



Mass Spectrometry

# IsoScale G Data Processing Algorithms for GIRMS

## Software Manual

Qtegra ISDS Software

BRE0031839

Revision D

May 2023



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# Using This Manual

This chapter provides information about this manual.

## Contents

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## About This Manual

This *IsoScale G Data Processing Algorithms for GIRMS* Software Manual explains the evaluation algorithms of Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

## Related Documentation

This *IsoScale G Data Processing Algorithms for GIRMS* manual represents the original mathematical document. It is valid for Thermo Scientific GIRMS instruments.

## Typographical Conventions

This section describes typographical conventions that have been established for Thermo Fisher Scientific manuals.

### Signal Words

Make sure you follow the precautionary statements presented in this manual. The special notices appear different from the main flow of text:

**Tip** Points out possible material damage and other important information in connection with the instrument.

### Viewpoint Orientation

The expressions *left* and *right* used in this manual always refer to the viewpoint of a person that is facing the front side of the instrument.

### Data Input

Throughout this manual, the following conventions indicate data input and output via the computer:

- Messages displayed on the screen are represented by capitalizing the initial letter of each word and by italicizing each word.
- Input that you enter by keyboard is identified by quotation marks: single quotes for single characters, double quotes for strings.
- For brevity, expressions such as “choose **File > Directories**” are used rather than “pull down the File menu and choose Directories.”
- Any command enclosed in angle brackets < > represents a single keystroke. For example, “press <F1>” means press the key labeled *F1*.
- Any command that requires pressing two or more keys simultaneously is shown with a plus sign connecting the keys. For example, “press <Shift> + <F1>” means press and hold the <Shift> key and then press the <F1> key.
- Any button that you click on the screen is represented in bold face letters. For example, “click **Close**”.
- Mathematical equations show × instead of · for the multiplication.



## Topic Headings

The following headings are used to show the organization of topics within a chapter:

### Chapter Name



### Second Level Topics



### Third Level Topics

### Fourth Level Topics

## Contacting Us

There are several ways to contact Thermo Fisher Scientific. You can use your smartphone to scan a QR Code™, which opens your email application or browser.

Contact	Link / Remarks	QR Code
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<b>Service Contact</b>	For technical support related to your instrument or software, visit the <b>Services &amp; Support</b> tab at <a href="http://www.thermofisher.com">www.thermofisher.com</a> or visit <a href="http://www.unitylabservices.com">www.unitylabservices.com</a> to find the customer care telephone line or email address for your geographical region.	

Contact	Link / Remarks	QR Code
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<b>Customer Feedback</b>	<b>To suggest changes to this manual</b>  You are encouraged to report errors or omissions in the text or index. Send an email message to the Technical Editor at <a href="mailto:documentation.bremen@thermofisher.com">documentation.bremen@thermofisher.com</a> .  The PDF versions of our manuals allow adding comments with Adobe Acrobat Reader or other freely available PDF reader programs.	

## Training

Thermo Fisher Scientific offers worldwide training on instruments and software. Experience has shown that maximum results can be obtained from a scientific instrument if the instrument operator receives an adequate training.

We recommend that the key users participate in a basic operator training. For information on training courses and enrollment, contact your local Thermo Fisher Scientific office.

## Introduction

This document describes the delta calculations performed by Qtegra IsoScale G, a part of Qtegra ISDS Software.

The calculations are based on the ion corrections of Isodat, Qtegra's predecessor in this field.

Numerical values used in this document relate to example calculations and tests that were used in the creation of the Qtegra IsoScale G code.

### Contents

- [Fraction and Ratios](#) on page 2-1
- [Delta Values](#) on page 2-2
- [Atom Percent](#) on page 2-4
- [Standards](#) on page 2-5

## Fraction and Ratios

The calculation of delta values is based on measurements of ratios of different isotopes of the same species. The letter  $R$  is used to denote ratios. A superscript on the left side shows the numerator mass of the ratio. The denominator is the main isotope of the species, for example:

$${}^{13}R = \frac{{}^{13}C}{{}^{12}C} \quad (1)$$

A similar notation is used for the fractional abundance  $F$ :

$${}^{13}F = \frac{{}^{13}C}{{}^{12}C + {}^{13}C} \quad (2)$$

## Delta Values

Delta values describe the difference between the ratio  $R$  of a measured sample and the ratio  $R_{Std}$  of a standard substance. Deltas are calculated like

$$\delta = \left( \frac{R}{R_{Std}} - 1 \right) \times 1000 \quad (3)$$

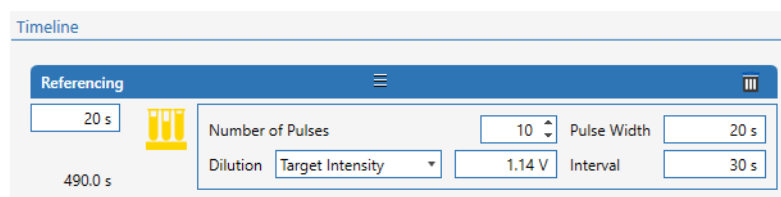
This equation can be inverted to get the ratio:

$$R = \left( \frac{\delta}{1000} + 1 \right) \times R_{Std} \quad (4)$$

Qtegra IsoScale G reports  $\delta$  values calculated using the working standard ratio as 'raw  $\delta$ ' values.  $\delta$  values calculated using the primary standard ratio are just called ' $\delta$ ' values.

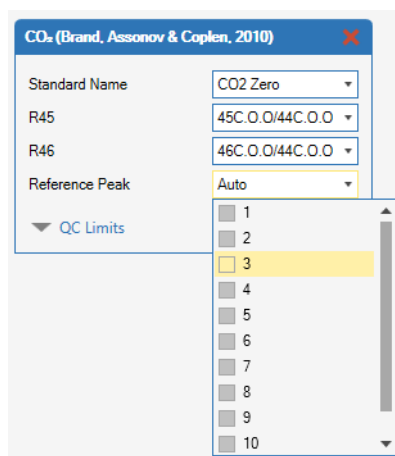
## Reference Peaks

In chromatography and EA measurements, the reference peaks used for  $\delta$  calculations are determined by matching measured peaks with the referencing actions from the timeline in the continuous flow method parameters (see [Figure 2-1](#)). A peak is used as a reference peak when it overlaps with a referencing peak from the timeline. This means the start of a measured peak must lie before the end of the referencing action and the end of the measured peak must lie after the start of a referencing action. To allow for typical gas travel times 6 seconds are added to the times from the timeline.

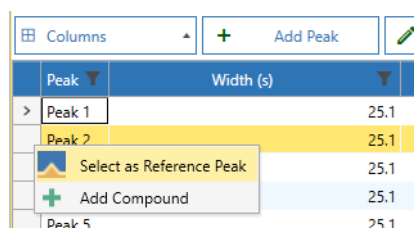


**Figure 2-1.** Referencing action in the timeline settings

The peak or peaks of the available reference peaks, which is actually used in the delta calculations, can be selected in the Delta Calculation parameters (see Figure 2-2) or from the shortcut menu (open with a right-click) in the results display (see Figure 2-3).



**Figure 2-2.** Delta Calculation parameters



**Figure 2-3.** Results display

If no reference peak is explicitly selected, a reference peak is automatically selected:

- If the first peaks of the measurement are standard peaks, the last one of them is used as a standard.
- If the last peaks of the measurement are standard peaks, the first one of them is used as standard.
- If no standard peak has been found at the start or end of the measurement, the first standard is used.

It is possible to select more than one reference peak. In this case, the average ratio of these peaks is used as the standard values in the  $\delta$  calculations.

## Atom Percent

Atom percent is the fractional abundance of an isotope expressed in percent:

$${}^{13}\text{Atom}\% = {}^{13}F \times 100 = \frac{{}^{13}\text{C}}{{}^{12}\text{C} + {}^{13}\text{C}} \times 100 \quad (5)$$

In the case of elements with two (dominating) isotopes, the fractional abundance can be calculated from the ratio, e.g.:

$${}^{13}F = \frac{{}^{13}\text{C}}{{}^{12}\text{C} + {}^{13}\text{C}} \quad (6)$$

$$= \frac{{}^{13}\text{C}/{}^{12}\text{C}}{{}^{12}\text{C}/{}^{12}\text{C} + {}^{13}\text{C}/{}^{12}\text{C}} \quad (7)$$

$$= \frac{{}^{13}R}{1 + {}^{13}R} \quad (8)$$

In this case atom percent values can be calculated this way:

$$\text{Atom}\% = 100 \times \frac{R}{1 + R} \quad (9)$$

They can be calculated from the delta values as well:

$$\text{Atom}\% = 100 \times \frac{R_{Std} \times \left( \frac{d}{1000} + 1 \right)}{1 + R_{Std} \times \left( \frac{d}{1000} + 1 \right)} \quad (10)$$

For elements with more isotopes, equations 6, 7 and 8 must be extended using the additional isotopes. For oxygen with the three isotopes  ${}^{16}\text{O}$ ,  ${}^{17}\text{O}$  and  ${}^{18}\text{O}$  this leads to:

$${}^{18}F = \frac{{}^{18}\text{O}}{{}^{16}\text{O} + {}^{17}\text{O} + {}^{18}\text{O}} \quad (11)$$

$$= \frac{{}^{18}R}{1 + {}^{17}R + {}^{18}R} \quad (12)$$

To be compatible with the calculations performed by Isodat, the atom percent values are calculated by Qtegra using equation 9 as if only two isotopes were present.

## Standards

The primary standards are the elemental ratios of reference substances. They are entered by the user in the Standard Editor.

**Table 2-1.** Common standards

Standards name	Isotopes	Ratio
VPDP (Vienna Pee Dee Belemnite)	$^{13}\text{C}/^{12}\text{C}$	0.0111802
	$^{18}\text{O}/^{16}\text{O}$	0.0020672
	$^{17}\text{O}/^{16}\text{O}$	0.0003860
Air-N <sub>2</sub>	$^{15}\text{N}/^{14}\text{N}$	0.0036782
VSMOV (Vienna Standard Mean Ocean Water)	$^2\text{H}/^1\text{H}$	0.00015575
	$^{18}\text{O}/^{16}\text{O}$	0.0020052
	$^{17}\text{O}/^{16}\text{O}$	0.0003799
CDT (Canon Diablo Meteorite)	$^{18}\text{O}/^{16}\text{O}$	0.0450045
	$^{17}\text{O}/^{16}\text{O}$	0.007878

Working standards are delta values measured for the primary standard with the setup used for the measurement. These values are entered into the Standard Editor as well.

From the working standard delta and the primary standard ratio, the working standard ratio can be calculated using equation 4.

During experiments the intensities of samples and standards are measured. Ratios are then calculated from the intensities. These measured ratios are molecular ratios, e.g.  $^3R$  or  $^{44}R$ . The molecular working standard ratios  $R_{wrk}$  must be calculated from the elemental standard values using equations obtained from the fractional abundances for the specific isotope system.

The standard ratios ( $R_{Std}$ ) are used to calibrate the sample ratios ( $R_{sample}$ ):

$$R_{calib} = \frac{R_{sample} \times R_{wrk}}{R_{Std}} \quad (13)$$

Qtegra IsoScale G supports various types of standard for different usages.

## Ref Gas Standards

Ref Gas Standards store the delta values of a reference substance used to calculate the delta values of unknown samples.

In the Delta Calculation parameters, delta values can be selected as standard.

## **Chromatography (CSIA) Standards**

Chromatography Standards store different delta values for different compounds of a reference substance.

They are selected in the Reference column of Chromatography LabBooks for Delta Standard (External Referencing), QC (Quality Control) and Ref Gas Calibration samples.

In EA LabBooks, Chromatography Standards can be selected for QC and Ref Gas Calibration samples.

## **EA (BSIA) Standards**

EA Standards provide weight percent standard values in addition to the delta values of the reference substance.

EA standards can be selected in EA LabBooks for Delta Standard (External Referencing), Weight Percent and Weight Percent and Delta Standard samples.

## **Dual Inlet Standards**

Like Ref Gas Standards, Dual Inlet Standards store the delta values of a reference substance.

The Dual Inlet standards are used in Dual Inlet LabBooks for Delta Standard (External Referencing), QC (Quality Control) and Ref Gas Calibration samples.



# Isotope Systems

This chapter describes the evaluation algorithms for the Qtegra ISDS Software used in the evaluation algorithms available by aQuant.

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## Hydrogen H<sub>2</sub>

The stable hydrogen isotopes used in GIRMS analyses are <sup>1</sup>H (99.9885%) and <sup>2</sup>H (0.0115%).

The fractional abundances of H<sub>2</sub> are

$${}^2F = {}^1F^1F \quad (14)$$

$${}^3F = 2 \times {}^1F^2F \quad (15)$$

This gives

$${}^3R = \frac{{}^3F}{{}^2F} = 2 \times {}^2R \quad (16)$$

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 2 and 3.

From the intensities, the  ${}^3R$  values are calculated for samples and standards.

The sample ratios  ${}^3R$  are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the calibrated molecular ratio  ${}^3R$  the elemental ratio  ${}^2R$ , delta  $\delta^2H$ , and atom percent  ${}^2Atom\%$  values can be calculated using equations 17, 3 and 10.

$${}^2R = {}^3R - 2 \times {}^2R \quad (17)$$

## Carbon Monoxide CO

The stable carbon isotopes used in GIRMS analyses are  ${}^{12}C$  (98.9%) and  ${}^{13}C$  (1.1%). The stable oxygen isotopes are  ${}^{16}O$  (99.757%),  ${}^{18}O$  (0.205%) and  ${}^{17}O$  (0.038%).

Assuming an equal statistical distribution of the isotopes, and no preferences in the molecule formation the abundances of the CO species are given by

$${}^{28}F = {}^{12}F^{16}F \quad (18)$$

$${}^{29}F = {}^{12}F^{17}F + {}^{13}F^{16}F \quad (19)$$

$${}^{30}F = {}^{12}F^{18}F + {}^{13}F^{17}F \quad (20)$$

Using equations 18, 19 and 20 we get formulas for the ratios  ${}^{29}R$  and  ${}^{30}R$ :

$${}^{29}R = \frac{{}^{29}F}{{}^{28}F} = {}^{13}R + {}^{17}R \quad (21)$$

$${}^{30}R = \frac{{}^{30}F}{{}^{28}F} = {}^{18}R + {}^{13}R^{17}R \quad (22)$$

The ratio  ${}^{17}R$  is calculated from  ${}^{18}R$  using the formula

$${}^{17}R = {}^{18}R^a \times K \quad (23)$$

The constants used by Qtegra are the values determined by Santrock, Studley and Hayes<sup>2</sup>:  $a = 0.516$  and  $K = 0.0099235$ . Alternative values can be entered by the user in the Delta Calculation editor.

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 28, 29 and 30.

From the intensities the  $^{29}R$  and  $^{30}R$  values are calculated for samples and standards.

The sample ratios are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the corrected molecular ratios, the elemental ratio can be calculated using equations 21 and 22:

$$^{13}R = ^{29}R - ^{17}R_{wrk} \quad (24)$$

$$^{18}R = ^{30}R - ^{13}R_{wrk} - ^{17}R_{wrk} \quad (25)$$

The  $^{17}R$  is calculated from  $^{18}R$  with equation 23.

From the ratios  $^{13}R$ ,  $^{17}R$ , and  $^{18}R$  the deltas  $\delta^{13}C$ ,  $\delta^{17}O$ , and  $\delta^{18}O$  and the according atom percent values can be calculated using equations 3 and 9.

## Carbon Dioxide CO<sub>2</sub>

The stable carbon isotopes used in GIRMS analyses are  $^{12}C$  (98.9%) and  $^{13}C$  (1.1%). The stable oxygen isotopes are  $^{16}O$  (99.757%),  $^{18}O$  (0.205%), and  $^{17}O$  (0.038%).

$$^{44}F = ^{12}F^{16}F^{16}F \quad (26)$$

$$^{45}F = 2 \times ^{12}F^{16}F^{17}F + ^{13}F^{16}F^{16}F \quad (27)$$

$$^{46}F = ^{12}F^{17}F^{17}F + 2 \times ^{12}F^{16}F^{18}F + 2 \times ^{13}F^{16}F^{17}F \quad (28)$$

Using equations 26, 27 and 28 we get formulas for the ratios <sup>45</sup>R and <sup>46</sup>R:

$${}^{45}R = \frac{{}^{45}F}{{}^{44}F} = {}^{13}R + 2 \times {}^{17}R \quad (29)$$

$${}^{46}R = \frac{{}^{46}F}{{}^{44}F} = 2 \times {}^{18}R + 2 \times {}^{13}R {}^{17}R + {}^{17}R {}^{17}R \quad (30)$$

<sup>13</sup>R and <sup>18</sup>R are determined numerically using the Newton-Raphson algorithm to find the roots of

$${}^{13}R + 2 \times {}^{17}R - {}^{45}R = 0 \quad (31)$$

$$2 \times {}^{18}R + 2 \times {}^{13}R {}^{17}R + {}^{17}R {}^{17}R - {}^{46}R = 0 \quad (32)$$

<sup>17</sup>R is calculated from <sup>18</sup>R with

$${}^{17}R = {}^{18}R^a \times K \quad (33)$$

The constants used by Qtegra are either the values determined by Brand, Assonov and Coplen<sup>5</sup> ( $a = 0.528$  and  $K = 0.01022444$ ), by Santrock, Studley and Hayes<sup>2</sup> ( $a = 0.516$  and  $K = 0.0099235$ ), or the values determined earlier by Craig<sup>1</sup> ( $a = 0.5$  and  $K = 0.008335$ ). Alternative values can be entered by the user in the Delta Calculation editor. To use the same conditions as in the mentioned publications, the appropriate primary standard ratios must be entered in the Standards editor.

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 44, 45 and 46.

From the intensities the <sup>45</sup>R and <sup>46</sup>R, values are calculated for samples and standards.

The sample ratios are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the ratios <sup>13</sup>R, <sup>17</sup>R and <sup>18</sup>R, the deltas  $\delta^{13}C$ ,  $\delta^{17}O$  and  $\delta^{18}O$  and the according atom percent values can be calculated using equations 3 and 9.

To calculate CO<sub>2</sub> delta values, it is necessary to specify standard values for both <sup>13</sup>R and <sup>18</sup>R because both are needed for the numerical solution of equation 31 and 32. The Delta Calculation editor in Qtegra displays an error message if this condition is not met. For standards used for Ref Gas Calibration, this is currently not the case.

## Carbon Dioxide Clumped

The CO<sub>2</sub> clumped calculation is used get the capital Δ values for the isotopologues with masses 47, 48, and 49 that contain more than one of the heavier C or O isotopes. This is the reason for the name “clumped”. The isotopes evaluated in this case are the same as in the CO<sub>2</sub> analyses (<sup>12</sup>C, and <sup>13</sup>C, and <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O).

The CO<sub>2</sub> clumped evaluation is performed using the abundances of the isotopes:

$${}^{12}A = \frac{1}{1 + {}^{13}R} \quad (34)$$

$${}^{13}A = \frac{{}^{13}R}{1 + {}^{13}R} \quad (35)$$

$${}^{16}A = \frac{1}{1 + {}^{17}R + {}^{18}R} \quad (36)$$

$${}^{17}A = \frac{{}^{17}R}{1 + {}^{17}R + {}^{18}R} \quad (37)$$

$${}^{18}A = \frac{{}^{18}R}{1 + {}^{17}R + {}^{18}R} \quad (38)$$

The isotopologue abundances are calculated from the isotope abundances using the permutations of the isotopes that can be used to create the isotopologue:

Mass 44: <sup>12</sup>C<sup>16</sup>O<sup>16</sup>O

$${}^{44}A = {}^{12}A({}^{16}A)^2 \quad (39)$$

Mass 45: <sup>12</sup>C<sup>16</sup>O<sup>17</sup>O, <sup>12</sup>C<sup>17</sup>O<sup>16</sup>O, <sup>13</sup>C<sup>16</sup>O<sup>16</sup>O

$${}^{45}A = {}^{13}A({}^{16}A)^2 + {}^{12}A{}^{16}A{}^{17}A \times 2 \quad (40)$$

Mass 46:  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ ,  $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ ,  $^{13}\text{C}^{16}\text{O}^{17}\text{O}$ ,  $^{13}\text{C}^{17}\text{O}^{16}\text{O}$ ,  $^{12}\text{C}^{17}\text{O}^{17}\text{O}$

$$^{46}A = ^{12}A^{16}A^{18}A \times 2 + ^{13}A^{16}A^{17}A \times 2 + ^{12}A(^{17}A)^2 \quad (41)$$

Mass 47:  $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ ,  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ ,  $^{13}\text{C}^{17}\text{O}^{17}\text{O}$ ,  $^{12}\text{C}^{17}\text{O}^{18}\text{O}$ ,  $^{12}\text{C}^{18}\text{O}^{17}\text{O}$

$$^{47}A = ^{13}A^{16}A^{18}A \times 2 + ^{13}A(^{17}A)^2 + ^{12}A^{17}A^{18}A \times 2 \quad (42)$$

Mass 48:  $^{13}\text{C}^{17}\text{O}^{18}\text{O}$ ,  $^{13}\text{C}^{18}\text{O}^{17}\text{O}$ ,  $^{12}\text{C}^{18}\text{O}^{18}\text{O}$

$$^{48}A = ^{13}A^{17}A^{18}A \times 2 + ^{12}A(^{18}A)^2 \quad (43)$$

Mass 49:  $^{13}\text{C}^{18}\text{O}^{18}\text{O}$

$$^{49}A = ^{13}A(^{18}A)^2 \quad (44)$$

The abundances can be used to calculate the mass abundance ratios, e.g.:

$$^{45}R_A = \frac{^{45}A}{^{44}A} \quad (45)$$

The capital deltas are then calculated from the mass abundance ratios and the reference sample ratios<sup>3,4</sup>:

$$\Delta_{47} = 1000 \times \left( \left( \frac{^{47}R}{^{47}A_A} - 1 \right) - \left( \frac{^{46}R}{^{46}R_A} - 1 \right) - \left( \frac{^{45}R}{^{45}R_A} - 1 \right) \right) \quad (46)$$

$$\Delta_{48} = 1000 \times \left( \left( \frac{^{48}R}{^{48}R_A} - 1 \right) - 2 \times \left( \frac{^{46}R}{^{46}R_A} - 1 \right) \right) \quad (47)$$

$$\Delta_{49} = 1000 \times \left( \left( \frac{^{49}R}{^{49}A_A} - 1 \right) - \left( \frac{^{46}R}{^{46}R_A} - 1 \right) - \left( \frac{^{45}R}{^{45}R_A} - 1 \right) \right) \quad (48)$$

## Nitrogen N<sub>2</sub>

The stable nitrogen isotopes used in GIRMS analyses are <sup>14</sup>N (99.6%) and <sup>15</sup>N (0.4%).

The fractional abundances of N<sub>2</sub> are

$${}^{28}F = {}^{14}F{}^{14}F \quad (49)$$

$${}^{29}F = 2 \times {}^{14}F{}^{15}F \quad (50)$$

This gives

$${}^{29}R = \frac{{}^{29}F}{{}^{28}F} = 2 \times {}^{15}R \quad (51)$$

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 28 and 29.

From the intensities the <sup>29</sup>R values are calculated for samples and standards. The sample ratios <sup>29</sup>R are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the calibrated molecular ratio <sup>29</sup>R the elemental ratio <sup>15</sup>R, delta δ<sup>15</sup>N and atom percent <sup>15</sup>Atom% values can be calculated using equations 52, 3 and 10.

$${}^{15}R = {}^{29}R - 2 \times {}^{28}R \quad (52)$$

## Nitrogen with Mass 30 Correction

The stable nitrogen isotopes used in GIRMS analyses are  $^{14}\text{N}$  (99.6%) and  $^{15}\text{N}$  (0.4%).

The fractional abundances of  $\text{N}_2$  are

$$^{28}\text{F} = {}^{14}\text{F}^{14}\text{F} \quad (53)$$

$$^{29}\text{F} = 2 \times {}^{14}\text{F}^{15}\text{F} \quad (54)$$

$$^{30}\text{F} = {}^{15}\text{F}^{15}\text{F} \quad (55)$$

This gives

$$^{29}\text{R} = \frac{{}^{29}\text{F}}{{}^{28}\text{F}} = 2 \times {}^{15}\text{R} \quad (56)$$

$$^{30}\text{R} = \frac{{}^{30}\text{F}}{{}^{28}\text{F}} = {}^{15}\text{R}^2 \quad (57)$$

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 28, 29, and 30.

From the intensities the  $^{29}\text{R}$  and  $^{30}\text{R}$  values are calculated for samples and standards. The sample ratios  $^{29}\text{R}$  and  $^{30}\text{R}$  are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the ratios  $^{29}\text{R}$  and  $^{30}\text{R}$  two values for the fractions  $^{15}\text{F}$  are calculated. Equation 56 gives with

$${}^{14}\text{F} = 1 - {}^{15}\text{F} \quad (58)$$

$$^{29}\text{R} = \frac{2 \times {}^{15}\text{F}}{{}^{14}\text{F}} \quad (59)$$

$$^{29}\text{R} = \frac{2 \times {}^{15}\text{F}}{1 - {}^{15}\text{F}} \quad (60)$$

$$^{29}\text{R}(1 - {}^{15}\text{F}) = 2 \times {}^{15}\text{F} \quad (61)$$

$$^{29}\text{R} - {}^{29}\text{R} \times {}^{15}\text{F} = 2 \times {}^{15}\text{F} \quad (62)$$



$${}^{29}R = 2 \times {}^{15}F + {}^{29}R \times {}^{15}F \quad (63)$$

$${}^{29}R = {}^{15}F \times (2 + {}^{29}R) \quad (64)$$

$${}^{15}F_{29} = \frac{{}^{29}R}{{}^{29}R + 2} \quad (65)$$

and equation 57 gives:

$${}^{30}R = \frac{{}^{15}F^2}{{}^{14}F^2} \quad (66)$$

$${}^{30}R \times {}^{14}F^2 = {}^{15}F^2 \quad (67)$$

$${}^{30}R \times (1 - {}^{15}F)^2 = {}^{15}F^2 \quad (68)$$

$$\sqrt{{}^{30}R} \times (1 - {}^{15}F) = {}^{15}F \quad (69)$$

$$\sqrt{{}^{30}R} - \sqrt{{}^{30}R} \times {}^{15}F = {}^{15}F \quad (70)$$

$$\sqrt{{}^{30}R} = {}^{15}F + {}^{15}F \times \sqrt{{}^{30}R} \quad (71)$$

$$\sqrt{{}^{30}R} = {}^{15}F \times (1 + \sqrt{{}^{30}R}) \quad (72)$$

$${}^{15}F_{30} = \frac{\sqrt{{}^{30}R}}{1 + \sqrt{{}^{30}R}} \quad (73)$$

From the two fractions for mass 15 a combined value is calculated by summing them weighted by the ratio on which they are based:

$${}^{15}F = {}^{15}F_{29} \times \frac{{}^{29}R}{{}^{29}R + {}^{30}R} + {}^{15}F_{30} \times \frac{{}^{30}R}{{}^{29}R + {}^{30}R} \quad (74)$$

The  ${}^{14}F$  value can be derived from the  ${}^{15}F$  value with equation 58. The fractions are then used to calculate the ratio  ${}^{15}R$ :

$${}^{15}R = \frac{{}^{15}F}{{}^{14}F} \quad (75)$$

With that the delta  $\delta^{15}N$  and atom percent  ${}^{15}Atom\%$  values can be calculated using equations 3 and 10.

## Nitrous Oxide N<sub>2</sub>O

The stable nitrogen isotopes used in GIRMS analyses are <sup>14</sup>N (99.6%) and <sup>15</sup>N (0.4%).

The stable oxygen isotopes are <sup>16</sup>O (99.757%), <sup>18</sup>O (0.205%) and <sup>17</sup>O (0.038%).

For this evaluation the nitrogen and oxygen isotopes <sup>14</sup>N, <sup>15</sup>N, <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O are used.

$${}^{44}F = {}^{14}F{}^{14}F{}^{16}F \quad (76)$$

$${}^{45}F = 2 \times {}^{14}F{}^{15}F{}^{16}F + {}^{14}F{}^{14}F{}^{17}F \quad (77)$$

$${}^{46}F = {}^{15}F{}^{15}F{}^{16}F + 2 \times {}^{14}F{}^{15}F{}^{17}F + {}^{14}F{}^{14}F{}^{18}F \quad (78)$$

Using equations 76, 77 and 78 we get formulas for the ratios <sup>45</sup>R and <sup>46</sup>R:

$${}^{45}R = \frac{{}^{45}F}{{}^{44}F} = 2 \times {}^{15}R + {}^{17}R \quad (79)$$

$${}^{46}R = \frac{{}^{46}F}{{}^{44}F} = {}^{15}R{}^{15}R + 2 \times {}^{15}R{}^{17}R + {}^{18}R \quad (80)$$

The ratio <sup>17</sup>R is calculated from <sup>18</sup>R using the formula 23:

$${}^{17}R = {}^{18}R^a \times K \quad (81)$$

with the Santrock, Studley and Hayes<sup>2</sup> values  $a = 0.516$  and  $K = 0.0099235$  by default. Alternative values can be entered by the user.

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 44, 45 and 46.

From the intensities the <sup>45</sup>R and <sup>46</sup>R values are calculated for samples and standards.

The sample ratios are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

Equations 79 and 80 can be used to get two equations

$$2 \times {}^{15}R + {}^{17}R - {}^{45}R = 0 \quad (82)$$

and

$$^{15}R^{15}R + 2 \times ^{15}R^{17}R + ^{18}R - ^{46}R = 0 \quad (83)$$

for the two unknowns  $^{15}R$  and  $^{18}R$  ( $^{17}R$  is calculated from equation 23). These two equations are solved numerically using the Newton-Raphson algorithm.

From the ratios  $^{15}R$ ,  $^{17}R$  and  $^{18}R$ , the deltas  $\delta^{15}N$ ,  $\delta^{17}O$  and  $\delta^{18}O$ , and the according atom percent values can be calculated using equations 3 and 9.

## Oxygen (O<sub>2</sub>)

The stable oxygen isotopes used in GIRMS analyses are  $^{16}O$  (99.757%),  $^{18}O$  (0.205%) and  $^{17}O$  (0.038%).

The fractional abundances of O<sub>2</sub> are:

$$^{32}F = ^{16}F^{16}F \quad (84)$$

$$^{33}F = 2 \times ^{16}F^{17}F \quad (85)$$

$$^{34}F = 2 \times ^{16}F^{18}F + ^{17}F^{17}F \quad (86)$$

This gives

$$^{33}R = \frac{^{33}F}{^{32}F} = 2 \times ^{17}R \quad (87)$$

$$^{34}R = \frac{^{34}F}{^{32}F} = 2 \times ^{18}R + ^{17}R^{17}R \quad (88)$$

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 32, 33 and 34.

From the intensities the  $^{33}R$  and  $^{34}R$  values are calculated for samples and standards.

The sample ratios are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the calibrated molecular ratios  $^{33}R$  and  $^{34}R$  the elemental ratios  $^{17}R$  and  $^{18}R$ , deltas  $\delta^{17}O$  and  $\delta^{18}O$  and atom percent  $^{17}Atom\%$  and  $^{18}Atom\%$  values can be calculated using equations 89, 90, 3, and 10.

$$^{17}R = \frac{^{33}R}{2} \quad (89)$$

$$^{18}R = \frac{(^{34}R - ^{17}R^{17}R)}{2} \quad (90)$$

## Oxygen Clumped

For the  $O_2$  clumped delta calculation the same calculations are performed as for the  $O_2$  delta calculation. Additionally, the ratios  $^{35}R$  and  $^{36}R$  are determined.

$$^{35}F = 2 \times ^{17}F^{18}F \quad (91)$$

$$^{36}F = ^{18}F^{18}F \quad (92)$$

This gives

$$^{35}R = \frac{^{34}F}{^{32}F} = 2 \times ^{17}R^{18}R \quad (93)$$

$$^{36}R = \frac{^{36}F}{^{32}F} = ^{18}R^{18}R \quad (94)$$

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 32, 33, 34, 35, and 36.

For the ratios  $^{35}R$  and  $^{36}R$  the deltas  $\delta^{35}O_2$  and  $\delta^{36}O_2$  are calculated using equation 3 and the capital deltas are calculated from<sup>6</sup>:

$$\Delta_{35} = \left( \frac{^{35}R_{measured}}{^{35}R} - 1 \right) \times 1000 \quad (95)$$

$$\Delta_{36} = \left( \frac{^{36}R_{measured}}{^{36}R} - 1 \right) \times 1000 \quad (96)$$

## Sulfur Oxide (SO)

The stable sulfur isotopes used in GIRMS analyses are  $^{32}\text{S}$  (94.93%),  $^{34}\text{S}$  (4.29%),  $^{33}\text{S}$  (0.76%), and  $^{36}\text{S}$  (0.02%). The stable oxygen isotopes are  $^{16}\text{O}$  (99.757%),  $^{18}\text{O}$  (0.205%) and  $^{17}\text{O}$  (0.038%).

### $^{32}\text{S}$ , $^{33}\text{S}$ , and $^{34}\text{S}$

$$^{48}\text{F} = ^{32}\text{F}^{16}\text{F} \quad (97)$$

$$^{49}\text{F} = ^{32}\text{F}^{17}\text{F} + ^{33}\text{F}^{16}\text{F} \quad (98)$$

$$^{50}\text{F} = ^{32}\text{F}^{18}\text{F} + ^{33}\text{F}^{17}\text{F} + ^{34}\text{F}^{16}\text{F} \quad (99)$$

Using equation 97, 98 and 99 we get formulas for the ratios  $^{49}\text{R}$  and  $^{50}\text{R}$ :

$$^{49}\text{R} = \frac{^{49}\text{F}}{^{48}\text{F}} = ^{33}\text{R} + ^{17}\text{R} \quad (100)$$

$$^{50}\text{R} = \frac{^{50}\text{F}}{^{48}\text{F}} = ^{18}\text{R} + ^{33}\text{R}^{17}\text{R} + ^{34}\text{R} \quad (101)$$

### $^{32}\text{S}$ , $^{33}\text{S}$ , $^{34}\text{S}$ , and $^{36}\text{S}$

$$^{48}\text{F} = ^{32}\text{F}^{16}\text{F} \quad (102)$$

$$^{49}\text{F} = ^{32}\text{F}^{17}\text{F} + ^{33}\text{F}^{16}\text{F} \quad (103)$$

$$^{50}\text{F} = ^{32}\text{F}^{18}\text{F} + ^{33}\text{F}^{17}\text{F} + ^{34}\text{F}^{16}\text{F} \quad (104)$$

$$^{52}\text{F} = ^{34}\text{F}^{18}\text{F} + ^{36}\text{F}^{16}\text{F} \quad (105)$$

Using equations 102, 103 and 104 we get formulas for the ratios  $^{49}\text{R}$  and  $^{50}\text{R}$ :

$$^{49}\text{R} = \frac{^{49}\text{F}}{^{48}\text{F}} = ^{33}\text{R} + ^{17}\text{R} \quad (106)$$

$$^{50}\text{R} = \frac{^{50}\text{F}}{^{48}\text{F}} = ^{18}\text{R} + ^{33}\text{R}^{17}\text{R} + ^{34}\text{R} \quad (107)$$

$$^{52}\text{R} = \frac{^{52}\text{F}}{^{48}\text{F}} = ^{34}\text{R}^{18}\text{R} + ^{36}\text{R} \quad (108)$$

The ratio  $^{17}R$  is calculated from  $^{18}R$  using the formula 23:

$$^{17}R = ^{18}R^a \times K \quad (109)$$

with the values  $a = 0.521$  and  $K = 0.0094912$ .

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 48, 49 and 50.

From the intensities, the  $^{49}R$  and  $^{50}R$  values are calculated for samples and standards.

The sample ratios are then calibrated using the measured standard ratios and the working standard ratio from the standard editor using equation 13.

From the corrected molecular ratios, the element ratio can be calculated using equations 100 and 101:

$$^{33}R = ^{49}R - ^{17}R_{wrk} \quad (110)$$

$$^{34}R = ^{50}R - ^{18}R_{wrk} - ^{17}R_{wrk} ^{33}R \quad (111)$$

From the ratios  $^{33}R$  and  $^{34}R$ , the deltas  $\delta^{33}S$  and  $\delta^{34}S$ , and the according atom percent values can be calculated using equations 3 and 9.

## Sulfur Dioxide (SO<sub>2</sub>)

The stable sulfur isotopes used in GIRMS analyses are  $^{32}S$  (94.93%),  $^{34}S$  (4.29%),  $^{33}S$  (0.76%), and  $^{36}S$  (0.02%). The stable oxygen isotopes are  $^{16}O$  (99.757%),  $^{18}O$  (0.205%) and  $^{17}O$  (0.038%).

### $^{32}S$ and $^{34}S$

Assuming an equal statistical distribution of the isotopes, and no preferences in the molecule formation the abundances of the SO<sub>2</sub> species are given by

$$^{64}F = ^{32}F^{16}F^{16}F \quad (112)$$

$$^{66}F = 2 \times ^{32}F^{16}F^{18}F + ^{34}F^{16}F^{16}F \quad (113)$$

Using equations 112 and 113 we get a formula for the ratio <sup>66</sup>R:

$${}^{66}R = \frac{{}^{66}F}{{}^{64}F} = {}^{34}R + 2 \times {}^{18}R \quad (114)$$

### <sup>32</sup>S, <sup>33</sup>S, and <sup>34</sup>S

Assuming an equal statistical distribution of the isotopes and no preferences in the molecule formation the abundances of the SO<sub>2</sub> species are given by

$${}^{64}F = {}^{32}F^{16}F^{16}F \quad (115)$$

$${}^{65}F = 2 \times {}^{32}F^{16}F^{17}F + {}^{33}F^{16}F^{16}F \quad (116)$$

$${}^{66}F = 2 \times {}^{32}F^{16}F^{18}F + {}^{32}F^{17}F^{17}F + 2 \times {}^{33}F^{16}F^{17}F + {}^{34}F^{16}F^{16}F \quad (117)$$

Using equations 116 and 117 with 115 we get formulas for the ratio <sup>65</sup>R and <sup>66</sup>R:

$${}^{65}R = \frac{{}^{65}F}{{}^{64}F} = {}^{33}R + 2 \times {}^{17}R \quad (118)$$

$${}^{66}R = \frac{{}^{66}F}{{}^{64}F} = 2 \times {}^{18}R + {}^{17}R^{17}R + 2 \times {}^{33}R^{17}R + {}^{34}R \quad (119)$$

### <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S

$${}^{64}F = {}^{32}F^{16}F^{16}F \quad (120)$$

$${}^{65}F = 2 \times {}^{32}F^{16}F^{17}F + {}^{33}F^{16}F^{16}F \quad (121)$$

$${}^{66}F = 2 \times {}^{32}F^{16}F^{18}F + {}^{32}F^{17}F^{17}F + 2 \times {}^{33}F^{16}F^{17}F + {}^{34}F^{16}F^{16}F \quad (122)$$

$${}^{68}F = {}^{32}F^{18}F^{18}F + {}^{34}F^{18}F^{16}F + {}^{36}F^{16}F^{16}F \quad (123)$$

Using equations 121, 122 and 123 with 120 we get formulas for the ratio <sup>65</sup>R, <sup>66</sup>R and <sup>68</sup>R:

$${}^{65}R = \frac{{}^{65}F}{{}^{64}F} = {}^{33}R + 2 \times {}^{17}R \quad (124)$$

$${}^{66}R = \frac{{}^{66}F}{{}^{64}F} = 2 \times {}^{18}R + {}^{17}R {}^{17}R + 2 \times {}^{33}R {}^{17}R + {}^{34}R \quad (125)$$

$${}^{68}R = \frac{{}^{68}F}{{}^{64}F} = {}^{18}R {}^{18}R + 2 \times {}^{34}R {}^{18}R + {}^{36}R \quad (126)$$

## Classical SO<sub>2</sub> Delta Calculation

For this evaluation only the most abundant sulfur and oxygen isotopes <sup>32</sup>S, <sup>34</sup>S, <sup>16</sup>O, and <sup>18</sup>O are used.

### Standard Values

Primary standards for SO<sub>2</sub> are <sup>18</sup>R and <sup>34</sup>R:

$$R_{primary} {}^{18}O/{}^{16}O = {}^{18}R_{primary} = 0.0020052 \text{ (VSMOW)} \quad (127)$$

$$R_{primary} {}^{34}S/{}^{32}OS = {}^{34}R_{primary} = 0.0450045 \text{ (CDT)} \quad (128)$$

Working standards are delta values measured for the primary standard with the setup used for the measurement. These values are entered into the standard editor as well.

$$d_{primary} {}^{18}O/{}^{16}O = {}^{18}d_{primary} = 0.0 \quad (129)$$

$$d_{primary} {}^{34}S/{}^{32}OS = {}^{34}d_{primary} = 0.0 \quad (130)$$

Equation 4 can be used to calculate the working standard ratio from the delta value:

$$R_{wrk} = \left( \frac{d_{wrk}}{1000} + 1 \right) \times R_{primary} \quad (131)$$

With our values we get

$${}^{18}R_{wrk} = 0.0020052 \quad (132)$$

$${}^{34}R_{wrk} = 0.0450045 \quad (133)$$



for the working standard ratios. (The same as the primary standard values because the delta value is zero.)

From the elemental standard ratios, the molecular standard ratio can be calculated:

$${}^{66}R_{wrk} = {}^{34}R_{wrk} + 2 \times {}^{18}R_{wrk} = 0.0490149 \quad (134)$$

## Evaluation of Measurements

Intensities for samples and standards are measured for the masses 66 and 64.

From the intensities the  ${}^{66}R$  values are calculated for samples and standards.

The sample ratios are then calibrated using the measured standard ratios and the working standard ratio from the standard editor:

$${}^{66}R_{calib} = {}^{66}R_{sample} \times \frac{{}^{66}R_{wrk}}{{}^{66}R_{Std}} \quad (135)$$

This calibrated ratio can be used to get the  ${}^{34}R$  of the sample using equation 114:

$${}^{34}R = {}^{66}R_{calib} - 2 \times {}^{18}R_{wrk} \quad (136)$$

The sulfur delta is calculated from equation 3:

$$\delta^{34}S = \left( \frac{{}^{34}R}{{}^{34}R_{primary}} - 1 \right) \times 1000 \quad (137)$$

The  ${}^{34}d$  value can be used to get the atom percent for  ${}^{34}S$  with equation 9:

$${}^{34}Atom\% = 100 \times \frac{{}^{34}R_{primary} \times \left( \frac{{}^{34}d}{1000} + 1 \right)}{1 + {}^{34}R_{primary} \times \left( \frac{{}^{34}d}{1000} + 1 \right)} \quad (138)$$

$$= 100 \times \frac{{}^{34}R}{1 + {}^{34}R} \quad (139)$$

## SO<sub>2</sub> (Masses 64, 65, 66) Delta Calculation

For this evaluation the isotopes <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O are used.

### Standard Values

$$R_{primary}^{18}O/^{16}O = {}^{18}R_{primary} = 0.0020052 \text{ (VSMOW)} \quad (140)$$

$$R_{primary}^{17}O/^{16}O = {}^{17}R_{primary} = 0.0003799 \text{ (VSMOW)} \quad (141)$$

$$R_{primary}^{34}S/^{32}OS = {}^{34}R_{primary} = 0.0450045 \text{ (CDT)} \quad (142)$$

$$R_{primary}^{33}S/^{32}OS = {}^{33}R_{primary} = 0.0078780 \text{ (CDT)} \quad (143)$$

With delta values of 0 using equation 4 the working standard ratios <sup>18</sup>R<sub>wrk</sub> and <sup>34</sup>R<sub>wrk</sub> are the same as <sup>18</sup>R<sub>primary</sub> and <sup>34</sup>R<sub>primary</sub>.

The ratios <sup>17</sup>R and <sup>33</sup>R are calculated from <sup>18</sup>R and <sup>34</sup>R using equation 23.

With  $a = 0.521$  and  $K = 0.0094912$  for oxygen we get

$${}^{17}R_{wrk} = 0.0003730313 \quad (144)$$

and with  $a = 0.515$  and  $K = 0.03924$  for sulfur we get

$${}^{34}R_{wrk} = 0.0079461326 \quad (145)$$

Using equations 118 and 119 the molecular standard ratios can be calculated:

$${}^{65}R_{wrk} = 0.0086921952 \quad (146)$$

$${}^{66}R_{wrk} = 0.0490209675 \quad (147)$$

### Evaluation of Measurements

Intensities for samples and standards are measured for the masses 66, 65 and 64.

From the intensities the <sup>65</sup>R and <sup>66</sup>R values are calculated for samples and standards and corrected with the working standard using equation 13.

From the corrected molecular ratios, the element ratio can be calculated using equations 118 and 119:

$${}^{33}R = {}^{65}R - 2 \times {}^{17}R_{wrk} \quad (148)$$

$${}^{34}R = {}^{66}R - 2 \times {}^{18}R_{wrk} - 2 \times {}^{17}R_{wrk} {}^{33}R - {}^{17}R_{wrk}^2 \quad (149)$$

From the ratios  ${}^{33}R$  and  ${}^{34}R$ , the deltas  $\delta^{33}S$  and  $\delta^{34}S$  and the according atom percent values can be calculated using equations 3 and 9.

The  ${}^{17}d$  value is calculated from the  ${}^{17}R_{wrk}$  ratio calculated with equation 23 and the primary standard ratio  ${}^{17}R_{primary}$  using equation 3.

$$\delta^{17}O = \left( \frac{{}^{17}R_{wrk}}{{}^{17}R_{primary}} - 1 \right) \times 1000 = -18.080284 \quad (150)$$

## SO-SO<sub>2</sub> Extended Delta Calculation

### Standard Values

Primary standards for SO are  ${}^{18}R$ ,  ${}^{17}R$ ,  ${}^{34}R$ , and  ${}^{33}R$ :

$${}^{18}R_{primary} = 0.0020052 \text{ (VSMOW)} \quad (151)$$

$${}^{34}R_{primary} = 0.0450045 \text{ (CDT)} \quad (152)$$

$${}^{33}R_{primary} = 0.0078780 \text{ (CDT)} \quad (153)$$

The ratio  ${}^{17}R$  is calculated from  ${}^{18}R$  using the equation 23. With  $a = 0.521$  and  $K = 0.0094912$  for oxygen we get

$${}^{17}R_{wrk} = 0.0003730313 \quad (154)$$

### Evaluation of Measurements

Intensities for samples and standards are measured for the masses 48, 49, 50, 64, 65, and 66.

From the intensities the  ${}^{49}R$ ,  ${}^{50}R$ ,  ${}^{65}R$ , and  ${}^{66}R$  values are calculated for samples and standards and corrected with the working standard using equation 13.

From the corrected molecular ratios, the element ratio can be calculated using equations 100, 101, 118, and 119:

$$^{33}R = 2 \times ^{49}R - ^{65}R \quad (155)$$

<sup>17</sup>R can be calculated either from <sup>49</sup>R or <sup>65</sup>R

$$^{17}R_{49R} = ^{49}R - ^{33}R \quad (156)$$

$$^{17}R_{65R} = \frac{(^{65}R - ^{33}R)}{2} \quad (157)$$

<sup>17</sup>R<sub>49R</sub> is used as the result for <sup>17</sup>R.

$$^{34}R = 2 \times ^{50}R - ^{66}R + ^{17}R_{49R} \ ^{17}R_{49R} \quad (158)$$

<sup>18</sup>R can be calculated from <sup>50</sup>R or <sup>66</sup>R:

$$^{18}R_{50R} = ^{50}R - ^{17}R_{49R} \times ^{33}R - ^{34}R \quad (159)$$

$$^{18}R_{66R} = \frac{(^{66}R - 2 \times ^{17}R_{65R} \times ^{33}R - ^{34}R - ^{17}R_{65R} \times ^{17}R_{65R})}{2} \quad (160)$$

The resulting <sup>18</sup>R is the average value of the two ratios:

$$^{18}R = \frac{(^{18}R_{50R} + ^{18}R_{66R})}{2} \quad (161)$$

From the ratios <sup>18</sup>R, <sup>33</sup>R, and <sup>34</sup>R, the deltas δ<sup>18</sup>O, δ<sup>33</sup>S, and δ<sup>34</sup>S and the according atom percent values can be calculated using equations 3 and 9.

δ<sup>17</sup>O is calculated from <sup>17</sup>R<sub>49R</sub> and the converted working standard <sup>17</sup>R<sub>wrk</sub>

$$\delta^{17}O = \left( \frac{^{17}R_{49R}}{^{17}R_{wrk}} - 1 \right) \times 1000 \quad (162)$$

## SO-SO<sub>2</sub> For <sup>36</sup>S Delta Calculation

### Standard Values

Primary standards for SO are <sup>18</sup>R, <sup>17</sup>R, <sup>34</sup>R, and <sup>33</sup>R:

$$^{18}R_{primary} = 0.0020052 \text{ (VSMOW)} \quad (163)$$

$$^{17}R_{primary} = 0.0003799 \text{ (VSMOW)} \quad (164)$$

$$^{34}R_{primary} = 0.0450045 \quad \text{(CDT)} \quad (165)$$

$$^{33}R_{primary} = 0.0078780 \quad \text{(CDT)} \quad (166)$$

$$^{36}R_{primary} = 1.00000 \quad \text{(CDT)} \quad (167)$$

The ratio <sup>17</sup>R is calculated from <sup>18</sup>R using the equation 23. With  $a = 0.521$  and  $K = 0.0094912$  for oxygen we get

$$^{17}R_{work} = 0.0003730313 \quad (168)$$

### Evaluation of Measurements

Intensities for samples and standards are measured for the masses 48, 49, 50, 52, 64, 65, 66 and 68.

From the intensities the <sup>49</sup>R, <sup>50</sup>R, <sup>52</sup>R, <sup>65</sup>R, <sup>66</sup>R, and <sup>68</sup>R values are calculated for samples and standards and corrected with the working standard using equation 13.

From the corrected molecular ratios, the element ratio can be calculated using equations 106, 107, 108, 124, 125, and 126:

$$^{33}R = 2 \times ^{49}R - ^{65}R \quad (169)$$

<sup>17</sup>R can be calculated from <sup>49</sup>R

$$^{17}R_{49R} = ^{49}R - ^{33}R \quad (170)$$

<sup>17</sup>R<sub>49R</sub> is used as the result for <sup>17</sup>R.

$$^{34}R = 2 \times ^{50}R - ^{66}R + ^{17}R_{49R} \quad (171)$$

<sup>18</sup>R can be calculated from <sup>50</sup>R or <sup>66</sup>R:

$${}^{18}R_{50R} = {}^{50}R - {}^{17}R_{49R} \times {}^{33}R - {}^{34}R \quad (172)$$

$${}^{18}R_{66R} = \frac{({}^{66}R - 2 \times {}^{17}R_{65R} \times {}^{33}R - {}^{34}R - {}^{17}R_{65R} \times {}^{17}R_{65R})}{2} \quad (173)$$

The resulting <sup>18</sup>R is the average value of the two ratios:

$${}^{18}R = \frac{({}^{18}R_{50R} + {}^{18}R_{66R})}{2} \quad (174)$$

<sup>36</sup>R can be calculated from <sup>52</sup>R or <sup>68</sup>R:

$${}^{36}R_{52R} = {}^{52}R - {}^{34}R {}^{18}R_{50R} \quad (175)$$

$${}^{36}R_{68R} = {}^{68}R - {}^{18}R {}^{18}R - 2 \times {}^{34}R {}^{18}R \quad (176)$$

The resulting <sup>36</sup>R is the average value of the two ratios:

$${}^{36}R = \frac{({}^{36}R_{52R} + {}^{36}R_{68R})}{2} \quad (177)$$

From the ratios <sup>18</sup>R, <sup>33</sup>R, and <sup>34</sup>R, the deltas δ<sup>18</sup>O, δ<sup>33</sup>S, and δ<sup>34</sup>S and the according atom percent values can be calculated using equations 3 and 9.

δ<sup>17</sup>O is calculated from <sup>17</sup>R<sub>49R</sub> and the converted working standard <sup>17</sup>R<sub>wrk</sub>

$$\delta^{17}O = \left( \frac{{}^{17}R_{49R}}{{}^{17}R_{wrk}} - 1 \right) \times 1000 \quad (178)$$

## Blank Correction

Blank correction can only be applied to EA measurements.

Blank corrections are performed by measuring an empty sample. The sample delta values ( $\delta$ ) are then corrected with the delta of blank scaled by the peak area ( $A$ ):

$$\delta_{corr} = \frac{\delta_{sample}A_{sample} - \delta_{blank}A_{blank}}{A_{sample} - A_{blank}} \quad (179)$$

If samples are diluted, the blank peak area is corrected ( $A_{corr}$ ) for the blank and sample dilution before use in equation 179:

$$A_{corr} = \frac{A_{blank} \times (1 - dilution_{sample})}{(1 - dilution_{blank})} \quad (180)$$

where

*dilution* = value between 0 (undiluted sample is measured) and 1 (only the diluent is measured and the correction cannot be applied)

In Qtegra ISDS Software, the blank correction from a 'Blank' sample is applied to all following samples until another 'Blank' sample is defined. Samples before the first 'Blank' sample are not blank-corrected.

Multiple adjacent 'Blank' samples are averaged.

If a 'Blank' sample is not evaluated (using the checkbox in the Sample List), it is not applied to the following samples.

The blank correction is applied to the first non-standard peak of each measurement of a sample.





## Drift Correction

The drift of measured delta values ( $\delta$ ) during a LabBook run can be compensated by measuring Drift Correction samples (e.g., every 5–10 samples). Drift correction is performed based on the slope of the  $\delta$  values in these Drift Correction samples.

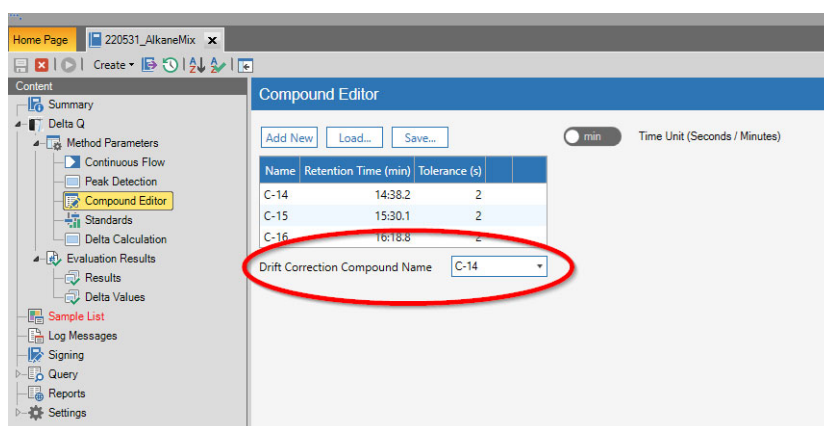
It is not necessary to specify a standard for a drift correction sample. Drift correction is only based on the change of measured delta values. Obviously the same sample must be used for all drift correction samples.

A linear regression line is fitted through the  $\delta$  values vs. measurement time  $t_{sample}$  (sample start time). The slope  $m$  of that line is then used to correct the other samples:

$$\delta_{corr} = \delta_{measured} - m \times t_{sample} \quad (181)$$

In **Dual Inlet measurements**, a slope is determined for each measured  $\delta$  value and then used to correct the  $\delta$  values of all samples.

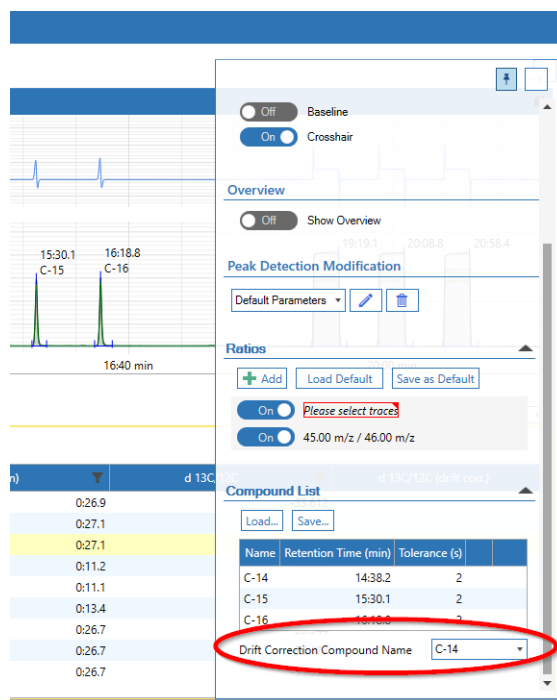
For **Time Resolved measurements**, in the Compound editor, a compound can be selected for use for drift correction. If such a compound is specified, the drift correction is performed based on the measured delta values of the peak with that compound. This works best for GC and LC measurements.



**Figure 5-4.** Compound Editor: Selecting the compound for drift correction

If **no drift correction compound** is specified, the linear regression is performed for each peak in the Drift Correction samples separately. The peaks of all other samples are corrected using the slope of the matching drift correction peak, which is suitable for EA measurements. Matching

peak means that the retention time of the peaks differ by less than 2 seconds (which is the same value as used to assign compounds to peaks, by default).



**Figure 5-5.** Compound List: Selection of compound for drift correction

For **GasBench measurements**, where the average values of deltas over multiple peaks are calculated, the drift correction is performed on the average values only and so working in the same way as in Dual Inlet measurements.

## External Referencing

External referencing corrects sample delta values with delta values of standards that were measured under the same conditions as the samples.

Multiple adjacent reference samples with the same standard are treated as one reference block. The average delta value of the samples in the reference block is used for correction.

Only reference blocks before an unknown are used to correct deltas of the unknown sample.

In chromatography measurement, standard values are assigned to individual peaks using the peak's compound names. The standard and the measured deltas of the peaks are used as individual points in the referencing.

### Contents

- [One Point Referencing](#) on page 6-2
- [Two Point Referencing](#) on page 6-2
- [Referencing with more than two Standards](#) on page 6-2
- [Reference Gas Calibration using an External Standard in Qtegra GC-IRMS](#) on page 6-3

## One Point Referencing

One point referencing is used when one reference standard is used to correct the sample delta values.

The correction factor  $c$  is calculated using the following equation:

$$c = \frac{\delta_{Std} - \delta_{meas}}{\frac{\delta_{meas}}{1000} + 1} \quad (182)$$

The correction factor is applied to the sample values using equation 183:

$$\delta' = \delta + c + \frac{\delta c}{1000} \quad (183)$$

## Two Point Referencing

For two point referencing two reference standards are used to correct the sample delta values.

Two correction factors *stretch* and *shift* are determined from the two standard delta values.

$$stretch = \frac{\delta_{Std1} - \delta_{Std2}}{\delta_{meas1} - \delta_{meas2}} \quad (184)$$

$$shift = \delta_{Std2} - \delta_{meas2} \times stretch \quad (185)$$

The correction factor is applied to the sample values using equation 186:

$$\delta' = \delta \times stretch + shift \quad (186)$$

## Referencing with more than two Standards

When more than two reference standards are used for correction, the shift and stretch values are determined from a linear regression over the reference deltas and the measured deltas of the standards.

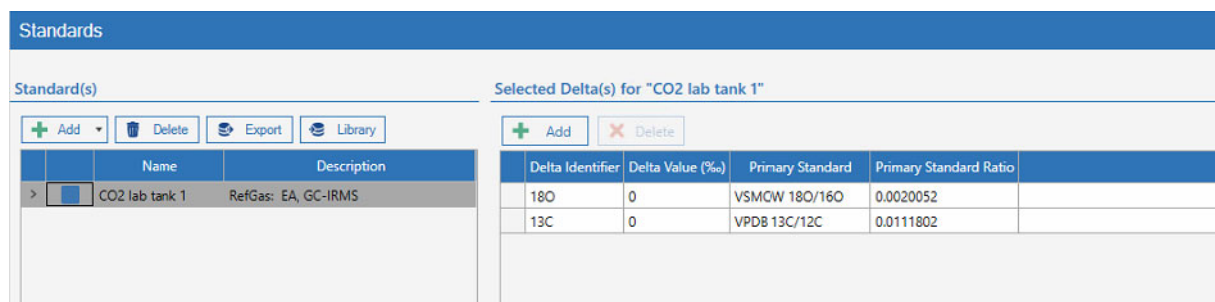
The shift value is the intercept from the linear regression and stretch is the slope.

Equation 186 is used to correct the sample delta values.

## Reference Gas Calibration using an External Standard in Qtegra GC-IRMS

### ❖ To use an external standard for reference gas calibration

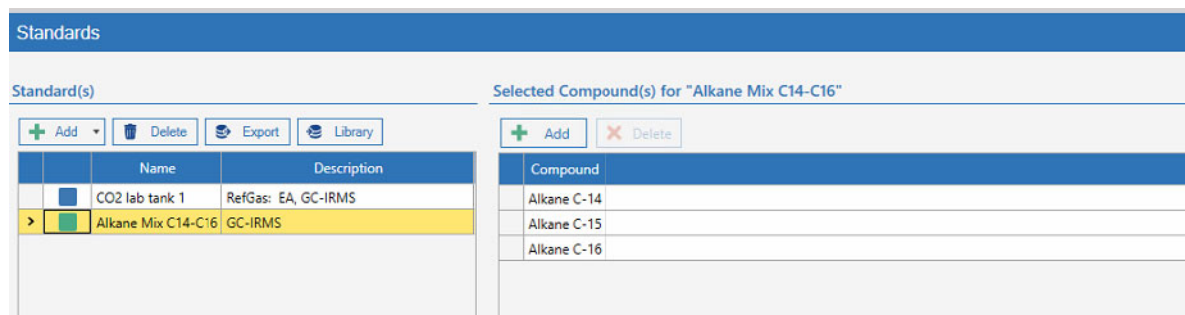
1. Assign your (CO<sub>2</sub>) laboratory tank standard in the Standards tab of the LabBook. Here, the 13C Delta Value ( $\delta^{13}\text{C}$ ) is set as 0‰ assuming the laboratory tank value is unknown.



Standard(s)		Selected Delta(s) for "CO2 lab tank 1"			
Name	Description	Delta Identifier	Delta Value (‰)	Primary Standard	Primary Standard Ratio
CO2 lab tank 1	RefGas: EA, GC-IRMS	18O	0	VSMOW 18O/16O	0.0020052
		13C	0	VPDB 13C/12C	0.0111802

**Figure 6-6.** LabBook Standards tab - 13C Delta Value

2. Assign your External Reference Standard mixture (here; Alkane Mix C14-C16).



Standard(s)		Selected Compound(s) for "Alkane Mix C14-C16"	
Name	Description	Compound	
CO2 lab tank 1	RefGas: EA, GC-IRMS	Alkane C-14	
Alkane Mix C14-C16	GC-IRMS	Alkane C-15	
		Alkane C-16	

**Figure 6-7.** Selecting compounds for Alkane Mix C14-C16

3. Select each compound of the external standard that is used for Reference Gas Calibration and **only** insert  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values (set  $\delta^{18}\text{O}$  to 0 as alkane has no oxygen).

The elements (C, O) and primary standards must be compatible between laboratory tank and external reference. Otherwise, the calculation will fail.

## External Referencing

Reference Gas Calibration using an External Standard in Qtegra GC-IRMS

The screenshot shows the 'Standards' window with three main sections:

- Standard(s):** A table with columns 'Name' and 'Description'. It lists 'CO2 lab tank 1' (RefGas: EA, GC-IRMS) and 'Alkane Mix C14-C16 GC-IRMS'.
- Selected Compound(s) for "Alkane Mix C14-C16":** A table with a 'Compound' column. It lists 'Alkane C-14', 'Alkane C-15', and 'Alkane C-16'. 'Alkane C-14' is highlighted.
- Selected Delta(s) for "Alkane C-14":** A table with columns 'Delta Identifier', 'Delta Value (%)', 'Primary Standard', and 'Primary Standard Ratio'. It lists two deltas: '13C' (Delta Value: -31.3, Primary Standard: VPDB 13C/12C, Ratio: 0.0111802) and '18O' (Delta Value: 0, Primary Standard: VSMOW 18O/16O, Ratio: 0.0020052).

**Figure 6-8.** Selecting Deltas for the compounds

4. In the Sample List, assign the Reference Gas Calibration standard if not already assigned. Select the correct external standard mixture as reference.

The screenshot shows the 'Sample List' window with a table of samples:

	Label	Status	Comment	Evaluate	Sample Type	Reference	Vial	Inject Volume [µl]	Inject
1	Alkane	●	<Comment>	☑	Ref Gas Calibration	Alkane Mix C14-C16	1	0.5	☑
2	Alkane	●	<Comment>	☑	Unknown		1	0.5	☑
3	Alkane	●	<Comment>	☑	Unknown		1	0.5	☑
4	Alkane	●	<Comment>	☑	Unknown		1	0.5	☑
5	Alkane	●	<Comment>	☑	Unknown		1	0.5	☑

**Figure 6-9.** Assigning the Ref Gas Calibration standard in the Sample List

5. Select the Results menu of Qtegra ISDS Software and check the value of Ref Gas Calibration standard (first row).

The reference gas pulse is calibrated according to the external reference values.

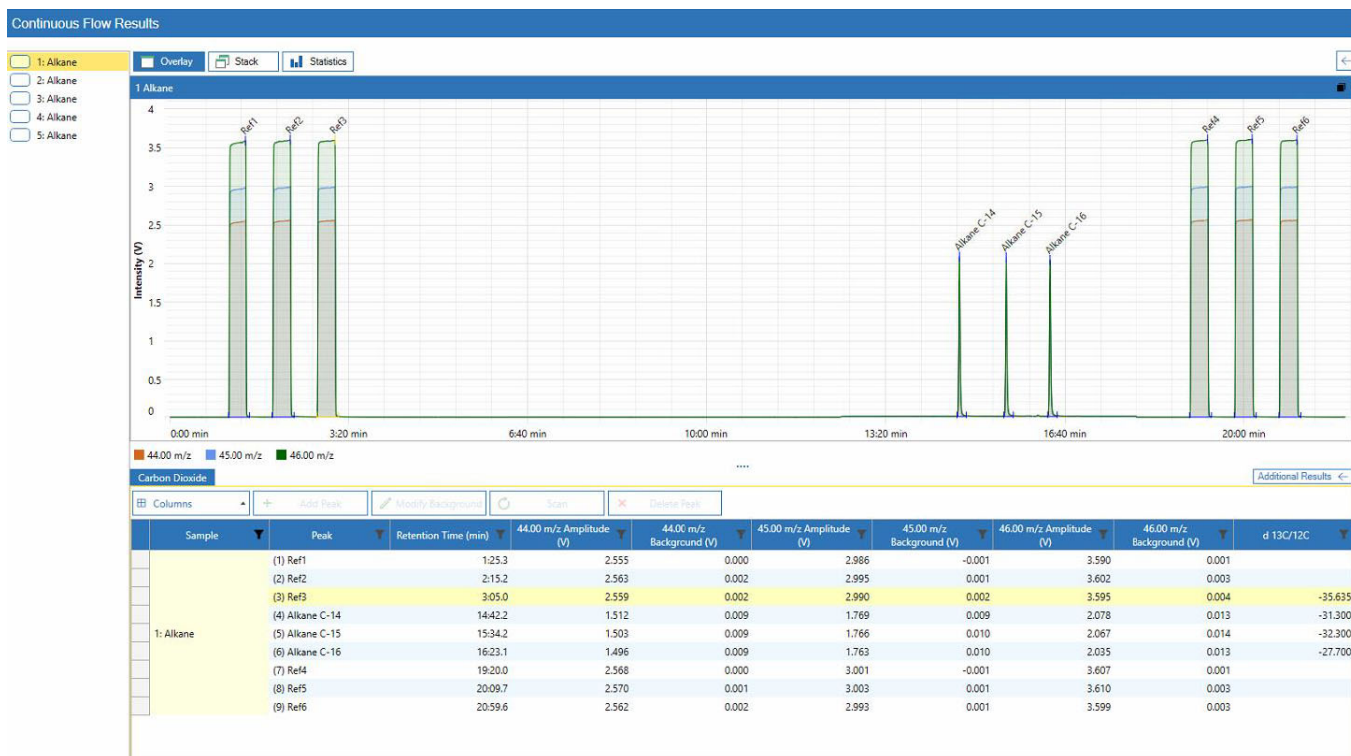


Figure 6-10. Checking the Ref Gas Calibration on the Results menu - 1: Alkane

6. Check the sample values. All Delta values are calculated based on the calibrated reference gas value.

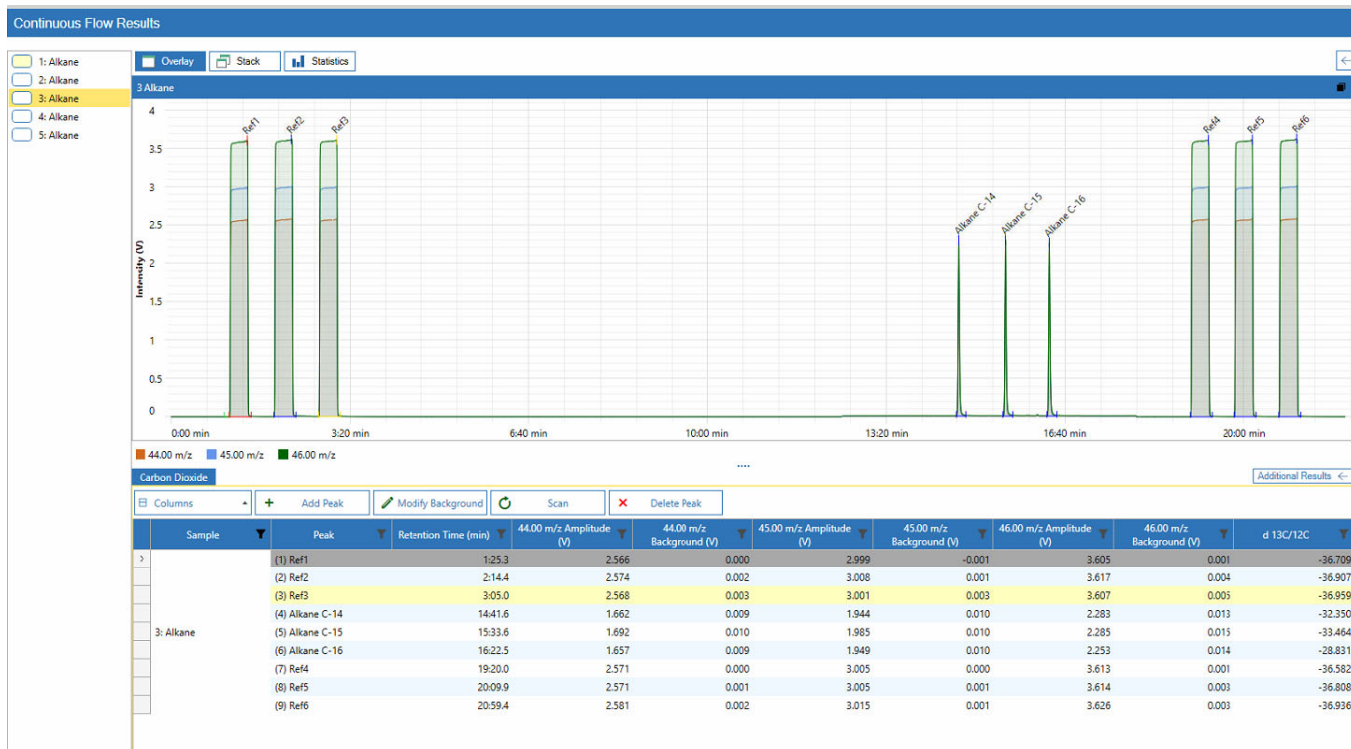


Figure 6-11. Checking the Ref Gas Calibration on the Results menu - 3: Alkane

## External Referencing

Reference Gas Calibration using an External Standard in Qtegra GC-IRMS



## Order of Correction

The corrections are performed in the following fixed order:

1. Linearity / H<sub>3</sub> correction (immediately after measurement or peak detection)
2. Blank Correction
3. Drift Correction
4. External Referencing

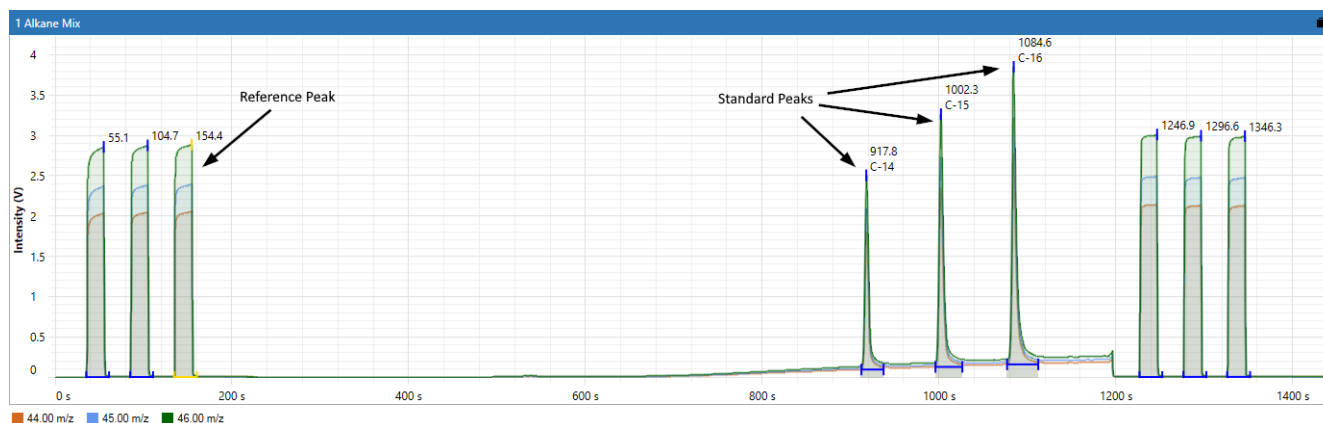
## Order of Correction

## Ref Gas Calibration

Ref Gas Calibration samples are used to correct the Reference Gas Standards used in delta calculations. The correction is performed by measuring a known standard and calculating an offset between the known standard and the Ref Gas Standard. This offset is then used to update the Ref Gas Standard delta for the following samples.

Practically, this is done by measuring a standard in a Ref Gas Calibration sample and calculating the delta values of the Reference Peak(s) using the measured standard. From these measured delta values for the Reference Peak(s) and the Reference Gas delta from the Standard list, an offset is calculated. This offset is then used to correct the Reference Gas Standard delta in the following measurements.

For dual inlet measurements, the Reference Gas Standard delta values are calculated using the known Dual Inlet Standard measured as the sample. This delta should be ideally be the delta value of the Reference Gas Standard. In reality, this will not be the case and the difference between measured delta and standard delta is used to calculate an offset to correct the standard in its later usages.



**Figure 8-1.** Ref Gas Calibration in chromatography measurements

For **Flash EA and chromatography measurements**, the procedure is essentially the same (see [Figure 8-1](#)): The delta values for the reference peaks are calculated using the sample peaks from the measured (CSIA) standard as reference. If multiple reference and sample peaks with standard information are available, all these peaks are used individually to calculate the reference delta and the offset to the delta of the reference standard. The average of the offsets is used to correct the further standard applications.

In **chromatography measurements**, the compounds assigned to the peaks must match the compounds identifying the individual standards in the CSIA standard.

If more than one Ref Gas Calibration sample is measured in a LabBook, the correction from a later sample is applied to the previous corrected sample. Individual corrections from chromatography peaks are as well applied in the order they were determined.

In each Ref Gas Calibration sample for each delta value in the standard, an offset is calculated that is applied to the standard in all following samples:

$$offset = \frac{\delta_{sample} - \delta_{std}}{\frac{\delta_{sample}}{1000} + 1} \quad (187)$$

The corrected working standard delta is then calculated from the working standard's delta and the offset:

$$\delta' = \delta + offset + \frac{\delta \times offset}{1000} \quad (188)$$

The delta values reported by Qtegra for the reference peaks of Ref Gas Calibration samples are the average values of the deltas calculated from the individual standard peaks (see [Figure 8-1](#)).

In the following, on Ref Gas Calibration samples, the delta values reported for the reference peaks are the corrected Ref Gas Standard values that are used in the delta calculations of these samples.

If a LabBook contains multiple Ref Gas Standards, the corrections of following samples are applied to the Ref Gas Standard values corrected by the previous corrections. This means that the corrections are chained.

## Weight Percent Calculation

In EA measurements the weight percent values for the individual elements (C, N, S, O, and H) can be determined. The Weight Percentages are calculated from the areas of the peaks for the individual elements on the TCD trace. The elements for the TCD peaks are determined from their retention time. The sample drop time (from the LabBook's method parameters) and the EA Transfer Time (from the Experiment Configuration) are added to the retention time and the TuneBook that was active at that time determines the element for the TCD peak.

The sample weight must be specified in the Sample List.

At least one Weight Percent standard sample must be measured in the LabBook. The standardization is then used in all following samples to determine the Weight Percent values.

For the standards the K-factor  $K$  is calculated using the sample weight *amount*, the known weight percent *wt%* and the peak area *area*:

$$K = \frac{wt\% \times amount}{area} \quad (189)$$

The K-factor is used to calculate the weight percent values for the following unknown samples:

$$wt\% = \frac{K \times area}{amount} \quad (190)$$

If more than one standard is used, the resulting K-factor can be either determined as the average values of all K-factors or from a linear regression of K-factor vs. area. The algorithm to be used can be selected in the Peak Detection parameters for the TCD (FlashEA) trace as Weight Percentage Calculation / Calibration Algorithm.

## Weight Percent Calculation

## Peak Finder

The peak finder in chromatography or FlashEA measurements uses the same algorithms and produces the same results as the peak finder used by the predecessor Isodat software.

The peak finder operates on the measured intensities on the Volt scale. After the peak finder has located and evaluated the peaks, the resulting areas ( $area_{corr}$ ) are scaled to the correct magnitude by scaling the values ( $area_{meas}$ ) with the amplifier resistance:

$$area_{corr} = \frac{area_{meas} \times R_{det}}{R_{trace}} \quad (191)$$

where

$R_{det}$  is the amplifier resistance of the detection trace

$R_{trace}$  is the amplifier resistance of the corrected trace

Ratios displayed in the chromatogram view of the Qtegra ISDS Software are calculated from the uncorrected (for amplifier resistance) Volt intensities.





## Dual Inlet

Qtegra IsoScale G supports three evaluation methods for Dual Inlet measurements.

<b>Change Over</b>	Multiple cycles of standard and sample measurements are performed. Ratios and deltas are calculated from the sample and standard intensity of one cycle.
<b>LIDI</b>	<p>In the beginning, multiple cycles of sample measurements are performed followed by the same number of standard measurements.</p> <p>Before the standard measurements are performed, the standard intensity is set to the same intensity as the previous sample measurement using pressure adjustment. Ratios and deltas are calculated from the sample and standard intensity of the same cycle number.</p>
<b>LIDI2 (LIDI bracketed)</b>	<p>The measurement is performed as LIDI. A standard block is measured before the first sample block and the actual standard value is calculated from the standard measured before and after the sample.</p> <p>The standard ratios of the pre- and post-standard measurements are fitted with a linear regression against the major mass intensities. To determine the standard ratio for a specific sample intensity, the standard ratios for that intensity are calculated from the linear fits.</p> <p>A linear interpolation is used between the two standard ratios to get the standard ratio at the time of the sample measurement.</p> <p>The reported end result for a sample are the average deltas with their standard deviation.</p>



## Data Categories

### Continuous Flow

<b>PeakData</b>	Contains per peak data (times, areas, ratios, deltas).
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### Dual Inlet

<b>BackgroundInterferenceCorrected</b>	Interference corrected background values.
<b>BackgroundInterferenceCorrection</b>	Interference correction values that were applied to the background values,
<b>BackgroundAverage</b>	Average of the (possibly interference corrected) background values.
<b>BackgroundStdDev</b>	Standard deviation of the (possibly interference corrected) background values.
<b>MeasureInterferenceCorrected</b>	Interference corrected measurement values.
<b>MeasureInterferenceCorrection</b>	Interference correction values that were applied to the measurement values.
<b>BackgroundCorrectedIntensity</b>	Background and possibly interference corrected intensities.
<b>PreStandardIntensity</b>	LIDI2 only: Standard intensities of the pre-ref measurement.
<b>PreStandardIntensityCorrection</b>	LIDI2 only: Interference correction values that were applied to the standard intensities of the pre-ref measurement.
<b>RawRatio</b>	LIDI2 only: The ratios calculated from the pre-ref standard intensities.
<b>RawPreStandardRatio</b>	LIDI2 only: Standard ratios of the pre-ref measurement (same values as RawRatio).
<b>SampleIntensity</b>	The sample intensities.

<b>SampleIntensityCorrection</b>	Interference correction values that were applied to the sample intensities.
<b>StandardIntensity</b>	The standard intensities.
<b>StandardIntensityCorrection</b>	Interference correction values that were applied to the standard intensities.
<b>RawSampleRatio</b>	The ratios calculated from the sample intensities.
<b>RawStandardRatio</b>	The ratios calculated from the standard intensities.
<b>StandardRatio</b>	The standard ratios (LIDI2 corrected in case of LIDI2).
<b>PreRefIntensityCategoryKey</b>	LIDI2 only: The pre-ref intensities calculated from the pre-ref standard ratios (RawPre-StandardRatio).
<b>PostRefIntensityCategoryKey</b>	LIDI2 only: The post-ref intensities calculated from the post-ref standard ratios (Raw-StandardRatio).
<b>RefIntensity</b>	LIDI2 only: The LIDI2 corrected intensities calculated from the standard ratios (StandardRatio).

## Delta Calculations

For each delta calculation in the LabBook, a category is created that contains the values (ratios, deltas, atom percent) provided by the delta calculation.

## References

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