

# **WATER TRIPLE POINT ANALYSIS COMPARING CELLS MADE FROM QUARTZ AGAINST THOSE FROM BOROSILICATE GLASS**

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## Abstract

Three years ago, at Tempmeko we presented the results of over 100 Water Triple Point Cells comparing these cells to a reference cell and to V-SMOW. These cells were made between 2001 and 2005 when K7 report of 22 laboratories Water Cells were intercompared by BIPM, and BIPM adopted V-SMOW as the isotopic ideal for the ITS-90 Water Triple Point Cell.

This article updates this information by adding a further three years results to the above and attempts to compare results of cells made of quartz glass to those made from borosilicate glass.

During 2005 and following the K7 data we modified our still to produce water of V-SMOW composition.

Of the hundreds of cells produced during 2005, 2006, 2007, 2008 and 2009 many have been UKAS certified, by comparing them to a Reference Cell.

Others have been sampled and the samples sent for isotopic analysis.

More and more customers have preferred quartz glass containers for the pure water in preference to the traditional borosilicate glass containers, on basis that the quartz cell has a drift rate  $1/10$  of that of borosilicate cells.

The authors have analysed the results of the comparisons and isotopic analysis to give an idea of the spread of results, and also to attempt to show what improvements result from the use of quartz rather than borosilicate glass.

This presentation summarises our results.

Keywords: Borosilicate, Isotopic, Quartz, Water Triple Point.

## Introduction.

The appendix at the back of this paper details the temperature of cells made from 2001 to 2009. The information in this appendix can be analysed in a number of ways as we describe below.

## Relationship to V-SMOW over the period 2001-2009.

Fig. 1 details each cells association to ITS 90 from intercomparisons with our reference cells and each cells isotopic association to V-SMOW through water analysis, from the end of 2005 through to 2009. (For continuity the results from the previous paper for 2001 through to mid 2005 are also shown).

The uncertainties attributed to our intercomparisons are  $\pm 15 \mu\text{K}$  and to the isotopic analysis  $\pm 2 \mu\text{K}$ .

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 the isotopic target was set to  $+15 \mu\text{K}$  above V-SMOW. The results show that the still has consistently performed within these 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)

Table 2 shows that the mean temperature for all our cells is within  $-1 \mu\text{K}$  of the ITS 90 and the mean isotopic temperature is  $+10 \mu\text{K}$  to V-SMOW, which gives a mean depression of  $-11 \mu\text{K}$  due to air and impurities.

## Borosilicate Cells v Quartz Cells

One of the main issues we looked at during this data gathering process was, when manufacturing Borosilicate 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

Three years ago 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]

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.

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

Graph 2, illustrates these results and shows that since 2005 the cell has drifted downward in temperature by some 35  $\mu\text{K}$ . 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. [2]

(White *et al.* 2005b) states 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. [3, 4]

This seems to be confirmed with our results for VSL-119.

### Conclusions

Since 2005, when our still was altered to produce cells of V-SMOW temperature  $\pm 20 \mu\text{K}$  the cells have met or exceeded this specification.

Regarding 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 conclude 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).

Having prepared this paper we plan to replace our day-to-day reference cells with Quartz versions.

## References.

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Graph 1.

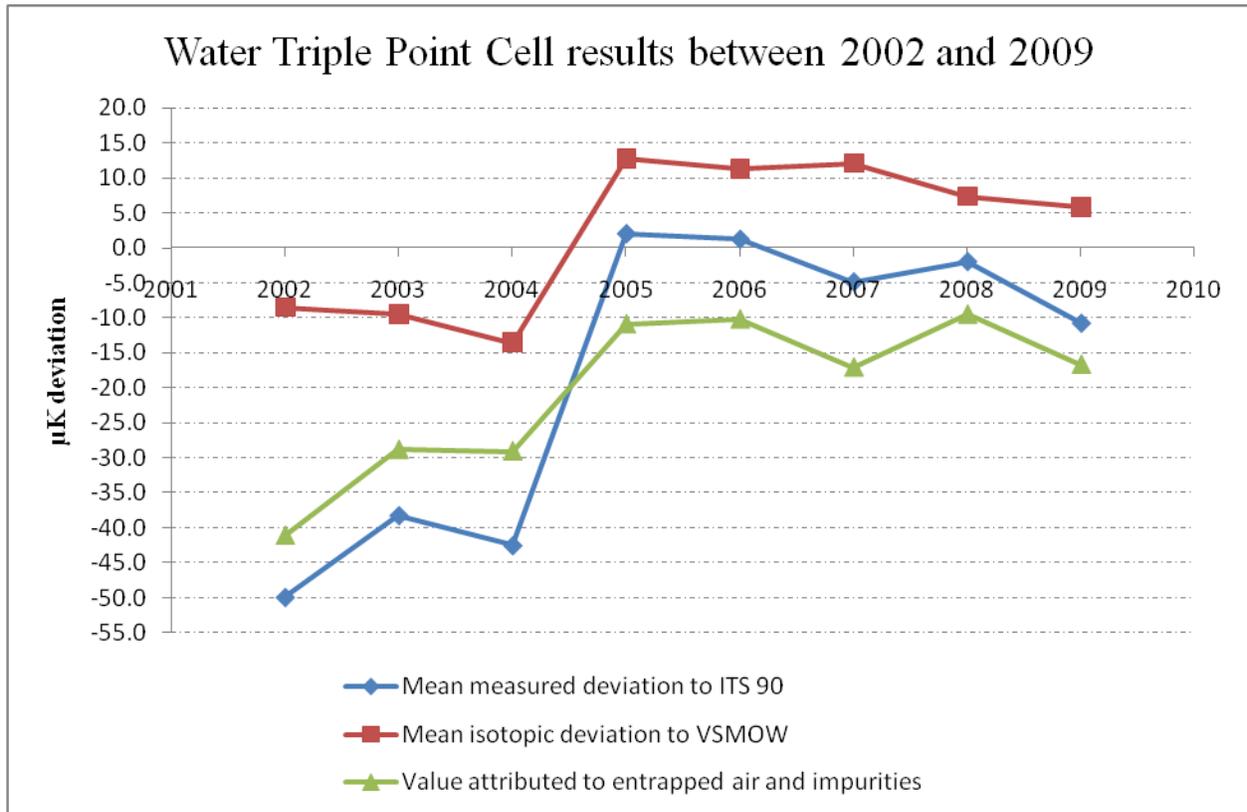


Table 1.

For all types of cells			
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

Table 2.

	All Cells (mid 2005 - 2009)		Quartz Cells only (mid 2005 - 2009)		Borosilicate Cells only (mid 2005 - 2009)	
	mean measured dev to ITS 90 ( $\mu\text{K}$ )	mean isotopic dev to V-SMOW ( $\mu\text{K}$ )	mean measured dev to ITS 90 ( $\mu\text{K}$ )	mean isotopic dev to V-SMOW ( $\mu\text{K}$ )	mean measured dev to ITS 90 ( $\mu\text{K}$ )	mean isotopic dev to V-SMOW ( $\mu\text{K}$ )
		-0.9	10.3	0.8	9	-1.1
Air & Impurities	-11.2		-8.2		-13.0	

Table 3.

VSL-119 v KT 001		
KT 001 = $-7\mu\text{K}$ to VSMOW		
Year	Dev to KT 001 ( $\mu\text{K}$ )	Dev to V-SMOW ( $\mu\text{K}$ )
2001	-10	-17
2006	-4	-11
2009	-39	-46

Graph 2.

