** to open the **Edit Samples In Progress** form. Select C as the **Prefix** and ^{13}C as the **Isotope**. Enter 5 in the **From** text box. Click **Query**. The analyses of C-5 are shown (Fig. 24). Note that two standard deviations are shown. To show the effect of including poor analytical data on Std Dev 1, click on the Ignore box for analysis D-116957. The **Final Delta** and both standard deviations are immediately updated. Note that **Std Dev 1** changes from 0.01 to 0.04. Click the same check box to ignore D-116957.

A **Final Delta** will not be calculated for a sample with a null value (or -999) in **Pen. Delta** field (penultimate delta). To demonstrate this, click the Ignore box of D-117195 to uncheck this box. Note that **Final Delta** and both standard deviations are cleared. Click the Ignore box of D-117195 so that a numerical value in **Final Delta** is displayed.

Date	Analysis.Pk	Port	Proc. Code	Comments	Penultimate Delta	Corr. Coefs.	Corrected Delta	Ign
C-5	**Reference**	**Q1**		**02 --> C [Cal] calcite**				
1/6/95	D-116957	77	312		+1.84	1.00000, -0.15	+1.69	X
1/6/95	D-116958	77	312		+2.03	1.00000, -0.15	+1.88	X
1/6/95	D-116959	77	312		+2.04	1.00000, -0.15	+1.89	
1/7/95	D-116993	84	312		+2.04	1.00000, -0.15	+1.89	
1/7/95	D-117003	89	312		+2.04	1.00000, -0.15	+1.89	
1/8/95	D-117011	73	312		+2.02	1.00000, -0.15	+1.87	
1/9/95	D-117023	75	312		+2.05	1.00000, -0.15	+1.90	
1/9/95	D-117031	84	312		+2.05	1.00000, -0.15	+1.90	
1/11/9	D-117053	75	312		+2.03	1.00000, -0.15	+1.88	
1/11/95	D-117067	83	312		+2.04	1.00000, -0.15	+1.89	
1/12/95	D-117089	74	312		+2.04	1.00000, -0.15	+1.89	
2/10/95	D-117107	83	312		+2.03	1.00000, -0.15	+1.88	
2/13/95	D-117121	74	312		+2.01	1.00000, -0.15	+1.86	
2/13/95	D-117129	78	312		+2.04	1.00000, -0.15	+1.89	
2/15/95	D-117154	76	312		+2.04	1.00000, -0.15	+1.89	
2/15/95	D-117178	89	312		+2.03	1.00000, -0.15	+1.88	
2/15/95	D-117182	71	312		+2.03	1.00000, -0.15	+1.88	
2/16/95	D-117195	71	312		-999.00	1.00000, -0.15		X
2/17/95	D-117251	89	312		+2.06	1.00000, -0.15	+1.91	
2/18/95	D-117263	83	312		+2.01	1.00000, -0.15	+1.86	
2/20/95	D-117328	74	312		+2.01	1.00000, -0.15	+1.86	
2/21/95	D-117330	77	312		+2.04	1.00000, -0.15	+1.89	
2/21/95	D-117332	81	312		+2.06	1.00000, -0.15	+1.91	
3/4/95	D-117399	85	312		+2.06	1.00000, -0.17	+1.89	
3/4/95	D-117407	85	312		+2.05	1.00000, -0.17	+1.88	
	Std Dev 1 = 0.01						**Final Delta = 1.89**	
	Std Dev 2 = 0.01							
C-6	**Johnson**	**DHC2-0.25**		**02 --> C[Cal] calcite**				
1/5/95	D-116943	70	312		-2.07	1.00000, -0.15	-2.22	
2/9/95	D-117093	75	312		-2.05	1.00000, -0.15	-2.20	
	Std Dev 1 = 0.01						**Final Delta = -2.21**	
C-7	**Johnson**	**DHC2-0.50**		**02 --> C[Cal] calcite**				
1/5/95	D-116945	71	312		-2.08	1.00000, -0.15	-2.23	
2/9/95	D-117095	76	312		-2.05	1.00000, -0.15	-2.20	
	Std Dev 1 = 0.02						**Final Delta = -2.22**	

Fig. 22. Example of Print Samples In Progress report.

Date	Analysis.Pk	Port	Proc. Code	Comments	Penultimate Delta	Corr. Coefs.	Corrected Delta	Ign
N-41	**Johnson**	**1286**			**60 --> N [N2O] nitrous oxide**			
Aliquot ID: Aliquot 5								
6/6/96	F-18208		124	m/z = 28 ion b	0.996	1.00000,		
6/6/96	F-18208		138	m/z = 40 ion b	2.078	1.00000,		
6/6/96	F-18208		140	m/z = 44 ion b	0.039	1.00000,		
6/6/96	F-18208		161	Ion gauge (sam	2.9372	1.00000,		
6/6/96	F-18208		162	Ion gauge (sta	2.93681	1.00000,		
6/6/96	F-18208		163	Major ion beam	1.00118	1.00000,		
6/6/96	F-18208		164	Major ion beam	1.0042	1.00000,		
6/6/96	F-18208		580	0.636 v	-2.85	1.00000, -0.28	-3.13	

Fig. 23. Example of Print Samples In Progress report with Print Aliquots IDs and Interfering Masses check boxes enabled.

Fig. 24. Edit Samples In Progress form.

One may easily view the results of compound specific isotopic analyses. As an example, set the Prefix to G, select ^{13}C from the Isotope combo box, and click **Query**. Move to sample G-6 by clicking **List** or the navigation buttons. Listed are δ^{13}C values for a sludge sample. To print a report of these data (Fig. 25), click **Close**, click **Print Samples In Progress**, select **Prefix** G, select **Isotope** 13C, enter 6 in the **From** text box, check the **Print Aliquot IDs** and the **Print Interfering Masses** check boxes, and click **Print**. The user should compare his or her printer output with that in Fig. 25 to ensure that no characters have been omitted. Note that no **Final Delta** value is calculated by LIMS. Such a value is probably not of much use because it is the average of the δ values of all of the aliquots. It is this value that would be stored in the Table of Samples and that would be displayed on the **Sample** form. Thus, it is necessary to use Samples In Progress for viewing and printing reports on compound specific analyses.

Open the **Edit Samples In Progress** form again if it was closed. Click **Prefix** G, select ^{13}C from the **Isotope** combo box, and click **Query**. Click **List** and select sample G-6. To delete the sample from the Table of Samples In Progress, click **Delete**. This act does not delete the sample (or analyses) from the database. It only removes the sample from the Table of Samples In Progress. To add it back, the user can click **Add Samples to Samples In Progress** on the Main Menu discussed below. Generally, the **Delete** button is rarely used because samples are removed automatically from the Table of Samples In Progress when the Final Delta is stored in the Table of Samples by clicking **Store Samples In Progress** as described below.

Click **List** and select sample G-13. The user can review the δ^{13}C values of Mr. Johnson's samples. Use the **List** button or the navigation buttons to move to another sample. The user can repeat for δ^{15}N values by selecting 15N from the **Isotope** combo box and clicking **Query**. No editing of the samples is necessary; thus, this completes the eighth task in Fig. 3. No sample reruns are necessary because we only planned to analyze each sample once. Thus, the ninth task in Fig. 3 is also completed.

Occasionally one may realize that the mean δ value calculated from several mass spectrometer analyses is in error and needs to be corrected. If the user has a good idea of what the true δ value of the sample should be, *e.g.*, the average of two "close" δ values, the **Add Ethereal** button can be clicked to add this value to the table of analyses. Clicking this button brings up the "Ethereal mass spectrometer." Enter the δ value for the sample—this is the corrected δ value, not the penultimate δ value. Ignore (check the **Ignore** check box) all of the other analyses of the selected sample. If all analyses except the Ethereal δ value are ignored by checking each **Ignore** check box, then the Ethereal δ value is stored in the Table of Samples when Store Samples in Progress is executed with the **Single Analysis** check box checked (see below). Such a case can arise, for example, when there are two analyses of a sample that are fairly close, but not close enough to satisfy the algorithm that calculates the Final Delta. If the sample were exhausted, the user could store an average of the two extant analyses.

The other buttons on the **Edit Samples In Progress** form are described below:

Retrieve is described below in the section titled "Add Samples to Samples In Progress" (see page 78).

Date	Analysis.Pk	Port	Proc. Code	Comments	Penultimate Delta	Corr. Coefs.	Corrected Delta	Ign

G-6   Johnson   Sludge 1   26 --> G [C & N] C- and N-bearing material

Aliquot ID: C4

| 2/18/96 | P-101 | 0 | 355 | | -25.55 | 1.00000, -0.36 | -25.91 | |

Aliquot ID: C5

| 2/18/96 | P-101.002 | 0 | 355 | | -25.35 | 1.00000, -0.36 | -25.71 | |

Aliquot ID: C6

| 2/18/96 | P-101.003 | 0 | 355 | | -23.33 | 1.00000, -0.34 | -23.67 | |

Aliquot ID: C7

| 2/18/96 | P-101.004 | 0 | 355 | | -23.55 | 1.00000, -0.34 | -23.89 | |

Aliquot ID: C8

| 2/18/96 | P-101.005 | 0 | 355 | | -23.81 | 1.00000, -0.34 | -24.15 | |

Aliquot ID: C9

| 2/18/96 | P-101.006 | 0 | 355 | | -24.35 | 1.00000, -0.34 | -24.69 | |

Aliquot ID: None

| 2/19/96 | P-110 | 0 | 355 | | -22.84 | 1.00000, -1.68 | -24.52 | |

Fig. 25. Example of report for $\delta^{15}N$ results of compound specific isotope-ratio analyses (C4 through C9).

Print allows the user to print analyses of the prefix, isotope, and range selected. However, it is not quite as flexible as the **Print Samples In Progress** form because the options of printing aliquot IDs or printing interfering masses are not offered.

Close the **Edit Samples In Progress** form.

Store Samples In Progress Form

Ranges of samples are "stored" (Final Delta values of samples in the Table of Samples In Progress are calculated and saved in the Table of Samples, and the sample is removed from the Table of Samples In Progress) with the **Store Samples In Progress** form. Click **Store Samples In Progress**. Select **Prefix** C and the **Isotope** combo box is updated and opened. Select ^{13}C. For the range choose a range large enough to include all the samples to be stored. Use 1 to 999. Click Store and the **Status** form will display the samples as they are stored. Only samples for which a Final Delta can be calculated are stored. Thus, there must be at least two analyses for every sample that is stored. Samples for which correction factors have not been determined cannot be stored because a Final Delta cannot be calculated for them. When the samples have been stored, click **OK**.

Store Mr. Johnson's samples for δ^{13}C and all others that have only a single analysis. Click **Store Samples In Progress**. To store samples that have only a single analysis, the user must check the **Store Single Analysis** check box. Click **Store Samples In Progress**. Click **Prefix** G, select **Isotope** ^{13}C, enter 1-999 for the sample range, check the **Store Single Analysis** check box, and click **Store**. When LIMS gets to sample G-5 it displays the message:

Sample G-5 has data for more than 1 peak. Therefore, a mean value will not be calculated and no value will be stored in the Samples Table.

Do you want this sample deleted from Samples In Progress?

Click **Yes** because the mean value of this sample is meaningless as discussed above. Deleting the sample from the Table of Samples In Progress does not delete any isotopic analyses or results. LIMS repeats the message for sample G-6. Click **Yes**. When the samples have been stored, click **OK**.

Repeat for **Prefix** G and **Isotope** ^{15}N. Mr. Johnson's samples have now been "stored," completing the tenth task in Fig. 3.

To print a report of Mr. Johnson's samples, click **Projects**. Double click on 6/6/95 Johnson to open the **Project** form. Click **Print Report** and a final project report is printed. To save isotopic data from this project in ASCII format on a diskette, click **Results** and click **Yes**. Insert a diskette into the computer. LIMS will advise the user that the file will create a file with 18 samples and will save the file with a default name of Johnson.txt on the diskette. The user can change this file specifier if desired. Click **Select** and the file is created. To save all of the information in the Table of Samples about each

sample in this project to a diskette in Excel 5.0 format, click **Results** and click **No**. Using LIMS default file specifier, the file G-13.xls is created on the diskette. Click **Close**. This completes the tasks on Fig. 3 for Mr. Johnson's samples and the results could be sent via mail or E-mail to him.

Add Samples to Samples In Progress Form

In the event that one wants to revise normalization coefficients for a sample and change the stored δ value, one will need to add the sample back into the Table of Samples In Progress. This can be done by clicking **Add Samples to Samples In Progress** on the Main Menu. The sample Prefix, the Isotope, and the sample range will need to be selected. If a sample is reanalyzed, the sample is automatically added to the Table of Samples In Progress.

One can also add a sample to the Table of Samples In Progress by clicking **Retrieve** on the **Edit Samples in Progress** form.

Normalization Equation Ranges Form

For audits, one may want to print the coefficients of the normalization equations and their ranges. This is done with the **Normalization Equation Ranges** form which is accessed by clicking **Normalization Equation Ranges** on the Main Menu. One needs to select a mass spectrometer and isotope from the **Normalization Equation List** combo box and enter the range of the mass spectrometer analyses.

This completes the discussion of the Example Database.

INSTALLING A NEW DATABASE FILE

A new database is installed when the user is ready to begin using LIMS in their laboratory. The database is a backend database that holds the samples, analyses, and projects of the user's laboratory. The user first needs to select from between two possible database files. If the database must be accessible by LIMS version 1.4 (the Access 2.0 version of LIMS), the user should install the Access 2.0 compatible database, LM4DATA.mdb. If only Windows 95 or NT 4.0 (or higher) platforms will be used for LIMS, the user should install Lm7data.mdb, which is only compatible with Access 97.

To install the new database, find the New Database diskette that contains the file that will be the backend database (either LM4DATA.mdb or Lm7data.mdb) and insert it into the computer. Locate the folder for the backend database. This is likely to be the folder in which Lm7datae.mdb now is found. Copy the new database file (either LM4DATA.mdb or Lm7data.mdb) from the New Database diskette to this folder. The user will need to delete the current backend database, change its name, or move it to another folder in order to force LIMS to query the user for the location of the new database.

When LIMS is opened, one or more mass spectrometers will need to be installed. Follow the instructions on page 91 and then close the **Mass Spectrometer Configuration** form. Click **New Project Login** on the Main Menu to open the **Login New Samples** form. Click **Add/Edit Customer** to open the **Customers** form. Customer # 001 should be visible. Click **Edit**. Replace MyLastName with the user's last name. Replace MyFirstName with the user's first name, *etc.* When finished, click **Save**. Click **List** or use the navigation buttons to view the customers in the table of customers. The customers "Test" and "Reference" will be found. "Test" is often used for samples that are employed to test a mass spectrometer or for fill-in samples whose δ values are not needed. "Reference" is normally used to designate reference materials. Click **Close** to close the **Customers** form and click **Cancel** to close the **Login New Samples** form.

When the **Login New Samples Form** opens, the **Country** combo box is set to the country selected in the **LIMS For Light Stable Isotopes Configuration Form**. See page 85 for instruction on how to set the default country to the user's country. The user should at this time set the software switches and other preferences on the **LIMS For Light Stable Isotopes Configuration Form**.

Click **Projects** on the Main Menu to open the **Search for Projects** form. Nineteen projects have already been created and should be shown. The submitter of five projects is Reference, and these are the H_2, CO_2, SO_2, N_2, and O_2 used as the references (standards) in continuous flow measurements. If one does not plan to employ continuous flow techniques, these projects can be deleted. There are fourteen Test projects. These are useful for testing. Several are for an elemental analyzer. Their samples are for empty boats and no boats for background determination. If other media are needed, now is a good time to add them (see page 93).

Stable isotope laboratories will typically employ a number of internally produced reference materials on a daily or weekly basis for their own quality assurance. The user should log all such reference materials into LIMS now. The known δ values versus VSMOW, VCDT, VPDB, AIR, or other

internationally accepted reference should be added to the table of references (see page 89).

The user should modify the **Alternative Field Names** on the **LIMS For Light Stable Isotopes Configuration** form (Fig. 17). For example, the user might be primarily interested in oceanographic samples and might prefer the names "Station", "Cast", "Niskin", and "Depth", for "User Def Caption 2", "User Def Caption 3", "User Def Caption 4", and "Elevation" (see page 85). If the user plans to employ the Excel 5.0 template for importing projects of samples entered by those submitting samples to the laboratory (this is strongly advised), the column headings will also need to be changed on the worksheet Alt.xls (see page 81). Note that the worksheet Alt.xls is protected, but there is no password. Thus, users can easily unprotect it, make the necessary changes, and protect it again. All yellow cells should remain unprotected; all others can be protected so that column headings cannot be changed accidentally by those submitting samples to the laboratory.

The new database is now ready for use.

The user should make backups of the backend database on a regular interval. Have at least two backups, for example, one for even days of the month and one for odd days of the month. In the author's laboratory, a copy is saved to another hard disk daily using an automatic backup program for .mdb files (Total Access Agent, http:/www.fmsinc.com). **The importance of regular, frequent backups cannot be stressed too strongly. If power fails while LIMS is writing to one's backend database, it will likely be corrupted and could be a total loss.** Thus, an uninterruptible power supply for the LIMS computer is very worthwhile.

IMPORTING PROJECTS USING THE EXCEL 5.0 TEMPLATE

An easy way for a user to create a project in LIMS is to import the sample headings and project information entered in an Excel 5.0 template file by the customer submitting the samples. This technique eliminates typographic errors by the laboratory staff. Any errors are the responsibility of the submitter of the samples.

The minimum required information that must be provided by the template file includes:

(1)   the submission date,

(2)   the name of the submitter (only last name may be needed if the last name is unique in the table of customers),

(3)   the numeric media code, and

(4)   Sample IDs for each of the samples submitted.

Other project information will be imported if it is present, *e.g.*, project purpose and location. Additional sample information, such as latitude, longitude, country, *etc.*, will be imported if it is present.

The LIMS diskette titled Excel 5.0 Template for Creating Sample Projects contains two Microsoft Excel 5.0 files: USGS.xls and ALT.xls. The two template files are unpopulated with data. The choice of which one to use is based on the following:

ALT.xls   This is for use by submitters who use a laboratory where Alternative Field Names are employed (see page 85). This probably includes the vast majority of users. The advantage of this template is that column headings can be changed to match the alternative field names.

USGS.xls   This is for use by users who submit samples to a laboratory that has not checked the **Alternative Field Names Enabled** check box on the **LIMS For Light Stable Isotopes Configuration** form, *e.g.*, the author's laboratory. The column names cannot be changed or importing will fail.

There is a significant difference in size between ALT.xls and USGS.xls, 97 kb and 425 kb, respectively. Most of this difference is due to the fact that USGS.xls contains all the states and counties in the U.S.

In order to use USGS.xls, the user only needs to ensure that the **Alternative Field Names Enabled** check box on the **LIMS For Light Stable Isotope Configuration** form is deselected. After a customer has entered his project and sample information in the spreadsheet, LIMS should import this information and create a project.

Part of Excel 5.0 template ALT.xls is shown in Fig. 26. In addition to customer information (last name, first name, address, *etc.*) and project information (submission date, title, and general location), the following fields are provided for sample information:

Sample ID	User Def Cap 2
Country Code	User Def Cap 3
State/Province Code	User Def Cap 4
Latitude	User Def Cap 5
Longitude	User Def Cap 6
Lat. Long. Accuracy	Cap 7
Collection Date/Time	Other Info
Ending Collection Date/Time	
Elevation	
Length Unit	
Top	
Bottom	

It is possible to change 10 of these (Sample ID, User Def Cap 2 through 6, Cap 7, Other Info, Top, and Bottom) using the **LIMS For Light Stable Isotope Configuration** form and selecting the **Alternative Field Names Enabled** check box. If this has been done, the user must change the names on the Excel template to match exactly or LIMS cannot import the project. The Excel template files can then be distributed to customers.

A Sample ID (or equivalent name if the user has changed the name of this column) must be provided for each sample. Sample IDs must be unique. LIMS will check to be sure that Sample IDs are unique and will not import a project if they are not unique. The Country Codes are listed on the spreadsheet titled "Countries." The State/Province Codes are listed on the spreadsheet titled "States-Provinces." Latitude and longitude can be entered as 45.3333 in the Degrees field or 45 in the Degrees field and 20 in the Minutes field. No characters other than numbers and decimal points should be entered (for example, do not enter 20" for 20 seconds). The Collection Date/Time and Ending Collection Date/Time should be entered in a format compatible with that in your Microsoft Windows settings. The ending date/time is used when collecting a precipitation or similar sample. The Elevation of the site must be a numeric entry. The unit of distance (meter or foot) is specified in the column Length Unit. Valid entries are *m* and *ft*. If the columns Top or Bottom are used, they must contain only numeric data (no alpha characters are allowed). The seven remaining fields, beginning with User Def Cap 2, can contain alphanumeric entries.

As supplied, the maximum length of entries that will be imported and stored in LIMS is:

Sample ID	35 characters
User Def Cap 2	40 characters
User Def Cap 3	20 characters
User Def Cap 4	20 characters
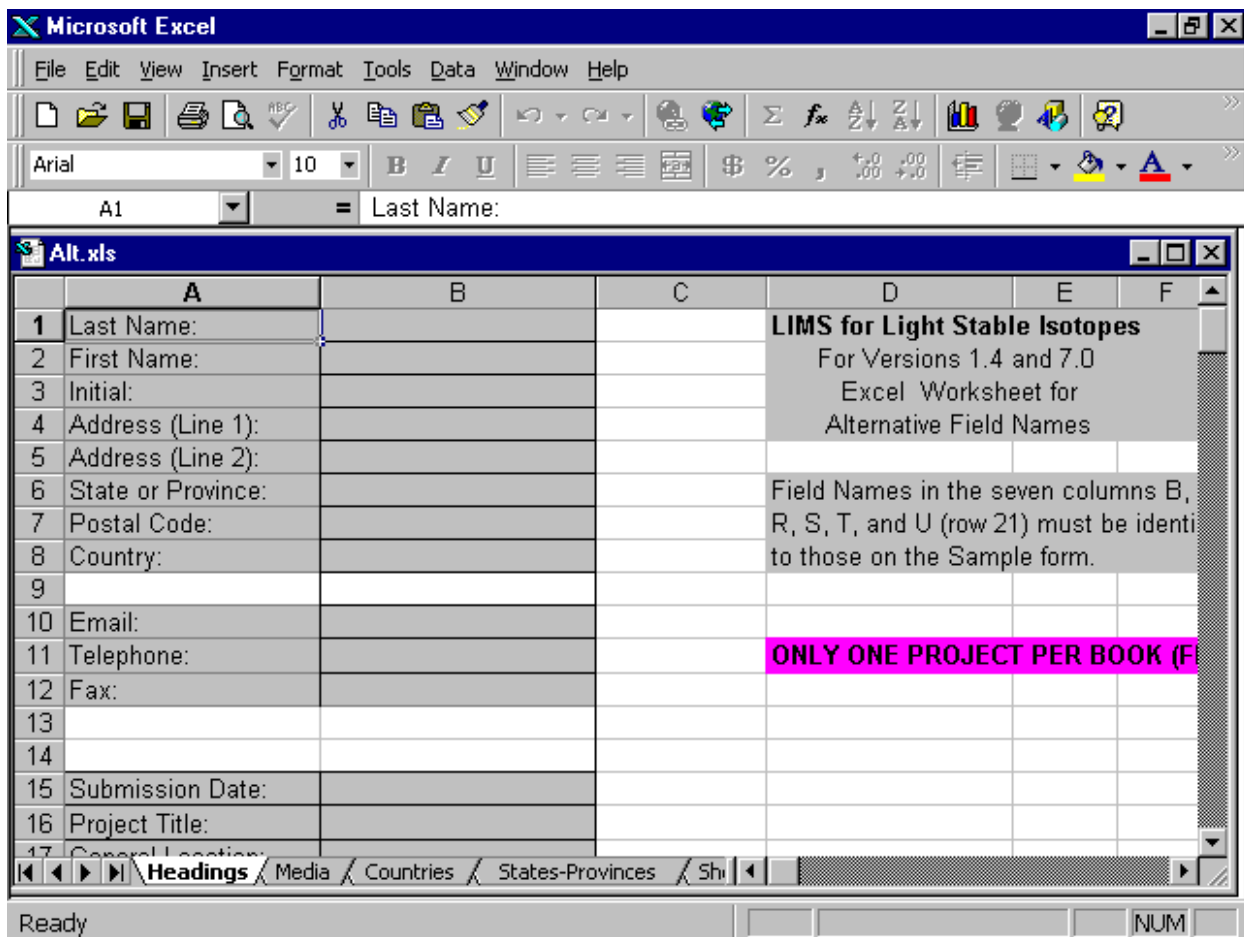
Fig. 26. Alt.xls Excel 5.0 template for creating projects.

User Def Cap 5	20 characters
User Def Cap 6	22 characters
Cap 7	26 characters
Other Info	70 characters

Any of these can be easily increased by the user—see the Microsoft Access Help or Microsoft 1997a, 1997b.

SPECIAL FEATURES

The **Special Features** button allows the user to change the configuration of LIMS and to add, delete, and edit mass spectrometers, procedure codes, media codes, *etc.* Clicking **Special Features** opens the **Special Features** subform. The user may be prompted for a password.

LIMS For Light Stable Isotopes Configuration Form

Clicking **Config** opens the **LIMS For Light Stable Isotopes Configuration** form (Fig. 17). This form allows the user to (i) edit eight alternative field (column) names (and "Top" and "Bottom") that appear as labels on the **Samples** form, (ii) change the color of most of the forms, (iii) set software switches, and (iv) edit the value of various tokens or parameters used in the software. All of these values are stored in the code module. When you click **Exit** on the Main Menu, LIMS makes a backup of these items in the Access database Lm7prefs.mdb (LM4PREFS.mdb in the Access 2.0 version of LIMS). If the user updates the code module Lm7code.mdb, LIMS will search for Lm7prefs.mdb. If LIMS finds it, it will ask the user if the configuration parameters should be updated. The user should choose in the affirmative.

Alternative Field Names

If users check the **Alternative Field Names Enabled** check box, they may change the names of eight fields on the **Sample** form (and **Range of Samples** report). For example, one might want one of the fields to be Dose if one is working with urine from diabetic patients. Generally one will use upper and lower case letters and the underscore character. In no case should the following five characters be used:

[ ] ' . !

Form Colors

To change the color of a form, first click **Edit**, choose a form from the **Form Colors** combo box, click on a color on the palette, and click **OK** on the color palette. Try it with the Main Menu first because it can be seen below the **LIMS For Light Stable Isotopes Configuration** form. One can reset the colors to the initial LIMS for Light Stable Isotopes colors by clicking **Set default colors**. If one has a video card that can produce more than 256 colors, one can click **Define Custom Colors** on the color palette to produce more colors than employed in LIMS (LIMS requires and assumes you have at least 256 colors).

Software Switches

The following software switch options may be selected:

1. Show latitudes and longitudes on forms and reports using decimal degrees (33.34221, for example) rather than DDMMSS (Degree Degree Minute Minute Second Second) format. Data in the LIMS Table of Samples are always stored in decimal degrees.

2. Display elevations and depths on forms and reports using meters instead of feet. Data in the LIMS Table of Samples are stored in feet. (This, of course, could be changed.)

3. Require working standard label to be an integer between 1 and 366.

4. Check for missing mass spectrometer analyses when starting LIMS.

5. Use 'Rel. to VPDB' for $\delta^{18}O$ values of carbonates instead of 'Rel. to VSMOW.'

6. Require port label identifiers on the mass spectrometers to be integers between 0 and 99.

7. Display "Headings Complete" text box on the **Project** form. This is useful when extensive amounts of information may need to be added to the **Sample** form, often after the samples are analyzed.

8. Reston features enabled. This switch changes several values to Reston default values. It enables an algorithm for preventing isotopic replicate analyses from being stored unless the standard deviation is sufficiently low, makes visible **NWQL**, **NAWID**, and **Access** buttons and forms, makes visible some buttons on the **Project** form, and enables several other features.

9. Debugging enabled will make numerous text boxes visible on forms. Once you toggle this check box, it is a good idea to exit LIMS and restart it.

Paper Size

The paper size token, US_PAPERSIZE, can be found by clicking **LIST**. It can have two values, 0 and -1. A value of 0 is used to select the A4 paper size and -1 selects U.S. standard paper (8.5 inches x 11 inches). The value for this token is changed by clicking **Edit**, replacing the value in the **Value** text box, and clicking **Save** to save the change.

Default Country

When the **Login New Samples** form opens, the **Country** combo box is set to the country selected by the token labelled "DEFAULT_COUNTRY" in the configuration table. To change the country to his

or her own country, identify the two character string that is used for the new country. This is done by clicking the Samples and Analyses on the Main Menu, entering a 1 for the sample number, clicking **Find**, opening the **Country** combo box, and scrolling to the new country. The first two character (CA for Canada, for example) are needed. To set the default country to this new country, click **Special Features** on the Main Menu, enter the password if requested, click **Config**, click **List**, select the token DEFAULT_COUNTRY, click **Edit**, change the two character token from "US" to that identified above, click **Save**, and click **Close**. The new default country can be checked by clicking **New Project Login**.

Other Parameters

The other tokens whose values can be changed are listed below:

ALT_SAMPLE_CAPTION_BOT	Caption for bottom (bottom of perforation) when alternative field names are enabled.
ALT_SAMPLE_CAPTION_TOP	Caption for top (top of perforation) when alternative field names are enabled.
CF_Std_OurLabID_AIR	The Our Lab ID of the mixed reference gas used for continuous flow analysis.
CF_Std_OurLabID_CO2	The Our Lab ID of the CO2 reference gas used for continuous flow analysis.
CF_Std_OurLabID_H2	The Our Lab ID of the H2 reference gas used for continuous flow analysis.
CF_Std_OurLabID_N2	The Our Lab ID of the N2 reference gas used for continuous flow analysis.
CF_Std_OurLabID_O2	The Our Lab ID of the O2 reference gas used for continuous flow analysis.
CF_Std_OurLabID_SO2	The Our Lab ID of the SO2 reference gas used for continuous flow analysis.
COMPANY_NAME	Name of company, university, or organization.
FINN_BLANK_CORR_EA_DATA	Set to -1 to import EA blank corrected delta values. Otherwise set to 0 to use non-blank corrected data.
FINN_COL_HEAD_13C	Unique identifier in $\delta^{13}C$ column in ISODAT dual inlet spreadsheet.

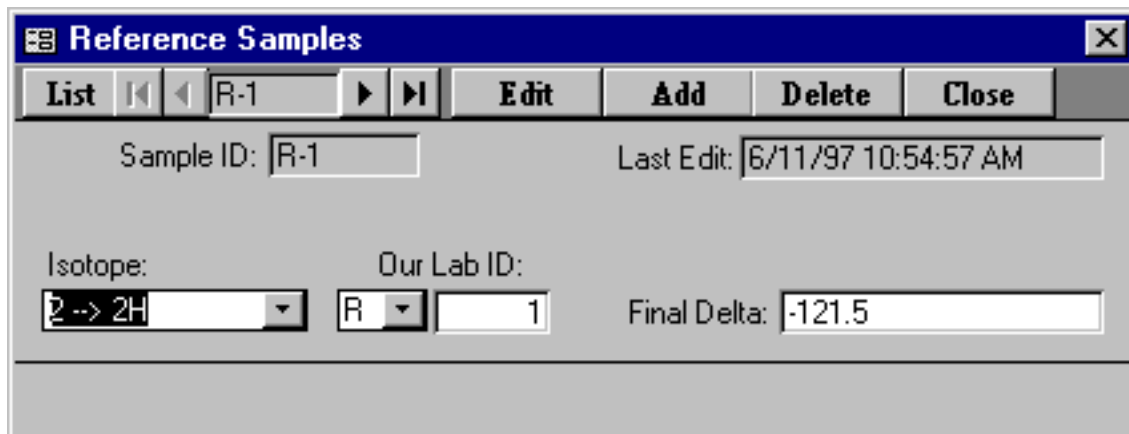|	
FINN_COL_HEAD_15N	Unique identifier in δ^{15}N column in ISODAT dual inlet spreadsheet.
FINN_COL_HEAD_17O	Unique identifier in δ^{17}O column in ISODAT dual inlet spreadsheet.
FINN_COL_HEAD_18O	Unique identifier in δ^{18}O column in ISODAT dual inlet spreadsheet for other than H2O samples.
FINN_COL_HEAD_18OH2O	Unique identifier in δ^{18}O column in ISODAT dual inlet spreadsheet for H2O samples.
FINN_COL_HEAD_2H	Unique identifier in delta 2H column in ISODAT dual inlet spreadsheet.
FINN_COL_HEAD_30Si	Unique identifier in delta δ^{30}Si column in ISODAT dual inlet spreadsheet.
FINN_COL_HEAD_34S	Unique identifier in δ^{34}S column in ISODAT dual inlet spreadsheet.
FINN_COL_HEAD_37Cl	Unique identifier in δ^{37}Cl column in ISODAT dual inlet spreadsheet.
FINN_COL_HEAD_GCC_13C	Unique identifier in δ^{13}C column in ISODAT GCC CF spreadsheet.
FINN_COL_HEAD_GCC_15N	Unique identifier in δ^{15}N column in ISODAT GCC CF spreadsheet.
FINN_COL_HEAD_GCC_18O	Unique identifier in δ^{18}O column in ISODAT GCC CF spreadsheet.
SHOW_CFC-11_12_&_113	Set to -1 to show CFC-11, 12 & 113 simultaneously on sample form and reports. Otherwise set to 0.
STORE_EA_CONCENTRATIONS	When set to -1, Finnigan EA concentrations are stored when isotopic compositions are imported. Otherwise set to 0.
STORE_INTERF_MASSES	When set to -1, interfering mass voltages are stored when isotopic analyses are imported. Otherwise set to 0.
STORE_ION_GAUGES	When set to -1, Finnigan ion gauge values are stored when isotopic analyses are imported. Otherwise set to 0.
STORE_MAJOR_VOLTAGES	Set to -1 to store ion gauge readings and major ion beam

volatages when importing analyses. Otherwise, set to 0.

STORE_UNEXPECTED_PROCEDURES	Set to -1, unexpected procedures (192 - 198) are stored when isotopic analyses are imported. Otherwise, set to 0.
UMASS_COL_HEAD_13C	Column header of $\delta^{13}C$ column in Micromass spreadsheet.
UMASS_COL_HEAD_15N	Column header of $\delta^{15}N$ column in Micromass spreadsheet.
UMASS_COL_HEAD_17O	Column header of $\delta^{17}O$ column in Micromass spreadsheet.
UMASS_COL_HEAD_18O_Other	Column header of $\delta^{18}O$ column in Micromass spreadsheet for samples other than water.
UMASS_COL_HEAD_18O_Water	Column header of $\delta^{18}O$ column in Micromass spreadsheet for water samples.
UMASS_COL_HEAD_2H	Column header of $\delta^{2}H$ column in Micromass spreadsheet.
UMASS_COL_HEAD_30Si	Column header of $\delta^{30}Si$ column in Micromass spreadsheet.
UMASS_COL_HEAD_34S	Column header of $\delta^{34}S$ column in Micromass spreadsheet.
UMASS_COL_HEAD_37Cl	Column header of $\delta^{37}Cl$ column in Micromass spreadsheet.

Reference Samples Form

The **Reference Samples** form (Fig. 27) is opened by clicking **Special Features** on the Main Menu and clicking **References**. This form is used to add, delete, or edit reference samples used in the normalization equation calculations. To add a reference sample, click **Add**, select the isotope from the **Isotope** combo box, select the sample prefix from the **Prefix** combo box, enter the integer sample number, and enter the "true value" in the **Final Delta** text box. To save results, click **Save**. To edit an existing reference click **List** or the navigation buttons to move to the reference. Click **Edit**, make the change, and click **Save**. Click **Delete** to delete a reference sample.

Prefixes & Next Sample # Button

The **Prefix** form is opened by clicking **Special Features** on the Main Menu and clicking **Prefixes & Next Sample #**. One can only edit the positive integer in the **Next Sample** text box. This is the integer used for assigning the next Our Lab ID in the **Login New Samples** form. If one changes this integer, one needs to be careful that samples with duplicate Our Lab IDs are not generated. This is a sure method of creating havoc in LIMS.

Fig. 27. Reference Samples form.

Mass Spectrometer Configuration Form

The **Mass Spectrometer Configuration** form (Fig. 28) is opened by clicking **Special Features** on the Main Menu and clicking **Mass Spec**. Install a new mass spectrometer as follows:

1. Click **Add**.

2. Enter a single letter code for the mass spectrometer. **Once a mass spectrometer is created, this single letter code cannot be changed** (the mass spectrometer must be deleted and a new mass spectrometer must be installed). One probably should avoid using the letters already used for sample prefixes (C, G, J, N, R, S, and W) and the letters O and I. The letter E is not available because it is used for the Ethereal mass spectrometer. The short name is used in several combo boxes.

3. Enter the vendor serial number which may be used by some mass spectrometer manufacturers on the file of isotopic results in order to identify the mass spectrometer that generated the isotopic results. If your mass spectrometer manufacturer supports LIMS, ask what entry needs to go into this field.

4. Enter an analysis import format appropriate for your mass spectrometer.

5. Enter a sample export format as appropriate for your mass spectrometer. If a user's manufacturer is not listed, "LIMS Default" can be selected. The user can then generate multi-sheet templates and (or) sample lists even though the file on the diskette generated by the template code cannot be used. The user may want to encourage mass spectrometer vendors to modify their mass spectrometer software so that it can make use of the LIMS sample export file.

6. Select all isotopes that will be analyzed by the mass spectrometer.

7. Enter the sample prefix of the most common sample analyzed. This field can be left blank.

8. Check the "Continuous Flow Capability" check box if appropriate.

9. Click **Save** to create your mass spectrometer.

One may edit most fields for an existing mass spectrometer. One cannot deselect an isotope if there are any analyses of that isotope in the table of analyses. Likewise, one cannot delete a mass spectrometer if there are any analyses for it in the table of analyses.

Fig. 28. Mass Spectrometer Configuration form.

Faraday Cup Information Form

When the user clicks **Faraday Cups** LIMS advises the user that Faraday cup information for all mass spectrometers can be edited. Click **Faraday Cups**. Click **OK** and the **Faraday Cup Information** form opens. For each Faraday cup of each mass spectrometer, one can assign an electrometer output coefficient. This is the expansion coefficient that is used when an interfering mass value is imported and that is printed on the **Samples In Progress** report for interfering masses. If analyses with interfering masses are imported and no Faraday cup electrometer output coefficients are found, a default value of 1 is employed.

Mass Spectrometer Error Codes Form

The mass spectrometer **Error Codes** form is opened by clicking **Special Features** on the Main Menu and clicking **Mass Spec Error Codes**. The existing error codes are used by the author's Microsoft Visual Basic mass spectrometric data acquisition and control software. One can add additional codes, delete these, or edit existing codes.

NAWID, NWQL, and Access Forms

NAWID, **NWQL**, and **Access** are program features used only by the U.S. Geological Survey and are only visible when Reston Features is enabled.

Media Form

The **Media** form is opened by clicking **Special Features** on the Main Menu and clicking **Media**. One can add, edit, and delete media in a manner similar to that used with the **Reference Samples** form above. The description can always be edited. The prefix cannot be edited if any samples of the medium have been logged in because labels may already exist on sample containers with this prefix. One is required to select one and may select two isotopes for a medium. These will become the low and high isotopes of the medium. An example of adding a medium is given on page 96. Information about deleting media codes is given on page 97.

Procedure Form

The **Procedure** form is opened by clicking **Special Features** on the Main Menu and clicking **Procedures**. One can add, edit, and delete procedure codes using this form in a manner similar to that used with the **Reference Samples** form above. Note that only the description of the procedure code can be edited. When LIMS was designed, it was decided to build in a relationship between the procedure codes (table 4) and the isotope codes (table 3) in order to minimize disk accesses and to speed up

the program. This relationship is:

Integer(Procedure code)/100 = Isotope code

Thus, all of the procedure codes for δ^2H lie between 200 and 299 because the isotope code for ^{2}H is 2 (table 3). The situation with oxygen is a little more complicated. It was decided that normalization coefficients for δ^{18}O of water should be in a list separate from that of other O-bearing substances. Thus, δ^{18}O procedure codes for water range from 800 through 809 and those for other O-bearing materials lie between 810 and 899. The situation for isotope codes 2 through 15 is summarized in table 5. The values for codes above 15 are analogous to the values for isotope code 15. If more than 100 procedure codes were needed for any isotope, one could easily modify the algorithm above. For example, the value of 100 could be changed to 1000. Then each isotope could have 1000 procedure codes.

To add a new procedure code and make use of it in LIMS is a two-step process. First, the user should add the procedure code to LIMS using this form. Next the user must link the procedure to each medium using the **Low Procedure Codes** form or the **High Procedure Codes** form. An example of adding a medium, procedures, low procedures, and high procedures is given on page 96. Information about deleting media codes, procedure codes, low procedure codes, and high procedure codes is given on page 97.

Low Procedure Codes Form

The **Low Procedure Codes** form is opened by clicking **Special Features** on the Main Menu and clicking **Low Procedures**. One can add, edit, and delete low procedure codes. The low procedure code links the low isotope of a medium to a procedure code. When a new procedure has been added to the table of procedures, the user can open the **Low Procedure Codes** form, click **Add**, select the medium, select the new procedure, and click **Save**. If this medium has entries in both the low and high procedures tables, then the user must ensure that procedure 000 (N/A) has been added to both the low and high procedures tables. This gives the user the possibility to select individually either the low or the high procedure code, but not to require both. For every medium, one and only one procedure should be selected as the default procedure. The default procedure is selected by assigning an asterisk to the Default field on the **Low Procedure Codes** form.

An example of adding a medium, procedures, low procedures, and high procedures is given below. Information about deleting media codes, procedure codes, low procedure codes, and high procedure codes is given on page 97.

High Procedure Codes Form

The **High Procedure Codes** form is opened by clicking **Special Features** on the Main Menu and clicking **High Procedures**. One can add, edit, and delete high procedure codes. The high procedure code

Table 5. Minimum and Maximum Sample Preparation Procedure Codes in LIMS version 7.0 as a Function of Isotope Code Between Codes 2 and 15.

Isotope	Isotope Code	Prefix	Minimum Procedure Code	Maximum Procedure Code
^{2}H	2	G	200	299
^{2}H	2	J	200	299
^{2}H	2	R	200	299
^{2}H	2	W	200	299
^{13}C	3	C	300	399
^{13}C	3	G	300	399
^{13}C	3	J	300	399
^{13}C	3	R	300	399
^{15}N	5	G	500	599
^{15}N	5	J	500	599
^{15}N	5	N	500	599
^{15}N	5	R	500	599
^{34}S	6	G	600	699
^{34}S	6	J	600	699
^{34}S	6	R	600	699
^{34}S	6	S	600	699
^{17}O	7	G	700	799
^{17}O	7	J	700	799
^{17}O	7	R	700	799
^{18}O	8	C	810	899
^{18}O	8	G	810	899
^{18}O	8	J	810	899
^{18}O	8	N	810	899
^{18}O	8	R	810	899
^{18}O	8	S	810	899
^{18}O	8	W	800	809
^{7}Li	10	G	1000	1099
^{7}Li	10	J	1000	1099
^{7}Li	10	R	1000	1099
^{11}B	11	G	1100	1199
^{11}B	11	J	1100	1199
^{11}B	11	R	1100	1199
^{30}Si	12	G	1200	1299
^{30}Si	12	J	1200	1299
^{30}Si	12	R	1200	1299
^{37}Cl	13	G	1300	1399
^{37}Cl	13	J	1300	1399
^{37}Cl	13	R	1300	1399
^{14}C	14	G	1400	1499
^{14}C	14	J	1400	1499
^{14}C	14	R	1400	1499
^{3}H	15	G	1500	1599
^{3}H	15	J	1500	1599
^{3}H	15	R	1500	1599

links the high isotope of a medium to a procedure code. High procedure codes are edited and added in the same manner as low procedure codes (see page 94). An example of adding a medium, procedures, low procedures, and high procedures is given below. Information about deleting media codes, procedure codes, low procedure codes, and high procedure codes is given on page 97.

How to Add Media, Procedures, Low Procedures, and High Procedures

Suppose a large project on the variability of $\delta^{18}O$ and $\delta^{30}Si$ of olivine samples is starting. Suppose $\delta^{18}O$ preparation will be by a new laser ablation technique and $\delta^{30}Si$ preparation will be by reaction with gaseous fluorine. Assume that some samples will have $\delta^{18}O$ analyses only and some will have $\delta^{30}Si$ analyses only. Add a new medium, two procedure codes, and low and high procedure codes. Because this will be a major project spanning decades, choose a unique prefix for the medium.

Click **Media** and click **Add**. Enter 85 (since 85 is not used) in the **Code** text box, "olivine" in the **Medium** text box, J in the **Prefix** combo box, and "olv" in the **Abbr** text box. Either one or two isotopes need to be selected. Click the $^{18}O/^{16}O$ and the $^{30}Si/^{28}Si$ check boxes. Click **Save** and LIMS will remind the user to add this medium to the list of media on the Excel 5.0 template for importing projects. Click **OK**. Click **Close**.

Now add two new procedure codes. From table 5 one knows that the $\delta^{18}O$ procedure needs to be between 810 and 899 because this is an O-bearing material that is not water. Choose 870 since it is not used. For the $\delta^{30}Si$ use 1225 since it is available. Click **Procedures** and click **Add**. Enter 870 in the **Code** text box, "DI, laser ablation, delta 18O" in the **Description** text box, and click **Save**. The **Amount of Sample** text box is not used (this text box is for future use in LIMS). Click **Add**. Enter 1225 in the **Code** text box, "DI, gaseous fluorine, Delta 30Si" in the **Description** text box, and click **Save**. Click **Close**.

Now link the medium and procedures. Let 870 be the low procedure code. Click **Low Procedures**. Click **Add**, select 85 from the **Medium** combo box, select 870 from the **Low Procedure** combo box, and set the **Default** combo box to * (this indicates that procedure code 870 will be selected as the default for the determination of $\delta^{18}O$ in olivine samples). Click **Save**. One needs the possibility to select only the $\delta^{30}Si$ preparation. This is done by adding the following additional low procedure code. Click **Add**. Select 85 for the **Medium** combo box, select "000 --> N/A" for the **Low Procedure** combo box, and click **Save**. Click **Close.** Now either 0 or 870 can be selected as the procedure code for the low isotope (^{18}O).

Repeat in a similar manner for the high procedure code. Click **High Procedures**. Click **Add**. Select 85 for the **Medium** combo box, select 1225 for the **High Procedure** combo box, select * for the **Default** combo box, and click **Save**. Click **Add**. Select 85 for the **Medium** combo box, select "000 --> N/A" for the **High Procedure** combo box, and click **Save**. Click **Close.** Now either 0 or 1225 can be selected as the procedure code for the high isotope (^{30}Si).

This completes the addition of a medium, procedure code, low procedure code, and high procedure code.

How to Delete Media, Procedures, Low Procedures, and High Procedures

Media codes, procedure codes, low procedure codes, high procedure codes must be deleted in the reverse order in which they are installed. Therefore, if a procedure code is to be deleted, all of the low and high procedure codes using this procedure must first be deleted. If a medium is to be deleted, all of the low and high procedure codes using this procedure must first be deleted. Media codes, procedure codes, low procedure codes, high procedure codes cannot be deleted if they have been used for samples or isotopic analyses in the database.

Creating and Editing Templates

Multi-sheet paper templates are used for two purposes: (i) to set out samples to be analyzed so that they correspond to the location of sample preparation vessels, and (ii) to provide a list of the sample that goes into each location on an elemental analyzer. Templates are populated with samples from the Table of Samples To Be Analyzed, and printed by clicking **Print Templates** on the Main Menu. However, before a template can be populated and printed, it must be designed and created. **Templates** on the **Special Features** subform opens the **Templates** form (Fig. 29) and allows the user to add or edit a template. The user may want to examine the templates in the example database. Templates for elemental analyzers and water equilibration devices can be found in the example database. The user should examine these templates prior to generating any templates. To view these templates (first make sure the example database is active—see page 20), click **Special Features** on the Main Menu, and click **Templates**.

Fig. 30 shows a photograph of the 48-port Micromass sample equilibration system in the author's laboratory and a template set up with 48 water samples for this preparation system. The multi-sheet paper template is shown in Figs. 31 and 32. Note that there are 12 samples in each of 4 rows (48 samples total) laid out on a four-page template. (Twelve samples, whether they be water, carbonates, or other samples, has been found to be a convenient number to put on one sheet of paper. If samples are larger, then fewer samples can be placed on each page, leaving desired positions blank.) Samples can be placed on the template the day prior to sample preparation; thus, a designated technician has time to check to make sure that each position on the template has the correct sample on it. This has led to a significant reduction in errors in the laboratory. The plastic holder in the front is used to load the samples from each row and to transport them to the equilibration system.

It is important to consider the layout of your multi-sheet template. Proper design can lead to important savings in sample preparation time and reduction of error by minimizing the possibility of a sample getting into the wrong sample port. As an example, for the 48-port CO_2-H_2O equilibration device above, there are four banks, A, B, C, and D. There are 12 sample ports on each bank. Thus, one might use the port names A1, A2, A3, ... B1, B2, ... D12. However, in the author's laboratory operators find it
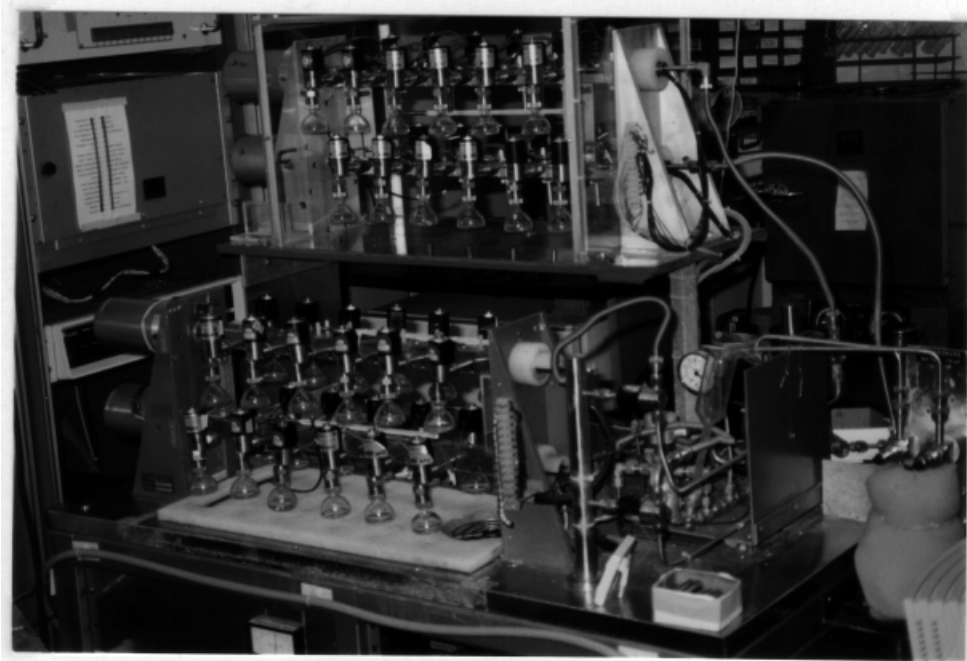
Fig. 29. Templates form.

Fig. 30. (a) Micromass CO_2-H_2O equilibration system in author's laboratory. (b) Template for this system set up with 48 samples.

Port	Sample #	Amount		Port	Sample #	Amount
11	W-69	_____		34	W-102	_____
09	W-5	_____		36	W-5	_____
07	W-70	_____		38	W-103	_____
05	W-71	_____		40	W-104	_____
03	W-72	_____		42	W-105	_____
01	W-73	_____		44	W-106	_____
23	W-74	_____		46	W-107	_____
21	W-75	_____		48	W-108	_____
19	W-6	_____				
17	W-6	_____				
15	W-5	_____				
13	W-76	_____				
02	W-77	_____				
04	W-78	_____				
06	W-79	_____				
08	W-80	_____				
10	W-81	_____				
12	W-82	_____				
14	W-83	_____				
16	W-84	_____				
18	W-5	_____				
20	W-85	_____				
22	W-86	_____				
24	W-87	_____				
35	W-88	_____				
33	W-89	_____				
31	W-5	_____				
29	W-90	_____				
27	W-91	_____				
25	W-92	_____				
47	W-93	_____				
45	W-94	_____				
43	W-95	_____				
41	W-96	_____				
39	W-97	_____				
37	W-98	_____				
26	W-99	_____				
28	W-100	_____				
30	W-101	_____				
32	W-5	_____				

Fig. 31. Example of List of Samples To Be Analyzed for the CO_2-H_2O equilibration template with 48 samples.

26/W-99	28/W-100	30/W-101		32/W-5	34/W-102	36/W-5		38/W-103	40/W-104	42/W-105		44/W-106	46/W-107	48/W-108
35/W-88	33/W-89	31/W-5		29/W-90	27/W-91	25/W-92		47/W-93	45/W-94	43/W-95		41/W-96	39/W-97	37/W-98
02/W-77	04/W-78	06/W-79		08/W-80	10/W-81	12/W-82		14/W-83	16/W-84	18/W-5		20/W-85	22/W-86	24/W-87
11/W-69	09/W-5	07/W-70		05/W-71	03/W-72	01/W-73		23/W-74	21/W-75	19/W-6		17/W-6	15/W-5	13/W-76
Page 1				Page 2				Page 3				Page 4		

Fig. 32. Example of the 4-page CO_2-H_2O water equilibration template with 48 samples. Note placement of pages side by side.

easier to identify each sample port by an integer; thus, 1, 2, ... 47, and 48 are used. Personnel find it quickest to load 12 samples at a time. The first 12 samples are 6 samples on one side of bank A and 6 samples on the same side of bank B. The next 12 samples are the samples on the other side of banks A and B. The third set of 12 samples consists of 6 samples on bank C and 6 on bank D. The last 12 samples are on the other side of banks C and D. This relatively complicated layout scheme allows personnel to load samples in a minimum of time and it minimizes the possibility of error in sample loading. It is presented to demonstrate to the reader that it is important to consider various scenarios for loading samples.

Before starting be sure that the reference samples you want to use as floating (see step 14 below) and fixed (see step 25 below) references are in the Table of Reference Samples. To add a template follow these steps:

1. Click **Special Features** on the Main Menu and then click **Templates**.

2. Click **Add**.

3. Enter a name for the template, such as "Pegasus." Each template must have a unique name.

4. Enter the description.

5. Select the mass spectrometer.

6. Select the sample export format if necessary.

7. Select the media for the template. The user will need to fill the Media Selected for Template list box with all of the media for the template. First click on a medium in the **Available Media** list box to highlight it. Then click **Add** to add this medium to the Media Selected for Template list box. As many media as required can be included. If you make a mistake, highlight the medium to be deleted in the Media Selected for Template list box, and click **Delete Medium**.

8. Select an isotope for the low procedure code if necessary.

9. Select the default low procedure code if necessary.

10. Select the default number of repeats for the low procedure if necessary. The default number of repeats is the number of times a sample added to the template will be analyzed. For example, in the author's laboratory, every water sample for H equilibration is analyzed twice.

11. Select an isotope for the high procedure code if necessary.

12. Select the default high procedure code if necessary.

13. Select the default number of repeats for the high procedure if necessary.

14. Select the sample that will serve as the floating reference. A floating reference is a reference sample that is randomly interspersed with samples. LIMS will determine the location of all floating reference samples using a random number generator. Only samples from the table of reference samples that have a medium found in the Media Selected for Template list box will appear in this combo box.

15. Enter the number of floating reference samples on your template. Often it is 10 to 15% of the total number of samples on a template.

16. Select a sample for unfilled positions. This sample is used to fill or pad the remainder of a template in the event that there are not sufficient samples in the Table of Samples To Be Analyzed to populate all the spaces in a template. Often a sample such as W-1, C-1, *etc.* is selected.

17. Select the printing option. Usually, one wants to print a multi-sheet template and a list of samples.

18. Click **Save**.

19. Click **Ports & References** to open the **Ports & References** form (Fig. 33) and design the multi-sheet paper template that will holds the samples. Even though one only wants to print a list of samples and not a multi-sheet template, one still needs to use this form to provide necessary information to LIMS (port identification, etc.).

20. Layout the multi-page template. The user will need to decide the following:
    a. Will all 12 positions on each page be used? If not, which will remain blank?
    b. What is the port number for each of the positions on the page that will hold a sample?
    c. Which ports should be left empty. These might be ones with vacuum leaks or such other problem that prevents their use.
    d. Which ports must always hold a reference sample, that is, a fixed reference sample.
    e. By default, the remaining ports can hold a floating reference sample. A floating reference sample "floats" from port to port and has no fixed location.

21. Click **Edit** to enable editing.

22. Page 1 of your template should be shown. Enter port numbers (or port identifiers for each of the 12 positions that should hold a sample.

23. Enter the list number of each port specified above. This is the ordinal number of the sample in the sample list printed out for the user. For example, the sample position that is always at the top of the list is 1, the second is 2, *etc.*

Fig. 33. Ports & Configuration form.

24. For each position that should be empty, select "Empty."

25. For each position that should be a fixed reference, select "Fixed Ref" and select the reference sample from the fixed reference ("Fixed Ref") combo box. The remaining positions should be identified as "Floating Ref" positions. This completes the entry for this page.

26. Click **Save** to save your entries.

27. If the template consists of only a single page, click **Close** and this completes the creation of the template. Otherwise, click **Add Page**.

28. Enter the entries on page 2 in a manner similar to that done for page 1.

29. Repeat data entry for remaining template pages.

30. When all pages are complete, click **Close**.

Additional pages may be added and entries may be edited by clicking **Edit**. If the user needs to delete a page, only the last page of a template can be deleted. This completes the creation of the template.

In order to use this template, the user will need to add samples to the Table of Samples To Be Analyzed. This can be done from the **Project** form (page 29) by clicking **Templates**, or from the **Samples To Be Analyzed** form (page 40). Once samples have been added to the Table of Samples To Be Analyzed, a list of samples (and a template of samples to analyze) can be printed (*e.g.*, see Figs. 31 and 32).

Using LIMS with ^{14}C

LIMS can be used for ^{14}C samples. ^{14}C media and procedures must be added to the default database because no media or procedures using them are otherwise available. The following illustrates how this is done.

Add a new medium containing ^{13}C and ^{14}C, and add a procedure code for ^{14}C. Click **Special Features**, entering the password if required, click **Media** from the **Special Features** subform, and click **Add** on the **Media** form. LIMS will prompt the user to select the Prefix last. Click **OK**. Enter "140" for the **Code**, enter "C-bearing material" for the **Medium**, and enter "14C" for the **Abbr**. Click the check boxes **13C/12C** and **14C**. Select **Prefix** "G," and click **Save**. (Note, that the user could have selected "C --> Carbonate." LIMS will remind the user that this medium should be added to the Excel Template file for Creating Sample Projects in case the user is using this feature (see page 81). Click **OK**. Click **Close** to close the **Media** form. Note that the user can create a medium containing only ^{14}C, or one containing ^{13}C and ^{14}C with Prefix C, *etc.*

Next add a new procedure for ^{14}C. Click **Procedures** on the **Special Features** subform. LIMS will display a message box advising the user of valid ranges of procedure codes for various isotopes, isotope ratios, and CFCs. Note that valid procedure codes for ^{14}C are between 1400 and 1499. Click **Ok**. Click **Add**. Enter "1400" for the **Code** and press the Enter key. LIMS will advise the user that a code for ^{14}C is being added. Click **OK.** Enter "14C by AMS" for the **Description**. Click **Save**. Click **Close** to close the **Procedure Codes** form.

The user next needs to link procedures to the medium created. Click **Low Procedures** on the **Special Features** form. Click **Add**. Select "140 -->G [14C] C-bearing material" from the **Medium** combo box. Select "352 --> DI, Quartz sealed tube, 800 deg. Delta 13C" from the **Low Procedure** combo box. If a user had several procedure codes for the same medium and needed to indicate to LIMS which should be used as a default (such as when importing isotopic analyses), the user could select "*" from the **Default** combo box in order to make the selected procedure code the default low procedure code. Click **Save** and close the **Low Procedure Codes** form by clicking **Close**.

Next click **High Procedures** on the **Special Features** subform to open the **High Procedure Codes** form. Click **Add**. Select "140 -->G [14C] C-bearing material" from the **Medium** combo box. Select "1400 --> 14C by AMS" from the **High Procedure** combo box. Click **Save** and close the **High Procedure Codes** form by clicking **Close**.

A media code, and procedures codes are now available for ^{14}C use in LIMS. To demonstrate this, click **New Project Login** on the **Main Menu**. Click the **Medium** combo box and verify that medium 140 is available.

Using LIMS with ^{3}H

LIMS can be used for ^{3}H samples. ^{3}H media and procedures must be added to the default database because no media or procedures using ^{3}H are otherwise available. The following illustrates how this is done.

Add a new medium containing ^{3}H, and add a procedure code for ^{3}H. Click **Special Features**, entering the password if required, click **Media** from the **Special Features** subform, and click **Add** on the **Media** form. LIMS will prompt the user to select the Prefix last. Click **OK**. Enter "150" for the **Code**, enter "3H-bearing material" for the **Medium**, and enter "3HC" for the **Abbr**. Click the check box **3H**. Select **Prefix** "G," and click **Save**. LIMS will remind the user that this medium should be added to the Excel Template file for Creating Sample Projects in case the user is using this feature (see page 81). Click **OK**. Click **Close** to close the **Media** form. Note that the user can create a medium containing only ^{3}H, or one containing ^{2}H and ^{3}H, for example.

Next add a new procedure for ^{3}H. Click **Procedures** on the **Special Features** subform. LIMS will display a message box advising the user of valid ranges of procedure codes for various isotopes, isotope ratios, and CFCs. Note that valid procedure codes for ^{3}H are between 1500 and 1599. Click **Ok**. Click

Add. Enter "1500" for the **Code** and press the Enter key. LIMS will advise the user that a code for ^{3}H is being added. Click **OK.** Enter "3H by electrolytic enrichment and LSC" for the **Description.** Click **Save.** Click **Close** to close the **Procedure Codes** form.

The user next needs to link procedures to the medium created. Click **Low Procedures** on the **Special Features** form. Click **Add.** Select "150 -->G [3H] 3H-bearing material" from the **Medium** combo box. Select "1500 --> 3H by electrolytic enrichment and LSC" from the **Low Procedure** combo box. If a user had several procedure codes for the same medium and needed to indicate to LIMS which should be used as a default (such as when importing isotopic analyses), the user could select "*" from the **Default** combo box in order to make the selected procedure code the default low procedure code. Click **Save** and close the **Low Procedure Codes** form by clicking **Close.**

A media code, and procedures codes are now available for ^{3}H use in LIMS. To demonstrate this, click **New Project Login** on the **Main Menu.** Click the **Medium** combo box and verify that medium 150 is available.

Using LIMS with CFCs

The CFCs, CFC-11, CFC-12, and CFC-113, are available in LIMS. CFC media and procedures must be added to the default database because no media or procedures using them are otherwise available. The following illustrates how this is done.

First add a new medium by clicking **Special Features**, entering the password if required, clicking **Media** from the **Special Features** subform, and clicking **Add** on the **Media** form. LIMS will prompt the user to select the Prefix last. Click **OK.** Enter "270" for the **Code**, enter "CFC-11, 12, & 113" for the **Medium**, and enter "CFCs" for the **Abbr.** Click the check boxes **CFC-11** and **CFC-12.** Select **Prefix** "G," and click **Save.** LIMS will remind the user that this medium should be added to the Excel Template file for Creating Sample Projects in case the user is using this feature (see page 81). Click **OK.** Click **Close** to close the **Media** form.

Next add two new procedures, one for CFC-11 and one for CFC-12. Click **Procedures** on the **Special Features** subform. LIMS will display a message box advising the user of valid ranges of procedure codes for various isotopes, isotope ratios, and CFCs. Note that valid procedure codes for CFC-11 are between 2700 and 2799, and for CFC-12 are between 2800 and 2899. Click **Ok.** Click **Add.** Enter "2700" for the **Code** and press the Enter key. LIMS will advise the user that a code for CFC-11 is being added. Click **OK.** Enter "CFC-11" for the **Description.** Click **Save.** The first procedure code has been added. Enter the second code by clicking **Add**, entering "2800" for the **Code**, entering "CFC-12" for the **Description**, and click **Save.** Click **Close** to close the **Procedure Codes** form.

The user next needs to link these two procedures to the medium created. Click **Low Procedures** on the **Special Features** form. Click **Add.** Select "270 --> G [CFCs] CFC-11, 12 & 113" from the

Medium combo box. Select "2700 --> CFC-11" from the **Low Procedure** combo box. If a user had several procedure codes for the same medium and needed to indicate to LIMS which should be used as a default (such as when importing isotopic analyses), the user could select "*" from the **Default** combo box in order to make the selected procedure code the default low procedure code. Click **Save** and close the **Low Procedure Codes** form by clicking **Close**.

Next click **High Procedures** on the **Special Features** subform to open the **High Procedure Codes** form. Click **Add**. Select "270 -->G [CFCs] CFC-11, 12 & 113" from the **Medium** combo box. Select "2800 --> CFC-12" from the **High Procedure** combo box. Click **Save** and close the **High Procedure Codes** form by clicking **Close**.

A media code, and procedures codes are now available for use in LIMS. To demonstrate this, click **New Project Login** on the **Main Menu**. Click the **Medium** combo box and verify that medium 270 is available.

LIMS allows users to display, print, and store CFC-113 results on a medium created for CFC-11 and CFC-12 using the token "SHOW_CFC-11_12_&_113" found in the **LIMS for Light Stable Isotopes Configuration** form. Setting this token to -1 will enable the label "CFC-113" to be visible on the **Samples** form, the **Project** report, and the **Sample Range** report.

ANALYSIS IMPORT FORMATS

Introduction

LIMS can import isotopic results from a file on a diskette. The formats that existed when this document was printed are discussed below. The user may discover that additional import formats have been added.

LIMS Default Analysis Import Format

The LIMS Default format for importing isotopic analyses is a Microsoft Access 2.0 .mdb database file. The specifications are listed below. The field names of the database file are listed in table 6.

Extension of the Microsoft Access file:	.mdb
Microsoft Jet engine version:	2.0
Name of Microsoft Access table:	tbl_IsotopicResults

Either of the first two fields can be null (rstr_MassSpec or str_VendorMSID). If rstr_MassSpec is null, then LIMS can use str_VendorMSID to interrogate the table of mass spectrometers to determine rstr_MassSpec.

LIMS_TBA.mdb must be an Access 2.0 database and not an Access 95 or 97 database so that it can be imported by users employing LIMS 1.4, the Access 2.0 version that runs on the Microsoft Windows 3.1 or Windows for Workgroups 3.11 platform.

The Microsoft Visual Basic 3 code fragment below shows how to create the Access 2.0 file, create the table tbl_IsotopicResults, and populate the table.

```
Dim dyn        As dynaset
Dim sz         As string
Dim qdf        As querydef
Dim tbl        As table
Dim db         As database

On Error GoTo 0

'Delete file named ANALYSES.mdb on drive A:.
On Error Resume Next
Kill ("A:\ANALYSES.MDB")
On Error GoTo e_Export_Click

'Create Microsoft Access file.  By default it is version 2.0.
Set db = CreateDatabase("A:\ANALYSES.MDB", DB_LANG_GENERAL, False)
sz = "CREATE TABLE tbl_IsotopicResults"
sz = sz & " (rstr_MassSpec TEXT (1),"
sz = sz & " str_VendorMSID TEXT (50),"
sz = sz & " lng_Analysis LONG,"
sz = sz & " lng_PeakNumber LONG,"
sz = sz & " rstr_Prefix TEXT (1),"
```

Table 6. Fields of the LIMS default table for importing isotopic analyses.

Field name	Data type	Maximum string size	Description
rstr_MassSpec	Text	1	Single letter mass spectrometer identification. Primary key of tbl_MassSpec. Does not need to be supplied as long as str_VendorMSID is supplied.
str_VendorMSID	Text	50	Mass spectrometer serial number or vendor identification number. Does not need to be supplied as long as rstr_MassSpec is supplied.
lng_Analysis	Number (long)		Analysis number. Unique integer that should be generated by the mass spectrometer and printed on the analysis report. This number must be able to be changed by user so that it can be set to required value in case mass spectrometer computer requires replacement.
lng_PeakNumber	Number (long)		Peak number. Acceptable values are 1 to 999. Default value for dual inlet mass spectrometers is 1.
rstr_Prefix	Text	1	Single letter sample prefix; C, G, J, N, R, S, or W (see table 1).
rlng_Sample	Number (long)		Integer sample number. Together with sample prefix, this forms the Our Lab ID, *e.g.*, W-45677.
str_AliquotID	Text	20	Aliquot identification.
str_Port	Text	5	Name or identifier of the sample port on the preparation unit, manifold, carousel, *etc.*
str_Std	Text	14	In dual inlet mass spectrometry, the name or identifier of the working standard.
dat_Analyzed	Date/Time		Date and time sample analysis of this peak is begun. Generally increments for each peak.
str_Comment	Text	32	Comment.
int_Procedure	Number (integer)		Procedure code from table tbl_Procedure (table 4).
dbl_PenultimateDelta	Number (double)		Penultimate delta value.
rint_Error	Number (integer)		Error code. Primary key of table tbl_Error. Default value is 0.
ysn_Ignore	Yes/No		Default value is No. Mass spectrometer can set this field to Yes if it can determine that isotopic analysis is unsatisfactory and should not be included in a calculation by LIMS of the final delta value. Usually this is the case when the dual inlet mass spectrometer software performs another isotopic analysis of the sample.

```
sz = sz & " rlng_Sample LONG,"
sz = sz & " str_AliquotID TEXT (20),"
sz = sz & " str_Port TEXT (5),"
sz = sz & " str_Std TEXT (14),"
sz = sz & " dat_Analyzed DATETIME,"
sz = sz & " str_Comment TEXT (32),"
sz = sz & " int_Procedure SHORT,"
sz = sz & " dbl_PenultimateDelta DOUBLE,"
sz = sz & " rint_Error SHORT,"
sz = sz & " ysn_Ignore BIT );"
Set qdf = db.CreateQueryDef("qdf_Create_tbl_IsotopicResults", sz)
qdf.Execute
qdf.Close
db.DeleteQueryDef ("qdf_Create_tbl_IsotopicResults")

Set tbl = db.OpenTable("tbl_IsotopicResults")

... set dynaset with analysis data here.

dyn.MoveFirst
  Do While Not dyn.EOF
    tbl.AddNew
    tbl("rstr_MassSpec") = dyn("rstr_MassSpec")
    tbl("str_VendorMSID") =  "My serial #"
    tbl("lng_Analysis") = dyn("lng_Analysis")
    tbl("lng_PeakNumber") = dyn("lng_PeakNumber")
    tbl("rstr_Prefix") = dyn("rstr_Prefix")
    tbl("rlng_Sample") = dyn("rlng_Sample")
    tbl("str_Port") = dyn("str_Port")
    tbl("str_Std") = dyn("str_Std")
    tbl("dat_Analyzed") = dyn("dat_Analyzed")
    tbl("str_Comment") = dyn("str_Comment")
    tbl("int_Procedure") = dyn("int_Procedure")
    tbl("dbl_PenultimateDelta") = dyn("dbl_PenultimateDelta")
    tbl("rint_Error") = dyn("rint_Error")
    tbl("ysn_Ignore") = 0
    tbl.Update
    dyn.MoveNext
  Loop
  tbl.Close
  Set db = Nothing
```

Analytical Precision Analysis Import Format

Analytical Precision saves analyses in a Microsoft MDB file with the specifications below (see table 7):

Microsoft Jet engine version: 2.0
Microsoft Access Table name: LIMSInput

Table 7. Fields of the Analytical Precision Microsoft Access table of isotopic analyses, LIMSInput.

Field name	Data type	Size	Comments
Counter	Long		Not used by LIMS
MassSpecID	String	9	This is the VendorID of the mass spec.
AnalysisCounter	Long		Analysis number.
PeakNo	Integer		Peak number.
Name	String	20	OurLabID must be here.
Position	Long		PortID
GasName	String	10	Not used by LIMS.
RunDate	Date/Time		Date/Time
Comment	Memo		First 32 characters should be saved in LIMS comment field.
Isotope	Integer		Isotope from tbl_Isotope.
Delta	Double		Delta value
RunCode	Long		Same as LIMS' error code.
Barcode	string	10	Equivalent to LIMS' Sample ID.

Europa Scientific Analysis Import Format

The format employed by Europa Scientific is a comma separated ASCII text file with all values in quotes (see table 8). Null values are indicated by "".

File name: Mercury.txt

An example of one line of data follows:

"U","45741","1","W","4578","Aliquot 2","10101","Y123","23/03/1997 23:15:17","","-9.23","200","0"

Finnigan MAT Analysis Import Format

The format for Finnigan ISODAT dual inlet, GC combustion (GCC), and EA (elemental analyzer) files are different and are discussed below. Importing isotopic data from any of these three formats into LIMS is a two step process:

1.   Save the isotopic data on a diskette in Lotus .wks format using the mass spectrometer's computer.

2.   Insert the diskette with the .wks file into the LIMS computer, click **Import Analyses**, and import the .wks file.

Table 8. Fields of the Europa Scientific file of isotopic analyses, Mercury.txt.

Item #	Description	Maximum String Length	Comment
1	mass spectrometer ID	1	LIMS mass spectrometer ID
2	analysis number	7	LIMS long integer
3	peak number	3	LIMS long integer
4	sample prefix	1	LIMS text with length of 1
5	sample number	6	LIMS long integer
6	aliquot ID	20	LIMS text with length of 20
7	port ID	5	LIMS text with length of 5
8	standard ID	14	LIMS text with length of 14
9	date/time	19	LIMS date/time
10	Comment	32	LIMS text with length of 32
11	penultimate delta		LIMS double
12	Procedure	4	LIMS integer
13	error code	5	LIMS integer

Finnigan MAT is currently investigating possible formats for incorporation into their ISODAT-NT software, now under development.

Dual Inlet Import Format

Importing Finnigan isotopic data is not always straight forward. An example of importing the dual inlet file Finn_DI.wks is given in the tutorial on page 57. If one opens this file with Excel, one finds the following 17 column headings in row 4:

1. date/time
2. spec.- no.
3. sample ident
4. standard name
5. Comment
6. SA
7. ST
8. SA28[V]
9. ST28[V]
10. SA29[V]
11. ST29[V]
12. d-29/28
13. std.dev. 29/28

14.   Baseline
15.   Interfering mass 1
16.   Interfering mass 2
17.   Interfering mass 3

This spreadsheet file was created with ISODAT version 5.2-0009 software using the following ISODAT configuration parameters:

*   2   Date
*   3   Spec.-No. / Sample Ident / Sample Size
*   6   Standard Name
*   8   Comment
*   13   Ion-Gauge
*   25   Delta Mean
*   26   Std.Deviation
*   50   New Page
*   52   Interfering Masses

For importing $\delta^{18}O$ values of water the user may want to put an asterisk on parameter 44, "sample (alpha H2O)." For importing $\delta^{18}O$ values of CO_2 gas, the user may want to put an asterisk on parameter 42, "Delta O-18 vs SMOW."

A few comments are in order. The date/time column is imported by LIMS. Column 2, the spec. no., is the LIMS analysis number. This must be a unique integer for use by LIMS. **Therefore, if a user needs to replace a computer or hard disk, the Spec No must be set during installation to the next unique integer analysis number.** Column four contains the standard name. Column five contains the analysis comment. Column three is used to provide information about the description of the sample and the analysis. Currently LIMS does not import Baseline information (column 14). LIMS does import some interfering masses (columns 15 through 17).

LIMS needs a value for the peak number. It uses a value of 1 as a default for dual inlet analyses.

Column three, sample ident, can contain as many as five items of information as shown an example below:

	Example Value
Our Lab ID	C-1
Aliquot ID	My test #34
Low Procedure Code	312
High Procedure Code	820
Comment	Temp = 41 C

When all five items are provided, they are delimited with forward slashes as:

Our Lab ID / Aliquot ID / Low Procedure Code / High Procedure Code / Comment

The minimum information needed by LIMS to import the analysis is Our Lab ID. LIMS will use default procedure codes for the medium if not provided. The following are examples for valid entries in column 3:

    C-1/My test #34/312/820/Temp = 41 C
    C-1 / My test #34 / 312 / 820 / Temp = 41 C
    C-1
    C-1 //// Temp = 41 C
    C-1 / My test #34 /// Temp = 41 C
    C-1/My test #34
    C-1 // 312 / 820
    C-1 // 820

Note that if the comment is provided as a unique column (column 5 in this example), then it should not be provided in column 3.

The $\delta^{15}N$ values are found in column 12 in this example. The column header is "d-29/28". LIMS needs a mechanism to uniquely identify the column of the δ values to be imported. Often δ values are found in several columns so the user must specify the correct column. The procedure the user follows is to open the **LIMS For Light Stable Isotopes Configuration** form by clicking **Special Features** on the Main Menu and then clicking **Config**. The user can click **List** and can click on the token "FINN_COL_HEAD_15N." Note that the value of this token is "d-29/28" and that the description of this parameter is that it is the descriptor that uniquely identifies the column with $\delta^{15}N$ data to be imported. Note that tokens are also available for several other δ values. In the case of $\delta^{18}O$, two tokens are provided. One is for importing water samples and the other is for all other oxygen bearing materials.

An example of a file containing $\delta^{18}O$ values from water samples is F_18wodi.wks. Another example of a file containing $\delta^{18}O$ values from water samples is Fh2o18di.wks. In this file, the unique column identifier is "18/16-O". Finnh2di.wks contains $\delta^{2}H$ results. Note that the unique column identifier containing the desired isotopic data is either "sample vs. SMOW" or "H3 factor" to choose column 7 or "std.dev. 3/2" to select column 11. "outl. corr" cannot be used because it is found in other columns. If the user is having difficulty importing isotopic data into LIMS, it is important to verify that the token specifying the column with the δ values to be imported is unique and spelled exactly as it appears. It cannot differ, even by a space. The author uses the copy and paste features of Windows to copy these column specifiers.

In order to import data from a file LIMS needs at a minimum the following columns: (i) date/time, (ii) spec.- no. (analysis number), (iii) sample ident with Our Lab ID, (iv) standard name, (v) δ value.

As shown in the example database (page 57), LIMS can import ion gauge readings and sample and standard ion beam voltages if these are present in the spreadsheet to be imported. The user enables importing of these values using the tokens "STORE_INTERF_MASSES" and "STORE_MAJOR_VOLTAGES" in the **LIMS For Light Stable Isotopes Configuration** form.

GCC Import Format

Two slightly different formats are generated for GCC analyses depending upon whether CO_2 or N_2 is being analyzed. F_gcc_n2.wks was generated from a Finnigan Delta Plus from caffeine. Note that the format is significantly different than that of dual inlet isotopic data. The $\delta^{15}N$ values are found in a column uniquely identified by "delta-29/28" and this is saved in the token "FINN_COL_HEAD_GCC_15N". The Our Lab ID must be found in either column "Sample Name #1", "Sample Name #2", or "Sample Name #3." As in the case of dual inlet data, aliquot IDs and procedure codes can be appended using forward slash as the record separator in columns 1, 2 or 3. There is little reason to put the comment in columns 1, 2, or 3 because a separate comment column is provided. LIMS will use the peak number found in the column with the specifier "Peak." Typically, one or more analyses will be a standard. This is identified by an asterisk in the column "STD." For such analyses LIMS will use the Our Lab ID found in the token "CF_Std_OurLabID_N2" in the **LIMS For Light Stable Isotopes Configuration** form.

F_GCC_CO2.wks was generated during installation of a Finnigan Delta Plus from analysis of CO_2 from a flame ionization mixture of organic compounds. The $\delta^{13}C$ values of CO_2 are found in a column uniquely identified by "delta-13/12" and this is specified with the token "FINN_COL_HEAD_GCC_13C" (see the **LIMS For Light Stable Isotopes Configuration** form). The $\delta^{18}O$ values of CO_2 are found in a column uniquely identified by "delta-18/16" and this is specified with the token "FINN_COL_HEAD_GCC_18O" (see the **LIMS For Light Stable Isotopes Configuration** form). The Our Lab ID must be found in either column "Sample Name #1", "Sample Name #2", or "Sample Name #3." As in the case of dual inlet data, aliquot IDs and procedure codes can be appended using forward slash as the record separator in columns 1, 2 or 3. LIMS will use the peak number found in the column "Peak." Typically, one or more analyses will be a standard. As above, this is identified by an asterisk in the column "STD." For such analyses LIMS will use the Our Lab ID found in the token "CF_Std_OurLabID_CO2" in the **LIMS For Light Stable Isotopes Configuration** form.

EA Import Format

Three slightly different formats are generated for GCC analyses depending upon whether SO_2, N_2 only, or CO_2 only or CO_2 and N_2 is being analyzed. Finn_EA.wks was generated on a Finnigan Delta Plus from C- and N-bearing samples. The format is similar to that of GCC analyses. The first 18 or so columns are similar or identical to those found in Finnigan GCC files. LIMS can import the values for C, N, or S concentration found in the column "CONC." They will be stored using procedure codes 189, 190, and 191, respectively. The amount of sample is listed in the column " Sample Wt. [mg] ." If the

comment is blank, LIMS will import the amount of sample and save it in the Comment field of the analyses table. The $\delta^{13}C$ and $\delta^{15}N$ values are found in columns 26 through 29. Both blank-corrected and non-blank-corrected δ values are reported. The user specifies which to import using the token "FINN_BLANK_CORR_EA_DATA" in the **LIMS For Light Stable Isotopes Configuration** form. Set it for -1 to import blank-corrected values, otherwise set it for 0. As in the GCC format, the Our Lab ID must be found in either column "Sample Name #1", "Sample Name #2",or "Sample Name #3." Aliquot IDs and procedure codes can be appended using forward slash as the record separator in columns 1, 2 or 3. There is little reason to put the comment in columns 1, 2, or 3 because a separate comment column is provided. LIMS will use the peak number found in the column "Peak." Typically, one or more analyses will be a standard. This is identified by an asterisk in the column "STD." For such analyses LIMS will use the Our Lab ID found in the token "CF_Std_OurLabID_CO2" in the **LIMS For Light Stable Isotopes Configuration** form. When N_2 is analyzed, LIMS will use for standards the Our Lab ID specified in the token "CF_Std_OurLabID_CO2." For SO_2 analyses LIMS will use for standards the Our Lab ID specified in the token "CF_Std_OurLabID_SO2." Files F_EA_N2.wks and F_EA_SO2.wks are examples of N_2 only and of SO_2 files. As of the version of ISODAT of September 1997, blank-corrected $\delta^{34}S$ values were not available. Therefore, $\delta^{34}S$ values imported by LIMS will be identical whether the token "FINN_BLANK_CORR_EA_DATA" in the **LIMS For Light Stable Isotopes Configuration** form is set to True (-1) or False (0).

If the user has set LIMS to import EA blank corrected δ values by setting the token, FINN_BLANK_CORR_EA_DATA, to true (-1) using the **Configuration** form (page 60), LIMS displays the following message:

> **At software development time [a date], Finnigan ISODAT software did not save blank corrected sulfur delta values with unique column headings, such as 'delta vs. CDT.'**

If the user clicks **OK**, the message above about Finnigan GCC analyses being found appears. The "At software development time ..." message appears because LIMS checks the spreadsheet to see if it is an EA analysis, and then to see if it is a GCC analysis. This is a temporary message until a future version of ISODAT provides blank corrected EA $\delta^{34}S$ values.

Micromass Analysis Import Format

Micromass uses comma separated variable (CSV) text files that can be imported into spreadsheet programs. An example of importing the dual inlet file Mm_H2.csv is given in the tutorial on page 59. The format of dual inlet files is relatively similar according to Micromass; however, the format for continuous flow samples has varied often. According to discussion of the author in March 1997 with Tim Brockwell of Micromass, providing a stable format for continuous flow measurements has not been given a high priority. Therefore, currently LIMS does not import Micromass continuous flow analyses.

Micromass dual inlet files often contain more than 150 columns; thus, standard importing tools of Access will not work. Examples of Micromass dual inlet files of δ^2H of water, $\delta^{15}N$ of other N-

bearing material, and $\delta^{18}O$ of water are provided by the files Mm_H2.csv, Mm_N2.csv, and Mm_O18w.csv, respectively. Column 1, "Sample Name", must contain the Our Lab ID. Just as for Finnigan importing, the Aliquot ID, the low procedure code, the high procedure code, and the comment can be appended together in this field using the record separator forward slash (see above). The user has the choice to select the column of δ values to be imported.

Note that no analysis number is maintained by Micromass software. Therefore, users are prompted by LIMS to input an analysis number that must be separately maintained by the user. The "Run Serial Number" that Micromass generates is stored in the comment field of the analyses table. If a comment has been entered, the two are appended.

The $\delta^{18}O$ values are found in column 39 in this example. The column header is "delta O18 wrt SMOW". LIMS needs a mechanism to uniquely identify the column of the δ values to be imported. Often δ values are found in several columns so the user must specify the correct column. The procedure the user follows is to open the **LIMS For Light Stable Isotopes Configuration** form by clicking **Special Features** on the Main Menu and then clicking **Config**. The user can click **List** and can click on the token "UMASS_COL_HEAD_18O_Water" Note that the value of this token is "Delta O18 wrt SMOW" and that the description of this parameter is that it is the descriptor that uniquely identifies the column with $\delta^{18}O$ values of water to be imported. Note that tokens are also available for $\delta^{18}O$ of other materials, $\delta^{13}C$, $\delta^{34}S$, *etc.* If the user is having difficulty importing isotopic data into LIMS, it is important to verify that the token specifying the column with the δ values to be imported is unique and spelled exactly as it appears. It cannot differ, even by a space. The author uses the copy and paste features of Windows to copy these column specifiers.

As for Finnigan files (see page 57 of the tutorial), LIMS can import ion gauge readings and sample and standard ion beam voltages if these are present in the spreadsheet to be imported. The user enables importing of these values using the tokens "STORE_INTERF_MASSES" and "STORE_MAJOR_VOLTAGES" in the **LIMS For Light Stable Isotopes Configuration** form.

When LIMS imports date and time from Micromass files it first tries to import them assuming they are in the format 18-03-1997 18:03. If that is unsuccessful, LIMS attempts to import them as valid dates for the existing Window's setting. Therefore, be careful not to enter 09/03/97, expecting that September 3, 1997 will be imported. LIMS will import it as March 9, 1997.

SAMPLE EXPORT FORMATS

Introduction

When the user generates a template of samples to be analyzed, LIMS creates a file on the user's diskette that contains the sample names, the position of the samples in the preparation system, and information about the isotopic analyses requested. The data acquisition and control software of the user's mass spectrometer can use this information to perform the requested isotopic analysis(es) of each of the user's samples. This technique eliminates typing in the sample heading and potential typographic errors. This method has been used in the author's laboratory for a decade.

LIMS Default Sample Export Format

LIMS saves information on samples to be analyzed in two files, as a Microsoft Access 2 .mdb database file and as a Microsoft Excel 5.0 file. The specifications of the database and table are listed below (table 9). Analytical Precision also saves information on samples to be analyzed in the same Microsoft Access 2.0 format.

Name of Microsoft Access file: LIMS_TBA.mdb
Name of Microsoft Access table: SamplesToBeAnalyzed
Name of Microsoft Excel 5.0 file: LIMS_TBA.xls

Sample Export Format for Analytical Precision

The sample export format used by Analytical Precision is the LIMS default format, discussed below.

Sample Export Format for Europa Scientific

The format employed by Europa Scientific is a comma separated text file with all values in quotes (see table 10). Each line corresponds to one sample. Missing information is presented as "".

Name of text file: ZEUS.TXT

Table 9. Fields of the LIMS default sample export table, SamplesToBeAnalyzed.

Description	Field name	Data type	Size
Date and time of template Generation	dat_Stamp	Date/Time	8
template name	rstr_TemplateName	Text	50
mass spectrometer ID	rstr_MassSpec	Text	1
mass spectrometer serial number or vendor ID	rstr_VendorMSID	Text	50
ordinal position of sample in list	rlng_OrdinalPositionInList	Number (Long)	4
port ID	rstr_Port	Text	5
flag; 1 = fixed reference sample in this port, 2 = floating reference sample in this port, and 3 = port is empty.	rlng_PortRefEmpty	Number (Long)	4
sample prefix	rstr_Prefix	Text	1
sample number	rlng_Sample	Number (Long)	4
aliquot ID	rstr_AliquotID	Text	20
low isotope	byt_Lisotope	Number (Byte)	1
low procedure	rint_Lprocedure	Number (Integer)	2
high isotope	byt_Hisotope	Number (Byte)	1
high procedure	rint_Hprocedure	Number (Integer)	2
method (for future use)	rstr_Method	Text	32

Table 10. Fields of LIMS sample export file for Europa Scientific.

Item #	Description	Maximum String Length
1	template name	50
2	mass spectrometer ID	1
3	mass spectrometer serial number or vendor ID	50
4	ordinal position in list	5
5	port ID	5
6	sample prefix	1
7	sample number	6
8	aliquot ID	20
9	Isotope of low procedure	2
10	Low procedure	5
11	Isotope of high procedure	2
12	high procedure	5

An example of two rows of data follow:

"EA 1","U","4KM33","1","10001","G","4451","Aliquot 1","3","380","5","584"
"EA 1","U","4KM33","2","10002","C","751","Aliquot 1","3","356","",""

Sample Export Format for Finnigan MAT

Finnigan MAT's sample export format is currently being developed on Finnigan's ISODAT-NT data acquisition and control software that operates on the Microsoft Windows NT platform.

Sample Export Format for Micromass

Currently Micromass has no sample export format.

FILES FOUND ON DISKETTES

The following files are included with LIMS—Version 7.0.

Program Files (4 diskettes, except only 1 diskette for LIMS 1.4)

Example Database
    Lm7datae.mdb (LM4DATAE.mdb is provided for LIMS 1.4)
    numerous examples of mass spectrometer analyses for importing

New Database
    Lm7data.mdb and LM4DATA.mdb

Excel 5.0 Template for Creating Sample Projects
    ALT.xls
    USGS.xls

Example Import Formats
    Several files of isotopic analyses that can be imported into the example database.

ACKNOWLEDGMENTS

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