

The South Bay data collection

Pre-mining documents to the present, 2003

Overview

Prepared by Boojum Research Ltd for
Talisman Energy Inc

November 2003

LIST OF CONTENTS

1.0	Introduction.....	1
1.1	Sampall/Chemall Database (File: SBTOTAL.MDB)	1
1.2	Titrino Database (File: SBTOTAL.MDB).....	4
1.3	Water Level/Elevation Database (File: SBWATERLEVELS.XLS)	6
1.4	Flow Database (File: SBFLOWS.XLS).....	6
1.5	Weather Database (File: SBWEATHER.XLS)	6
1.6	Maps Database	7
1.7	Field Books Database (File: SBTOTAL.MDB)	7
1.8	Lab Records	7
1.9	Photo/Slides Record	7
1.10	Report Database	8

LIST OF TABLES

Table 1:	SAMPALL Data Structure (Field and Descriptions).....	3
Table 2:	SAMPALL Data Structure (Field and Values).....	4

LIST OF APPENDICES

Appendix 1:	Boojum Research Total Database 2.0 User Manual 1.0
Appendix 2:	Further Development of A Titrino Approach of Model Detection Based on Buffer Intensity: Metal Mixtures
Appendix 3:	Evaluation of Titrino data

1.0 Introduction

The South Bay Waste Management Area (SBWMA) was decommissioned using a variety of innovative, but non-conventional, techniques which relied heavily upon extensive and frequent collections of data. That same data is also essential to any assessment of the Ecological Engineering measures implemented at the site by Boojum Research Limited over the past 16 years.

The data is organized into ten distinct formats.

1. Sampall/Chemall Database
2. Titrino Database
3. Water Levels Database
4. Flows Database
5. Weather Database
6. Maps Database
7. Field Books Database
8. Lab Records
9. Photo/Slides Records
10. Reports Database

1.1 Sampall/Chemall Database (File: SBTOTAL.MDB)

Initially, data from the site was recorded in Lotus spreadsheets. This included results of the analysis of water and soil samples collected in 1987. By 1991, when the complexity of the data had begun to overwhelm the spreadsheets, the information was transferred to Paradox, a relational database. Each sample was numbered and referenced by way of the site location that yielded it, the methods by which it was gathered and prepared, and the outside laboratory to which it was assigned for elemental analysis and the results of that analysis. In 1999, the database was upgraded again to Access.

As of May 2003, the database contained information pertaining to 4329 samples. Information generated by all of the regularly monitored stations, for example C1, C8 and C11 can be accessed through a clickable map. Eventually, this feature will be extended to all non-standard stations as well. The codes for some samples have yet to be unified. At

present the locations can be found through the use of the map database where pdf files are provided, sorted by area within the site, and within these folders by year.

Paper copies of all of the data stored electronically, including assayer records and information from the certified analytical laboratories have been preserved as well. As part of Boojum's QA/QC measures, spiked samples, blank samples and certified materials such as standard leaves were submitted for analysis. Samples were returned to the Boojum laboratory and stored until the data are interpreted and published. The samples analyzed since January 1998 by the Saskatchewan Research Council are held in storage at the SRC facility in Saskatoon until the data are interpretation is completed.

A draft manual to the database is provided in Appendix 1.

The file **SBTOTAL.MDB** consists of two major tables, **SAMPALL** and **CHEMALL**, each containing specific data sets.

The **SAMPALL** database contains:

- Assayer number (a unique identifier of each sample)
- Date of sampling
- Date of shipping/preparation
- Site location
- Sampling location
- Habitat (short description of habitat of the sample)
- Horizontal (location where sample was collected)
- Vertical (location where sample was collected)
- Code (describing the sample type)
- Flag (notes on special conditions)
- Description (short description of the type of sample: pies, PO4 experiment, etc ...)
- Type of chemical parameters which re to be analyzed by the laboratory
- Filter paper number (only when filter papers were washed and pre-weight for TSS determination and or elemental content)

- Laboratory to which the sample was shipped to
- Floppy and filename number on which the data are recorded

A summary of the column descriptors is given in Table 1.

Table 1: SAMPALL Data Structure (Field and Descriptions)

Field	Description
ASSAYER #	10112
PROJECT	SOUTH BAY
DATE SAMP#	1/30/2003
DATE SHIP#	2/18/2003
SITE LOCAT#	SAND PIT
SAMPLING LOCAT#	MSP11
HABITAT	
HORIZONTAL	
VERTICAL	
CODE	FA
FLAG	
DESCRIP	
ANAL#	ICP25+S
FILT#PAP##	
LABORATORY	SRC2003-1
FLOPPY #	11.149
FILE NAME	SB0301.XLS

The **CHEMALL** database contains the following information

- pH, Eh, temperature, electrical measurements taken in the field.
- the above parameters are often re-measured in the Boojum Laboratory
- the results of elemental analyses conducted by a succession of certified analytical laboratories.

Samples analyzed for nutrients, as well as for their elemental composition, require different methods of preservation, so multiple samples were shipped to the laboratory for each analytical request. In most cases, the results are combined in the database. Table 2 provides an example of the parameters entered to combine all the chemical analysis of the sample analyzed.

Table 2: SAMPALL Data structure (Field and Value)

Field	Value	Field (Continued...)	Value	Field (Continued...)	Value	Field (Continued...)	Value
Ag	-0.001	N-tot		Zn	22	SO3	
Al	4.1	Na	3.3	Zn-tot		SO4	
As		Nb		Zr	-0.001	NO2	
AS-DIS		Ni	0.029	L#O#I# ¹		NO3	
B	0.004	NI-DIS		F*Temp		NO2+NO3	-0.1
Ba	0.017	Ort-p		F*pH		NH3	15.6
Be	-0.001	P	0.01	F*Cond		NH4	
Bi		P-tot		F*Eh		PO4	
C		Pb	-0.002	F*Acid		CO3	
Ca	8	S	53	F*Alk# ²		HCO3	
Cd	0.01	Sb		F*Fe3+		OH	
Ce		Se		F*Fe2+		TDS	
Co	0.064	Si	5.3	L*Temp	19.4	T#S#S# ³	
Cr	-0.001	Sn		L*pH	3.863	TKN	16
Cu	0.037	Sr	0.044	L*Cond	506	DOC	
Fe	6.3	Te		L*Eh	571	TOC	1
Fe-tot		Th		L*Acid	188.5	TIC	
Hg		Ti	-0.001	L*Alk#		Ra 226	
K	1.7	U		L*Fe3+		RA_DIS	
La		U-DIS		L*Fe2+		Pb 210	
Mg	2.5	V	-0.001	Br		Po 210	
Mn	1.9	W		Cl		TH_230	
Mo	0.001	Y		F		HARDN	

F*: Field measurements, L*: Lab measurements, 1: Loss On Ignition, 2: Alkalinity, 3: Total Suspended Solids
The unit depends of the sample type

1.2. Titrino Database (File: SBTOTAL.MDB)

This database summarizes the titrations curves, obtained as a result of the determination of alkalinites or the acidity values. This defines the buffering capacity of the water between the pH value of 8.3 and 4.5. These values in themselves do not provide as much information as the shape of the curve which indicates the contribution of the metals to the buffer capacity. So the database **SBTOTAL.MDB** therefore also contains the file **SBTITMAIN** and **SBTITRATION**. As of May, 2003, this database contained 6269 entries.

The Table **SBTITMAIN** is similar to the Table **SAMPALL**. It contains all the information about the sample as well as general information about titration of the sample like initial pH and the value of acidity/alkalinity. The table **SBTITRATION** contains all

the related titration curves. These two tables are linked through the unique identification code assigned to each sample at the beginning of the titration process. The number of entries in **SBTITRATION** is greater than in **SAMPALL/CHEMALL**, as we used the titration curve to assess potential changes in the water characteristics, some of which were induced by the restoration efforts made on the site. If no changes were noted in the curve between sampling intervals, the sample was not submitted to the analytical laboratory, a cost-saving measure that allowed obtaining monitoring data but eliminated the need to analyze about 2000 samples.

1.2.1 Titrations as a monitoring tool – a program in development

The potential of the titration curve, to interpret large data sets on a statistical and mathematical level, and as a practical monitoring tool was initially explored by an undergraduate student at the University of Waterloo under the supervision of Dr. Alan Werker. The work was completed with the conclusion, that the methodological approach was valid (Appendix 2). Dr. Gunther Meinrath, at the Technical University, Bergakademie in Freiberg, Germany is presently refining the monitoring tool.

The reclamation effort at the SBWMA requires such a tool. The reclamation strategy for the site relied upon such natural water-cleansing processes as the precipitation of dissolved metals and their adsorption onto the surfaces of particulates, bacteria and algae. Unlike the abrupt precipitation of dissolved metals, induced by the addition of neutralizing agents, these processes are gradual but continuous and, in fact, continue to affect the quality of water samples after they are collected. The oxidation of iron, in particular, can transform the chemical characteristics of mine waste water, usually quite rapidly.

Dr. Meinrath has proposed that an ongoing, electronic record of titration curves, compiled on-site by the Beckman Auto-titrator, would serve the purpose. The comparison of current and past curves would provide an almost immediate indication of changes in the concentration of dissolved metals. And do so very economically. A computer program is currently being developed that should yield estimates of actual concentrations

based on the titration curve. Appendix 3 presents work completed to date relating the titration curve and the metal content.

1.3. Water Level/Elevation Database (File: SBWATERLEVELS.XLS)

These Excel files contain all water levels measurements made in the field by the operator from 1986 to 2003 relative to on-site benchmarks as well as in meters above sea level. Water level monitoring focused generally on the tailings, which were monitored on 200 occasions between 1986 and June 2003. The object was to obtain an understanding of the seasonal water level fluctuations of the water table in the tailings.

The benchmarks were set by indicators on the piezometers pipes and on still wells from some adjoining water bodies. The piezometer locations were originally determined with the help of aerial survey flown for the site from which a topographical contour map was derived. The photos are provided in the map database. When additional piezometers were installed, the site was resurveyed and the elevations connected. One survey was carried out with a Total Station and finally a last survey with a GPS unit.

This database also contains details about the installation of the piezometers such as the elevation of the screen, and the tip. The file **SBSTRATIGRAPHY.XLS** contains the stratigraphy of South Bay piezometers. Details on the installation are found in the respective reports in the report database.

1.4. Flows Database (File:SBFLOWS.XLS)

The Excel file **SBFLOWS.XLS** contains measured flows (converted to L/sec) collected at locations relevant to contaminant loadings, mainly the Mine Site and Mud Lake. It covers a period of 1992 to 2003. A reasonable set of field measurements was obtained, which was verified through drainage basin run-off estimates.

1.5. Weather Database (File: SBWEATHER.XLS)

This Excel file contains daily weather records for the years 1990 to 2002. The database was established a year after the installation of the first round of piezometers in the tailings area and the mine site. The file contains the data reported for weather stations in

Ear Falls, from 1990 to 1996, Red Lake from 1997 to 2000 and from both stations in 2001 and 2002. The daily record contains:

- Maximum temperature
- Minimum temperature
- Total rainfall
- Total snowfall
- Total precipitation

1.6. Maps Database

The changing topography of the SBWMA and the shifting emphasis of the treatment scenario created a need for a variety of data gathering techniques at a variety of locations; construction activities literally eliminated the locations of some monitoring stations and created the need for new monitors elsewhere. The regulatory monitoring stations associated with the SBWMA are linked electronically to the database. However many locations will be linked at a later stage in the project. These locations can be identified in the interim in the Map Database.

1.7. Field Books Database (File: SBTOTAL.MDB)

This Excel spreadsheet in the Access database **SBTOTAL.MDB** is a directory of field books, referencing the field trips and the data which have been collected. These are stored for inspection at the Boojum Research facility.

1.8. Lab Records:

Laboratory books, covering the complete span of the project, contain all measurements of SBWMA samples and the results of related experiments. Samples were recorded on arrival in the Boojum laboratory in the titration book, while samples shipped out for analysis were assigned an Assayer number. The books are available for inspection at Boojum Research Limited.

1.9. Photo/Slides Records

The photographs are all available electronically, sorted by year and labeled. They are accessible through a simple viewing program, where a brief history for the year can be

inspected, to obtain an easy reference to the activities of the year. The photos can be accessed through a small Visual Basic program by the year which allows fast access to the photos. The database contains more than 1300 photographs.

1.10 Reports Database

All draft, final reports, progress reports, relevant memos, data sets, relevant correspondence, field reports, and task lists are accessible in pdf format through an Access window. The report is searchable using Acrobat. The Report database contains about 110 reports, memos etc. The publications on South Bay or about research related to the processes applied there are not included in this report database, but are available at Boojum Research Ltd.

Boojum Research Total Database 2.0

User's Manual

July 17 2003

TABLE OF CONTENTS

1.0 OVERVIEW	- 1 -
2.0 STARTUP MENU CHOICES	- 1 -
2.1 SAMPALL MENU CHOICES	- 1 -
2.1.1 Select What You Want Here	- 1 -
2.1.2 Form 1: Screen 2. Select Data.....	- 2 -
2.1.3 Select by Assayer Number	- 2 -
2.1.4 Select from Map.....	- 2 -
2.1.5 Search by Location.....	- 3 -
2.2 PROGRAM REQUIREMENTS	- 4 -
2.3 TROUBLE SHOOTING PROGRAM ERRORS	- 5 -

TO BE CONTINUED

1.0 OVERVIEW

The Access program Total.mdb contains two main sections, Sampall/Chemall and Titration. They are displayed on the first menu after the welcome window.



Figure 1: Opening statement

The Sampall/Chemall side of the program consists of two tables, which contain Sample Descriptive Information and analysis information respectively. The titration section, a third database also has two main tables, Titration's and titration sample descriptions. Currently there are over 6,200 titration's in the database.

The program consists of a number of windows with clickable buttons to access the various functions.

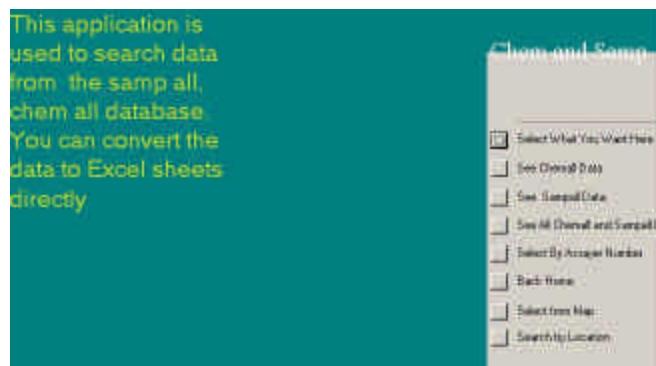


Figure 2: Search Options

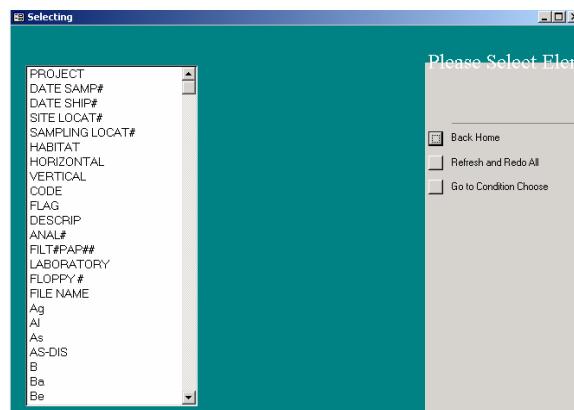
2.0 STARTUP MENU CHOICES

The Startup form presents two choices: SAMPALL and TITRATION to select from.

2.1 SAMPALL MENU CHOICES

2.1.1 Select What You Want Here

The first screen of this form presents the field list from the Sampall, Chemall tables. It allows selection of the required fields for the query being made. Clicking on the field toggles between selected (black) and unselected (white).



2.1.2 Form: 1 Screen: 2 Select Data

This Screen allows the user to select the selection criteria for the query being created. The combo box in the upper centre of the form allows the user to select which field the section criteria is to be taken from.

Multiple selections are allowed (e.g. 1992, 1997, 1999) click on the desired data in the left hand list box, deselect by

clicking again.

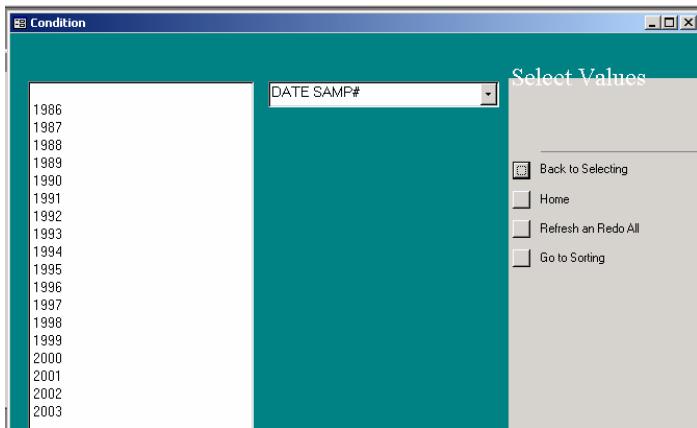
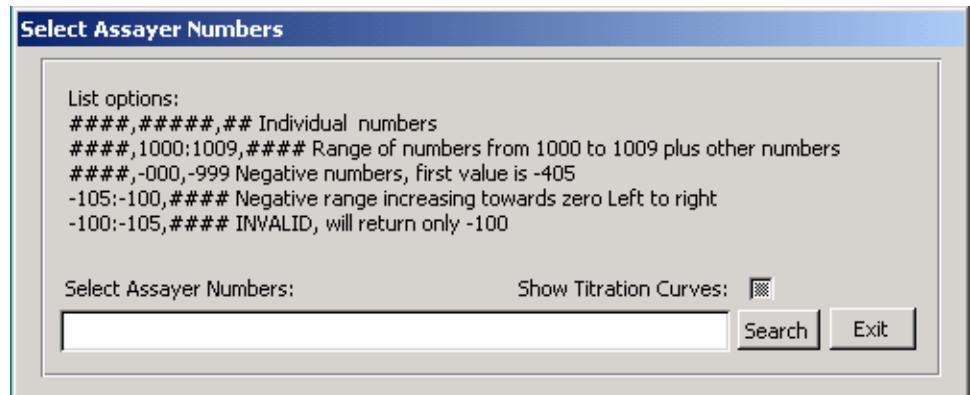


Figure 2.2: Select Data

2.1.3 Select by Assayer Number

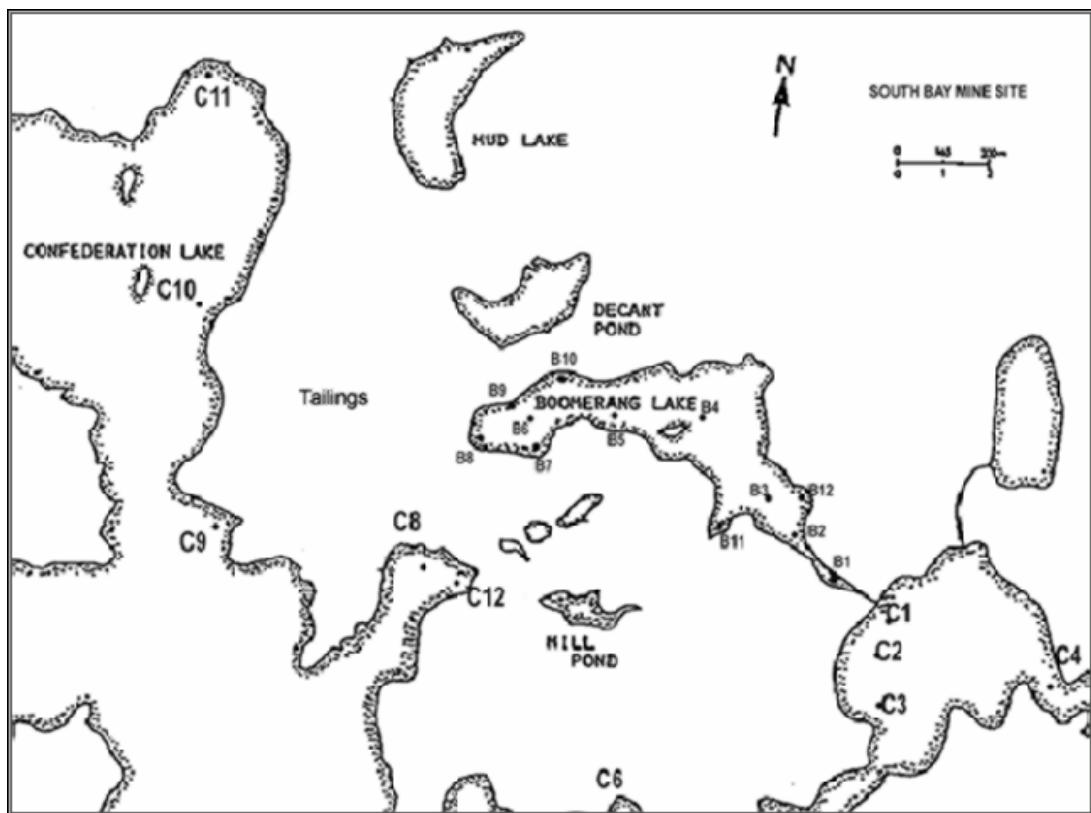
Select Assayer form allows input of the assayer numbers from the printed records, or drawn from the database through queries. The main function is to output them to Excel in an easy to use standard form



(ICP or individually selected elements) for research and report creation.

2.1.4 Select from Map

This map is an example of what is possible in the database, other maps can easily be added and the sampling points can be used to return data from different sources, i.e. from the sampall/chemall or the titration description or curves. The map currently brings up the sampling location (eg. C1, B1, C10...) information based on the titration description table, or from the site locations from the same table (Mill Pond, Boomerang Lake ...)



2.1.5 Search by Location

The Search by location form provides access to samples based on the Sampling location, refined by Project and/or Site. After choosing the sampling location, the database is searched, after a few moments (depending on the speed of your machine) the Date From and Date To boxes are filled with the date of the first and last sample in the entire dataset along with the total number of samples. (Total Returned) If more than 50 samples are returned in this dataset, the dataset should be refined by changing the date field(s).

SampChem Search Form

Project:	<input type="button" value="Refine By Project"/>	Site:	<input type="button" value="Refine By Site"/>	Sampling Location:
<input type="button" value=""/>		<input type="button" value=""/>		
Date From:	Date To:	Total Returned: 5	<input type="button" value="Get Date Range"/>	<input type="button" value="Export To Excel"/>
<input type="button" value=""/>		<input type="button" value=""/>	<input type="button" value=""/>	<input type="button" value="Home"/>

To change the date field's click inside the date box and enter a date in the format day-month-year where Month is three character alpha and the Year is a full 4 digits. E.g. 28-Feb-1997. Change the year and press enter to accept the date change. After you press enter the program will update the dataset and find the sample with the closest date after the changed date and will return a new total number of samples (Total Returned)

2.2 PROGRAM REQUIREMENTS

Hardware

IBM COMPATIBLE Pentium 233 or better, SVGA Colour monitor (800x600 or better)

Memory: 64mb (Windows 98) 128mb (Windows 2000,XP), Hard Drive Space (100 mb)

Software

Windows 98, 2000 or XP

Microsoft Office 2000 Professional or Microsoft XP Professional or standalone Excel and Access

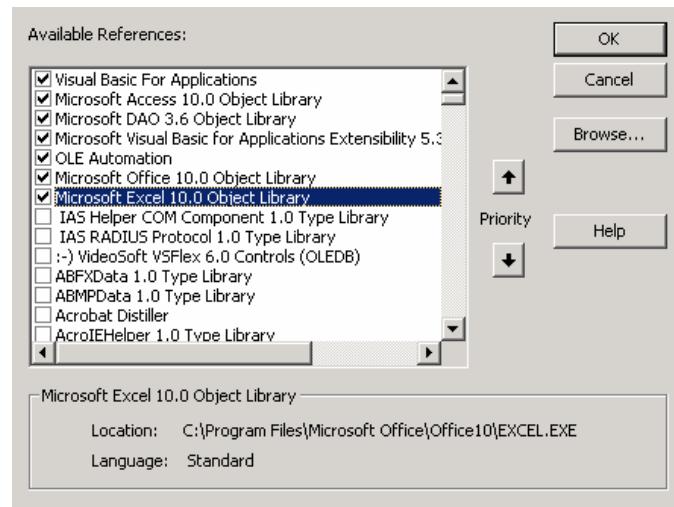
2.3 TROUBLE SHOOTING ERRORS

MISSING REFERENCE

The number one problem with Access is its dependency on the Microsoft Office Suite Libraries. If the program breaks and you are stranded in the Visual basic debugger with an error like:

```
MsgBox      (str(Err.Number)) +  
Err.Description + Err.HelpFile)
```

The most likely problem is that you have a different version of Office installed on your computer. To cure this problem, stop the debugger press on the square icon (looks like stop on a tape player) then click on



the menu item: *Tools: References*

One of the checked References will be notated as: *MISSING*.

uncheck the reference and scroll down through the list to find:

Microsoft Excel (9.0 or 10.0 depending on which version of Access the program was last compiled in) Object Library or Graph Library. Please note that ALL of the references shown in the box above must be checked with the Access and Excel references either version 9 or 10.

NO SEARCH RESULTS

The program has a problem when a search returns no results, the cache is not cleared and each new search will return no results. To solve this problem close the form and this automatically clears the cash.

No data in Table

The program does not check for empty data records at the time of plotting (performance issue), if the curve is missing the program will produce an error and drop into the debugger. Please note the curve id (in the excel sheet) and report it to boojum for repair.

TO BE COMPLETED.....

Further Development of A Titrino Approach of Model Detection Based on Buffer Intensity: Metal Mixtures

Alan Gideon Werker

June 20, 2002

Margarete Kalin, Principal
Boojum Technologies Limited
468 Queen Street East
LL2 Box 19
Toronto, Ontario
M5A 1T7

re: Further Titrimetric Analysis and Report

Dear Margarete,

as promised I have worked to advance the interpretation and the method of applying alkalimetric titration for the determination of metals in AMD samples. Please find enclosed my report which represents a more in depth and further analysis of the data that was collected as part of Viktors Kulneiks work term placement.

The results of this further development are encouraging and I look forward to discussing the work with you further. The report and supporting analysis represent 5 days of my time at \$600 CDN/day. I would be grateful if you could please arrange remuneration for this service by cheque mailed to my address at the University of Waterloo.

In the meanwhile, I am looking forward to seeing you when I am back in Canada. I wish you all the best for your Boojum midsummer celebrations tomorrow. I am sorry not to be able to join in with the festivities this year.

Sincerely,



Further Development of a Titrimetric Approach of Metal Detection

Based on Buffer Intensity: Metal Mixtures

Alan Gideon Werker, Ph.D. P.Eng.

*Assistant Professor, Department of Civil Engineering
University of Waterloo, Waterloo Ontario Canada, N2L 3G1
agwerker@uwaterloo.ca*

Abstract

From a preliminary investigation to determine an analytical approach to quantify metal concentrations by alkalimetric titration it was found that buffer intensity could be used for individual metals in solution. However, mixtures of metals are to be expected in samples of acid mine drainage (AMD). In addition other compounds in the water of AMD samples could further complicate the matrix and a titrimetric approach of metal analysis. Therefore, as a second and necessary step to further develop a titrimetric approach for metal analysis of AMD samples, mixtures of metals (iron, zinc, and aluminum) in acidified distilled water were considered. In this second investigation it was of interest to determine if the titration, of individual metals in solution, was influenced by the presence of other metals. In addition, the potential for titrimetric determination of the balance of ferric and ferrous iron in solution was considered. The data acquired for the present investigation suggested that the metals do not seem to interact significantly during titration. Therefore, metal quantification from buffer intensity can be performed from direct correlation to standards of individual metals. The results of determining the balance of ferric and ferrous iron were also promising. The precision of the titrimetric method that was applied could stand to be improved if a more accurate determination of metal concentration is necessary. One strategy to improve upon the current methodology would be to incorporate an internal standard into the samples before titration.

Introduction

The most promising route for the development of a method of metal analysis by titration with a strong base such as sodium hydroxide seems to be to correlate buffer intensity to corresponding metal concentrations (Werker, 2000). Buffer intensity refers to the molar amount of base required to increase the pH of an aqueous solution by one unit per litre of sample. The buffer intensity (β) at a given pH during titration is estimated from the slope on a titration curve:

$$\beta = \frac{dC_b}{dpH} \quad (1)$$

where C_b is the moles of titrant added per litre sample. The buffer intensity as a function of pH can be derived from alkalimetric titration data for water samples that have been acidified with a strong acid such as sulphuric acid *a priori*.

Sample acidification is required to dissolve the metal content such that all metal ions interact with the titrant. The dissolved metal content of an aqueous sample can be determined by filtration prior to acidification as outlined in Standard Methods. Sample acidification will not be the same as acid digestion and will therefore only release the metals in the sample that can be readily brought into solution at low pH. The objective of acidification is to dissolve but still preserve the metal oxidation state so that the amount of a metal and its valence can be determined

simultaneously. The form a the metal can be especially important towards understanding the biogeochemical processes at play at the location and time of sampling.

Points of elevated buffer intensity at a given pH during titration may relate to the concentrations of individual or combinations of metals in solution. Increases in buffer intensity will also be related to other weak acids in solution such as ions of the carbonate system. Therefore, the information of buffer intensity should also be complimented by other standard water quality analyses to compensate for interfering organic or inorganic compounds. Sample acidification could also be used a means of removing inorganic carbon while dissolving the metals present.

Solutions of pure metal ions have been shown to exhibit characteristic β -functions (Werker, 2000) that should be related to the sequestration of hydroxide ions due to ligand formation, complexation, and precipitation of individual metals during titration. The sample acidity will also correlate to the total metal content in acid mine drainage (AMD). However, it is of interest to identify which metal species most dominant the AMD when working to evaluate remediation of AMD sites.

While buffer intensity correlates directly to metal concentration in standard solutions of individual metals, the potential for complexity in ligand formation, complexation, and precipitation within AMD samples containing a suite of metals could significantly limit a titrimetric approach to metal identification and quantification. Since this complexity should also be present within standard solutions of metal mixtures, the objective of the present investigation was to establish the extent to which buffer intensity correlates to individual metal species within aqueous metal mixtures. The investigation was a necessary step towards the development of buffer intensity as an economical and simple metric for metals in AMD samples.

The titrimetric method of metal mixture quantification was evaluated within an otherwise ideal aqueous matrix. It was of interest to determine (1) if mixtures of metals reacted independently in solution during titration and (2) if the titrimetric approach could be helpful towards resolving the distribution of iron species in solution.

Methods and Materials

One litre stock solutions (1000 mg/l) of ferric iron and ferrous iron, zinc and aluminum were prepared by weighing the necessary mass of the metal salts (FeCl_3 , FeSO_4 , ZnSO_4 , and $\text{Al}_2(\text{SO}_4)_3$). Each metal stock solution pH was adjusted to 2 (as measured using a Corning 315 pH/ion pH electrode) by additions of 0.1 N sulphuric acid. Solutions containing FeSO_4 were stored in the refrigerator to prevent oxidation, although a low pH will also reduce the oxidation rate as well. Combinations of the stock solutions were prepared in 50 or 100 mL volumetric flasks, based on 5 or 10 mL stock solution aliquots, sealed with paraffin paper, and thoroughly mixed. The conductivity (Orion conductivity/temperature meter), redox potential (Corning M103), temperature (Orion), pH of each sample were measured and duplicate samples were taken, and acidified with 36N sulphuric acid pending ICP analysis. ICP quantification of the metal mixtures was performed at the University of Waterloo on a Spectroflame Modula FSM-08 (Spectro Analytical Instruments - Sequential Optical Emission Spectrometer UV monochromator 160-480nm with a standard sample introduction system).

Samples (5mL aliquots) of the as prepared metal mixtures were used for titration with the 702 SM Metrohm Titrino automatic titrating device. Since conductivity is related to the amount of dissolved metal, conductivity can be used to select the most appropriate normality of titrant to

be applied. Typically, for conductivities between 6000 and 12000 $\mu\text{S}/\text{cm}$, 0.1N NaOH is used. For conductivities less than 6000 $\mu\text{S}/\text{cm}$, a reduced titrant normality (0.01N NaOH) is more appropriate. The titrant addition rate needed to be adjusted so that the Titrino acquired a maximum number of pH levels during the automatic titration. However, the program that exports the Titrino measurement data files is restricted to a maximum of 201 measured pH values.

In the present investigation, for conductivities above 6000 $\mu\text{S}/\text{cm}$ a 0.1 N NaOH titrant was used with a titrant dosing volume of 0.05 mL. For conductivities below 6000, a 0.02 N NaOH titrant was used with the same dosing volume. This rule of thumb appeared to allow for an adequate number points to be generated to provide for a well-defined titration curve within the restrictions of the data acquisition software.

Assessment of the β -function requires that the slope of the titration curve be evaluated. The expectation is that the titration curve is a smooth continuous function. A number of approaches to estimate the slope from the data series were explored. Ultimately, the titration data were reduced for the present investigation by numerical differentiation, applying a Savitzky-Golay type sliding polynomial function to obtain the least-squares estimate of the first derivative of the discretised pH versus C_b curves. The sliding polynomial was used to estimate buffering intensity from pH 2 to 10 with a 0.1 pH interval.

Results and Discussion

The set of metal mixtures that were prepared for the present investigation are reported in Table 1. Each sample was analyzed by ICP and the corresponding resultant *as measured* metal concentrations in solution are also given. Various combinations of the 4 metals were chosen to cover a range of total metal concentrations from zero to approximately 1500 mg/L. Individual metal concentrations The resultant zinc and aluminum concentrations tended to be greater (12 and 18 percent respectively) than expected while the iron concentrations were consistently lower than *as prepared*. The lower than prepared total iron concentrations appeared to have been due to significantly less ferric iron in solution than prepared. Ferric iron is quite hygroscopic and so the estimated 21 percent less than expected ferric iron for the set of mixtures is not unusual. The resultant ferrous iron was estimated to lie within 4 percent of the prepared concentrations.

For each titration (Figure 1) a 9 point, third order Savitzky-Golay type sliding polynomial was used to estimate the slope of the titration curve and the β -function (Figure 2) was generated. The β -functions were evaluated at pH levels from 2 to 10 with a 0.1 interval by interpolation as part of the Savitzky-Golay analytical approach. The data were aligned in this manner in order to be able to compare the buffer intensity data for all the mixtures. During the analysis it was considered that it would be desirable to somehow internally reference each titration. Some variability in the titration data were expected due to differing titrant concentrations. As a first approach for an internal reference it was assumed that the buffer intensity in the neighbourhood of pH 2 would be due only to sulphuric acid neutralization. Therefore, the buffer intensity at pH 2.1 was selected as an internal reference to normalize each β -function (Figure 2).

A crude estimation of the direct correlation between the normalized buffer intensity and each individual metal concentration was made (Figure 3). From these calculations it was apparent that zinc, ferrous iron and ferric iron exhibit similar response factors while aluminum exerted a much more pronounced influence on buffer intensity. Each metal in the mixtures seemed to influence the buffer intensity in distinct ranges of pH as previously observed for pure metal solu-

tions. Therefore, the respective as measured metal concentrations were correlated to buffer intensity in their corresponding region of greatest response as follows: Iron ($\beta_{2.7}$ and $\beta_{7.5}$), Zinc ($\beta_{6.5}$), and aluminum ($\beta_{4.2}$). The correlation with total iron was distinct in that iron was present in two oxidation states and it was the only metal that exhibited a strong quadratic correlation. Therefore the most general representation of the equation used to relate buffer intensity to metal concentration by regression analysis was as follows:

$$M^{+n} = A_0 + A_1 \beta_A + A_2 \beta_A^2 + B_1 \beta_B + B_2 \beta_B^2 \quad (2)$$

Table 1. As prepared versus as measured (ICP) metal concentrations.

Sample	Prepared Sample (mg/L)					ICP Measurements (mg/L)		
	Fe ⁺²	Fe ⁺³	Fe (Total)	Zn ⁺²	Al ⁺³	Fe (Total)	Zn ⁺²	Al ⁺³
1	0	0	0	0	0	0	0	1
2	0	1,000	1,000	0	0	790	-1	4
3	0	800	800	0	0	629	-2	4
4	0	600	600	0	0	473	-2	4
5	0	400	400	0	0	315	-2	4
6	0	200	200	0	0	165	0	1
7	0	0	0	1,000	0	-1	1,138	4
8	0	0	0	800	0	-1	901	4
9	0	0	0	600	0	-1	670	4
10	0	0	0	400	0	-1	459	4
11	0	0	0	200	0	0	233	1
12	1,000	0	1,000	0	0	977	-2	5
13	800	0	800	0	0	775	-2	4
14	600	0	600	0	0	580	-2	4
15	400	0	400	0	0	373	-2	4
16	200	0	200	0	0	202	0	1
17	0	800	800	200	0	626	222	4
18	100	800	900	100	0	739	113	4
19	200	800	1,000	0	0	828	-1	4
20	0	200	200	800	0	149	934	4
21	200	0	200	800	0	183	893	4
22	100	100	200	800	0	168	899	4
23	800	200	1,000	0	0	956	-1	4
24	800	100	900	100	0	857	109	4
25	0	400	400	100	0	308	110	4
26	50	400	450	50	0	357	54	4
27	100	400	500	0	0	410	-1	4
28	0	100	100	400	0	76	447	4
29	100	0	100	400	0	93	444	4
30	50	50	100	400	0	85	453	4
31	400	100	500	0	0	462	-1	4
32	400	50	450	50	0	426	54	4
33	400	0	400	100	0	393	109	4
34	0	300	300	200	0	234	221	4
35	100	300	400	100	0	328	107	4
36	200	300	500	0	0	427	-1	4
37	0	200	200	300	0	153	336	4
38	100	100	200	300	0	171	337	4
39	200	0	200	300	0	191	333	4
40	300	200	500	0	0	452	-1	5
41	300	100	400	100	0	375	110	4
42	300	0	300	200	0	291	225	4
43	200	0	200	400	400	190	444	475
44	400	0	400	200	400	384	215	476
45	400	0	400	400	200	388	442	233
46	100	0	100	200	200	95	222	231
47	200	0	200	100	200	191	111	234
48	200	0	200	200	100	192	219	117

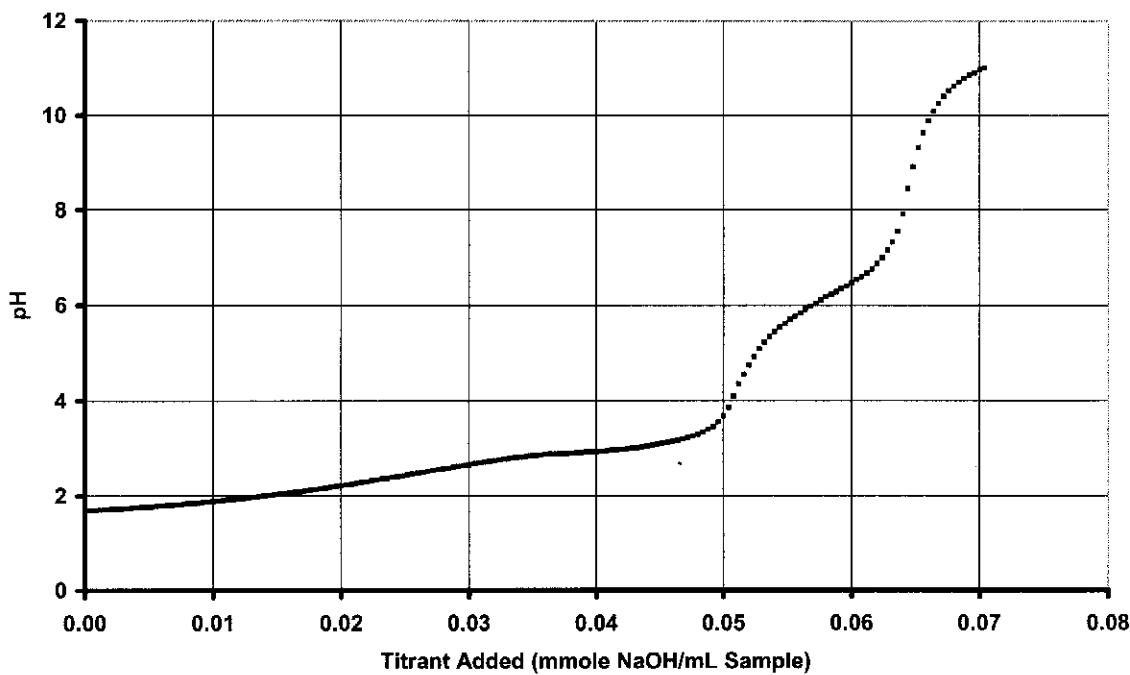


Figure 1. Typical example of the titration curve from one of the model mixtures of metals in solution (800 mg/L ferric iron and 200 mg/L zinc as prepared).

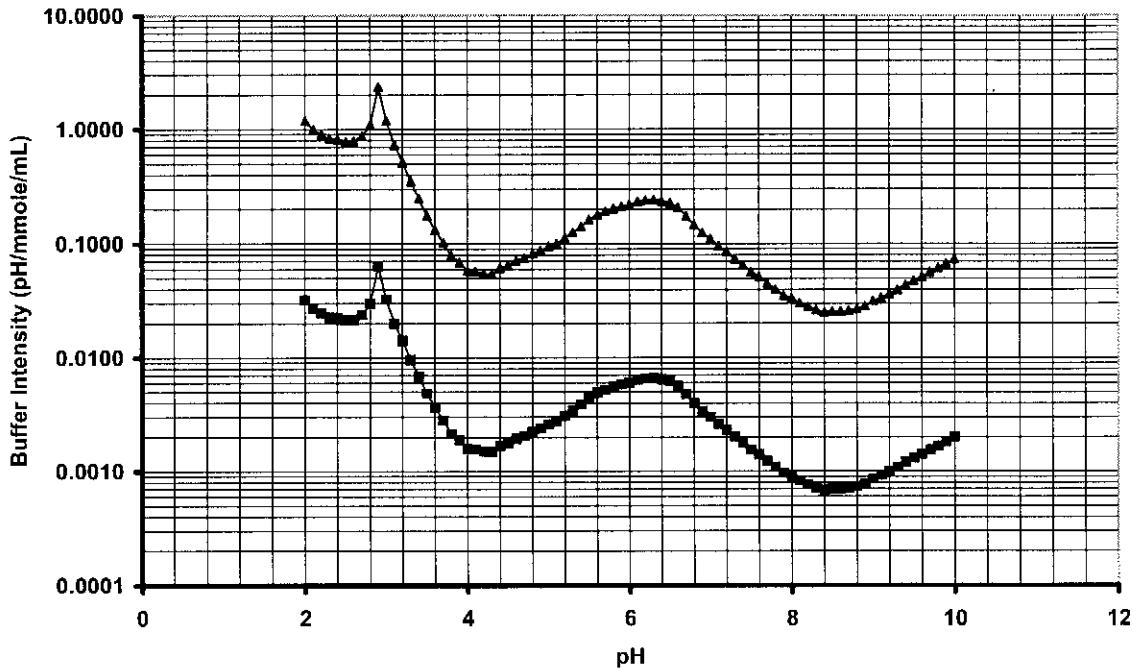


Figure 2. The resultant β -function from the data presented in Figure 1 (■). The β -functions were normalized to the buffer intensity at pH 2.1 (▲).

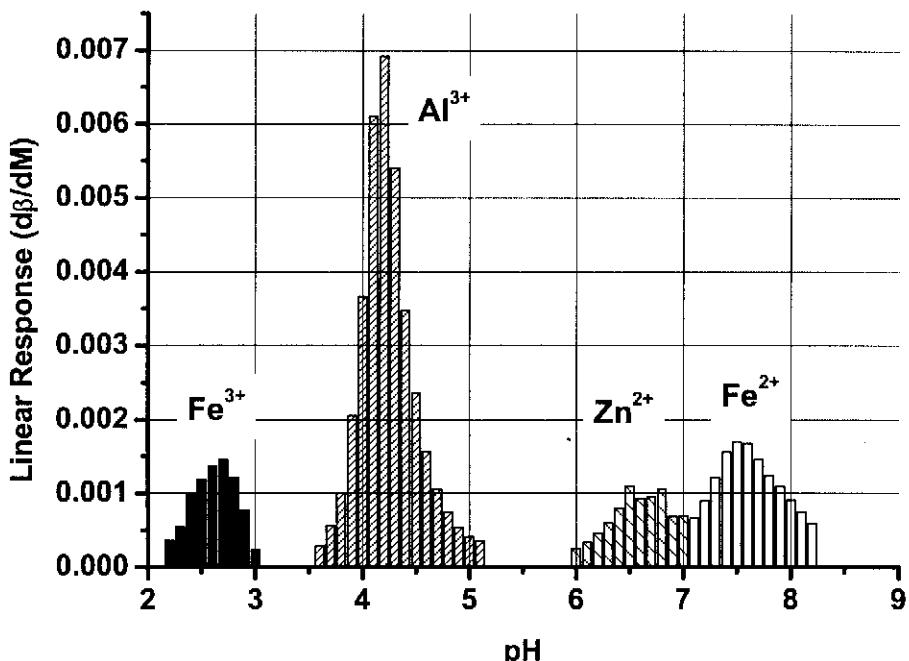


Figure 3. The approximate linear response for the metals considered for the purposes of the present investigation. The titrimetric method was most sensitive to aluminum. The other metals exhibited similar response factors.

Table 2. The results of linear regression for the 4 metals at their respective pH levels of elevated response in terms of buffer intensity.

M ⁺ⁿ	pH _A	pH _B	r ²	A ₀	A ₁	A ₂	B ₁	B ₂
Fe ⁺³ +Fe ⁺²	2.7	7.5	0.84	-289 ± 104	1091 ± 313	-212 ± 212	778 ± 219	-83 ± 179
Al ⁺³	4.2		0.98	0 ± 3	145 ± 3			
Zn ⁺²	6.5		0.89	-88 ± 22	1011 ± 53			

where M⁺ⁿ is the metal concentration, β_A and β_B are the buffer intensities at pH levels A and pH B. {A₀, A₁, A₂} and {B₁, B₂} are the constants of the correlation from regression analysis. The results of the regression analysis are summarized in Table 2. Scatter plots (Figures 4 to 6) of the total iron, aluminum and zinc ICP measured versus buffer intensity model concentrations help to indicate the ability of the titrimetric method to resolve the amounts of the respective metal ions in solution.

The scatter plots suggest a significant variability. However, there did not seem to be any strong evidence that this observed variability was due to the presence of other metal ions in solution. Therefore, it seems that the individual metal concentrations can be resolved from changes in their corresponding buffer intensities but the current methods do not yield great precision.

It was not surprising that the best correlation was found with aluminum which also exhibited the greatest response factor (Figure 3). This outcome suggests that the best way to improve the current level of precision with the other metals with lower relative response factors would be to work to either better standardize the titration methods or to spike the samples with an internal

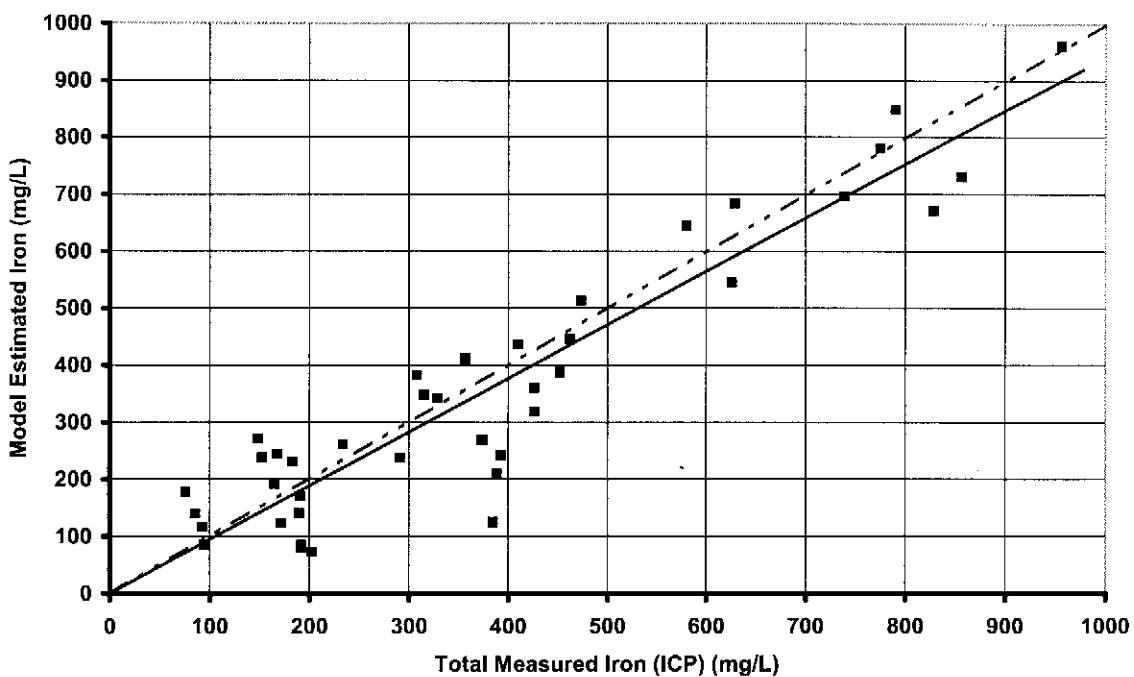


Figure 4. The outcome of the correlation between measured (ICP) and buffer intensity for total iron in metal mixtures containing iron, zinc, and aluminum.

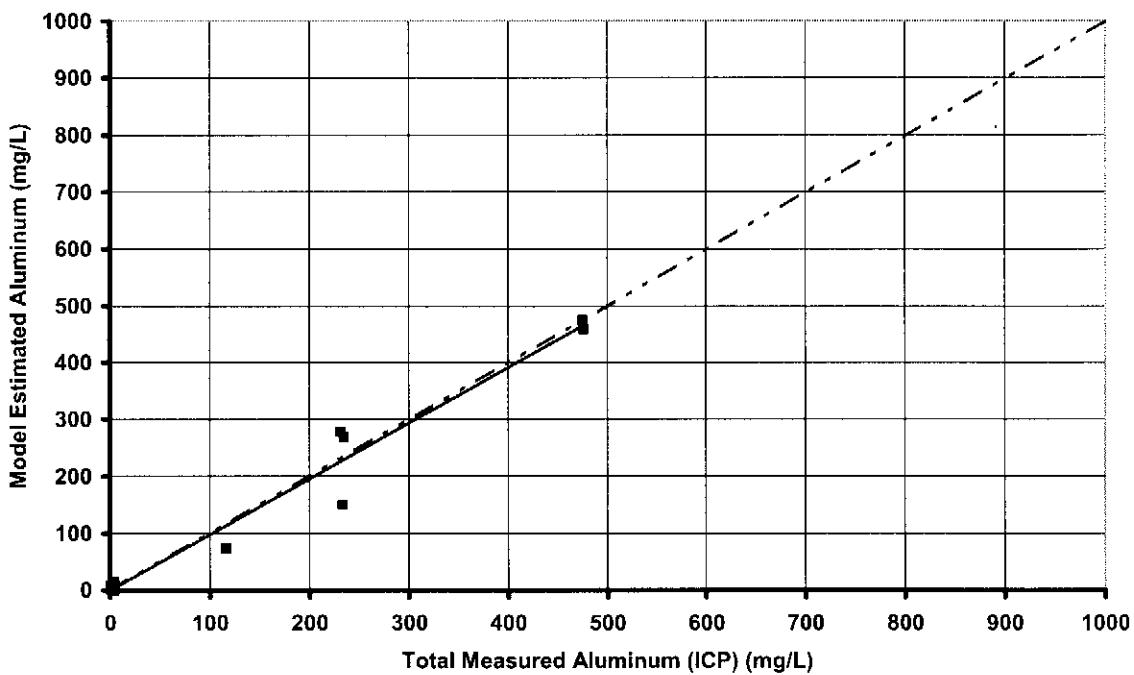


Figure 5. The outcome of the correlation between measured (ICP) and buffer intensity for aluminum in metal mixtures containing iron, zinc, and aluminum.

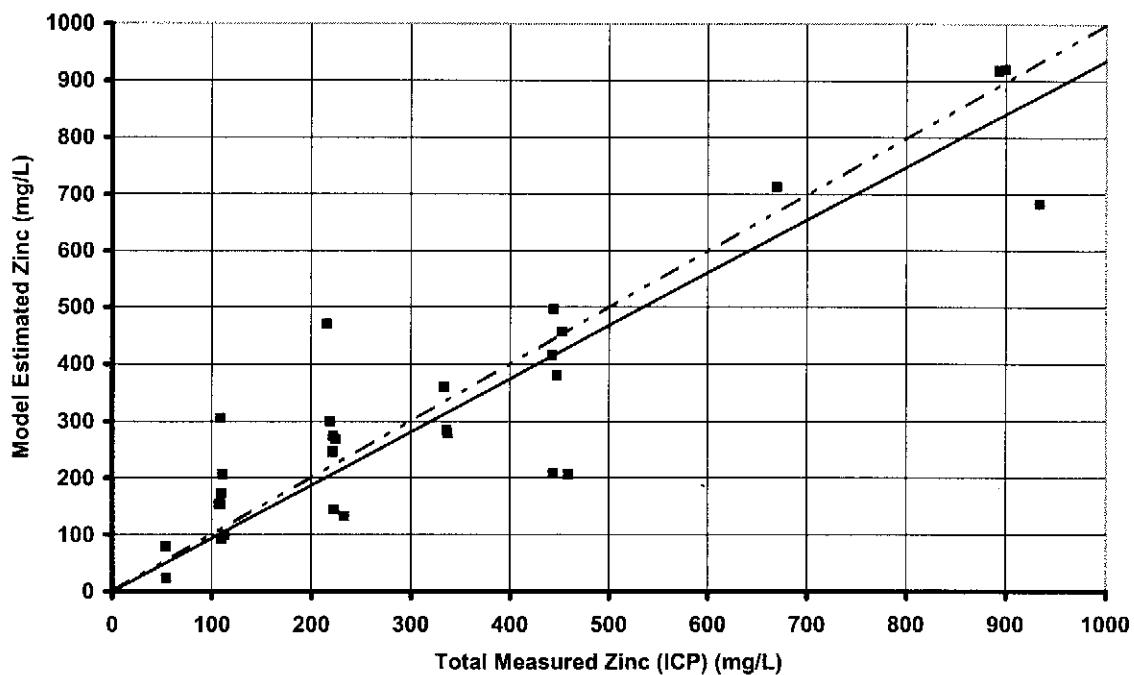


Figure 6. The outcome of the correlation between measured (ICP) and buffer intensity for total iron in metal mixtures containing iron, zinc, and aluminum.

standard. Ways to standardize the titration methods would help by reducing the sample to sample variability in the resolved buffer intensity at the respective pH levels. If ways to achieve such standardization are not possible or practical then an internal standard would provide a buffer intensity at a non-interfering pH level to reference the β -function from one sample to the next. If it is not possible to find a suitable metal or other cation for use as an internal standard, then applying the method of standard additions with the metal of interest could be a means to internally reference the titrations for improved sample to sample precision.

It was of further interest to recognize that while total iron was derived for the purpose of comparing ICP to titrimetric quantification, the titrimetric method enabled the further resolution of ferric and ferrous iron in solution. Accounting for the systematic differences between the *as prepared* and *as (ICP) measured* concentrations of iron in solution (Table 1), it was possible to estimate the balance of ferric and ferrous iron in all of the prepared mixtures. The concentrations of ferric and ferrous iron were then also estimated from the buffer intensities at pH 2.7 and 7.5 respectively assuming a linearly additive response:

$$Fe^{+3} = A_0 + A_1 \beta_{2.7} + A_2 \beta_{2.7}^2 \quad (3)$$

$$Fe^{+2} = B_1 \beta_{7.5} + B_2 \beta_{7.5}^2 \quad (4)$$

Figures 7 and 8 relate the reasonably good fit of the titrimetric determination of iron to the concentrations derived with knowledge of the ICP data and the *as prepared* amounts. Therefore, the

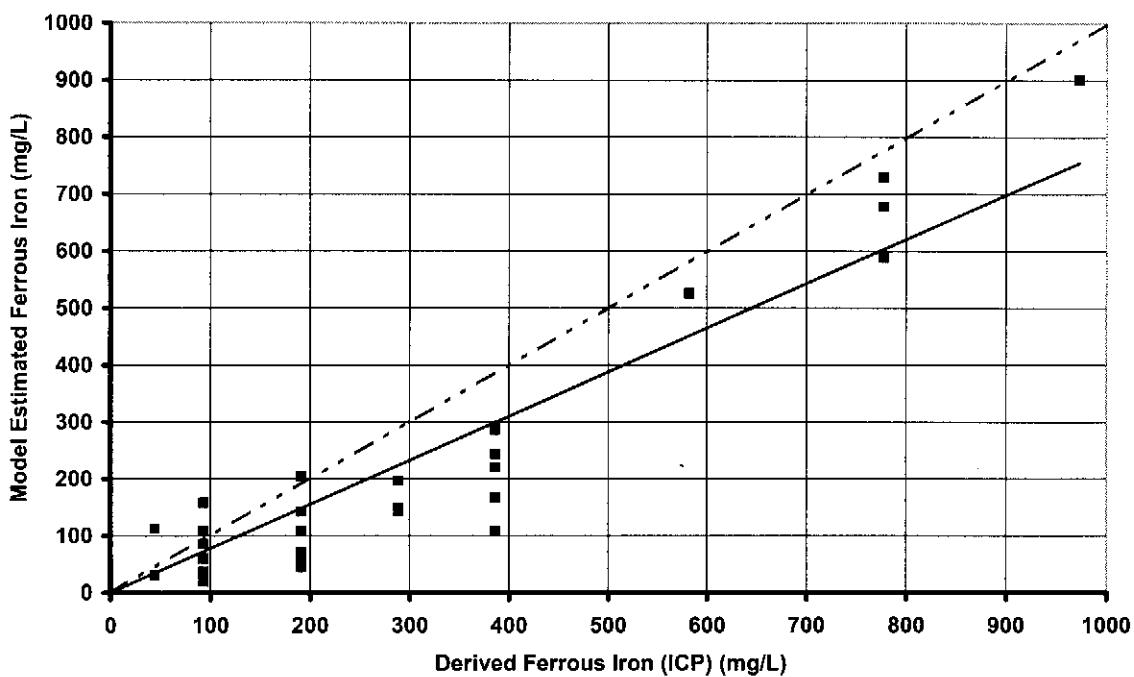


Figure 7. The outcome of the correlation between measured (ICP) and buffer intensity for ferrous iron in metal mixtures containing iron, zinc, and aluminum.

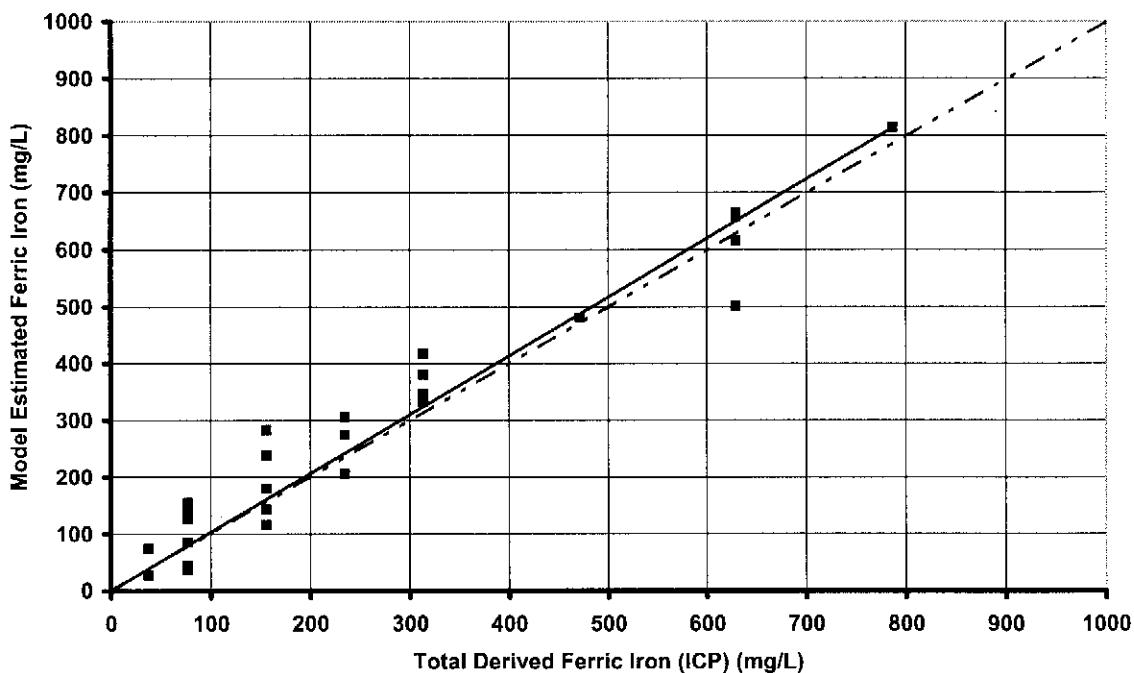


Figure 8. The outcome of the correlation between measured (ICP) and buffer intensity for ferric iron in metal mixtures containing iron, zinc, and aluminum.

titrimetric approach does provide a rather simple but powerful technique to resolve the oxidation state of iron in solution. Knowledge of the oxidation state of iron from field samples could be most informative when considering the nature of the biogeochemical conditions and processes in the field when looking to monitor and control acid mine drainage.

Conclusions

The present investigation has served to indicate that in laboratory samples mixtures of metals (iron, zinc and aluminum) appear to interact independently with hydroxide ions during alkali-metric titration from pH levels of less than 2. Quantification of the individual metal concentrations was possible. In addition, the titrimetric approach can be used to consider the redox state of iron, or mixtures of ferric and ferrous iron in solution.

The precision of the titrimetric method for metal quantification could be improved and it is recommended to either consider ways to better standardize the actual titration or to introduce an internal reference (standard) into the samples.

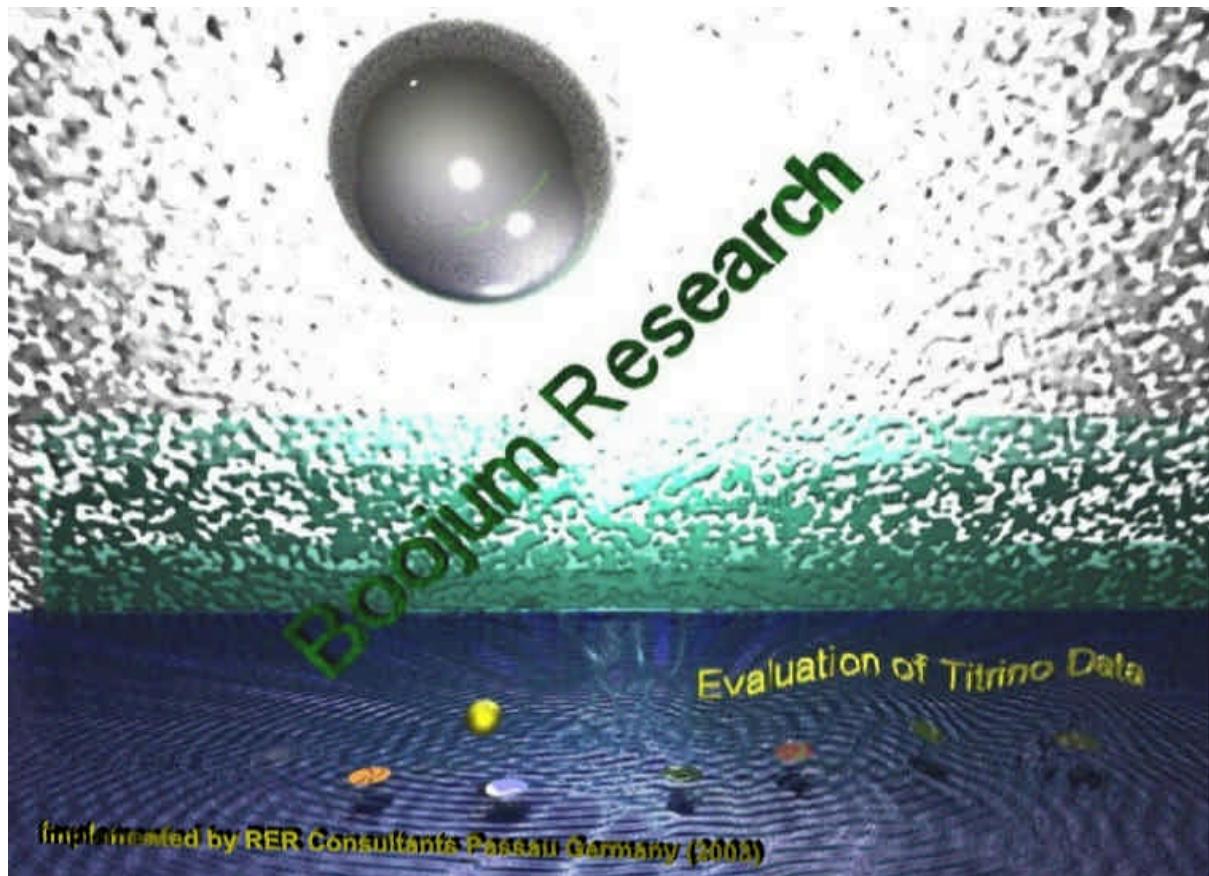
Acknowledgements

This report represents an original analysis of the data that was collected by Mr. Viktors Kulneiks who was hired by Boojum Research and sponsored by NSERC under the USRA program for the winter semester of 2001. The ICP analysis of the samples was performed by Mr. Mark Sobon as part of the project undertaken by Mr. Kulneiks. Mr. Kulneiks was jointly supervised by Margarete Kalin at Boojum and Alan Werker at the University of Waterloo.

References

Werker, A.G. (2000). Titrimetric Determination of Metal Concentrations in AMD Samples – Preliminary Consideration of Data Analysis Methods, Boojum Research Limited, Toronto, Ontario.

Manual



preliminary - preliminary - preliminary - preliminary - preliminary - preliminary

written by: G. Meinrath
Passau / Germany

last addition: October 17, 2003

Table of Contents

Table of Contents	2
Disclaimer of Warranty	2
Introduction	3
Installation	4
Program Description	4
Main window: File: Open	4
Data file conventions	7
Main window: File: Save: Titrations	8
Main window: File:Save:Concentrations	9
Main window: Process	10
Process: Graphics: View Data	11
Process: Graphics: View Standard	11
Process: Evaluate	11
Process: Simplex	14
Main window: Windows	15

Disclaimer of Warranty

Unless specified in this agreement, all express or implied conditions, representations and warranties, including any implied warranty of merchantability, fitness for a particular purpose or non-infringement are disclaimed, except to the extend that these disclaimers are held to be legally invalid.

To the extend not prohibited by the law, in no event will Boojum Research Ltd., RER Consultants or the author or the programmer of the code be liable for any lost revenue, profit or data, or for special, indirect, consequential, incidental or punitive damages, however caused regardless of the theory of liability, arising out of or related to the use of or inability to use this software, even if Boojum Research Ltd.or RER Consultants has been advised of the possibility of such damages. In no event will Boojum Research Ltd.'s or RER Consultants' liability to you, whether in contract, tort (including negligence), or otherwise exceed the amount paid by you for Software under this agreement. The foregoing limitations will apply even if the above stated warranty fails of its essential purpose. This agreement is effective until terminated. You may terminate this agreement by destroying all copies of software. This agreement will terminate immediately without notice from Boojum Research Ltd. or RER Consultants if you fail to comply with any provision of this agreement. Upon termination, you must destroy all copies of software.

All reverse engineering of the code is explicitly forbidden. All algorithms applied are published in the general literature. The implementations used in the program have been extensively tested using test cases and benchmarks from literature.

Introduction

Modern automatic titration devices allow the convenient routine determination of acid and base capacities of natural aqueous solutions. The information collected during titration is digitally stored and available for post-titration analysis. These titration files may hold information about the substances responsible for an observed acid/base capacity.

Often organic matters consume added acid/base. In the past 20 years, humic and fulvic materials have attracted much attention as natural polyelectrolytes affecting the buffer capacities of natural aqueous systems. These polyelectrolytes commonly hold several functional groups capable to act as buffering agents. Their titration curves commonly exhibit a diffuse, uncharacteristic titration curve.

However, under certain circumstances metal ions may form the overwhelming amount of buffering agents. These metal ions exhibit characteristic titration curves with interpretable steps. Especially in mine waters, where high amounts of only a few metal ions are present, the semi-quantitative evaluation of titration curves is capable to identify the metal ions.

Hence, under such circumstances automatic titration devices may be considered as a convenient and affordable tool for remote direct on-line surveillance of former mining sites or water bodies potentially threatened by effluents from mining sites. For that purpose, high analytical accuracy isn't the primary goal. A titration device can never compete in that respect with sophisticated equipment like ICP-OES or electrochemical analytical equipment. It has, however, considerable advantage over these equipment in terms of costs (investment and running costs), size and electrical energy demand. Titration devices are small and, hence, easily to hide and to transport. Electricity demand can be satisfied by solar panels. In contrast to many electrode sensors (arrays), titration equipment is also robust against adverse environmental effects like extreme pH values, high amounts of dissolved solid materials and temperatures.

A quantitative relationship exists between the amount of material in solution and the amount of titrant used to reach a certain pH value. The hydrolytic process, which involves the formation of several hydroxo complexes, takes place in a limited range of pH values. The trivalent ions, especially Fe^{3+} and Al^{3+} , precipitate at low pH values,

while certain divalent ions, Fe^{2+} and Mg^{2+} , precipitate at near-neutral pH. The majority of divalent ions, especially Mn^{2+} and Zn^{2+} , precipitate at high values above pH 9. The algorithms implemented in this computer code are able to normalise and adapt a large number of a large number of titration curves curve, to analyse these curves simultaneously, to estimate the amount of certain metal ions, to provide a numerical estimate of reliability of the evaluation as well as a graphical comparison of the fitted and experimental titration curves. All these procedures only take a few seconds.

Installation

The code is provided as a Visual Basic code. The installation files consist of a setup routine (Setup.exe) and the titrino.cab file which holds all necessary installation files. The Setup.lst file is required by Setup.exe.

The manual.pdf file is also part of the cab file. It is therefore automatically transferred with the executables. There is no need to copy the file from the installation CD to the hard disk.

The setup routine also installs 50 experimental titration curves. These titration curves are those originally provided by Boojum Research Ltd. as example files for the development of this code. The files are slightly renamed in order to have an easier selection of the titration data files for the input. The code in its present form is however able to load and analyse all files following the file format conventions. The file format conventions will be explained in more detail in the section "Menue: Open". The files are ASCII files consecutively giving pairs of mL and pH. The volume information and the titrand concentration must also be specified in the input files.

The Titrino program is assumed to be installed in the directory d:\Titrino. Please adapt the file names in all operations described in the following parts of the manual if the actual installation has been made in a different directory.

Program Description

Main window: 800 x 600

The program is started either by clicking the Titrino.exe in the Explorer or from the Start Menu entry created during the installation or by clicking the desk top icon (if available). The following window opens:

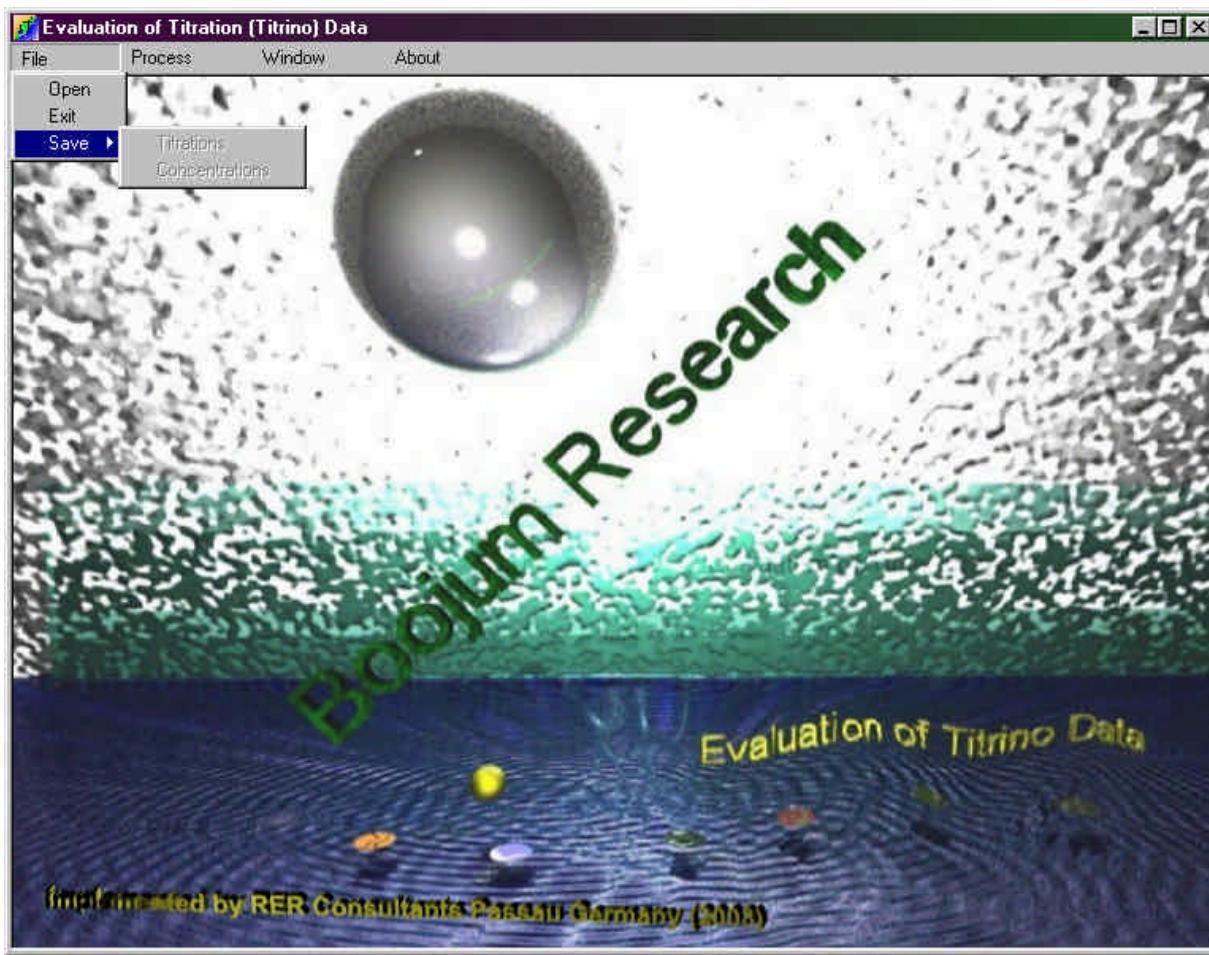


Figure 1: Titrino program main window with the "File" menu opened.

The menu bar holds the four items "File", "Process", "Window", "About". In most circumstances, only the items "File" and "Process" are of interest. Menu item "About" names programmer, commissioner and copyright holders. This menu item will not be mentioned any further.

The File menu allows to select the titration data files to be analysed by "Open". The menu item "Exit" immediately shuts down the program. There is no further option allowing to undo this operation. "Save" has two sub menus allowing to save the normalised and adapted titration curves ("Titrations") or the list of calculated concentrations ("Concentrations"). If no data has been loaded, both sub menu items are unavailable.

Main window: File:Open

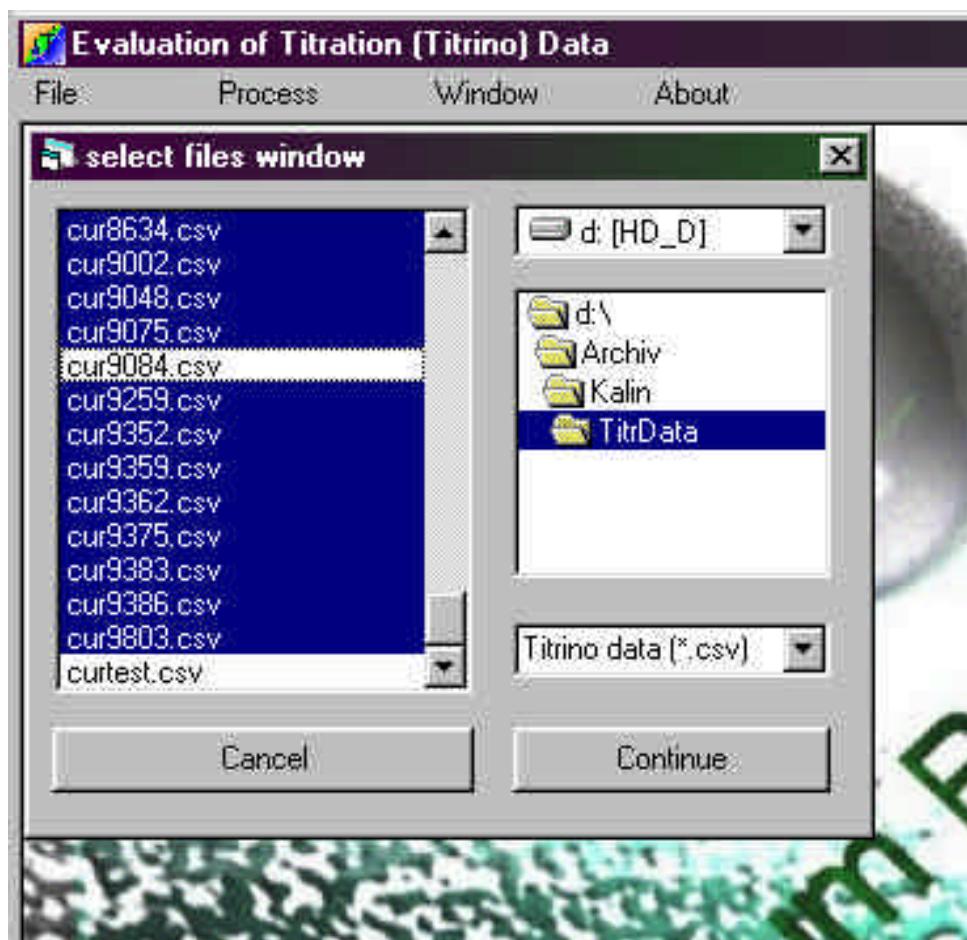


Figure 2: The dialog "File:Open"

The dialog "File:Open" follows the common Windows conventions. The user may select the drive, the sub directory and the extention of the files to be loaded. Clicking the "Continue" button opens the files and closes the window. The dialog may be terminated without loading files by clicking the "Cancel" button.

Files are selected by either clicking them with the left mouse button and by multiple selection with the left mouse button. Selected files may be deselected using the <Strg> key while clicking on them with the left mouse button.

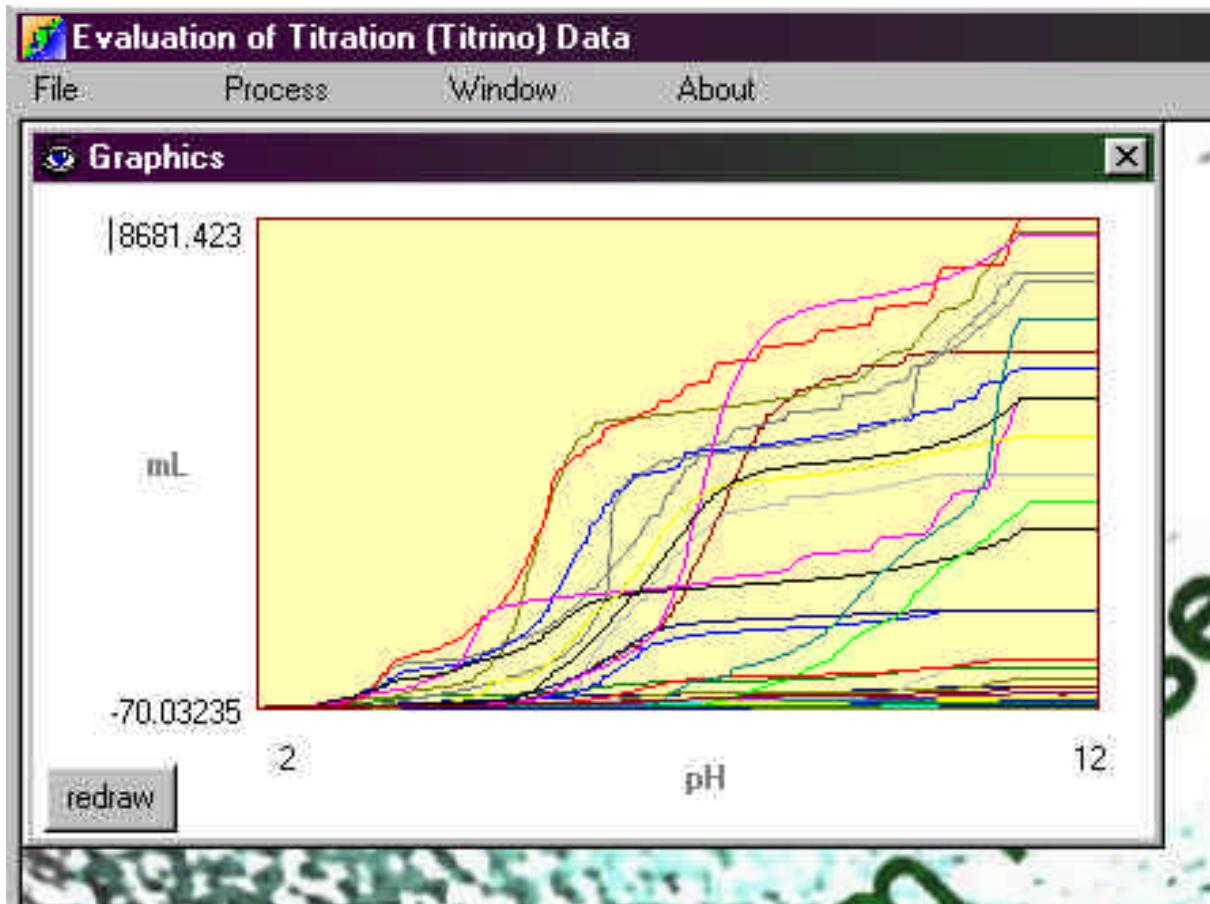


Figure 3: Graphical presentation of loaded and normalised titration curves

The program automatically normalises the loaded data by subtracting the titrant volume needed to cause pH shifts due to pure water and creating titration curves in a common pH region. This region is generally pH 2 to pH 12.

The Graphics window may be enlarged and moved by dragging the borders of the window. The graphical representations are appropriately adapted. There is, however, no further information provided in the window allowing to recognise a specific file by its colour. Such a legend would be either overly large or illegible if larger amounts of files are analysed simultaneously - as is intended for this program.

Data file conventions

The computer code is designed to compare certain properties of titration curves obtained under differing conditions. Differing conditions can be, e.g., the amount of solution titrated or the concentration of the titrand. Hence, the program needs to get information

about the conditions applied in recording the data. On basis of the information, the program needs to normalise the titration curves to achieve comparable data.

In the present case, the program expects that the data are available as ordered ASCII data. Ordering has to be increasing with pH. The data must be presented as x,y data pairs with one data pair per line. The pairs must be separated by a comma with the volume information in units of mL preceding the corresponding pH value.

Information about the titrated volume in mL and the concentration of the titrand in mol L⁻¹ must be provided in the first line of the data set using comma as delimiter.

In figure 4, the first lines of a data set are shown. From these informations, the programs creates data files which start at pH 2 and end at pH 12 normalised to a volume of 1 L.

10,0,01
0,5,35
0,01,5,472
0,02,5,647
0,03,5,846
0,04,5,862
0,05,6,036
0,06,6,056
0,07,6,184
0,08,6,205
0,09,6,336
0,09999999,6,36
0,11,6,593
0,12,6,82
0,13,6,84
0,14,7,383

Figure 4: First lines of a titration data set. The first line gives titrated volume (in units of mL) and concentration of titrand (in units of mol L⁻¹). The following data gives data pairs of amount of titrand added and corresponding pH.

Main window: File:Save:Titrations

Upon clicking "Save:Titrations", a file "Titration_Data.dat" is created in the same directory where the titration curve files have been loaded from. This file does overwrite an existing file of the same name without further notice.

The file "Titration_Data.dat" holds an array of the normalised titration data in comma separated ASCII format. These data are those actually treated by the program. In the

saved form, the data in "outfile.dat" can be imported into an appropriate graphical presentation program, e.g. for documentation as shown in figure 5 for the commercial program Origin.

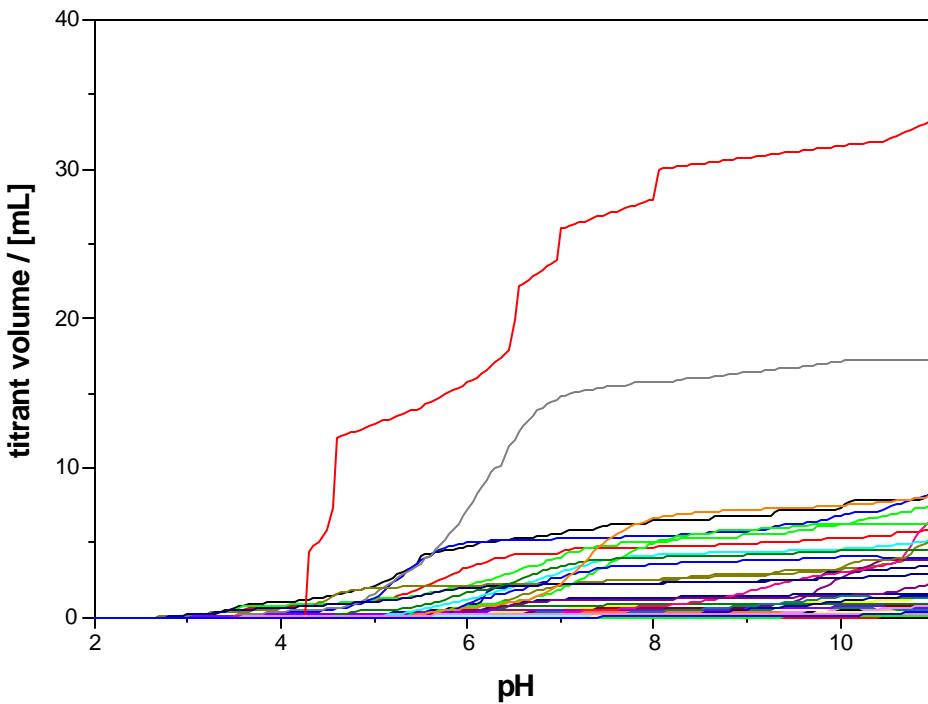


Figure 5: Normalised titration data after saving in "Titration_Data.dat" and importing into ORIGIN.

Main window: File:Save:Concentrations

If appropriate concentration data has been calculated by the program, the menu item "Save:Concentrations" is active. Upon selecting this menu option, a file "Concentration_Data.dat" is created in the same directory where the titration curve files have been loaded from. This file does overwrite an existing file of the same name without further notice.

The file "Concentration_Data.dat" holds the calculated amount of components in a row for each titration data file. If titrations have been evaluated by selecting both the "Evaluate" item and the "Simplex" item in the "Process" menu (see below), the both values are separated by a slash. The uncertainty specified is not valid for the "Simplex" result.

```

cur5266.csv: M+2 (Mn, Zn): -8.907337E-02 (-1899 %) mg :Fe+2: 1.66953 (189. %) mg :Mg: 1.020707 (155. %) mg :Fe+3:-11
cur5804.csv: M+2 (Mn, Zn): -1129.718 (-12.0 %) mg :Fe+2: 814.6689 ( 3.10 %) mg :Mg: 154.5984 (8.21 %) mg :Fe+3: 64.0701
cur5831.csv: M+2 (Mn, Zn): -1.328182 (-294. %) mg :Fe+2: 3.535544 (20.6 %) mg :Mg: 2.718035 (13.4 %) mg :Fe+3: .106579
cur5848.csv: M+2 (Mn, Zn): 354.5526 / 48.30722 (18.6 %) mg :Fe+2: 310.0932 / 253.7365 (3.96 %) mg :Mg: 3.971782 / 32.4
cur5918.csv: M+2 (Mn, Zn): 1.490979 (108. %) mg :Fe+2: 2.079072 (14.4 %) mg :Mg: .3416636 (44.1 %) mg :Fe+3: -601071
cur5924.csv: M+2 (Mn, Zn): -33.148 (-15.8 %) mg :Fe+2: 11.94297 (8.20 %) mg :Mg: 3.7302 (13.1 %) mg :Fe+3: -1259336 (-3
cur6000.csv: M+2 (Mn, Zn): -2.449003 (-31.5 %) mg :Fe+2: .1125892 (128. %) mg :Mg: .7533603 (9.60 %) mg :Fe+3: 7.97971
cur6004.csv: M+2 (Mn, Zn): 4.867043 (62.1 %) mg :Fe+2: 2.453413 (23.0 %) mg :Mg: 2118899 (133 %) mg :Fe+3: -1.92701

```

Figure 6: A section of the "Concentration_Data.dat" file. The file "cur5848.csv" has been evaluated by the two methods methods.

Figure 6 shows a section from a "Concentration_Data.dat" file, where one file has been evaluated by both possible methods. The first value is for the principal component value (obtained via the "Evaluate" process) while the value after the slash is obtained via linear regression (obtained via the "Simplex" process"). The uncertainty given in brackets is always obtained by the so-called "Clifford calculational method" from the principal component analysis.

Main window: Process

The menu item "Process" has five options. Only the first three, "Graphics", "Evaluate" and "Simplex" are of interest for the user at the present state of the development. Hence, the items "Cross Valid." (performs coloum cross validation) and "Target Iter." (performs target iteration for a user specified range of factors) will not be discussed further. These parts of the code are both for demonstrating some aspects of the given titration data by the programmer and the further development of the code (if necessary). Both features also help analysis of given data sets and trouble shooting.

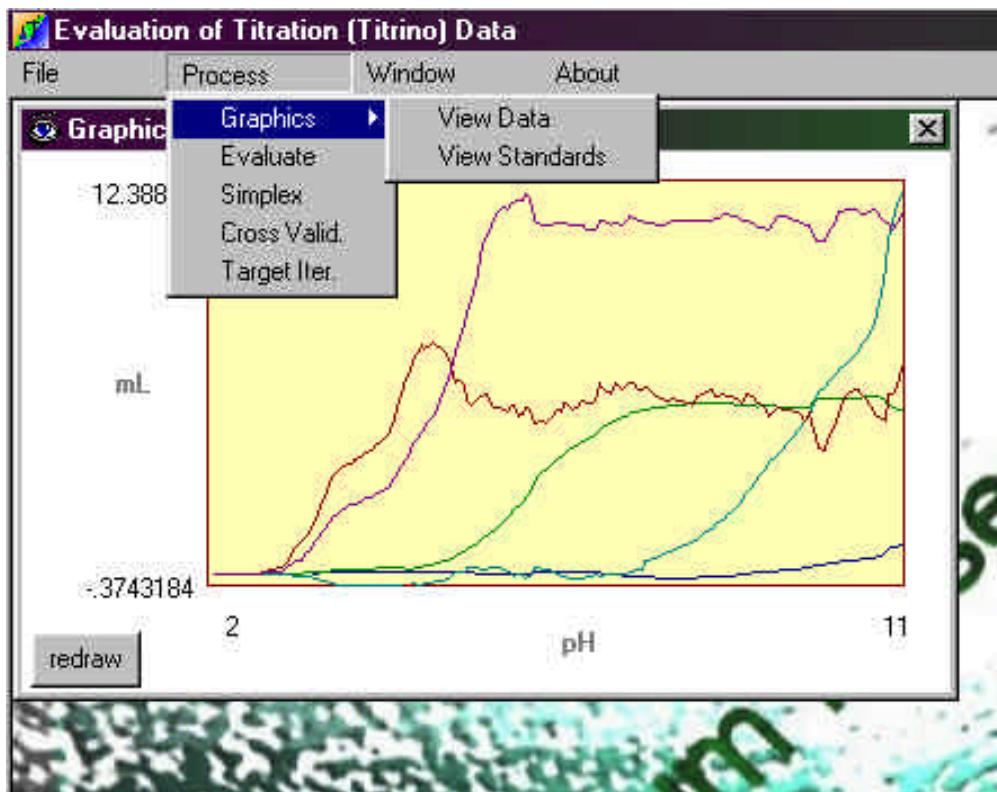


Figure 7: Menu item "Process" with the "Graphics" sub menus opened.

Process: Graphics: View Data

The item Process: Graphics: View Data allows the user to take a look on the experimental data at any time. Selecting this feature immediately opens a graphics window with the normalised titration data.

Process: Graphics: View Standards

On basis of the fifty example data sets, the factors contributing to the titration data (causing the titration curves) have been semi-quantitatively identified. These factors are provided to the program as starting values. In the evaluation process, these data are modified to suit other data sets. Clicking this option allows the user to visualise the modified factors.

Process: Evaluate

The menu item Proces: Evaluate starts the actual evaluation process yielding semi-quantitative estimates of the amounts of certain metal ions in a titrated solution. Two windows are created by Process: Evaluate: a graphics window showing the adapted factors and a table window holding in columns the estimated ion concentrations. The evaluation process takes just seconds. A typical window is shown in figure 8.

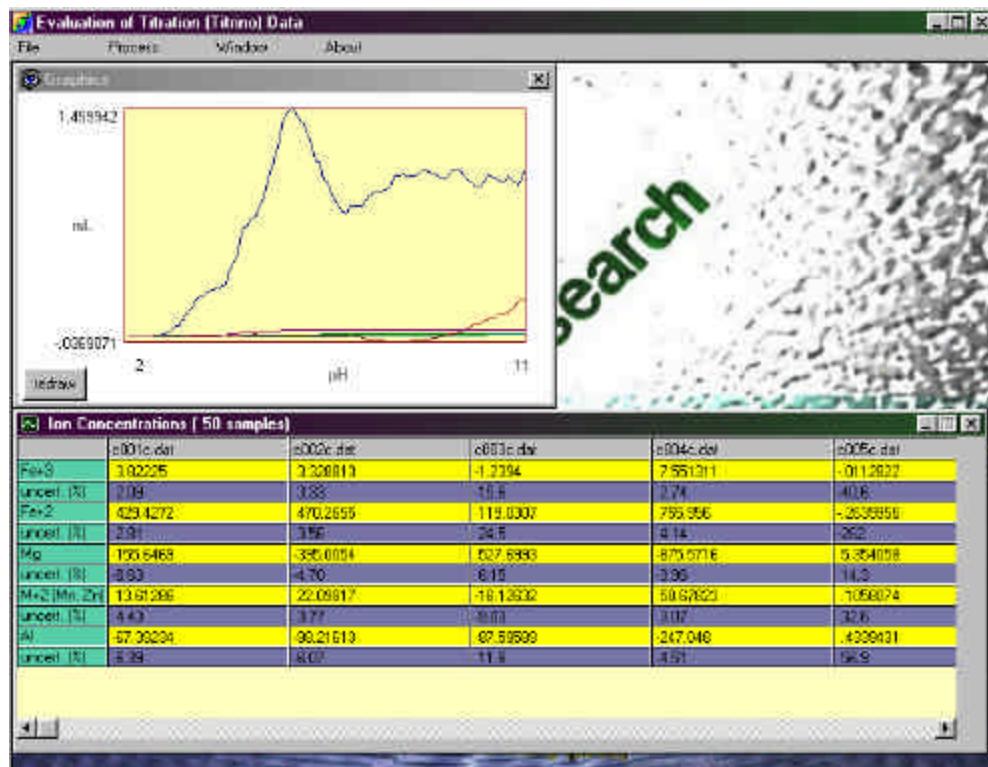


Figure 8: Main window with tabled evaluated data and graphics window holding the adapted factors.

The graphical windows explains itself. The table holds the estimated ion concentrations in mg / L in the yellow fields and an estimate of uncertainty in the gray fields (giving a 90% confidence in % of the estimated ion concentration). From the available informations, the ions Fe(III), Fe(II), Al(III) and Mg(II) are identified as the characteristic substances in solution. Other ions due not contribute significantly to the shape of the titration curve within the limits of titration accuracy. The program additionally is able to recognise divalent cations, notably Mn(II) and Zn(II) if the titration is conducted to values above pH 10. Within the available data set, only two such data files where present.

The estimate of uncertainty is a further element of quality assurance. An uncertainty estimate larger than the measured effect itself renders this value negligible. In several cases, entries in the yellow fields have negative sign. Computers do not like the value

Zero. Due to the high correlation between the factors the algorithm will decide to increase one factor and compensate this excess by setting an appropriate other factor to negative values. Larger negative entries may be caused by an outlying titration curve (in the present set of fifty titration curves, sample cur5804.csv has been recognised as an outlying observation).

If the negative values are overly large the data provided for a given file should be considered with caution. However, smaller negative entries are acceptable and do not render an evaluation as irrelevant. It should be noted that a titration curve is not as selective as a sophisticated instrument of analysis, e.g. an ICP-OES spectrometer. Future experience with analysing titration curves will show how to compensate and correct tailed results for presence of negative entries. It should be noted, nevertheless, that negative entries are part of the data treatment procedure.

Upon clicking at a column in the table "Ion Concentrations", the graphics window presents the experimental (normalised) titration curve (in blue colour) together with the fitted curve (in green colour). This graphical comparison is a further element of quality control. Larger deviations render an interpretation questionable. In addition, an additional window opens giving some details for the selected sample.

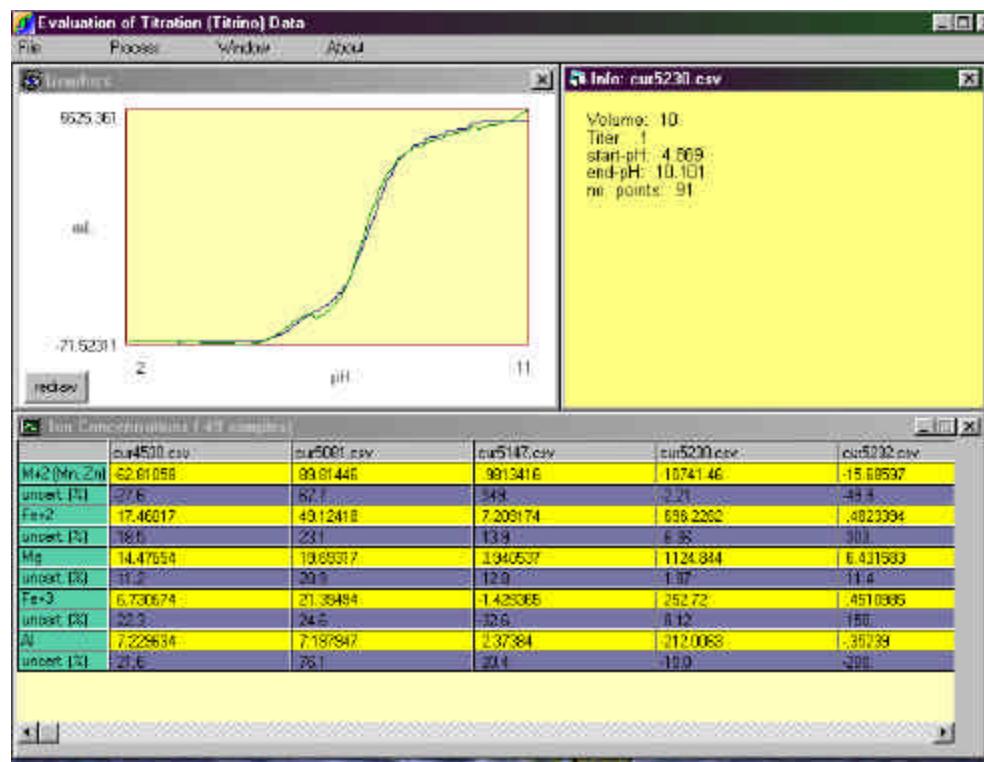


Fig. 9: "Info" window appearing upon clicking a column in the "Ion concentrations" window. The "Graphics" window gives the titration curve (blue) together with the fitted curve (green).

Process: Simplex

Larger negative values are a nuisance. Given the current quality of the the likely shape of titration curves of individual components and the inconsistencies in the titration data, larger negative values are unavoidable for some titration curves. Taking the data file cur5147.csv as an example it has to be realised that the pH region 3.5 to 10.5 in 20 mL of titrated sample solution is documented by 6 data points only. In case of data file cur9084.csv the large deviation of the titration curve may be explained by a wrongly stated titrand concentration or sample volume.

To spot such 'weak' data sets is one task for which this program has been designed. In its present version 2.0 beta it should not be mistaken as a ready-to-use tool but as a first approach to a previously unexplored field of exploration.

Nevertheless, data sets with larger negative concentration values are unsatisfactory. Therefore, a second algorithm has been included which is able to analyse individual titration curves on basis of the least-squares optimisation criterion with a rather strict non-negativity boundary condition. This algorithm is termed "Simplex" due to its special geometric design in the data space.

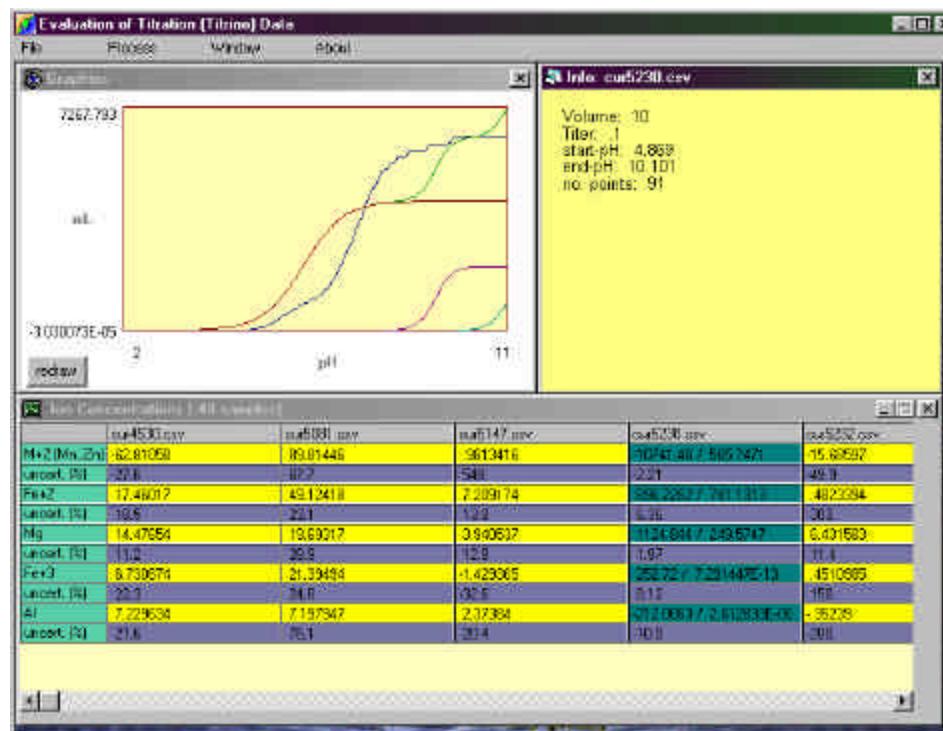


Figure 10: Analysis of the titration curve cur5230.csv by "Process:Simplex". The data curve with individual components is shown in the Graphics window. The respective

colum in the Ion Concentrations window is changed into blue. The Simplex results are given after the slash.

After the data has been analysed using the "Process:Evaluate" menu item, the "Process:Simplex" menu item becomes available. Selecting a titration data file in the "Ion Concentrations" window and selecting "Process:Simplex" starts the data analysis. The result is shown in the Graphics window (blue: titration curve, green: calculated titration curve. Other curves represent the contributions of individual components).

The relevant numerical data is included into the Ion Concentrations table. A column representing a titration curve analysed by the Simplex feature is changed into blue and the Simplex estimates are added following a slash.

Main window: Windows

The Windows menu gives a list of opened windows. It is a convenient way to bring a hidden or partially covered window to the top.