SUPPLEMENTARY FILE

to the paper

Validation of digestion and element separation methods and a new data reduction program (IsotopeHf®) for Lu-Hf isotope dilution analysis by MC-ICP-MS

by

Reneé González-Guzmán, Bodo Weber, María D. Tazzo-Rangel, and Luigi Solari

published in

Revista Mexicana de Ciencias Geológicas, 2016, 33(2), p. 254-269.

Package 'IsotopeHf'

July 11, 2016

Type Package

Title Hf isotope reduction Toolkit for R: IsotopeHf

Description The main functionality of the package is to provide reliable Lu-
Hf data from Neptune® MC ICP MS measurements.

Version 0.7.9

Encoding UTF-8

Date 2015-03-8

Author Reneé González Guzmán

Maintainer Reneé González Guzmán `<rguzman@cicese.edu.mx>`

Copyright CICESE

Depends R (>= 3.1.1)

Imports plyr,ggplot2,dplyr,knitr

License BSD (>= 3) + file LICENSE

LazyData TRUE

VignetteBuilder knitr

NeedsCompilation yes

RoxygenNote 5.0.1

R topics documented:

IsotopeHf-package   *Hf isotope reduction data Toolkit for R*

Description

This package imports mass spectrometer raw data files from Neptune® MC ICP MS, facilitates the
visualization of temporal trends and scatter during measurements and implements point-by-point
application of mass fractionation correction, isobaric correction, isotope dilution computation, and
spike stripping. In addition, provides a set of tools that compute useful Hf isotope parameters.

Details

Package:	IsotopeHf
Type:	Package
Version:	0.6.9
Date:	2015-02-15
License:	BSD-3

BHVO.Hf   *BHVO-1 basalt (Hf)*

Description

The 'BHVO.Hf' data frame has 80 rows and 11 columns, which are the measurements from a Hf
BHVO-1 basalt aliquot.

Details

Variables:

- **Time** (POSIXct format)
- **172 Mass**
- **174 Mass**
- **175 Mass**

- **176 Mass**
- **177 Mass**
- **179 Mass**
- **180 Mass**
- **181 Mass**
- **182 Mass**
- **Sample ID**

See Also

[BHVO.Lu](#),[Standard.Hf](#),[Standards.Lu_Re](#)

Examples

```
## Not run:
#Preloaded data
data (BHVO.Hf)
head (BHVO.Hf)
## End(Not run)
```

BHVO.Lu *BHVO-1 basalt (Lu)*

Description

The 'BHVO.Lu' data frame has 40 rows and 11 columns, which are the measurements from a Lu BHVO-1 basalt aliquot.

Details

Variables:

- **Time** (POSIXct format)
- **170 Mass**
- **172 Mass**
- **173 Mass**
- **174 Mass**
- **175 Mass**
- **176 Mass**
- **177 Mass**
- **185 Mass**
- **187 Mass**
- **Sample ID**

See Also

BHVO.Hf,Standard.Hf,Standards.Lu_Re

Examples

```
## Not run:
#Preloaded data
data (BHVO.Lu)
head (BHVO.Lu)
## End(Not run)
```

---

errorutils	*A collection of some functions commonly used for setting uncertain-ties.*

Description

General functions for the calculation of uncertainties and outlier detection.

Usage

```
outlier2sigma(data)
SD(data)
RSD(data)
SE(data)
```

Details

Variables:

- **SD** This function computes the standard deviation.
- **RSD** This function computes the coefficient of variation expressed as a percentage.
- **SE** This function computes the 2-standard error (2S.E.=$1.96\sigma/\sqrt{(n)}$). Note: the real range of error is 95% confidence level.
- **outlier2sigma** If outliers are detected by the 2σ method, this function can remove it with 'NA' values.

Examples

```
## Not run:
data <- round(rnorm(80, mean = 0.283100, sd = 0.000018),6)
SD(data)
##
RSD(data)
##
SE(data)
##
outlier2sigma(data)
## End(Not run)
```

Hf180corr	*180Hf unspiked correct data*

Description

Computes the corrected ^{180}Hf/^{177}Hf ratio and its uncertainty from standard solution or unspiked samples aliquot.

Usage

```
Hf180corr(data,outlier = TRUE)
```

Arguments

data	a data file from the output of the function `readHf`.
outlier	logical indicating whether you want outlier data rejection.

Details

This function calculates the mass bias factor (Rusell et al., 1978) and corrects the interferences on ^{180}Hf (from ^{180}Ta and ^{180}W) to compute a corrected ^{180}Hf/^{177}Hf ratio from unspiked sample data.

Value

A corrected ^{180}Hf/^{177}Hf value and its uncertainties are returned. This function has a graphic output.

References

Russel W.A, Papanastassiou D.A., Tombrello, T.A., 1978, Ca isotope fractionation on the earth and other solar system materials: Geochimica at Cosmochimica Acta, 42,1075-1090.

See Also

`HfIDcorr`,`Hfcorr`

Examples

```
## Not run:
#from preloaded data
data (Standard.Hf)
Hf180corr(Standard.Hf)
##############

#from .FIN2 file
##It is important set the work directory #setwd (path)
#getwd()To know the actual directory
data<-readHf()
Hf180corr(data)
## End(Not run)
```

Hfcorr   *Hf unspiked correct data*

Description

Computes the corrected $^{176}\text{Hf}/^{177}\text{Hf}$ ratio and its uncertainty from standard solution or unspiked sample aliquot.

Usage

```
Hfcorr(data, intLu.corr = FALSE, intYb.corr = FALSE, outlier = TRUE)
```

Arguments

data	a data file from the output of the function readHf.
intLu.corr	logical that carry into effect the interference correction of ^{176}Lu on ^{176}Hf from 175 Mass intensity.
intYb.corr	logical that carry into effect the interference correction of ^{176}Yb on ^{176}Hf from 172 Mass intensity.
outlier	logical indicating whether you want outlier values rejection.

Details

This function calculates the mass bias factor (Russel et al., 1978) and can correct the interferences on ^{176}Hf (from ^{176}Yb and ^{176}Lu) to perform corrected $^{176}\text{Hf}/^{177}\text{Hf}$ ratio from unspiked sample data. Additionally, computes isotope ratios measured in Hf aliquot to monitor the isobaric interference on ^{176}Hf, like $^{172}\text{Yb}/^{176}\sum$ and $^{175}\text{Lu}/^{176}\sum$ (Bast et al., 2015). Note: $^{176}\sum = {}^{176}\text{Yb} + {}^{176}\text{Lu} + {}^{176}\text{Hf}$.

Value

A corrected $^{176}\text{Hf}/^{177}\text{Hf}$ value and its uncertainties are returned. To prove the data quality, the interference monitors are shown. This function has a graphic output.

References

Russel W.A, Papanastassiou D.A., Tombrello, T.A., 1978, Ca isotope fractionation on the earth and other solar system materials: Geochimica at Cosmochimica Acta, 42,1075-1090.

Bast, R., Scherer, E.E., Sprung, P., Fischer-Gõdde, M., Stracke, A., Mezger, K., 2015, A rapid and efficient ion-exchange chromatography for Lu–Hf, Sm–Nd, and Rb–Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS: Journal of Analytical Atomic Spectrometry, 30, 2323–2333.

See Also

HfIDcorr,Hf180corr

Examples

```
## Not run:
#from preloaded data
data (Standard.Hf)
Hfcorr(Standard.Hf, outlier = FALSE)
##############

#from .FIN2 file
##It is important set the work directory #setwd (path)
#getwd()To know the actual directory
data<-readHf()
Hfcorr(data, outlier = FALSE)
## End(Not run)
```

HfIDcorr   *Hf spiked correct data*

Description

Computes elemental concentration of Hf, corrected ^{176}Hf/^{177}Hf ratio and its uncertainty from spiked sample aliquot.

Usage

```
HfIDcorr(data,SampleWeight = NA, SpikeWeight = NA, intLu.corr = FALSE, intYb.corr = FALSE)
```

Arguments

|	
data	a data file from the output of the function [readHf]().
SampleWeight	the sample weight (g). This value is used to calculate Hf concentration.
SpikeWeight	the spike added (g). This value is used to calculate Hf concentration.
intLu.corr	logical that carry into effect the interference correction of ^{176}Lu on ^{176}Hf from 175 Mass intensity.
intYb.corr	logical that carry into effect the interference correction of ^{176}Yb on ^{176}Hf from 172 Mass intensity.
outlier	logical indicating whether you want outlier values rejection.

Details

This function calculates the Hf concentration from isotope dilution equations (Gopalan, 2002). It is important to note that values from WR-1 spike (University of Münster) are used by default. This function calculates all necessary corrections for spiked samples (mass bias (Russel et al., 1978), interference and spike (Chu et al., 2011) corrections). Additionally, computes isotope ratios measured in Hf aliquot to monitor the isobaric interference on ^{176}Hf like ^{172}Yb/$^{176}\sum$ and ^{175}Lu/$^{176}\sum$ (Bast et al., 2015). Note: $^{176}\sum = {}^{176}$Yb + ^{176}Lu + ^{176}Hf.

Value

A corrected ^{176}Hf/^{177}Hf value and its uncertainty are returned. It is critical for calculating the concentration add the weights of both the sample and the spike into the command. To prove high data quality, the observed interference monitors are shown. This function has a graphic output. See below.
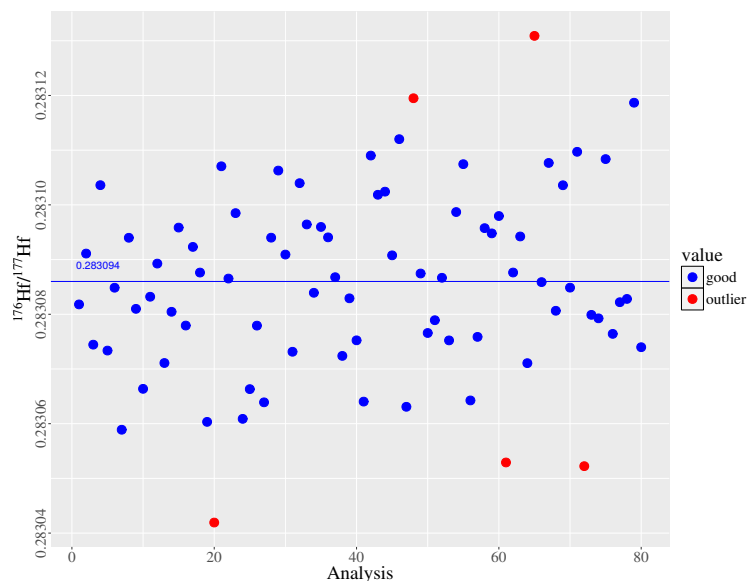
References

Russel W.A, Papanastassiou D.A., Tombrello, T.A., 1978, Ca isotope fractionation on the earth and other solar system materials: Geochimica at Cosmochimica Acta, 42,1075-1090.

Gopalan, K., 2002, Direct correction for mass fractionation of spiked isotopic ratios from dynamic multicollector measurements: Geochemical journal 36(1), 83 - 89.

Chu, Z.Y., Yang, Y.H., Jinghui, G., Qiao, G.S., 2011, Calculation methods for direct internal mass fractionation correction of spiked isotopic ratios from Multi-collector mass spectrometric measurements: International Journal of Mass Spectrometry, 299 (2), 87-93.

Bast, R., Scherer, E.E., Sprung, P., Fischer-Gõdde, M., Stracke, A., Mezger, K., 2015, A rapid and efficient ion-exchange chromatography for Lu–Hf, Sm–Nd, and Rb–Sr geochronology and the routine isotope analysis of sub-ng amounts of Hf by MC-ICP-MS: Journal of Analytical Atomic Spectrometry, 30, 2323–2333.

See Also

Hfcorr,Hf180corr

Examples

```
## Not run:
#from preloaded data
data (BHVO.Hf)
```

```
HfIDcorr(BHVO.Hf, outlier = FALSE)
##############

#from .FIN2 file
##It is important set the work directory #setwd (path)
#getwd()To know the actual directory
data<-readHf()
HfIDcorr(data, outlier = TRUE,SampleWeight = 0.1000, SpikeWeight = 0.0315)
## End(Not run)
```

Hftools   *Hftools*

Description

Computes useful parameters of Lu-Hf pair.

Usage

```
Hfi (ratio, lu = NA, hf = NA, age = NA)
Eps (ratio)
EpsT (ratio, lu = NA, hf = NA, age = NA)
TDm (ratio,lu = NA, hf = NA)
TDm2 (ratio, lu = NA, hf = NA, age = NA)

allHf (ratio, lu = NA, hf = NA, age = NA)
```

Arguments

ratio	^{176}Hf/^{177}Hf ratio.
lu	Lu concentration (ppm).
hf	Hf concentration (ppm).
age	age in Ma.

Details

Functions:

- **Hfi** This function computes initial ^{176}Hf/^{177}Hf ratios.
- **Eps** This function computes εHf values.
- **EpsT** This function computes initial εHf values.
- **TDm** This function computes one-stage model ages.
- **TDm2** This function computes two-stage model ages.
- **allHf** This function runs all the parameters.

Initial isotope values are calculated at t = age in Ma, using $\lambda^{176}Lu = 1.867 \times 10^{11}$ (Scherer et al. 2001; Scherer et al., 2003; Söderlund et al., 2004). The εHf_i is calculated following CHUR (CHondrite Uniform Reservoir) values: $^{176}Hf/^{177}Hf = 0.282785$ and $^{176}Lu/^{177}Hf = 0.0336$ (Bouvier et al., 2008). The Depleted Mantle (DM) values used are after Vervoort (2011): $^{176}Hf/^{177}Hf = 0.28321$ and $^{176}Lu/^{177}Hf = 0.0399$. Two-stage crustal residence model ages are calculated assuming $(^{176}Lu/^{177}Hf)$avg. crust = 0.015 (Condie et al., 2005).

Value

Numeric: $^{176}Hf/^{177}Hf_i$, εHf, εHf_i, one- and two-stage model ages

References

Scherer, E.E., Munker, C., Mezger, K., 2001, Calibration of the Lutetium-Hafnium Clock: Science 293, 683–687.

Scherer, E.E., Mezger, K., Münker, C., 2003, The ^{176}Lu decay constant discrepancy: terrestrial samples vs. meteorites: Meteoritics and Planetary Science Suppl 38, 5263.

Söderlund, U., Patchett, P.J., Vervoort, J.D., Isachsen, C.E., 2004, The ^{176}Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions: Earth and Planetary Science Letters 219, 311–324.

Condie, K.C., Beyer, E., Belousova, E., Griffin, W.L., O'Reilly, S.Y., 2005, U–Pb isotopic ages and Hf isotopic composition of single zircons: The search for juvenile Precambrian continental crust: Precambrian Research 139, 42-100.

Bouvier, A., Vervoort, J.D., and Patchett, P.J., 2008, The Lu-Hf and Sm-Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets, Earth and Planetary Science Letters, 273, 48-57.

Vervoort, J.D., Plank, T., Prytulak, J., 2011, The Hf-Nd isotopic composition of marine sediments: Geochimica at Cosmochimica Acta, 75, 5903-5926.

Examples

```
## Not run:
sample<-c("03-1b-1","unknown","03-2a-1","03-2a-2","zircon-1","zircon-2")
ratio<-c(0.282261,0.282432,0.282254,0.282261,0.282191,0.282200)
lu<-c(0.62,0.52,0.59,0.53,26.8,46.7)
hf<-c(25.64,19.90,28.72,14.79,6990,9780)
age<-rep(1000,6)
table<-allHf(ratio,lu,hf,age)
rownames(table) <- sample
print(table)

## End(Not run)
```

Description

Computes elemental concentration of Lu as well as ^{175}Lus/^{176}Lun ratio and its uncertainties from spiked sample aliquot.

Usage

```
LuIDcorr(data,SampleWeight = NA, SpikeWeight = NA, intHf.corr = FALSE, Slope=NA, outlier = TRUE)
```

Arguments

data	a data file from the output of the function [readLu]().
SampleWeight	the sample weight (g). This value is used to calculate Lu concentration.
SpikeWeight	the spike added (g). This value is used to calculate Lu concentration.
intLu.corr	carry into effect the interference correction of ^{176}Hf on ^{176}Lu from the measured intensity of ^{177}Hf.
Slope	the slope value of the log-log plot of the standard (Lu-Re) in a given work session. See [SlopeReLu]().
outlier	a logical indicating whether you want outlier data rejection.

Details

This function computes the Re-Lu doping method (Scherer et al., 1999) in order to return Lu data. It is important to note that values from WR-1 spike (University of Münster) are used by default.

Value

A corrected ^{175}Lus/^{176}Lun value and its uncertainty are returned. It is critical for calculating the concentration add the weights of the sample and the spike as well as the slope value (log-log plot Re-Lu) into the command. The mass-bias factors of Yb, Lu, and Re are also returned. This function has a graphic output.

References

Scherer, E, Munker, C, Rehkamper, M, Mezger, K., 1999, Improved precision of Lu isotope dilution measurements by MC-ICP-MS and application to Lu-Hf geochronology: Eos Suppl 80(46), 1118.

See Also

[Hfcorr](),[HfIDcorr](),[SlopeReLu]()

Examples

```
## Not run:
#from preloaded data
data (BHVO.Lu)
LuIDcorr(BHVO.Lu, outlier = FALSE, SampleWeight = 0.1198, SpikeWeight =0.0334, S = 0.67202)
###############

#from .FIN2 file
##It is important set the work directory #setwd (path)
#getwd()To know the actual directory
data<-readLu()
LuIDcorr(data, outlier = TRUE, SampleWeight = 0.1198, SpikeWeight =0.0334, S = 0.67202)
## End(Not run)
```

Pearson   *Pearson*

Description

The 'Pearson' data frame has 10 rows and 4 columns, which are Pearsson's x-y data used in York's function example.

Details

Variables:

- **x** (x-value)
- **sx** (absolute error)
- **y** (y-value)
- **sy** (absolute error)

References

Pearson, K., 1901, On Lines and planes of closest fit to systems of points in space: Philosophical Magazzine, 2(6), 559-572.

See Also

York

Examples

```
## Not run:
#Preloaded data
data (Pearson)

## End(Not run)
```

---

readHf   *Read file Hf.FIN2*

Description

Reads the selected file with .FIN2 extension.

Usage

```
readHf(data)
```
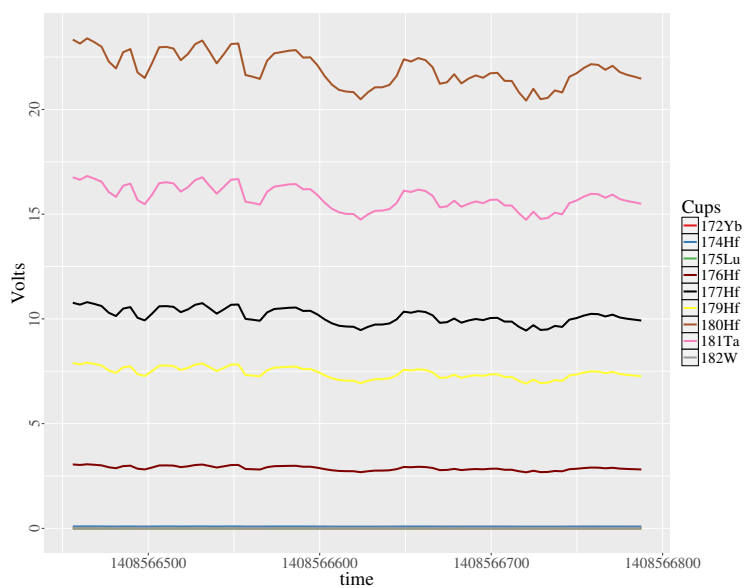
Arguments

data   path to the .FIN2 file (.FIN2 is the output extension from Thermo Neptune®
                    MC-ICP-MS, same as .csv extension).

Details

This function reads the indicated file. The argument must to be the complete path to a file. If it does
not contain an absolute path, the file name is relative to the current working directory (getwd()). This
function creates a data frame with the measured voltages of the Mass spectrometer to determine Hf
concentrations. The time is changed to POSIXct format.

Value

If a .FIN2 file is selected, then a data frame is returned. This function has a graphic output, see
below.

See Also

[readLu](#)

Examples

```
## Not run:
#It is important set the work directory
#getwd()#To know the actual directory
#setwd(path)#To change directory
data<-readHf()

## End(Not run)
```

---

readLu   *Read file Lu.FIN2*

Description

Reads the selected file(s) with .FIN2 extension.

Usage

```
readLu(data)
```

Arguments

data   path to the .FIN2 file (.FIN2 is the output extension from Thermo Neptune®
                     MC-ICP-MS, same as .csv extension).

Details

This function read(s) the indicated file(s). The argument must to be the complete path to a file(s).
If it does not contain an absolute path, the file name is relative to the current working directory
(getwd()). This function creates a data frame with the measured voltages of the Mass spectrometer
to determine Lu concentrations. The time is changed to POSIXct format.

Value

If a .FIN2 file is selected, then a data frame is returned. This function has a graphic output.

See Also

[readHf](#)

Examples

```
## Not run:
#It is important set the work directory
#setwd(path)#To change directory
#getwd()#To know the actual directory
data<-readLu(getwd())

## End(Not run)
```

SlopeReLu   *Slope of Re-Lu (log-log) plot*

Description

Computes the slope, intercept and other parameters from a linear array in a log-log diagram.

Usage

```
SlopeReLu(data)
```

Arguments

data   path to the .FIN2 files (.FIN2 is the output extension from Thermo Neptune®
                MC-ICP-MS, same as .csv extension).

Details

Computes a weighted regression following the approach of York et al. (2004) (see [York](#)). It is calculated from a standard solution containing both Re and Lu, which is measured interspersed with unknown samples in a given analytical session. All files of these measurements must be in the same folder.

Value

It is returned the regression coefficients from the $\ln(^{187}Re/^{185}Re)$ vs. $\ln(^{176}Lu/^{175}Lu)$ diagram and its uncertainties. This function has a graphic output.

References

Scherer, E, Munker, C, Rehkamper, M, Mezger, K., 1999, Improved precision of lu isotope dilution measurements by MC-ICP-MS and application to Lu-Hf geochronology: Eos Suppl 80(46), 1118.

York, D., Evensen, N.M., López-Martínez, M., De Basabe-Delgado, J., 2004, Unified equations for the slope, intercept, and standard errors of the best straight line: American Journal of Physics, 72, 367-375.

See Also

[LuIDcorr](#),[York](#)

Examples

```
## Not run:
#It is important set the work directory
#setwd(path)#To change directory
#getwd()#To know the actual directory
SlopeReLu()
## End(Not run)
```

Standard.Hf   *Standard.Hf*

Description

The 'Standard.Hf' data frame has 80 rows and 11 columns, which are the measurements from a JMC 475 standard solution.

Details

Variables:

- **Time** (POSIXct format)
- **172 Mass**
- **174 Mass**
- **175 Mass**
- **176 Mass**
- **177 Mass**
- **179 Mass**
- **180 Mass**
- **181 Mass**
- **182 Mass**
- **Sample ID**

See Also

BHVO.Lu,BHVO.Hf

Examples

```
## Not run:
#Preloaded data
data (Standard.Hf)
head (Standard.Hf)
## End(Not run)
```

Standards.Lu_Re   *Standards.Lu_Re*

Description

The 'Standards.Lu.Re' data frame has 320 rows and 11 columns, which are the measurements from a standard solution containing both Re and Lu, which is measured interspersed with unknown samples in an analytical session.

Details

Variables:

- **Time** (POSIXct format)
- **170 Mass**
- **172 Mass**
- **173 Mass**
- **174 Mass**
- **175 Mass**
- **176 Mass**
- **177 Mass**
- **185 Mass**
- **187 Mass**
- **Sample ID**

See Also

BHVO.Lu, SlopeReLu, LuIDcorr

Examples

```
## Not run:
#Preloaded data
data (Standards.Lu.Re)
head (Standards.Lu.Re)
## End(Not run)
```

| York | *York regression* |

Description

Computes the linear weighted regression (with correlated errors in bivariate data).

Usage

```
York (data)
```

Arguments

data   data frame with x,y,sx, and sy values (sx and sy must be absolute errors).

Details

This function generates a best-fit line using the weighted regression method following the approach of York et al. (2004). In some analytical applications, it may be required. In this case of Pearson's data (Pearson, 1901), the results are compared with other softwares (see Table below). A graphical output displaying the fitted trend line with the data points is also shown for comparison.
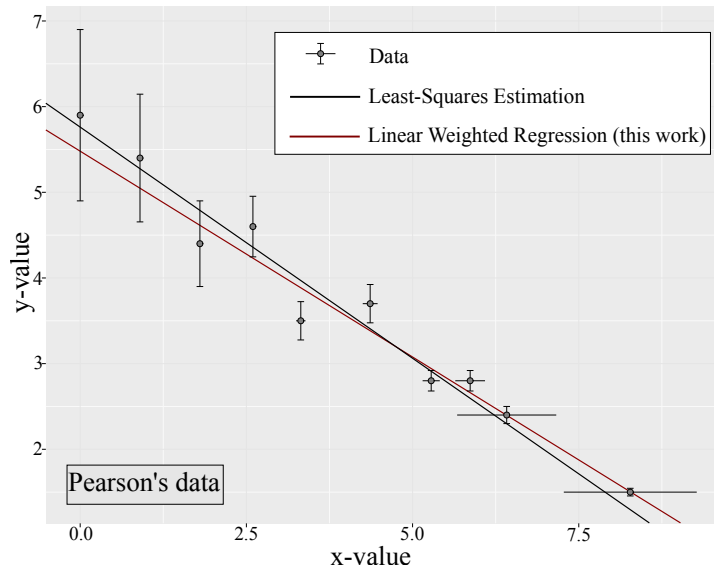
Tool	Intercept	Std. error	Slope	Std. error	r^2
[1]LSM	5.47991	0.295713	-0.485033	0.058256	NA
[2]Excel®	5.47991	0.359247	-0.4805333	0.070620	NA
[3]Matlab®	5.47991	0.294971	-0.4805334	0.057985	0.96
This function	5.47991	0.294971	-0.4805336	0.057985	0.96
R (LSE)	5.76119	0.18949	-0.53958	0.04213	0.95

Value

The output displays the slope, the intercept, and their uncertainties as well as the linear correlation coefficient of the fitted data.

References

Pearson, K., 1901, On Lines and planes of closest fit to systems of points in space: Philosophical Magazzine, 2(6), 559-572.

[1]York, D., Evensen, N.M., López-Martínez, M., De Basabe-Delgado, J., 2004, Unified equations for the slope, intercept, and standard errors of the best straight line: American Journal of Physics, 72, 367-375.

[2]Cantrell, C.A., 2008, Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems. Atmospheric Chemistry and Physics Discussions, 8, 6409-6436.

[3] Thirumalai, K., Singh, A., Ramesh, R., 2011, A MATLAB code to perform weighted linear regression with (correlated or uncorrelated) errors in bivariate data: Journal of The Geological Society of India, 77(4), 377-380.

See Also

Pearson, SlopeReLu, LuIDcorr

Examples

```
## Not run:
#from preloaded data
data (Pearson)
York(Pearson)
##############

##--  Pearson's data  --##
x <- c(0.0, 0.9, 1.8, 2.6, 3.3, 4.4, 5.2, 6.1, 6.5, 7.4)
y <- c(5.9, 5.4, 4.4, 4.6, 3.5, 3.7, 2.8, 2.8, 2.4, 1.5)
sx <- c(0.031623, 0.031623, 0.044721, 0.035355, 0.070711, 0.111803, 0.129099, 0.223607, 0.745356, 1.000000)
sy <- c(1.000000, 0.745356, 0.500000, 0.353553, 0.223607, 0.223607, 0.119523, 0.119523, 0.100000, 0.044721)
data <- data.frame(x,y,sx,sy)
York(data)

## End(Not run)
```

Index