

FROM OVER 1000 WATER TRIPLE POINT CELLS MADE BETWEEN 2001 AND 2010, 10% HAVE BEEN COMPARED IN ISOTOPIC ANALYSIS AND ABSOLUTE TEMPERATURE TO V-SMOW (ITS-90)

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Introduction

Figure 1 at the end of this paper details the temperature of cells made from 2001 through to 2010. The information in this appendix can be analysed in a number of ways as we describe below.

Relationship to V-SMOW over the period 2001-2010

Fig. 1 details each cell's association to ITS-90 from intercomparisons with our reference cells and each cell's isotopic association to V-SMOW through water analysis, from 2001 through to 2010.

The uncertainties attributed to our intercomparisons are $\pm 15\mu\text{K}$ [1] and to the isotopic analysis $\pm 2\mu\text{K}$ (see Appendix 2).

Using this cell data, Graph 1 illustrates the mean value to the ITS 90 and V-SMOW for each year. Note that during the first part of 2005 the target temperature of the still was adjusted to achieve $\pm 20\mu\text{K}$ to ITS-90 and not 0 to $\pm 40\mu\text{K}$ which were the previous limits.

By subtraction we can derive the value attributed to trapped air and impurities, these are also shown on Graph 1 and summarised in Table 1.

We can further analyse the data from Fig.1 (2005 to 2009) to separate the Borosilicate cells from the Quartz cells. (See Table 2)

Borosilicate Cells v Quartz Cells

One of the main issues we looked at during this data gathering process was, when manufacturing cells where and when do the impurities arise?

Do they emanate from the still itself or are they caused by initial leaching of the cell as it is filled?

Looking at Table 2, there is no significant difference between levels of air and impurities in Borosilicate and Quartz glass cells with mean depressions of $-13\mu\text{K}$ and $-8\mu\text{K}$ respectively. This would suggest that the small amounts of impurities present in the finished cell are actually in the water as it leaves the still. The amount of leaching as the cell is filled could be quantified as less than $5\mu\text{K}$.

Drift in Borosilicate Reference Cell

In 2007 [1] we reported no measurable change in our reference cells based on 2001 and 2006 intercomparisons to our reference 'Ball Cell' (a water triple point cell made of Borosilicate glass with a design based on an article by Stimpson in 1943). [1, 2, 3]

This Ball Cell (KT 001) can be re distilled prior to each realisation to remove any dissolved glass and/or trace impurities from the water, leaving primarily the isotopic composition to influence the realisation temperature. A water sample from this cell was sent for isotopic analysis and the results reported a deviation of $-7\mu\text{K}$ from V-SMOW with equivalent uncertainties of $\pm 2\mu\text{K}$.

One of our reference cells VSL-119 has been in regular use since 2001 and during autumn of 2009 it was decided to repeat the 2001 and 2006 intercomparison, again using KT 001 as the reference cell [4].

The method of intercomparison was identical to that carried out in 2001 and 2006 [1] and the summary of the results is given in Table 3.

Graph 2, illustrates these results and shows that since 2001 the cell has drifted downward in temperature by some $35\mu\text{K} \pm 15\mu\text{K}$ 2 sigma. This fits with Dr Hill's mean drift rate of $-4\mu\text{K}/\text{year}$ based on the dissolution of Borosilicate glass into the water except that the drift of VSL-119 was concentrated after 5 years of drift free use. [5] (VSL-119 was produced in 1998)

(White *et al.* 2005) state that drift rate is likely to increase with time and is dependent on the treatment of the glass prior to the manufacture of the cells. It is assumed that the dissolution of the borosilicate glass is uniform; however, as the leaching contributes to the dissolution, the dissolution of the glass is generally not uniform. [6, 7]

This seems to be confirmed with our results for VSL-119 – this cell was not produced by us, we do not know the glass preparation technique.

Conclusions

Cells made of Borosilicate glass, analysing the data suggests that the amount of air and impurities present following manufacture is similar to that of Quartz glass cells, which would suggest that small amounts of

impurities may be present in the water, as the cell is filled, the source of which may be the still itself.

Insufficient data is available to conclude anything about the long term stability of Quartz glass cells, although it has been speculated that they should be 10x more stable than Borosilicate cells.

Long term testing of one of our reference cells against a stable reference has confirmed the general feeling that Borosilicate cells can exhibit significant drift in a relatively short period of time (non uniform) and therefore should be replaced on a regular basis (every 5 years).

Graph 1 shows that our target specification of +0 to -40microK up to 2005 and 0 ±20µK to V-SMOW.2 from 2005 have been achieved.

Graph 1: Annual Average Deviations from V-SMOW.2

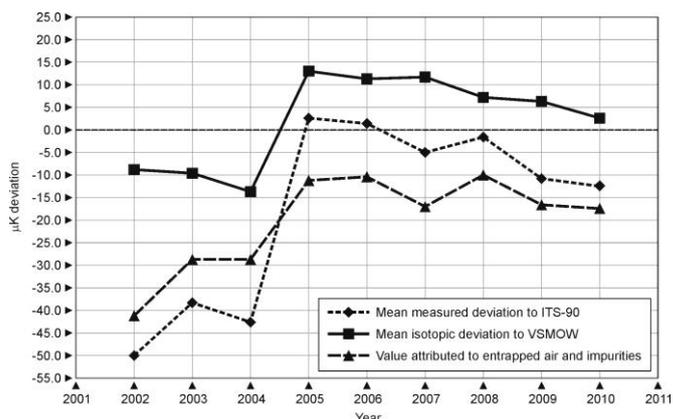


Table 1: Derived from Graph 1 above

For all types of cells (Deviation from V-SMOW)			
Year	mean measured dev (µK)	mean isotopic dev (µK)	Air and Impurities (µK)
2002	-50.0	-8.5	-41.1
2003	-38.3	-9.5	-28.8
2004	-42.6	-13.6	-29.0
2005	2.0	12.8	-10.8
2006	1.2	11.3	-10.1
2007	-4.9	12.1	-17.0
2008	-2.0	7.4	-9.4
2009	-10.8	5.8	-16.6
2010	+2.0	+2.0	+2.0

Appendix 1

Figure 1: Cell Temperature Deviations from V-SMOW.2

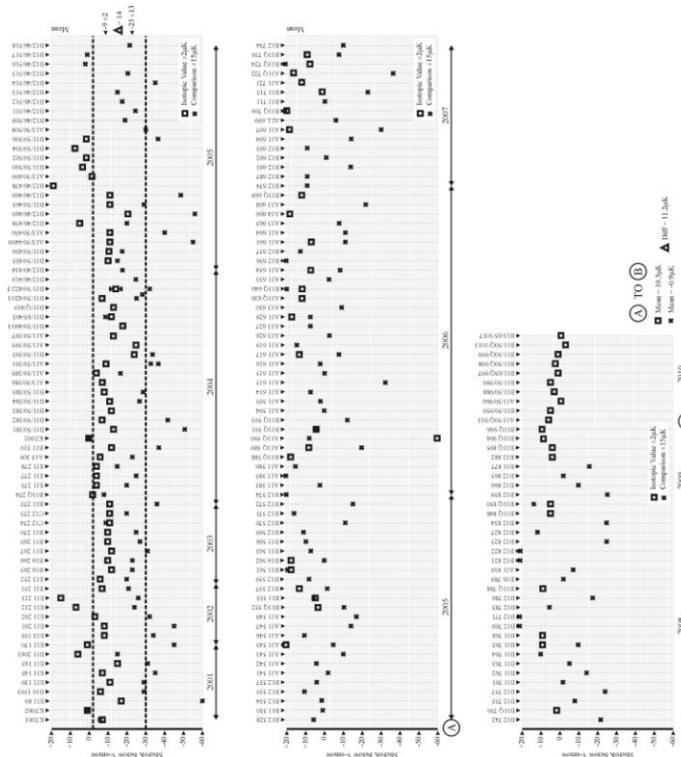


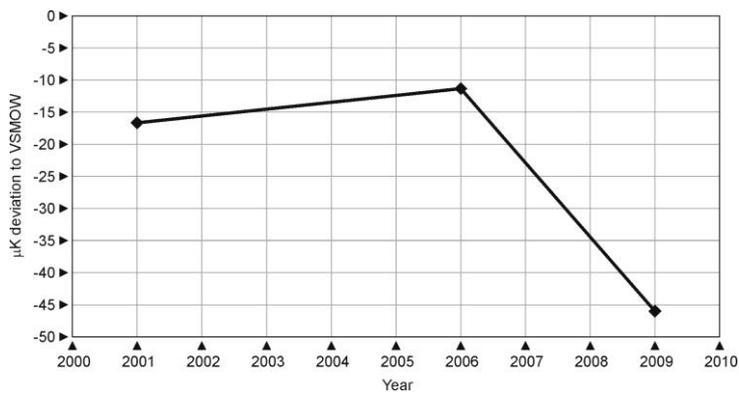
Table 2: Air and Impurities in Quartz and Borosilicate Cells 2005-2009

	All Cells (mid 2005 - 2009)		Quartz Cells only (mid 2005 - 2009)		Borosilicate Cells only (mid 2005 - 2009)	
	mean measured dev to ITS 90 (µK)	mean isotopic dev to V-SMOW (µK)	mean measured dev to ITS 90 (µK)	mean isotopic dev to V-SMOW (µK)	mean measured dev to ITS 90 (µK)	mean isotopic dev to V-SMOW (µK)
Air & Impurities	-11.2	-8.2	-13.0	-11.9	-1.1	11.9

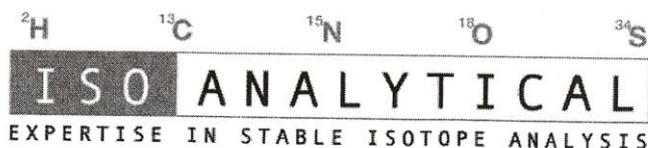
Table 3: Drift over 9 years of a Borosilicate Glass Reference Cell

VSL-119 v KT 001		
KT 001 = -7 μ K to VSMOW		
Year	Dev to KT 001 (μ K)	Dev to V-SMOW (μ K)
2001	-10	-17
2006	-4	-11
2009	-39	-46

Graph 2: Drift over 9 years of a Borosilicate Glass Reference Cell



Appendix 2: Report of Isotopic Analysis of Water Samples



LABORATORY REPORT

Prepared for: Isothermal Technology Limited Contact: Andrew Dolman
Iso-Analytical Reference No: **101203-2** Client Reference: **10PO2766**

Material: Water Analysis: Deuterium and Oxygen-18

Date Arrived: 03/12/2010 Report Date: 24/12/2010

Prepared by: Charles Belanger Results File: 101203-2-results.XLS

We have completed analysis of the samples. The results of analysis can be found as an e-mail attachment in MS Excel format. The analysis proceeded as follows:

Deuterium analysis

Deuterium analysis of the samples was performed in triplicate by the equilibration technique. In brief, a sample aliquot was pipetted into Exetainer tubes and an insert vial containing 5 % platinum on alumina added. The tubes were sealed and then filled with pure hydrogen. Samples were left to allow complete equilibration of the water with the hydrogen gas. Allowing the deuterium enrichment of the hydrogen gas to become proportional to the deuterium enrichment of the water. Reference standard waters were prepared in the same manner. Analysis was undertaken by continuous-flow isotope ratio mass spectrometry using a Europa Scientific ANCA-GSL and GEO 20-20 IRMS.

The samples were measured against three reference standards. The first standard being IA-R054 with $\delta^2\text{H}_{\text{V-SMOW}} = +4.93 \text{ ‰}$, the second IA-R052 with $\delta^2\text{H}_{\text{V-SMOW}} = -157.12 \text{ ‰}$ and the third IA-R053 with $\delta^2\text{H}_{\text{V-SMOW}} = -61.97 \text{ ‰}$. All three standards are traceable to the primary reference standards V-SMOW2 (Vienna-Standard Mean Ocean Water) and V-SLAP2 (Vienna-Standard Light Antarctic Precipitation) distributed by the IAEA. The IA-R054 standard was used as the reference to which the samples and other standards were measured. The IA-R052 standard was used for calibration of $\delta^2\text{H}$ and the IA-R053 standard was used as a check of this calibration. The results for check samples of IA-R053 are included in the results file.

Oxygen-18 analysis

Oxygen-18 analysis of the samples was performed in triplicate by the equilibration technique. In brief, a sample aliquot was pipetted into Exetainer tubes then flushed with pure CO₂. Then samples are then left to equilibrate to allow complete equilibration of the water with the CO₂ gas. Reference waters, including quality control check samples, were prepared in the same manner. The samples and references were then analysed by continuous flow using a Europa Scientific ANCA-GSL and GEO 20-20 IRMS.

The samples were measured against three reference standards. The first standard being IA-R054 with $\delta^{18}\text{O}_{\text{V-SMOW}} = +0.56 \text{ ‰}$, the second IA-R052 with $\delta^{18}\text{O}_{\text{V-SMOW}} = -19.64 \text{ ‰}$ and the third IA-R053 with $\delta^{18}\text{O}_{\text{V-SMOW}} = -10.18 \text{ ‰}$. All three standards are traceable to the primary reference standards V-SMOW2 (Vienna-Standard Mean Ocean Water) and V-SLAP2 (Vienna-Standard Light Antarctic Precipitation) distributed by the IAEA.

The IA-R054 standard was used as the reference to which the samples and other standards were measured. The IA-R052 standard was used for calibration of $\delta^{18}\text{O}$ and the IA-R053 standard was used as a check of this calibration. The results for check samples of IA-R053 are included in the results file.

Reproducibility of measurement for deuterium and oxygen-18

The results table includes a calculation of the standard deviation (1sd) for triplicate analysis of samples. This value, along with the standard deviation from the quality control check samples will give you a good indication of the reproducibility of analysis. Triplicate analysis is normally undertaken for natural abundance water samples to provide a robust mean value and to detect the occurrence of outliers.

For routine quality control of deuterium and oxygen-18 analysis in natural abundance water by the equilibration-IRMS method, we use a 1sd limit of 3 ‰ for $\delta^2\text{H}$ and 0.2 ‰ for $\delta^{18}\text{O}$. That is to say, we repeat analyses where a result from a triplicate analysis yields a 1sd of > 3 ‰ for $\delta^2\text{H}$ and > 0.2 ‰ for $\delta^{18}\text{O}$.

Sample Storage and Disposal

The unused portions of the samples will be returned to you if you request us to do so, otherwise the samples will be placed in storage for a period of three months after which time they will be disposed of.

LABORATORY REPORT: Results Files

Client Details

Name: Isothermal Technology Ltd.
 Contact: Andrew Dolman
 PO No. 10PO2766

Sample Details

Number: 2
 Material: Waters

Sample Tracking

IA Reference No.: 101203-2
 Date of Arrival: 03/12/2010

Analysis Details

Isotope(s) : Deuterium
 Oxygen-18
 Method: Equilibration IRMS
 Report Date: 24/12/2010

Deuterium Analysis Results

Sample Identification	Result δ ² H (ppm)	Result δ ² H _{V-SMOW} (‰)	Mean δ ² H _{V-SMOW} (‰)	Std. Dev. δ ² H _{V-SMOW} (‰)
1013/1014	155.11	-4.05		
"	155.10	-4.09		
"	155.28	-2.95	-3.70	0.65
1017	155.67	-0.43		
"	155.77	0.23		
"	155.52	-1.40	-0.53	0.82

Quality Control Reference Standards-Deuterium Analysis

Reference Standard	Result δ ² H _{V-SMOW} (‰)
IA-R053	-63.38
"	-62.21
"	-62.60
mean=	-62.73
1sd=	0.59
accepted=	-61.97
n	3

Sample Identification	Result δ ¹⁸ O (ppm)	Result δ ¹⁸ O _{V-SMOW} (‰)	Mean δ ¹⁸ O _{V-SMOW} (‰)	Std. Dev. δ ¹⁸ O _{V-SMOW} (‰)
1013/1014	1998.63	-1.28		
"	1998.72	-1.24		
"	1998.63	-1.28	-1.27	0.03
1017	1999.64	-0.77		
"	2000.16	-0.51		
"	1999.71	-0.74	-0.68	0.14

Quality Control Reference Standards-Oxygen-18 Analysis

Reference Standard	Result δ ¹⁸ O _{V-SMOW} (‰)
IA-R053	-10.21
"	-10.21
"	-10.14
mean=	-10.18
1sd=	0.04
accepted=	-10.18
n	3

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