ZAGRADA—THE NEW ZAGREB RADIOCARBON DATABASE

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ABSTRACT. After introducing the liquid scintillation counting (LSC) method and graphite target preparation for accelerator mass spectrometry (AMS) measurements in the Zagreb Radiocarbon Laboratory, the existing database software designed only for gas proportional counting (GPC) (using a DOS operating system) could not satisfy the requirements for parallel conduction of several techniques. This has been enabled recently by the development of the new relational database ZAGRADA, which—using SQL scripts and constraints defined by primary and foreign keys—enforces high data integrity and provides better performances in data filtering and sorting. The structural scheme of this database conceptually comprises 4 basic modules with data on the samples, chemical pretreatment and preparation, measurements and data on the final results. A user-friendly graphical user interface has been designed to perform various actions and data manipulation to the database. The implementation of a new database for ^{14}C samples has significant contribution to scientific research performed in the Radiocarbon and Tritium Laboratory and to quality assurance and quality control, and will enable better and easier communication with customers.

INTRODUCTION

In the Radiocarbon and Tritium Laboratory at the Rudjer Bošković Institute (Zagreb, Croatia), 3 different techniques for ^{14}C dating have been used. Gas proportional counting (GPC) was used from 1968 until abandoned in 2007. Thereafter, liquid scintillation counting (LSC) by Quantulus 1220™ was implemented in 2001 and 2 preparation techniques were developed: CO_2 absorption (LSC-A) and benzene synthesis (LSC-B) (Horvatinčić et al. 2004). Benzene samples can be measured in Teflon®-copper 7-mL vials, in Teflon 3-mL vials, and in 7-mL low-potassium glass vials, while for absorbed samples we use 20-mL glass vials (Krajcar Bronić et al. 2009a). In 2008, preparation of milligram-sized samples for accelerator mass spectrometry (AMS) dating was implemented (Krajcar Bronić et al. 2009b, 2010). Prepared graphite targets are sent to be measured at the AMS facility of the Scottish Universities Environmental Research Centre (SUERC) in Glasgow, Scotland.

The need for computer processing and data storage in a database was realized very soon after starting ^{14}C measurements in the early 1970s. The creation of a sophisticated database was possible only after introducing PCs in the laboratory, so the software package CARBO was designed (Obelić 1989), using the DOS operating system, MS FORTRAN 77, and dBASE III PLUS.

The CARBO software was designed for a single measurement technique (GPC) and was not appropriate for parallel processing of several techniques introduced in the laboratory within the last years. Moreover, its upgrade was not pragmatic because the DOS-related programs are outdated and obsolete. These facts initiated the development of a new Microsoft Windows®-oriented relational database named ZAGRADA (ZAGreb RAdiocarbon DAtabase), which will integrate all old data from the CARBO database since 1968 along with results of newly introduced techniques.

Here, we describe the design of the new database, which may serve as a template for other ^{14}C laboratories that are conducting (or planning to conduct) 2 or more measurement techniques in parallel and want to set up their own database for sample administration.

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DATABASE STRUCTURE

The most widely used method of storing large amounts of data generated by a laboratory is the relational database. Relational databases can store more than individual data items and enable relations among the data, thus providing much of its utility. The relational model design specifies the way in which data will be arranged and related.

ZAGRADA is developed by using relational database architecture provided by the MS SQL Server 2005 environment, which is most commonly used as a modern relational database management system (RDBMS). In order to avoid storing data anomalies in the database, ZAGRADA's data model is optimized using database normalization techniques. Normalization is a systematic way of ensuring that a database structure is suitable for general-purpose querying and free of certain undesirable characteristics such as insertion, update, and deletion of anomalies that could lead to a loss of data integrity (Codd 1990; Kline et al. 2008). The design of ZAGRADA's relational model enables high-level data organization and systematization, thus providing a software package capable of processing detailed data obtained from several measurement techniques. Utility database objects realized as stand-alone database tables are also implemented to provide service to the core database model as well as better software performance. These tables store temporary information necessary for intermediate data processing and their content is automatically cleared by stored procedures within the RDBMS when done. Using SQL procedures, triggers, and constraints defined by primary and foreign keys, ZAGRADA enforces high data integrity and provides better performances in data filtering and sorting. Additionally, an SQL task monitored by the SQL Server Agent component is also introduced to perform database backups at predefined periods of time, configured through the graphical user interface (GUI). In order to facilitate data handling and processing in ZAGRADA, the GUI is designed to be user-friendly and to perform various actions on data, e.g. input, corrections, searching, sorting, and output to printer.

The package ZAGRADA is designed in terms of client-server architecture. It is run on a PC configured as a server to which client PCs in the workgroup can connect. Each user has his own GUI on his computer, which enables communication with the database and manipulation of its content. The access to ZAGRADA is controlled through identification by a user name and a password. Once logged in, the Main Menu appears with entry points for the various program components: Samples, Preparation, Measurements, Results, Reports and Administration.

The new database consists of 21 tables (Table 1), comprising 4 basic groups: (1) data on samples; (2) data on sample pretreatment and preparation; (3) data on measurements; and (4) data on final (mean) results. The core database model is presented in Figure 1.

The first module, containing all the sample data, is described by the main table *Samples*, connected with subordinate tables containing data about site names and customers that delivered each sample (tables *LabCodes*, *Locations, SitenameDetails*, *Institutions*, *Persons*). The description of each sample starts with the laboratory number, the principal code conventionally accepted within the *Radiocarbon* community (Z- for the Zagreb laboratory). The type of material (wood, charcoal, carbonate, bones, etc. according to the list given in Obelić [1989]) is listed by laboratory code, while $\delta^{13}C$ values with related errors (according to Stuiver and Polach [1977]) could be either default values associated in the table *LabCodes* with the material type or measured values entered manually. Samples with certain common characteristics (e.g. the same site or within a certain project) are denoted by the same series code listed in the table *Series*. A drop-down list of scientific disciplines (archaeology, geology, etc.) associated with samples is the same as given in Obelić (1989). Detailed information about sample material and a description followed by stratigraphic position within the sampling site, expected

Table 1 Description of database tables.

Table name	Main content
Samples	Basic data about each sample denoted by laboratory number Z-xxxx
LabCode	Connection of material type with $\delta^{13}C$ values (Stuiver and Polach 1977)
Locations	Sample location (name, neighboring settlement, province, etc.)
SitenameDetails	Site name details (latitude, longitude, altitude)
Persons	Persons: collectors, submitters and/or customers
Institutions	Institutions to which belong collectors, submitters or customers
Series	List of series codes
SuggestedMeasurements	List of possible techniques and their combinations
Pretreatments	Pretreatment data
MeasuringTechnique	Decided measuring technique
Absorption	Details on CO_2 absorption procedure
Benzene	Details on benzene preparation procedure
BenzeneApparatus	Details on benzene preparation rigs
AMS	Details on graphite preparation
Measurements	Details on LSC and AMS measurement containing individual results
Vials	Data about vials for LSC measurement
Runs	Details on runs in LSC
Results	Mean results of LSC-A, LSC-B, and AMS measurements
ResultsGPC	Mean results of GPC measurements retrieved from old program CARBO
Users	Details on user accounts and passwords
TempMeasurements	Temporary table for complex mathematical operations and normalization

age and cultural period, context of the sample, and information about sample storage are given by the submitters and/or collectors. Their names are listed in the *Persons* table, linked with related institutions in order to enable their easy access using the drop-down list of names within each institution (table *Institutions*). Although usually the collector, the submitter, and the customer is the same person coming from the same institution, we allowed a general case that they are different by enabling separate fields for submission, collection, and customer. Details of sites and sample locations are also given in appropriate tables and include geographic latitude and longitude, as well as altitude. The decision on which technique will be used, the suggested pretreatment, and the priority for sample preparation is given by laboratory staff. A paper is then printed out with selected data for the laboratory log-book and recording of subsequent laboratory procedures, pretreatment, and preparation.

Data on pretreatment are stored in the *Pretreatments* table containing total sample weight, weight of the aliquot taken for pretreatment, comments about pretreatment procedures, and subsequent CO_2 production.

Details of each preparation procedure are stored in one of the tables *Absorption*, *Benzene*, or *AMS*, respectively, with additional code numbers associated with the various measurement techniques:

- **LSC-A** (CO_2 absorption): additional code number Dxxxx;
- **LSC-B** (benzene synthesis): additional code number Bxxxx;
- **AMS** (graphite preparation): additional code number Axxxx.

A sample is usually prepared by only 1 method, depending on the sample quantity (e.g. samples with <1 g of carbon will undergo AMS preparation, otherwise will undergo preparation for measurement by LSC) or the required precision (e.g. archaeological samples will undergo the more precise LSC-B method, while environmental samples for monitoring purposes will usually undergo LSC-A

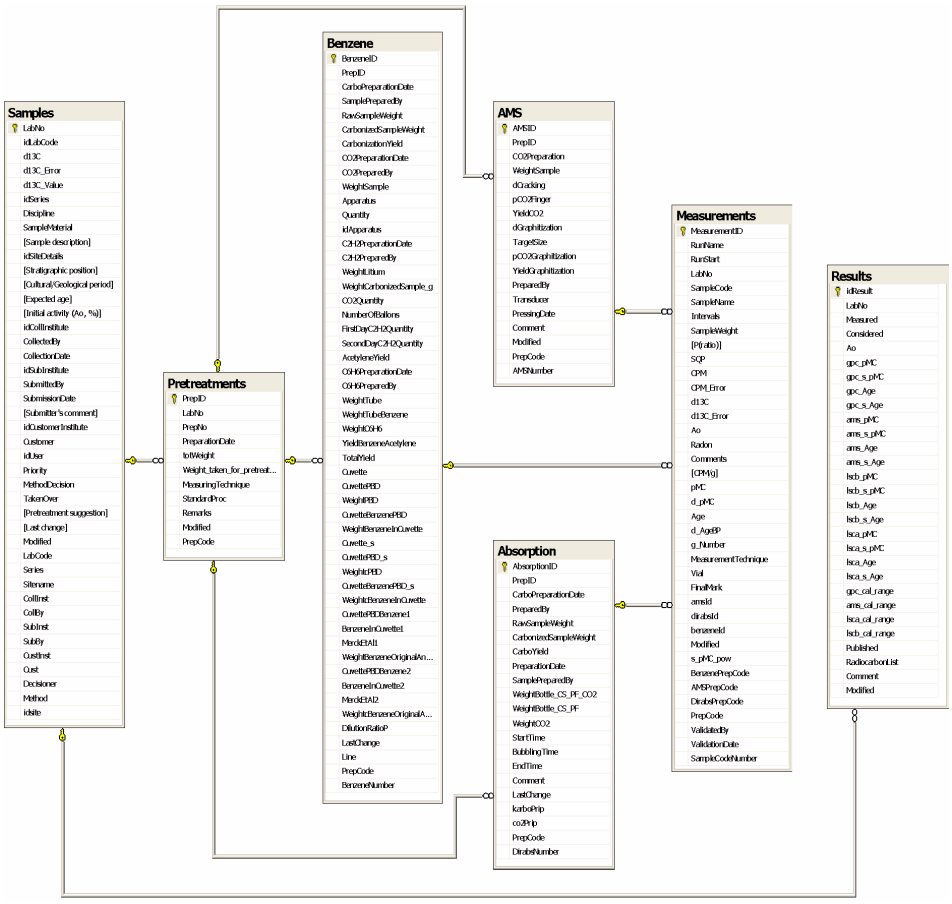

Figure 1 Core database tables with their respective content

method) (Krajcar Bronić et al. 2009a,b, 2010). However, in some cases the same sample could be prepared by different techniques simultaneously (intercomparison studies or intralaboratory checks). Therefore, it is possible to have multiple additional code numbers for the same principal code number Z. There is also the possibility for multiple preparations by the same technique, e.g. usually LSC-A samples are prepared in duplicates.

Data on individual measurement results are stored in the table *Measurements*. Data measured by LSC, either benzene (code **B**) or absorbed CO_2 (code **D**), are retrieved from the Registry.txt file produced by the program WinQ[2] and subsequently processed by the spectrum analysis program EASY View[3]. Since EASY View does not transfer all data necessary for further calculations (such as sample identification, CPM [counts per minute] error, SQP quenching parameter, CPM in radon window) into its final "All Samples" sheet, we created separate MS Excel files for ^{14}C activity calculation for both preparation methods, which are subsequently imported into the ZAGRADA database. For AMS

[2]Wallac WinQ, Windows software for controlling Wallac 1220 Quantulus™, version 1.2, PerkinElmer Life Sciences 2000.
[3]Wallac EASY View software, Spectrum analysis program for 1220 Quantulus & System 1400 DSA liquid scintillation counters, Version 1.0, Release 3.4, PerkinElmer Life Sciences 1998.

measurements (code **A**), data are compatible with the database of the AMS laboratory where graphite is measured (in our case, SUERC) and are entered manually into the database.

Individual measurement results from the *Measurements* table can be presented in separate windows. This window contains also previous results (if any) of a sample for a certain measurement method. Each result, regardless of measurement technique, has been judged by laboratory staff acceptance or rejection and is subsequently printed out for the laboratory archives.

The table *Results* contains mean values of all accepted results from *Measurements* for each laboratory number Z-xxxx and each measurement method separately and information necessary for reporting ^{14}C activity. Mean values of old measurement results performed by GPC and retrieved from the CARBO database are stored in a stand-alone database object *ResultsGPC* of the new database scheme. The window containing distribution of all measurement results of all measurement methods of a certain sample is presented in Figure 2. Thus, this window allows comparison of the respective results in the case when a sample was measured by different techniques (GPC, AMS, LSC-A, or LSC-B). Mean values of all positively judged results measured by the same technique can be found on the same windows as Final results. It is also possible to manually enter calibrated ranges calculated by respective calibration programs (in our case, OxCal; Bronk Ramsey 1995, 2001). The final results of a sample described by the principal code Z can be printed out as a Result Sheet, then stored for documentation records.

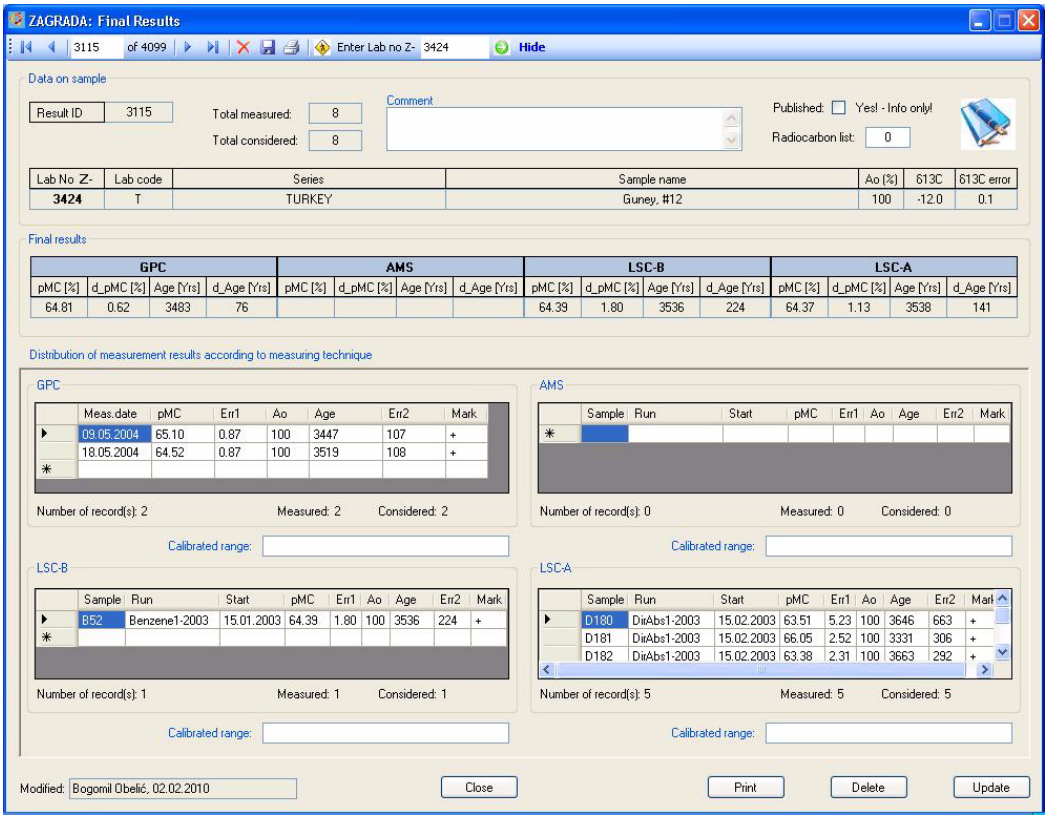

Figure 2 Example of the window containing distribution of measurement results of GPC, LSC-A, and LSC-B measurement methods, as well as mean values results obtained by each of these methods.

Reliable measurements of ^{14}C activity require continuous monitoring of reference (standard) samples, either inactive (containing no ^{14}C) or active (standard reference materials of precisely known ^{14}C activity). The ZAGRADA database allows preparation of control charts for such materials from the table *Measurements* for each preparation technique separately, LSC counting of benzene in different types of vials, direct absorption counting, and AMS. ZAGRADA enables creating reports by sorting selected groups of samples according to codes (Z, B, D, A), materials, sites, measurement dates, series names, etc. It also allows exporting of data to a MS Excel or PDF file, to be used in custom-made report documents.

Data redundancy is avoided by introducing the drop-down lists with predefined items from database records, such as of disciplines, series, customers, and institutions. In addition, some regular expressions implemented in the software prompt the user in case one tries to insert similar data that might already be presented in the database under a different record (e.g. site names, series names, institution names, etc.). Access to the database and its usage is restricted to dedicated laboratory personnel only, but in the future software upgrades may make it possible to post the tables on the internet. All invalid actions performed by laboratory users are controlled and prevented by regular expressions as mechanisms within the program logic. Each application window has implemented support to track last changes providing the user name with the respective date when changes were made.

The component Administration manages users' accounts and several configuration parameters as file paths for database backups. It is also used to administer and update general data on laboratory codes and sample series and for provisioning of some laboratory technical data related to the apparatus, devices, and lines used to obtain data on measurements.

CONCLUSIONS

The new database ZAGRADA enables processing and storing of data obtained by different preparation and measurement techniques at the Rudjer Bošković Institute Radiocarbon Laboratory. ZAGRADA uses state-of-the-art methods that ensure data integrity at the highest level; control of data input is ensured by database normalization and regular expressions. A modern database management system enables multi-user access, which contributes to the high efficiency of the laboratory. The implementation of a new database for ^{14}C samples contributes significantly to the scientific research performed in the Radiocarbon and Tritium Laboratory and to quality assurance and quality control, and will provide better and easier communication with customers. The presented structure may also help other ^{14}C laboratories in setting up their own relational databases.

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