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THERMAL EXPANSION COEFFICIENT OF WATER FOR VOLUMETRIC CALIBRATION

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Abstract: This paper describes an accurate determination for the water thermal expansion coefficient starting from CIPM water density equation. This thermal expansion coefficient, as it is determined, is to be used in the volume determination according to the volumetric method.

Keywords: water, thermal expansion coefficient, volumetric, CIPM water density equation.

1. INTRODUCTION

The volumetric method is widely used for volume determination. This method is normally used when using weighing instruments is impracticable or on site calibrations. For example, this is the case of volume measurements related to legal metrology.

The volumetric method consists of delivering a quantity of liquid from a calibrated standard (reference standard), into a standard capacity measure. The volume at temperature t, is determined using the following formula:

$$V_{\mathrm{TCMr}} = V_{\mathrm{RS0}}\left[1-\gamma_{\mathrm{RS}}(t_{0\mathrm{RS}}-t_{\mathrm{RS}})+\beta(t_{\mathrm{TCM}}-t_{\mathrm{RS}})+\gamma_{\mathrm{TCM}}(t_{\mathrm{r}}-t_{\mathrm{TCM}})\right] \quad (1)$$

where

V_{TCMr} is the volume of the test capacity measure at t_{r} °C

V_{RS0} is the volume of the reference standard at its reference temperature $t_{0\mathrm{RS}}$

$t_{0\mathrm{RS}}$ is the reference temperature of the reference standard

t_{RS} is the temperature of water in the filled reference standard before pouring

t_{TCM} is the temperature of water in the test capacity measure after its filling

γ_{RS} is the coefficient of cubical thermal expansion of the reference standard

β is the thermal expansion coefficient of water at the average test temperature, 0,5 ($t_{\mathrm{RS}} + t_{\mathrm{TCM}}$)

γ_{TCM} is the coefficient of cubical thermal expansion of the test capacity measure

t_{r} is the temperature the volume is to be determined at.

It is clear that the thermal expansion coefficient of water, β, is a quantity that has to be well known as a function of temperature in order to get accurate results in the volume determination through this method.

If β is to be determined at reference temperature t_0 = 0,5 ($t_{\mathrm{RS}} + t_{\mathrm{TCM}}$), and Δt = 0,5 ($t_{\mathrm{TCM}} - t_{\mathrm{RS}}$) equation (1) can be expressed as follows,

$$V_{\mathrm{TCMr}} = V_{\mathrm{RS0}}\left[1-\gamma_{\mathrm{RS}}(t_{0\mathrm{RS}}-t_{\mathrm{RS}})+2\beta\Delta t+\gamma_{\mathrm{TCM}}(t_{\mathrm{r}}-t_{\mathrm{TCM}})\right] \quad (2)$$

2. THERMAL EXPANSION COEFFICIENT DETERMINATION

In order to have an accurate determination of the thermal expansion coefficient of water the most adequate way is to use the density equation of water. The most accurate one is the CIPM density equation [1], which provides the density of water from 0ºC to 40 ºC. This temperature range is sufficient for most applications:

$$\rho = a_5\left[1-\frac{(t+a_1)^2(t+a_2)}{a_3(t+a_4)}\right] \quad (3)$$

$a_1/{}^\circ\mathrm{C} = -3.983035 \pm 0.00067$

$a_2/{}^\circ\mathrm{C} = 301.797$

$a_3/{}^\circ\mathrm{C}^2 = 522528.9$

$a_4/{}^\circ\mathrm{C} = 69.34881$

a_5 is the density of water at 101 325 Pa and – a_1ºC. The value for a_5 is not going to be important for the water thermal expansion coefficient determination.

For the reference temperature, t_0, the following condition has to be fulfilled:

$$V(t) = V(t_0)(1+\beta(t-t_0)) = \frac{V(t_0)}{\rho(t)}\rho(t_0) \quad (4)$$

If $t - t_0 = \Delta t$ and $a_i' = a_i + t_0$ (but this is unnecessary for a_3) expression (5) is obtained:

$$\beta\Delta t = \frac{\rho(t_0)}{\rho(t)} - 1 = \frac{\left[1 - \frac{a_1'^2 a_2'}{a_3 a_4'}\right]}{\left[1 - \frac{(\Delta t + a_1')^2(\Delta t + a_2')}{a_3(\Delta t + a_4')}\right]} - 1 \qquad (5)$$

As a result equation (6) is obtained

$$\beta \cdot \Delta t = \frac{\Delta t\left[(\Delta t + a_1')^2 + a_2'\left(\Delta t + a_1'\left(2 - \frac{a_1'}{a_4'}\right)\right)\right]}{a_3(\Delta t + a_4') - (\Delta t + a_1')^2(\Delta t + a_2')} \qquad (6)$$

So the thermal expansion coefficient has been found accurately:

$$\beta = \frac{\left[(\Delta t + a_1')^2 + a_2'\left(\Delta t + a_1'\left(2 - \frac{a_1'}{a_4'}\right)\right)\right]}{a_3(\Delta t + a_4') - (\Delta t + a_1')^2(\Delta t + a_2')} \qquad (7)$$

3. INFLUENCE OF THE REFERENCE TEMPERATURE

Parameters a_i' only depend on the selection of the reference temperature t_0. This temperature is 20ºC in most cases, but it may not be. In table 1 the thermal expansion coefficient of water as a function of the reference temperature t_0 and the measurement temperature t is presented. As can be observed there is a huge variation depending on these parameters.

Thermal expansion coefficient /10^{-6} ºC^{-1}									
t/t_0	0	5	10	15	20	25	30	35	40
0	-67,82	-24,80	14,01	49,36	81,82	111,85	139,82	166,03	190,72
2	-50,04	-7,96	30,03	64,64	96,46	125,92	153,37	179,11	203,37
4	-33,03	8,17	45,38	79,31	110,52	139,43	166,39	191,69	215,55
6	-16,72	23,64	60,11	93,40	124,04	152,44	178,94	203,82	227,31
8	-1,06	38,51	74,30	106,97	137,06	164,98	191,05	215,54	238,66
10	14,02	52,83	87,96	120,06	149,64	177,10	202,76	226,87	249,66
12	28,54	66,65	101,15	132,71	161,80	188,82	214,09	237,85	260,32
14	42,56	79,99	113,91	144,94	173,57	200,19	225,08	248,51	270,67
16	56,11	92,90	126,26	156,80	184,99	211,21	235,76	258,87	280,74
18	69,23	105,41	138,24	168,31	196,08	221,93	246,14	268,95	290,55
20	81,95	117,55	149,86	179,49	206,87	232,36	256,25	278,78	300,12
22	94,29	129,34	161,17	190,37	217,37	242,53	266,12	288,36	309,45
24	106,29	140,80	172,17	200,96	227,61	252,44	275,74	297,73	318,58
26	117,96	151,97	182,90	211,30	237,60	262,13	285,15	306,89	327,52
28	129,33	162,85	193,36	221,39	247,36	271,60	294,36	315,86	336,27
30	140,41	173,47	203,58	231,26	256,91	280,87	303,38	324,65	344,86
32	151,23	183,85	213,57	240,91	266,26	289,95	312,22	333,28	353,29
34	161,80	194,00	223,35	250,36	275,43	298,86	320,90	341,75	361,57
36	172,15	203,93	232,93	259,63	284,42	307,60	329,42	350,07	369,72
38	182,27	213,67	242,32	268,73	293,25	316,20	337,81	358,27	377,74
40	192,19	223,21	251,54	277,66	301,93	324,65	346,05	366,33	385,64

Table 1: Water expansion coefficient as a function of the reference temperature t_0 and temperature t.

4. SIMPLIFIED FORMULATION

The use of equation (7) implies the calculation of β for every measurement temperature, t. If the same reference temperature t_0 is always used a simplified formulation may be used. This may be interesting if simplification of the calculations is required.

The formula for this linear approximation comes from the Taylor series close to $t = t_0$.

$$\beta_{\text{approx}} = \frac{\left[a_1'^2 + a_2' a_1'\left(2 - \frac{a_1'}{a_4'}\right)\right]}{a_3 a_4' - a_1'^2 a_2'} + \Delta t \cdot$$

$$\frac{\left[(2a_1' + a_2')(a_3 a_4' - a_1'^2 a_2') - (a_3 - 2a_1' a_2' - a_1'^2)\left(a_1'^2 + a_2' a_1'\left(2 - \frac{a_1'}{a_4'}\right)\right)\right]}{(a_3 a_4' - a_1'^2 a_2')^2}$$

(8)

It can be sufficient depending on how far the temperature t is from the reference temperature t_0 or the required uncertainty.

If only the first term is considered (no dependence with t) the difference between the linear approximation of β (equation (8), only the first term) and the real β (equation (7)) may be huge, as provided in table 2.

Difference between β_{approx} and β_{real} /10^{-6} ºC^{-1}									
t/t_0	0	5	10	15	20	25	30	35	40
0	0,00	40,77	73,95	101,56	125,05	145,46	163,55	179,90	194,91
2	-17,78	23,94	57,93	86,27	110,41	131,40	150,01	166,82	182,26
4	-34,79	7,81	42,59	71,61	96,35	117,88	136,98	154,24	170,08
6	-51,10	-7,66	27,85	57,51	82,83	104,88	124,44	142,11	158,33
8	-66,77	-22,53	13,67	43,94	69,80	92,33	112,33	130,39	146,97
10	-81,84	-36,85	0,00	30,85	57,23	80,21	100,62	119,06	135,98
12	-96,36	-50,67	-13,19	18,21	45,07	68,49	89,29	108,08	125,32
14	-110,38	-64,01	-25,95	5,97	33,29	57,13	78,30	97,42	114,96
16	-123,94	-76,92	-38,30	-5,88	21,87	46,10	67,62	87,06	104,89
18	-137,06	-89,43	-50,27	-17,39	10,78	35,38	57,24	76,98	95,08
20	-149,77	-101,57	-61,90	-28,57	0,00	24,95	47,12	67,15	85,52
22	-162,12	-113,36	-73,21	-39,45	-10,50	14,79	37,26	57,57	76,18
24	-174,11	-124,82	-84,21	-50,05	-20,74	4,87	27,64	48,20	67,05
26	-185,78	-135,99	-94,94	-60,38	-30,73	-4,81	18,23	39,04	58,12
28	-197,15	-146,87	-105,40	-70,48	-40,49	-14,29	9,02	30,07	49,36
30	-208,23	-157,50	-115,62	-80,34	-50,05	-23,56	0,00	21,28	40,78
32	-219,05	-167,87	-125,61	-89,99	-59,40	-32,64	-8,84	12,65	32,35
34	-229,63	-178,02	-135,39	-99,45	-68,56	-41,55	-17,52	4,18	24,06
36	-239,97	-187,96	-144,97	-108,72	-77,55	-50,29	-26,05	-4,15	15,92
38	-250,09	-197,69	-154,36	-117,81	-86,38	-58,89	-34,43	-12,34	7,90
40	-260,01	-207,23	-163,58	-126,74	-95,06	-67,34	-42,68	-20,40	0,00

Table 2: Difference between the linear approximation of β, β_{approx},(equation (8), only the first term) and the real β, β_{real},(equation (7)).

If both terms are considered this difference between the linear approximation of β (equation (8), both terms) and the real β (equation (7)) is provided by table 3.

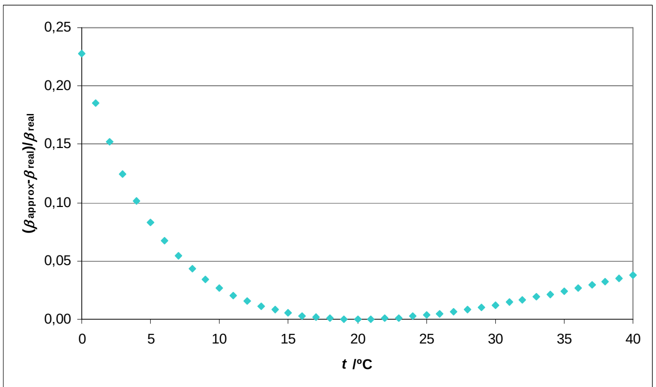
It is clear that taking only one term into consideration (no dependence of β with t) the committed errors are considerable. Thanks to the second term (this is, a linear dependence with t is considered) the results are much better, but it is not sufficient in general terms.

Difference between β_{approx} and β_{real} /10^{-6} ºC^{-1}									
t/t_0	0	5	10	15	20	25	30	35	40
0	0,00	2,10	6,83	12,64	18,66	24,40	29,63	34,20	38,06
2	0,41	0,73	4,24	9,21	14,65	20,02	25,01	29,44	33,25
4	1,58	0,08	2,32	6,40	11,24	16,19	20,91	25,19	28,91
6	3,45	0,08	1,00	4,16	8,36	12,87	17,29	21,38	25,00
8	5,97	0,67	0,24	2,45	5,97	10,01	14,11	17,99	21,49
10	9,08	1,82	0,00	1,22	4,03	7,58	11,34	14,99	18,34
12	12,74	3,48	0,23	0,43	2,51	5,54	8,93	12,33	15,52
14	16,91	5,60	0,90	0,05	1,38	3,86	6,87	10,00	13,01
16	21,54	8,16	1,97	0,04	0,60	2,52	5,12	7,96	10,78
18	26,61	11,12	3,42	0,39	0,15	1,48	3,66	6,21	8,81
20	32,07	14,45	5,21	1,07	0,00	0,74	2,48	4,71	7,09
22	37,91	18,14	7,33	2,05	0,14	0,26	1,55	3,45	5,60
24	44,10	22,14	9,75	3,30	0,54	0,03	0,85	2,41	4,31
26	50,62	26,44	12,45	4,82	1,19	0,03	0,37	1,57	3,22
28	57,44	31,03	15,41	6,59	2,06	0,24	0,09	0,93	2,31
30	64,54	35,88	18,61	8,58	3,15	0,66	0,00	0,46	1,56
32	71,90	40,97	22,04	10,78	4,44	1,26	0,09	0,16	0,98
34	79,51	46,29	25,69	13,18	5,91	2,03	0,34	0,02	0,54
36	87,36	51,82	29,53	15,77	7,56	2,97	0,74	0,02	0,23
38	95,42	57,56	33,56	18,53	9,37	4,06	1,29	0,15	0,06
40	103,68	63,49	37,77	21,46	11,33	5,30	1,97	0,41	0,00

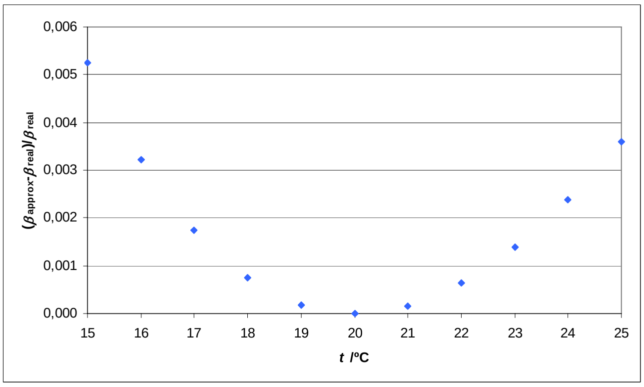
Table 3: Difference between the linear approximation of β, β_{approx}, (equation (8), both terms) and the real β, β_{real}, (equation (7)).

Only if the difference between t and t_0 are less than 3 ºC these differences are close to the uncertainty values, which will be seen in section 5. In some calibrations these maximum temperature differences are fulfilled so the approximation is useful if uncertainty for β is not important.

Plot 1 and 2 show these results for reference temperature t_0 = 20ºC.



Plot 1: Difference for the thermal expansion coefficient of water between the linear approximation, β_{approx} (both terms) and β_{real} for a reference temperature t_0 = 20 ºC in the range from 0 ºC to 40 ºC.



Plot 2: Difference for the thermal expansion coefficient of water between β_{real} and its linear approximation β_{approx} (both terms) for a reference temperature t_0 = 20 ºC in the range 15 ºC to 25 ºC.

5. SOURCES OF UNCERTAINTY

CIPM density formula

Reference [1] provides a formula for the relative uncertainty associated to the CIPM density equation:

$$u(\rho(t))/10^{-6} = 0.0715 - 0.22050t + 0.00285748t^2 - 0.0001175515t^3 + 0.00000156852t^4 \quad (9)$$

Applying the document JCGM 100 [6] to the first part of equation (5) the uncertainty contribution for β is obtained:

$$u(\beta(t)) = \frac{\rho(t_0)}{\Delta t \cdot \rho(t)} \left(u(\rho(t_0))^2 + u(\rho(t))^2 \right)^{1/2} \quad (10)$$

Obviously there is a problem in equation (10) when $t_0 = t$. When using equation (2) the sensitivity coefficient will be Δt, which is cero, so according to [6] higher order terms are required. Apart from that further correlations should be taken into account. In practice the measurement conditions do not allowing ensuring lower uncertainties than 0,5 ºC so it can be considered $t = t_0$ + 0,5 ºC without loss of generality for the purpose of determining uncertainty calculation. This also applies to the other uncertainties contributions when necessary.

In plot 3 this contribution to the uncertainty is presented as a function of temperature for a reference temperature t_0 = 20ºC.

Dissolved air

The density of water has been given under the assumption that the water is air-free. Obviously this fact is difficult to ensure in most calibrations. Bignell [3] has determined the difference in density, between air-free and air-saturated water. Between 0 ºC and 25 ºC this difference in kg/m^3 can be described by the following formula:

$$\Delta\rho = s_0 + s_1 t \qquad (11)$$

$s_0 = -4.612 \times 10^{-3}$

$s_1 = 0.106 \times 10^{-3} / {}^{\circ}\mathrm{C}^{-1}$

An alternative is the recent work of Harvey et al [4], which extends from 0 ◦C to 50◦C with results that agree within their uncertainty, so an extension up to 40 ºC for the range of this equation can be assumed.

It is accurate enough to make no correction and consider the maximum correction as an uncertainty. In plot 3 this contribution to the uncertainty is presented as a function of temperature for a reference temperature t_0 = 20ºC.

Compressibility

The density of air-free water has been given at a pressure of 101 325 Pa. Based on the work of Kell [5], the density at 101 325 Pa must be multiplied by this factor

$$1 + \left(k_1 + k_2 t + k_3 t^2\right)\Delta p \qquad (12)$$

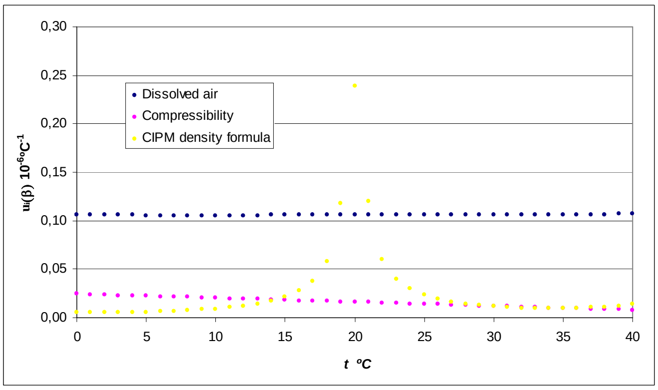
$\Delta p/\mathrm{Pa} = p/\mathrm{Pa} - 101\,325$

$k_1/(10^{-11}\ \mathrm{Pa}^{-1}) = 50.74$

$k_2/(10^{-11}\ \mathrm{Pa}^{-1}\ {}^{\circ}\mathrm{C}^{-1}) = -0.326$

$k_3/(10^{-11}\ \mathrm{Pa}^{-1}\ {}^{\circ}\mathrm{C}^{-2}) = 0.004\ 16$

It is accurate enough to make no correction and consider the maximum correction as an uncertainty. In plot 3 this contribution to the uncertainty is presented as a function of temperature for a reference temperature t_0 = 20ºC and Δp = 10 000 Pa (which covers most cases).



Plot 3: Contributions to the uncertainty for the water thermal expansion coefficient at reference temperature t_0 = 20 ºC as a function of temperature *t*.

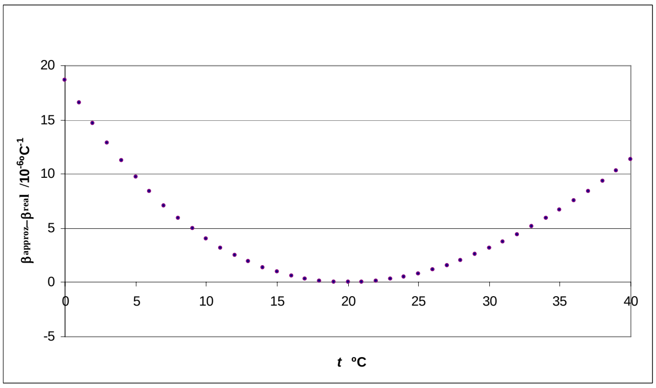
Purity

According to [1] the purity of water only affects to the parameter a_5. This parameter has no effect on the thermal expansion coefficient (equation (6)), so purity seems not to have a very important influence.

Use of the simplified formulation

The use of the simplified formulation (β_{approx} with both terms) maybe a high contribution to the uncertainty, the more the further the test temperature *t* is from the reference temperature t_0.

It is clear from plot 4 that this contribution is going to be the dominant one for temperature far from the reference temperature.



Plot 4: Contribution to the uncertainty for the water thermal expansion coefficient at reference temperature t_0 = 20 ºC as a function of temperature *t* caused by the use of the simplified formulation.

Uncertainty budget

When considering all the contributions it is clear that all but one come for corrections that have not been performed, so according to JGCM 100 [6] these contributions should be added linearly.

In table 4 these results are presented for β (without approximations). It is clear that when $t = t_0$ the uncertainty contribution increases, but this effect is compensated by the fact that it will be multiplied by Δt in the uncertainty evaluation.

In table 5 these results are presented for β (with linear approximation). Only if the difference between *t* and t_0 are less than 3 ºC the uncertainty contribution for the use of the simplified calculation has the same order of magnitude than the other ones, although it is always the dominant but for $t_0 = t$. Anyway, for some calibrations it may be sufficient.

$u(\beta_{real})$ $(k = 1)/10^{-6}$ ºC^{-1}									
t/t_0	0	5	10	15	20	25	30	35	40
0	0,33	0,15	0,14	0,14	0,14	0,13	0,13	0,13	0,13
2	0,18	0,15	0,14	0,14	0,13	0,13	0,13	0,13	0,13
4	0,16	0,16	0,14	0,14	0,13	0,13	0,13	0,13	0,13
6	0,15	0,16	0,14	0,14	0,13	0,13	0,13	0,12	0,13
8	0,14	0,14	0,15	0,14	0,13	0,13	0,13	0,12	0,13
10	0,14	0,14	0,19	0,14	0,13	0,13	0,13	0,12	0,13
12	0,14	0,14	0,16	0,15	0,14	0,13	0,13	0,12	0,13
14	0,14	0,14	0,15	0,22	0,14	0,13	0,13	0,12	0,13
16	0,14	0,14	0,14	0,22	0,15	0,13	0,13	0,12	0,13
18	0,14	0,14	0,14	0,16	0,18	0,14	0,13	0,12	0,13
20	0,14	0,13	0,14	0,15	0,36	0,14	0,13	0,12	0,13
22	0,13	0,13	0,13	0,14	0,18	0,16	0,13	0,13	0,13
24	0,13	0,13	0,13	0,13	0,15	0,24	0,13	0,13	0,13
26	0,13	0,13	0,13	0,13	0,14	0,23	0,14	0,13	0,13
28	0,13	0,13	0,13	0,13	0,13	0,15	0,17	0,13	0,13
30	0,13	0,13	0,13	0,13	0,13	0,14	0,34	0,14	0,14
32	0,13	0,13	0,13	0,13	0,13	0,13	0,17	0,16	0,14
34	0,13	0,13	0,13	0,13	0,13	0,13	0,14	0,26	0,15
36	0,13	0,13	0,13	0,12	0,13	0,13	0,14	0,28	0,18
38	0,13	0,13	0,13	0,13	0,13	0,13	0,14	0,18	0,26
40	0,13	0,13	0,13	0,13	0,13	0,13	0,14	0,16	0,48

Table 4: Combined uncertainty (k = 1) for the water thermal expansion coefficient as a function of reference temperature t_0 = 20 ºC and temperature t.

$u(\beta_{approx})$ $(k = 1)/10^{-6}$ ºC^{-1}									
t/t_0	0	5	10	15	20	25	30	35	40
0	0,33	2,3	7,0	13	19	25	30	34	38
2	0,58	0,88	4,4	9,3	15	20	25	30	33
4	1,7	0,24	2,5	6,5	11	16	21	25	29
6	3,6	0,24	1,1	4,3	8,5	13	17	22	25
8	6,1	0,82	0,40	2,6	6,1	10	14	18	22
10	9,2	2,0	0,23	1,4	4,2	7,7	11	15	18
12	13	3,6	0,39	0,58	2,6	5,7	9,1	12	16
14	17	5,7	1,0	0,26	1,5	4,0	7,0	10	13
16	22	8,3	2,1	0,27	0,75	2,7	5,2	8,1	11
18	27	11	3,6	0,55	0,33	1,6	3,8	6,3	8,9
20	32	15	5,3	1,2	0,36	0,88	2,6	4,8	7,2
22	38	18	7,5	2,2	0,32	0,42	1,7	3,6	5,7
24	44	22	9,9	3,4	0,69	0,26	0,98	2,5	4,4
26	51	27	13	5,0	1,3	0,26	0,51	1,7	3,3
28	58	31	16	6,7	2,2	0,40	0,26	1,1	2,4
30	65	36	19	8,7	3,3	0,79	0,34	0,60	1,7
32	72	41	22	11	4,6	1,4	0,26	0,32	1,1
34	80	46	26	13	6,0	2,2	0,48	0,28	0,69
36	87	52	30	16	7,7	3,1	0,88	0,30	0,41
38	96	58	34	19	9,5	4,2	1,4	0,33	0,32
40	104	64	38	22	11	5,4	2,1	0,58	0,48

Table 4: Combined uncertainty (k = 1) for the linear approximation of the water thermal expansion coefficient as a function of reference temperature t_0 = 20 ºC and temperature t.

6. CONCLUSIONS

In this paper a formula for the thermal expansion coefficient for the water has been presented. This formula is based on the CIPM water density equation and it is valid from 0 ºC to 40 ºC. The interest in this formula is its use in the volumetric calibrations.

It has been studied the influence of the reference temperature and a simplified formulation for small differences between reference and measurement temperatures have been included.

The sources of uncertainty have been studied and their contribution for an overall uncertainty evaluated. These sources are: CIPM density formula, dissolved air, compressibility and purity of the water and, additionally, the use of the simplified formulation. This last contribution is the dominant one in most cases.

7. REFERENCES

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