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Key problems in early wine-spirit thermometers and the "true Réaumur" thermometer

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Abstract

The main problems of early wine-spirit thermometers, with special reference to the eighteenth century, are considered with a holistic approach based on historical sources, physical mechanisms, and mathematical relationships. Thermometers were hardly comparable and were vulnerable at extreme temperatures, including calibration. Wine-spirit and the vapor pressure exerted at different temperatures, especially in proximity of the boiling points of spirit and water, are analyzed, because they caused the failure of glass tubes. The method suggested by Réaumur of completely removing air from the tube when it was sealed and the opposite one by Micheli du Crest of leaving some air inside are discussed, as well as advantages and disadvantages of using wine-spirit at different mole fractions of ethyl alcohol and water. The original, so-called "true Réaumur" thermometer, its calibration, scale, and response are investigated. The equations that evaluate the deviation from linearity for various factors are derived. Equations are given to convert readings taken with the "true Réaumur" and other early thermometers to Celsius, and at the same time correcting them from the departures due to wine-spirit and the particular calibration. Finally, the direct Celsius scale has been found to be known earlier than believed, in 1740.

Keywords Early thermometers \cdot Thermometric liquid \cdot Wine-spirit thermometers \cdot Physics of boiling \cdot Calibration \cdot Réaumur thermometers

1 Introduction

Long instrumental series constitute the most important source of information about past climate, and efforts are continually made to recover, validate, correct, and interpret early

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records. Recovery, correction, homogenization, and analysis of long instrumental series are a key part of climatology but require a multidisciplinary approach (ESM1). Several early thermometers have been studied, either from the point of view of the history of science (Bolton 1900; Boffito 1929; Birembaut 1958; Middleton 1966; Frisinger 1983; Landsberg 1985; Borchi and Macii 1997, 2009; Kington 1997; Talas 2002; Chang 2004; Gauvin 2012; Camuffo 2019), or to analyze temperature records representative of the Little Ice Age and the transition to global warming (Parker et al. 1992; Camuffo and Jones 2002; Brázdil et al. 2005, 2012; Winkler 2009; Böhm et al. 2010; Przybylak et al. 2010; Rousseau 2009, 2019; Camuffo and Bertolin 2012; Camuffo et al. 2016, 2017, 2020a, b; Brönnimann et al. 2018; White et al. 2018; Brugnara et al. 2020; Slivinski et al. 2019). However, the limited theoretical knowledge of the early instrumental period, construction technology, calibration points, and operative protocols require further investigations.

The most widely used thermometric liquids were wine-spirit, e.g., Florentine thermometers (Magalotti 1666), Réaumur (1730, 1731), and du Crest (1741), and mercury, e.g., Fahrenheit (1724) and De Luc (1772). Newton preferred linseed oil (Newton 1701; Camuffo and della Valle 2017) but had problems with the viscosity of the oil adhering to the tube. Wine-spirit became the most popular liquid for technical reasons. du Crest (1741) commented: it is twenty times easier to build good wine-spirit thermometers than good mercury thermometers, because the bulb could be smaller for the larger sensitivity; the internal section of the capillary tube could be thinner because there is not a strong surface tension effect as in mercury; there is no need to purify mercury, to dry tubes and use tubes with well calibrated cross-section. When the cross-section is not uniform, where it becomes wider the height of the liquid column is depressed; when becomes thinner, the height is enhanced. As the cross-section is proportional to the square of the radius, the effect is more evident with larger tubes, e.g. mercury. To control that tubes had uniform section, du Crest (1741) inserted a drop of mercury inside the tube obtaining a liquid rod whose length was inversely proportional to the square of the internal tube radius. Applying a gentle air pressure, it was possible to move this liquid rod along the tube and verify that the tube had constant section.

A serious difficulty was that wine-spirit thermometers had non-comparable readings (Derham 1709; Martine 1740; du Crest 1741, 1765; De Luc 1772; Lambert 1779). Today it is known that ethyl alcohol departs from linearity, and if there was some water mixed to it, the departure was larger (Osborne et al. 1913). This fact was recognized when du Crest (1765) and De Luc (1772) compared the response of different thermometers dipped in the same calibration bath. The results were also reported by Lambert (1779), Gaussen (1789), Goubert (1789), and Wildt (1825). The equations to evaluate the difference between readings taken with mercury and wine-spirit thermometers have been derived (Camuffo and della Valle 2016) and are reported in Section 2. In winter, the difference between mercury and wine-spirit is small, while in summer, it may reach marked departures, e.g., wine-spirit underestimates temperatures by 5 °C at 30 °C, as usual in Mediterranean countries.

Another difficulty was calibration, not well standardized. A bad practice was to dip only the bulb inside the calibration bath, e.g., Nollet (1748, 1770) (ESM2), or up to the mid-level of the range. It was less common to dip the whole thermometer inside the bath as du Crest correctly did. A variety of reference points existed (Chang 2004), including melting ice and boiling water (Renaldini 1694); human blood (Newton 1701; Fahrenheit 1724); mixture of ice and salts (Fahrenheit 1724); deep cellars (de La Hire 1718; du Crest 1741); and the *Temperate* of the city, cellars, or even the Earth (Martine 1740; du Crest 1758). The *Temperate* was a basic reference temperature represented by an average value, or equal proportions of heat and cold.

In theory, Réaumur (1730, 1731) conceived a volumetric calibration, based on a single calibration point, i.e., freezing water, but then he took advantage of additional reference points, i.e., boiling spirit and all the abovementioned ones. The two points based on the physical transitions of water had serious technological implications, especially because calibration constituted an essential step in building thermometers, for instance to determine the exact amount of the wine-spirit to fill the instrument before sealing the tube.

In particular, the glass on the upper end of the tube was brought near the melting point with a lantern flame. Then it was thinned and drawn to a capillary orifice and finally hermetically sealed by fusion. A critical issue was whether to leave some air in the free volume between the thermometric liquid and the top or completely remove all air (Fig. 1a, b). In the latter case, the bulb was gently heated, the liquid lifted to the upper end of the tube until all air was completely expelled, and then the capillary was sealed (Trail 1828). With mercury thermometers, this operation was easy. With wine-spirit, the operation was difficult because, at the high temperature of melting glass, alcohol boiled violently and was flammable.

There was no consensus on two conflicting theories, i.e., if it was better to remove all air (Réaumur 1730, 1731) or to leave a small air pocket inside, as suggested by du Crest (1741, 1757) and adopted by Nollet (1748). In addition, when calibrated at boiling water temperature, spirit thermometers presented serious drawbacks for the appearance of bubbles or because



Fig. 1 Anatomy of a thermometer. **a** Réaumur thermometer with scale from -20° to $+40^{\circ}$ R (from Cotte 1774). **b** Vertical cross-section. B, bulb; LC, liquid column; L, level reached by the liquid; R, internal radius of the tube; V, liquid-free volume on the top of the tube; H, height of V. **c** Horizontal cross-section of the tube showing the net pressure ΔP against the convex side, i.e., compression for higher external pressure. (**d**) The same but with net pressure ΔP pushing against the concave side of the glass, i.e., expansion, e.g., upper calibration point. (**e**) Thermometer with glasswork fixed to the wooden tablet with iron wires at three levels: L1 and L2 (very typical) and L3 on the hook on the top to avoid slipping down (not frequent) (from Cotte 1774)

some glass tubes could break (Delisle 1724; Martine 1740; du Crest 1741, 1757; Nollet 1748; Brander 1770). Initially, following Renaldini (1694), Réaumur decided to seal the tube removing air as far as possible: "less air is left in the tube when sealing, less problems will follow afterwards" (Réaumur 1731). However, 10 years later, du Crest noted that some wine-spirit evaporated inside the tube and that the evaporation increased when the thermometer was left for long time in the boiling water. The phenomenon was more evident in thermometers that had a very small air pocket left inside the tube when it was hermetically sealed. Therefore, he suggested to leave some air inside (du Crest 1741). Years later, du Crest (1757) gave a more explicit explanation: "the boiling water temperature is more or less high if the weight of the atmosphere (i.e. the atmospheric pressure) is greater or smaller. Consequently, if one leaves inside the instrument. In addition, most of physicists are not aware of that. When I gave to Mr de Maupertuis one of four early thermometers that I built in Paris financed by Mr Auzu, and he [Auzu] may witness his surprise, because he [de Maupertuis] believed that it was not possible, and justified his surprise because the wine-spirit boils earlier than water."

Jean Antoine Nollet, who was the second and most famous Réaumur pupil and instrument maker, abandoned the original Réaumur directive and closely followed the suggestion by du Crest (1741): "In a thermometer, the wine-spirit boils earlier if air has been perfectly removed from the tube. The earliest thermometers that had been built following the Réaumur directives cannot resist to boiling water for the above reason. However, they can be adapted to resist leaving some air inside because its spring opposes the ebullition when the liquid temperature becomes high. Therefore, the glass tube should be thicker than usual, to resist to the internal pressure" (Nollet 1748) (Fig. 1c).

The strategy of leaving some air inside the tube and increasing glass thickness was universally adopted. The need for thicker tubes is obvious. The strategy of air pockets, however, needs a thorough physical investigation to evaluate its performance.

Another open question concerned the stability, or drifts, related to the behavior of thermometric liquids, glass, and their interactions (ESM3).

The first aim of this paper is to analyze the physical system of wine-spirit in thermometers when the temperature reaches the boiling point of wine-spirit (78.3 °C), and then the boiling point of water (100 °C). In addition, it is aimed to discuss the same system deprived of air, or with an air-pocket.

The second aim is to analyze the response of the innovative wine-spirit thermometer invented by René-Antoine Ferchault de Réaumur. The historical context is well documented in contemporary sources and modern papers. Papers written by Réaumur to comment observations made with his thermometer are listed in ESM4; some comparisons made by Maraldi in 1741 are discussed in ESM5.

Since its origins in the seventeenth century, the thermometric scale was defined linearly, dividing the distance between two calibration points into equally spaced intervals. Probably inspired to air thermometers (Amontons 1702; Camuffo 2002a), Réaumur imagined a degree defined volumetrically, in terms of a fraction of the total volume of liquid that had expanded from the bulb (ESM6). Like air thermometers, this thermometer was theoretically based on only one calibration point, i.e., freezing water, and the thermometric liquid reached the maximum volume expansion at 80/1000 when the wine-spirit boiled. This was the maximum obtainable calibration temperature because Réaumur dipped the tube with wine-spirit into the water calibration bath, but the tube was left open on the top. Réaumur noticed that at a certain temperature, the wine-spirit started to boil, and after a certain time, the water too started to boil. He supposed that boiling wine-spirit had the same temperature as the water of the bath. This

conclusion was misleading. Somebody started to think: the true calibration point was boiling water or boiling alcohol? And wine-spirit at what purity level?

In the 1730s, Nollet built thermometers strictly following the directives of Réaumur (1730, 1731). These thermometers were named "*true* Réaumur" thermometers (TRT) to distinguish them from another type, also named after Réaumur, but born around 1739 for a misinterpretation of the Reaumur's obscure papers (ESM7).

A formula to convert TRT readings is very relevant because TRT was initially used in France and became dominant in Switzerland where most records are still unexploited (Pfister et al. 2019; Brugnara et al. 2020). In addition, some early data, e.g., Utrecht, were transformed into this scale. Rousseau (2019) published TRT records in Paris and transformed into modern units using the key given by Réaumur (1740), i.e., $1^{\circ}R_{T} = 1.148 \ ^{\circ}C$. This paper analyzes the real response of TRT and in addition compares this coefficient with the accurate calibration made by De Luc (1772).

This paper is aimed to make a physical analysis of this system and produce accurate equations to convert to Celsius the readings of the original TRT. In addition, to compare TRT with the second generation of Réaumur thermometers, the wine-spirit distorted thermometers, and the novel centigrade scale, i.e., Celsius and the Lyon thermometer (Savérien 1753).

2 Materials and methods

This complex matter is considered from a holistic point of view. For the historical approach, the original sources have been considered to be an input, as well as the modern investigations. For the physical approach, some calculations have been made, based on the classical thermodynamics, in particular the changes of physical states, the laws of vapors and gases, and the equilibrium partial pressures over binary solutions.

The saturation pressure of ethyl alcohol has been computed with the Antoine equation (Antoine 1888; Ambrose et al. 1975; Schroeder et al. 2014):

$$\log_{10}p = A - \frac{B}{C+T} \tag{1}$$

where *A*, *B*, and *C* are component-specific constants that respectively hold 8.20417, 1642.89, and 230.300 in the temperature range -57 < T < 80 °C and 7.68117, 1332.04, and 199.200 in the range 77 < T < 243 °C; *T* is the temperature in Celsius.

The saturation pressure of water has been computed with the empirical Sonntag (1990) equation:

$$p_{\text{sat}}(T) = 6.112 \times 10^{7.65T/(243.12+T)}$$
(2)

that is accurate even in proximity of the boiling point, differently from the equation by Magnus (1844), later refined by Tetens (1930).

As the composition of wine-spirit is crucial (Camuffo and della Valle 2016), and the Réaumur thermometers had different mole fractions of water mixed to ethyl alcohol expressed as % ABV (alcohol by volume), calculations have been made using the Raoult law (Raoult 1887):

$$P_T = \chi_A P_A + \chi_W P_W \tag{3}$$

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where P_T is the total pressure, χ_A and P_A the mole fraction and the partial pressure of the component A (ethyl alcohol), and the same for W (water). This equation is for ideal binary mixtures of volatile liquids, while ethyl alcohol and water do not constitute an ideal mixture and present a positive departure from linearity. However, when the mole fraction of water is not too big, as in thermometers, the approximation is good (Brown and Martin 1951; Fawcett 2004; Blandamer et al. 2005). For instance, with a mixture containing 95.6% of ethyl alcohol, the boiling point departure is -0.1 °C.

The equation used to transform wine-spirit readings T_{WS} into readings taken with a linear mercury thermometer T_{Hg} is explained in Camuffo and della Valle (2016):

$$T_{\rm Hg} = -0.0025 \ T_{\rm WS}^2 + 1.25 \ T_{\rm WS} \tag{4}$$

The opposite relationship, i.e., from mercury to wine-spirit, has been derived in this work from the De Luc (1772) calibration:

$$T_{\rm WS} = 0.0023 \ T_{\rm Hg}^2 + 0.77 \ T_{\rm Hg} \tag{5}$$

3 To leave some air or not when sealing the tube?

3.1 Mixture ethyl alcohol/water and pressure inside the capillary tube

When, for the upper calibration point, wine-spirit thermometers were dipped into hot water, and the temperature of the calibration bath exceeded the boiling point of wine-spirit, tubes could be broken for the high vapor pressure (Fig. 1c). The pressure exerted inside the tube by the binary mixture of ethyl alcohol and water has been calculated with the Raoult law. The calculation has been made for the pure components, and for mixtures 90 to 50% ABV representing different levels of refined wine-spirit with two or more distillations, or water of life (e.g., brandy, cognac) with simple distillation (Chomel and Marret 1732; Camuffo and della Valle 2016). The vapor pressure originates on the liquid-free volume on the top of the tube but is then transmitted to the liquid in the tube and the bulb. The highest pressure is reached with pure spirit (100% ABV). In early wine spirit thermometers (70-95% ABV), the pressure ranges between 1893 and 2260 hPA (Fig. 2, left scale). Increasing the mole fraction of water, the pressure decreases but at low rate, e.g., at boiling water temperature, wine-spirit 90% ABV has pressure reduced by 5.4%, 80% ABV by 10.8%, and 50% ABV by 27%. The most popular wine-spirit thermometers lie between 70% ABV and 95% ABV. The mole fraction of water cannot be too high because the freezing point is raised (Raoult 1882) and in severe frost conditions the thermometer may break. Increasing the mole fraction of water, the boiling temperature too will increase (ESM8).

This may explain why Réaumur and Nollet preferred wine-spirit with considerable mole fractions of water. They deliberately left unknown the wine-spirit concentration used. Martine (1740) measured that highly rectified wine-spirit (95% ABV?) boiled at 79.5 °C, brandy (40% ABV?) at 87.8 °C, and the wine-spirit used by Réaumur boiled at an intermediate level, i.e., 82.2 °C. du Crest (1741) wrote that the mixture was composed of $^{3}/_{4}$ wine-spirit and $^{1}/_{4}$ water, i.e., 75% ABV. du Crest and his instrument maker Brander (1770) preferred highly refined



Fig. 2 Vapor pressure inside the glass tube of a thermometer exerted by pure wine-spirit, pure water, and binary mixtures from 50 to 90% ABV. Left hand scale: absolute values of the pressure inside the tube. Right hand scale: difference ΔP between the internal pressure (i.e., vapor mixture) and the external barometric pressure (atmosphere), i.e., the effective pressure exerted on the glass tube ($\Delta P < 0$ inward and compression; $\Delta P > 0$ outward and expansion)

spirit burning gunpowder (ESM8) because it was more resistant to frost in polar regions. In Réaumur thermometers with 75% ABV, the vapor pressure was 13.5% lower in comparison with 95% ABV used by du Crest.

The absolute value of the pressure inside the tube was not the critical factor, but the difference of pressure ΔP across the glass wall of the tube, i.e., the pressure inside the tube minus the atmospheric pressure that represents the effective pressure experienced by glass (Fig. 2, right scale). The consequences are analyzed by considering ΔP in three intervals.

At normal ambient temperatures, the atmospheric pressure outside the tube is higher than the vapor pressure inside. The net resultant $\Delta P < 0$ is directed against the convex side, and the tube undergoes compression forces (Fig. 1c). Normally thermometers operate in such conditions. The situation may become critical in the extreme cold when the external atmospheric pressure is not adequately counteracted by the internal pressure, and ΔP reaches – 1000 hPa with the risk that the tube breaks. Therefore, thermometers for extreme cold conditions should be adequately robust.

The turning point $\Delta P = 0$ occurs at the boiling point (i.e., 78.3 °C) of wine-spirit (e.g., 95%ABV) under standard atmospheric pressure, i.e., 1013 hPa. The turning point slightly shifts toward higher temperatures when wine-spirit has lower ABV values, e.g., 87 °C for 50% ABV. The turning point is above normal weather conditions but is met in the calibration bath. Despite the attention reserved to this particular temperature, it does not represent a critical threshold for the tube. As opposed, it represents the safest condition: the glass has no pressure gradients and is fully relaxed.

In the calibration bath, when the temperature exceeds the boiling point of the thermometric liquid at standard atmospheric pressure, the pressure inside the tube becomes higher and higher. The net resultant $\Delta P > 0$ is directed outward, pushing against the concave side, and glass is expanded by tractive forces (Fig. 1d). Approaching the temperature of boiling water, ΔP may reach or even exceed 1000 hPa, and the tube risks to break if glass is not strong enough.

Voltaire (1737) complained that TRT could not resist to boiling oil (ESM9). If he had olive oil, the smoke point is 200 °C, and the pressure inside the tube would reach 19 atm; if soybean or sunflower oil, the smoke point is 230 °C with pressure 33.6 atm. However, the real problem seems having been that Voltaire tried to measure a temperature exceeding the allowed range of the thermometer; the liquid column reached the top of the tube, pushed against it but could not expand anymore, and broke the top.

The results of the above calculations show that the maximum ΔP value exerted on the glass tube is the same either at very low calibration values obtained with a mixture of ice and salts (e.g., sodium chloride and ammonium chloride) or at the upper calibration point (i.e., boiling water), except for the direction: at low temperatures, it is directed inward and, at high temperatures, outward.

The absolute values of ΔP are very similar at the two fixed points, but with opposite sign. The difficulties met in proximity of the upper point may be explained considering the values of ΔP in combination with its direction. When $\Delta P < 0$, the force is directed against the external curvature that is convex, while when $\Delta P > 0$ against the internal curvature that is concave. This hypothesis may be supported by several examples, e.g., in architecture, arches and vaults support heavy loads on their convex side; eggs can bear loads on the convex side but are easily broken from inside by newly born chickens. However, the literature does not give a clear answer.

Some historical tests (Fairbairn 1860) conducted on glass tubes with different sizes but larger than 0.5 in., made of the best flint glass (sand 52%, red lead oxide 22%, potash carbonate 24%), common green glass (sand 53.5%, soda sulfate 22.5%, lime carbonate 24%), and white crown glass (sand 67.1%, soda sulfate 25.5%, lime carbonate 7.4%), found no difference in vulnerability when internal or external pressures were applied. This is a dated study but has the advantage of having tested three different types of glass used in early instruments.

The standard EN 1595 (1997) concerning modern borosilicate glass tubes establishes that the maximum resistance is inversely proportional to the internal diameter. Therefore, the smaller the curvature radius, the higher the pressure that can be supported by the tube.

Another hypothesis for the different impact of internal and external pressures is that, when the glass tube is subjected to internal pressure, the traction on the wall thickness leads to strain existing flaws on the glass surface, helping these flaws to propagate (Pattillo 2019). This may explain why high temperatures may be more dangerous than low ones.

This discussion shows that the matter is complex, but high pressures, especially when acting inside the tube, may damage the thermometer. Therefore, special care was needed (i.e., glass composition type and tube size, as well as wine-spirit purity) to make thermometers resistant to the upper calibration point. This explains a bad practice in the upper calibration point, i.e., dipping into the hot bath only the bulb and leaving outside the upper part of the thermometer, with the saturated vapor at milder conditions (ESM2). This reduced the peak of high pressure.

3.2 The boiling point in open and closed tubes

The boiling point of water was a basic problem. Cavendish (1766) controlled the upper point of some famous thermometers, i.e., Adams, Bird, Nairne, and Ramsden, and found that they differed by two or three degrees. In the eighteenth century, scientists realized that the boiling point depended on atmospheric pressure and decided to calibrate thermometers when the

barometer reached a selected value, e.g., 27 Paris inches and 9 lines (du Crest 1741). However, the barometric value was imprecise because the corrections for temperature and latitude were still unknown. The atmospheric pressure affects the boiling point at the rate 2.8 $\times 10^{-2}$ °C hPa⁻¹, and in summer (i.e., 30 °C) the bias may reach 0.25 °C. Fortunately, the effect on the melting point was negligible, i.e., 8×10^{-6} °C hPa⁻¹. The temperature correction for mercury expansion was neglected. This caused an error of + 3.3 hPa at 20 °C and + 5.3 hPa at 30 °C. The most accurate pressure determinations were in winter, when the room with the barometer was around 0 °C. The effect of gravity for latitude can be ignored when the site is close to the reference latitude 45°; the bias accounts for some 0.7 hPa but with opposite sign at latitudes 40° and 50°, 1.2 hPa at 35° and 55°, and 1.6 hPa at 30° and 60°.

Réaumur (1730, 1731) recognized that wine-spirit boiled before water and that the threshold was around 78 °C, because he operated with open tubes and could see the wine-spirit bubbling and steaming. However, he and his colleagues could not know the physics of ebullition that a volatile liquid boils when its saturation pressure equals the pressure external to the liquid, and what happened when the tube was sealed.

In an open system under standard conditions, ebullition occurs when saturation pressure equals the atmospheric pressure, e.g., 1013 hPa. At this point, the expansive force of the steam dissolved inside the liquid exceeds the external, compressive pressure, and *ebullition* begins. Boiling is a powerful mechanism for molecules to pass from the liquid to the vapor state. However, the external pressure remains unaffected because the vapor is continually dispersed within the open environment and ebullition continues until all the liquid will be vaporized.

As opposed, in the case of a spirit thermometer with the tube sealed without leaving some air inside, the liquid-free volume on the top of the tube contains only the vapors released by wine-spirit. In this closed system, the molecules transferred from the liquid tend to raise the vapor pressure until ebullition is stopped. Therefore, the wine-spirit is at boiling conditions at every temperature, but boiling is not macroscopically visible because the saturation equilibrium is continually and dynamically reached. At every temperature, and every temperature change, this mechanism always keeps at saturation level, or brings to it, the liquid-free volume on the top of the tube. When temperature increases, some more molecules will escape from the liquid to establish the new saturation level, i.e., microboiling, as noted by Delisle (1724) and du Crest (1741). When temperature decreases, the vapor mixture will become super-saturated, and the excess of vapor will condense to establish a new equilibrium.

The scientists of the eighteenth century could not know that, inside a closed tube, irrespectively it had been emptied of air or not, the vapor is always at saturation. Therefore, there is not a single boiling point, but all temperatures, over the whole thermometer range, are equally at boiling conditions. The idea that inside a closed tube the spirit boils around 78.3 °C is wrong, and this temperature is the safest one. Problems arose when the calibration bath reached 90–95 °C, and the internal pressure became too high.

3.3 Advantages and disadvantages of leaving some air inside the capillary tube

Unresolved problems were the advantage or the disadvantage of leaving some air inside the tube, when it was sealed, and who was right: Réaumur (1731) who preferred an empty space deprived of air, or du Crest (1741, 1757) who preferred to leave some air inside.

In the small liquid-free volume on the top of the tube, the basic equation regulating the total pressure P_{tot} is:

$$P_{\text{tot}} = P_{\text{air}} + P_{\text{spirit}} + P_{\text{water}} = \frac{\left(n_{\text{air}} + n_{\text{spirit}} + n_{\text{water}}\right) \Re T}{V}$$
(6)

where P_{air} , P_{spirit} , and P_{water} and n_{air} , n_{spirit} , and n_{water} are the partial pressures and the mole fractions of air, pure spirit, and water, respectively; \Re the universal constant of gases; T the temperature in Kelvin; and V the liquid-free volume left between the thermometric liquid and the upper top of the tube. V is continually variable and decreases when T increases. The key difference is that air is a gas, and the number of molecules n_{air} remains unchanged, while spirit and water release or uptake molecules, and their number n_{spirit} and n_{water} changes continually to keep the saturation equilibrium. Therefore, the total pressure inside the tube is due to a binary mixture of vapors (Raoult law) with the addition of a third partial pressure, P_{air} , due to the air left inside. This additional pressure is proportional to the quantity of air left inside the tube and has a strong double dependence on temperature, i.e., the direct proportionality with T in the numerator of Eq. (6) and the inverse proportionality with V in the denominator because V is reduced when T increases raising the liquid column.

Inside the tube, this air pocket increased the internal pressure, and the effect was magnified at high temperatures. Under this aspect, Réaumur who considered risky to leave some air inside was right. The problem of the high pressure was overcome by selecting resistant glasses, thicker tubes, and probably thinner internal diameters. On the other hand, the addition of air suggested by du Crest brought the total pressure above the saturation pressures of wine-spirit, and the system passed from the neutral equilibrium in which every temperature was equally a boiling point, to a new equilibrium of being always a little below the boiling point, but never reaching it. Probably, this additional pressure was not fundamental but improved the situation, avoiding the formation of micro-bubbles and the risk that the liquid column was (reversibly) broken (i.e., separated in two or more parts) by the formation of vapor bubbles (called voids), especially in the case of accidental hits. Under this aspect, du Crest was right.

4 The "true Réaumur" thermometer

4.1 Identification characteristics

Réaumur did not realize that wine-spirit had problems and considered it the best thermometric liquid because it was easy to work, had a large expansion coefficient, and was resistant to frost. He thought to avoid the problems met at the upper calibration point by devising a different calibration. His calibration (ESM10) was based on a fixed point only: the freezing point of water. He obtained it with a mixture of crushed ice and marine salt and corresponded to $-1 \,^{\circ}C$ (De Luc 1772). Réaumur (1730, 1731) graduated the scale with a small phial, adding known volumes of spirit under isothermal conditions. Then he dipped in a bath of water at increasing temperatures his thermometer filled of wine-spirit but with the tube still open on the top. He noted that, when wine-spirit started to boil, the liquid volume considered 1000 at freezing temperature was expanded to 1080. Therefore, he established that the new scale was from the basic volume of the freezing point (defined $0^{\circ}R_{T}$) to the volume at boiling point of wine-spirit (defined $80^{\circ}R_{T}$). Herewith $^{\circ}R_{T}$ will be used to avoid confusion with the next Réaumur scale $^{\circ}R$. When De Luc (1772) extrapolated the R_{T} scale till the boiling point of water, the latter was found to be $100.4^{\circ}R_{T}$. In theory, the thermometer was conceived with only one fixed point, but then boiling spirit became the

second fixed point. In addition, as Réaumur was not sure that his solution was so good, he added some auxiliary reference points, i.e., the cold mixture of ice and salts, the body temperature, and the temperature of the cellars of the Meteorological Observatory, Paris (Réaumur 1730; De Luc 1772; van Swinden 1778; Lambert 1779; Gaussen 1789).

4.2 Scales that might be confused with the "true Réaumur"

The early R_T scale, used in the 1730s, was from freezing water (0° R_T = -1 °C) to boiling wine-spirit (80 R_T ~78.3 °C), divided into 80 degrees.

In 1740, Martine published a series of criticisms to Réaumur, i.e.: (i) The melting and freezing points occur at the same temperature, except when the freezing point was artificially obtained with salts. Réaumur and most thermometers of the Royal Society had this point "very erroneously graduated". (ii) The calibration method made with phials at the same temperature disregarded the fact that glass and wine-spirit expand differently. (iii) "Réaumur was in the wrong" when he evaluated the boiling point making confusion between spirit and water (Martine 1740). Although Martine published his book in 1740, the print of the chapter concerning thermometry was dated August 1738, and certainly Réaumur read it.

After, Réaumur abandoned thermometers, and Nollet produced a second type without explaining the change or acknowledging the failure. The new production was started in 1739, because in 1740, in Padua, Giovan Battista Morgagni began a series of observations with this new thermometer (Camuffo 2002b). From 1740 onward, the name Réaumur became improperly a brand to indicate spirit or even mercury thermometers calibrated at melting ice (0 °R = 0 °C) and boiling water (80 °R = 100 °C), also divided into 80 degrees. De Luc (1772) called "true Réaumur thermometers" the early thermometers built according Réaumur (1730) to distinguish them from those built after 1739 that he called "false Réaumur".

Nobody commented that TRT was similar to the Celsius scale. It is known that Anders Celsius proposed a centigrade scale but reversed, i.e., 0° the boiling water and 100° freezing water (Celsius 1742). However, his milestone article had limited reception because it was written in Swedish. Around 1747, his colleague Carl von Linné (*Linnaeus*) turned upright the Celsius scale to make it more convenient to describe the biological life of plants and animals (Renou 1876). Surprisingly, Martine (1740) compares various thermometer scales (ESM11), including the Celsius as we use it today, and not in the reversed form, as we believed. In addition, the date 1740 is earlier than the officially known: 1742.

In 1743, in Lyon, France, Jean-Pierre Christin proposed the same centigrade scale from melting ice and boiling water, known as *thermometer of Lyon* (Savérien 1753). To his contemporaries, the centigrade scale was not considered innovative, because it had the same fixed points as Renaldini, Réaumur, and De Luc, but with 100 divisions instead of 80, which implied a modest increase in resolution, i.e., 20% higher. Unfortunately, for the prestige of Réaumur reputation, this alternative approach was not adequately considered. The 100-degree scale, initially called "centigrade" in French and "centesimal" in English and German, either derived from Celsius, Linnaeus, or Lyon thermometer, became popular at the end of the eighteenth century, when the decimal-based metric system was adopted.

4.3 How to convert TRT readings

To compare TRT readings, Réaumur gave an average interpolation coefficient, disregarding that TRT is not linear, although he was aware of this problem (De Luc 1772; Lambert 1779).

His conversion formula was as follows: $10^{\circ}R_{T}$ corresponded $20^{2}/_{3}$ °F, i.e., 11.48 °C (Réaumur 1740). However, it is possible to obtain a precise polynomial relationship between ° R_{T} and °C over the whole temperature range, as well as the accuracy of the linear interpolation 1 ° R_{T} = 1.148 °C. This can be made taking advantage of a precise TRT calibration made by De Luc (1772) and later reported by Toaldo (1775), van Swinden (1778), Lambert (1779), Gaussen (1789), and others (ESM10). De Luc (1772) dipped in the same calibration bath a TRT and a mercury thermometer as a reference and sampled at regular temperature intervals (i.e., 5.5 °C) for a heating-cooling calibration cycle. Some minor fluctuations can be noted for the non-uniform cross-section of the capillary tube, but these are small and do not affect the best-fit interpolation. The cycle was performed in a water bath, so the information below the freezing point is missing.

The difference ΔT_{TRT} between TRT and a mercury thermometer is reported in Fig. 3a together with the deviation from linearity of wine-spirit, and all values transformed into °C. The similarity between these two plots suggests that ΔT_{TRT} can be interpreted as a combination of two specific departures, one due to wine-spirit and one for the particular choice of the



Fig. 3 Comparison of departures. **a** Difference between a true Réaumur thermometer and a reference mercury thermometer; the deviation from linearity of wine-spirit composed of ethyl alcohol 95% ABV; the above alcohol deviation with summed the further departure for having selected the freezing water (i.e., $0^{\circ}R_{T} = -1 ^{\circ}C$); and the boiling point of alcohol (i.e., $80^{\circ}R_{T} = 78.3 ^{\circ}C$) as reference points. **b** Difference between the Réaumur (1740) linear interpolation and De Luc (1772) calibration

reference points, i.e., freezing water (i.e., $0^{\circ}R_{T} = -1^{\circ}C$) and the boiling point of ethyl alcohol (i.e., $80^{\circ}R_{T} = 78.3^{\circ}C$). With this calibration, and the typical wine-spirit departure, TRT closely follows the Lyon and Celsius-Linnaeus thermometer.

We start step by step analyzing the various departures. The best-fit equation to transform TRT readings (T_{TRT}) into Celsius scale and correct them as they were taken with a mercury (Hg) thermometer (T_{Hg}) is:

$$T_{\rm TRT} = 0.0025 \ T_{\rm Hg}^2 + 0.7404 \ T_{\rm Hg} + 0.9664 \tag{7}$$

The departure ΔT_{TRT} (°C) from the Celsius scale is:

$$\Delta T_{\rm TRT} = T_{\rm TRT} - T_{\rm Hg} = 0.0025 \, T_{\rm Hg}^2 - 0.2599 \, T_{\rm Hg} + 0.8746 \tag{8}$$

A further departure ΔT_{WS} caused by the non-linearity of wine-spirit 95% ABV is symmetrical and is given by:

$$\Delta T_{\rm WS} = 0.0024 \ T_{\rm Hg}^2 - 0.238 \ T_{\rm Hg} \tag{9}$$

The additional departure ΔT_{CP} (°C) for the particular choice of freezing water and boiling spirit as calibration points is:

$$\Delta T_{\rm CP} = 1 - 0.017 \ T_{\rm Hg} \tag{10}$$

The sum ΔT_{Tot} of the two above departures is:

$$\Delta T_{\rm Tot} = \Delta_{\rm WS} + \Delta_{\rm CP} = 0.0024 \ T_{\rm Hg}^2 - 0.255 \ T_{\rm Hg} + 1 \tag{11}$$

The difference ΔT_{TRT} that characterizes TRT is skew and may be divided into two branches: in the interval 0–50 °C, ΔT_{TRT} closely approaches ΔT_{Tot} , and in the interval 50–100 °C, it better approaches ΔT_{WS} . Only the former interval is of meteorological interest.

Wrapping up, TRT readings (T_{TRT}) taken in R_T can be transformed into Celsius and at the same time corrected for the above two departures (i.e., as they had been taken with a precise mercury thermometer T_{He}) using the bulk equation:

$$T_{\rm Hg} = -0.0026 \ T_{\rm TRT}^2 + 1.2545 \ T_{\rm TRT} - 0.5966 \tag{12}$$

The response of TRT is represented in Fig. 4a, b together with other basic thermometers and their transformations to Celsius.

The parabolic departure from linearity of TRT, as well as all wine-spirit thermometers, is larger in warm climates and limited in the cold regions. Anyway, the figure shows that the difference between TRT and a wine-spirit thermometer with Celsius scale is very small and may pass unobserved. It may be not distinguishable at all if also the thermometer with Celsius scale was calibrated at the freezing point (i.e., -1 °C) instead of the melting point (i.e., 0 °C).

The linear transformation key $1^{\circ}R_{T} = 1.148 \text{ °C}$ given by Réaumur (1740) through the Fahrenheit scale in the 0–50 °C interval is reasonably good, i.e., within ± 1 °C, and then departs at the higher temperatures until it will reach – 13 °C at 100 °C (Fig. 3b). In the 0–50 °C interval, the best-fit linear interpolation value is $1^{\circ}R_{T} = 1.154 \text{ °C}$ with Pearson determination coefficient $R^{2} = 0.99$.

It should be noted that the choice of the lower point changed over time (De Luc 1772; Lambert 1779; Gaussen 1789; Avogadro 1840). Initially, Réaumur (1730) and Nollet made the calibration using freezing point and boiling water. The interval between these two points

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Fig. 4 a Overview of the response of selected thermometers (and related units): "true Réaumur" thermometer ($^{\circ}R_{T}$) after the De Luc (1772) calibration; the same but after the Réaumur (1740) interpretation key; Réaumur mercury and wine-spirit thermometers ($^{\circ}R$); and Celsius mercury and wine-spirit thermometers ($^{\circ}C$). **b** Expanded view in the meteorological range

corresponded to 101 °C divided into 80 °R, and the readings $T_{\text{Hg,F}}$ of a perfectly linear Réaumur thermometer, i.e., mercury or mercury-equivalent, had the following conversion to Celsius:

$$T(^{\circ}C) = \frac{101}{80} T_{\text{Hg,F}}(^{\circ}R) - 1$$
(13)

where 1°R = 1.2625 °C. The calibration with artificial ice was useful in summer when natural ice was not available. In the late 1730s, after the comments made by Martine (1740), the lower calibration point passed from freezing water to melting ice. The interval corresponded to 100 °C divided into 80 °R, and the readings $T_{\text{Hg,M}}$ had the

conversion:

$$T(^{\circ}C) = \frac{100}{80} T_{\text{Hg,M}}(^{\circ}R)$$
(14)

where 1 $^{\circ}R = 1.25 ^{\circ}C$. The latter constitutes the well-known conversion law popularly used from the second half of the eighteenth century, till the twentieth century, and still survives in France. If metadata are missing, the correct scale, i.e., Eq. (13) or Eq. (14), may be recognized analyzing the temperature of the snow days (Camuffo 2019; Camuffo et al. 2020b).

The magnified diagrams (Fig. 4b) convert readings taken with the above thermometers to Celsius, obtaining values already corrected for the deviations from linearity. The same figure may help to recognize early readings with the following procedure. Enter the unknown readings on the abscissa; move vertically up to the line of the selected thermometer; then move horizontally to left to obtain the related readings in Celsius.

It must be noted that some wine-spirit thermometers were not calibrated at the above fixed points, but by comparison with an accurate mercury thermometer in the meteorological temperature range. The reference and the thermometer under calibration were dipped into the same bath of hot water. The bath was left to cool, and selected temperature levels were considered. The reference levels were transferred to the tube of the wine-spirit thermometer by fastening a silk thread or a woolen yarn. After, the glasswork was fixed with iron wire on the wooden tablet where the numerical values of the calibration were reported. The other degrees of the scale were determined by linear interpolation and/or extrapolation (Toaldo 1775; Camuffo 2002a). With this particular calibration, wine-spirit thermometers became clones of the mercury reference; they were linear and were named "precise," "mercury-equivalent." In early drawings, or in science museums, they can be easily recognized because their scale is interrupted before100 °C, e.g., 40°R (50 °C) (Fig. 1a).

5 Discussions and conclusions

The most frequent questions raised by climatologists when recovering or analyzing early instrumental series are discussed.

When should we suspect that the thermometer could be TRT? When and where was it used? TRT were built in the 1730s but continued to be used over time. Réaumur had a strong political position and was vice and then director of the *Académie Royale des Sciences* (ARS), Paris. He promoted scientific cruises around the world, from cold Arctic to hot Africa, and Réaumur himself, or his correspondents, published some climate data in the *Histoire et Mémoires de l'Académie Royale des Sciences*, Paris, or the *Philosophical Transaction of the Royal Society*, London. Manuscripts with TRT records were kept in ARS archives (Angot 1895). In France, known records span from 1732 to 1757 and in Switzerland till midnineteenth century. In Italy, TRT was never used, while the "false Réaumur" (i.e. the second type with 80° referred to boiling water) is documented since 1740.

When should we suspect that the thermometer had low ethyl alcohol concentration? Réaumur used wine-spirit with low purity, possibly to increase resolution and minimize the glassware disturbance. The degree of purity was undefined and variable, making thermometers hardly comparable between them (ESM3, ESM5, ESM10), except when calibration was made cloning a mercury thermometer.

From what temperature should we apply corrections? The largest bias of wine-spirit thermometers calibrated at the two water transition points occurs in summer. Above 10 $^{\circ}$ C, the error exceeds 1 $^{\circ}$ C.

How to recognize the scale and related calibrations points? If metadata miss this information, the only possibility is to convert the original record to all scales one may suspect to be, and compare the transformations with contemporary readings of the same site, or sites nearby, or with averages of the same site but in other periods, and start excluding the most unlikely results. In winter, the snow benchmark may be useful to detect drifts, or if the site was well ventilated or biased. It cannot be applied to distinguish different scales with 0 °C as fixed point, because at this particular value, or in close proximity, all thermometers give the same readings.

A key issue is the physics of saturated vapors and boiling that was unknown. When Réaumur made his calibration, he dipped a glassware containing wine-spirit, but with open top, in a water bath over the fire. When the water bath reached and then exceeded the boiling temperature of wine-spirit, he saw that wine-spirit was boiling, but he did not understand that its temperature remained constant even when water reached its ebullition point. The only effect of the heat passing from the water bath to wine-spirit was to increase the ebullition intensity and the evaporation rate of wine-spirit. Around 1739, Nollet started producing thermometers with 80° corresponding to the boiling point of water, without writing any explanation. Martine, du Crest, and De Luc had the intuition that the key was to do the calibration after the tube had been sealed.

Early wine-spirit thermometers were vulnerable to high internal or external pressures. Two opposite strategies were devised by Réaumur (i.e., aqueous spirit, no air left inside the tube) and du Crest (i.e., highly refined spirit and a small air pocket left inside the tube). In an open system, when the saturation pressure of a liquid equals the external pressure, the equilibrium is never reached and the liquid starts to boil and will continue to boil until all liquid has been vaporized. In a closed system, like a tube sealed on the top, the pressure is due to the saturation pressure generated by wine-spirit that remains at boiling condition at every temperature. This is a dynamic equilibrium where all temperatures are equally boiling points. However, the ebullition is not visible because it immediately stops because the molecules transferred from the liquid to the small volume on the upper part of the tube raise the pressure, stopping boiling.

Inside the tube, pure ethyl alcohol exerts the highest pressure, and if one increases the mole fraction of water, the pressure decreases. This explains why Réaumur preferred to use wine-spirit with low alcohol content. However, in the wine-spirit mixture, the water fraction had to be limited, because increasing the molality of water, the freezing point of the mixture increases, and in frost conditions risks to break the thermometer. Instrument makers could solve the pressure challenge using high-quality glass, thicker tubes, and smaller internal cross-sections.

du Crest (1741) suggested to leave some air inside the tube to increase the internal pressure and stay just below the boiling point. Brander (1770) claimed that a higher pressure increased the resistance of the tube to the boiling point, but this was incorrect. The advantage of some air was that at every temperature, the liquid remained slightly below the boiling point, thus avoiding the formation of micro-bubbles and reducing the risk of forming separation breaks in the liquid column, not of breaking the glass! The air pocket generated an additional partial pressure that increased very much at the high temperatures and made thermometers more vulnerable.

The critical factor was not the absolute value of the pressure inside the tube, but the difference of pressure across the tube wall. The boiling point of wine-spirit (i.e., 78.3 °C)

constitutes the safest condition because the pressure inside the tube equals the external one and the glass is in neutral equilibrium without pressure gradients. As opposed, when the temperature of boiling water was approached, the pressure of wine-spirit exceeded 1 atm, and the tube risked to break if the glass was not adequately resistant.

In literature, TRT has been carefully investigated from the historical point of view, but never in physical terms. This analysis shows that TRT readings may be misinterpreted for a wine-spirit thermometer with Celsius or Lyon scale. Best-fit equations have been derived from De Luc (1772) to convert TRT readings into Celsius, at the same time correcting them from the departures due to wine-spirit.

If the accurate polynomial equation is left for a linear conversion, De Luc (1772) calibration gives $1^{\circ}R_{T} = 1.154 \text{ °C}$ instead of the crude transformation $1^{\circ}R_{T} = 1.148 \text{ °C}$ given by Réaumur (1740).

Additional equations have been found for the most frequent options, i.e., mercury and winespirit, either Réaumur or Celsius thermometers. These equations constitute the key to recover and analyze unexploited records.

Finally, it has been found that the Celsius scale was known earlier than believed, since 1740. Martine (1740) witnessed that it was an increasing scale, i.e., identical to the scale we use today, not reversed (ESM11).

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Electronic Supplementary Material

Title: Key problems in early wine-spirit thermometers and the "True Réaumur" thermometer

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ESM 1. Supplement to Section 1: How this paper fits with the involved disciplines

Recovery, correction and homogenization of long instrumental series is a key branch of climatology but requires a multidisciplinary approach, including physics, mathematics and history (Fig.ESM1). Physics is necessary to understand involved mechanisms, behaviour and response of instruments, calibration, operation and exposure bias. Mathematics is needed to handle and process data, but especially to perform critical test to verify hypotheses or to extract from the records some key information that was not included in logs and books. When reading logs and books, one may find what the early author deliberately intended to write. As opposed, mathematics may constitute a subtle



Fig.ESM1. Disciplines involved in this research. This paper lies in their common area. The professional fields of competence of the author are physics, mathematics and climatology

form of investigation to know not only what the early author did, but also what he was unable to understand or failed to write. Reading original sources is typical of both scientists and historians. However, in the early instrumental period, manuscripts and books were written using a language composed of terms and concepts at an embryonic stage typical of scientific thoughts under development, and also including several untenable ideas. Their interpretation requires high scientific competence to discriminate what might be extracted from thoughts that sometimes fall outside of reality.

In this paper, one of the three Referees, likely a historian for his/her comments, outlined that it should be explained how and where the author's methodology fits within the current scholarship and how this paper fits in the context of "*experimental history of science*" taking as useful reference the paper by Fors et al. (2016) *«From the library to the laboratory and back again: Experiment as a tool for historians of science*». These

Authors mention several examples of historians that have considered various fields, e.g. cultural heritage, anthropology, pharmacy, alchemy, physics and so on. The most stressed activity is the experimental approach to recover a particular practice from the past, and historians applied to reproduce experiments, but with subtle distinctions between *reworking, reproducing, replicating, reconstructing, re-enhancing, restaging* and so on. The conclusion was that such activity is always performed by historians, who explore a different discipline, but "*the main goal is a better historical*

understanding of the texts". Finally, the method should serve the purpose of re-evaluating historical episodes and contexts. An intriguing circular research is shown, that starts from historians, works with history, and returns to historians some better refined historical interpretations. Using a mathematical language, this might be defined "*a virtuous loop within the same cultural domain*". In addition, they do a beautiful job, but they are unable to transform their readings into mathematical equations to be used by everyone.

This paper lies in another context. The author is a physicist, specialized in climatology, and applies his mathematical and technical knowledge to interpret instruments and climate data, in this case temperature. Early instrumental observations were taken with instruments and methodologies different form the modern ones, standardized following the World Meteorological Organization (WMO). To combine early records with modern records, it is necessary to make them homogeneous. Therefore, the first task of a physicist, when he analyses a set of data, is to assess their reliability and correct for possible bias. To do this, he must know the characteristics of early instruments and so on, that unfortunately are often missing in the original documents. The only possibility is to seek for this vital information in the early sources, either manuscripts or printed papers in their original languages, or extract them with help of mathematical tests.

Returning to the previous classification, the position of every scientist is to be open-mind, observing and interpreting observations as objectively as possible, carefully avoiding any preconceived idea or philosophical position. The aim of this paper is to extract information from a certain cultural domain (e.g. historical documents), transform and transfer this information (with help of physics and mathematics) to a different cultural domain (i.e. climatology) to study climate changes. This may be defined "to establish a virtuous link between different domains, i.e. to build a bridge that connects historical sources with climate study". This bridge is built with words, but especially with mathematical equations that may be used by everyone.

The author is used to work in multidisciplinary projects but is not a historian, even if the activity of carefully reading early books may be common to humanists an in particular to historians. Of course, he appreciates reading early documents and history of science, and has been doing it for fifty years. Returning to the classification of Fors et al. (2016), one of the goals of this paper is *a "better physical understanding of early texts"*, that may be only made by well experienced physicists.

The final aim is to recovery, correct and homogenize early instrumental observations before applying statistical tools to analyse early and modern weather data, assess climate changes and draw sound climate conclusions that might have a strong impact on the global policy and society. As typical for physicists, ideas and results are synthetized in words, drawings, plots and especially mathematical formulae. As typical for scientists, the interest and the quotation concern the original document that reports a certain discovery or a key progress, irrespective of who later repeated, summarized or made overview. On the other hand, from the point of view of the history of sciences, humanities and social sciences, any innovative idea or hypothesis that had some impact on the culture or the society is highly relevant. If that idea had been later confirmed or not by reality, may be of secondary importance. Who launched the idea, who shared or repeated it, how long this idea was believed and so on are all key items and merit to be considered and quoted.

This paper is aimed to give a correct physical interpretation to the original writings about early thermometers, individuate claimed and real problems, transform criticisms and comments into mathematical equations, verify the physical conditions of thermometers under calibration and use, identify different scales and provide equations to transform early readings into different scales and recognize the type of thermometer used when this was not specified in the metadata. The target user is the scientific community that recovers and analyses long temperature series, and studies climate changes, as well as historians interested to this topic.

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ESM 2. Supplement to Section 1: Early thermometer calibration

In the 18th century, a common bad practice was to dip into the calibration bath only the bulb, as in **Fig.ESM2a** showing the laboratory of Nollet, and the instrument maker (Nollet?) while is calibrating a thermometer.



Fig.ESM2a. Calibration of thermometers. A view of a physics lab while a scientist is dipping the bulb (B) and the lower part of the tube into a pot (C) of boiling and steaming water. The upper part of the tube, with the wooden tablet. remains outside, in milder conditions. On the left corner, a vessel (G) with crushed ice mixed to salts for the lower point. (From Nollet 1748).

On the other hand, somebody else, like du Crest (1741), correctly dipped the whole thermometer into the calibration bath.

Another view of the laboratory of Nollet, while he is calibrating a small Réaumur thermometer by comparison with a big reference thermometer (called *étalon* in French) is shown in **Fig.ESM2b** (Tome III, Plate VII, Fig.4 and Fig.5 from Nollet 1770):



Fig.ESM2b. Details of the Nollet physics lab. On the left side: a big Réaumur thermometer that is calibrated volumetrically with phials and is used as a reference (étalon). On the right side: a smaller Réaumur thermometer that is calibrated by comparison with the reference. On the table: on the left, a pot of boiling water (E) with a dipped thermometer (C) for the upper calibration point; on the right, some glass phials hold on the round serving stand. On the floor, a wooden tub with ice and а thermometer (C) dipped inside for the lower calibration point. On the Table top, Fig.1 and Fig.2 are not related to this context. (From Nollet 1770, courtesy of gallica.bnf.fr Bibliothèque nationale de France)

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ESM 3. Supplement to Section 1: Stability of thermometers: wine-spirit, mercury and glass

3.1. Stability of wine-spirit

A key issue is the long-term stability of thermometers, and possible drifts due to chemical transformations of wine-spirit, or glass, or both. It is known that ethanol may degrade over time because of photocatalytic oxidation, possibly affecting the wine-spirit volume. Catalytic active substances might be contained in the glass, especially in historical glasses, and UV radiation might trigger the process in thermometers exposed outside. This problem may be found cited in modern reports concerning thermometry (Cross et al. 2009) as a potentially relevant issue, but this aspect has never been investigated. As opposed, several laboratory tests have been performed to obtain products derived from ethyl alcohol for industrial purposes or to remediate polluted environments. For instance, Sauer and David (1996) studied the photo-catalysed oxidation of ethanol and acetaldehyde in humidified air. Using two photo-catalysts and UV radiation they found that under such extreme conditions, ethanol was photo-oxidized to acetaldehyde and formaldehyde intermediates, and eventually to carbon dioxide and water products.

Once established that a reaction is theoretically possible, the point is if this may occur at so a high rate to produce an appreciable change of the wine-spirit volume, or may affect its expansion coefficient. In the early instrumental series, thermometers were used from short periods up to a maximum of two or three decades. In the 18th century, before the advent of the Societas Meteorologica Palatina, Mannheim (Hemmer 1783), thermometers with wooden tablets were not resistant to outdoor exposure, especially to rain, direct sunshine or relative humidity changes (Camuffo 2019). In the first half of the 18th century they were generally kept indoors, as recommended by the Royal Society, London (Jurin 1723). Around mid-18th century they were exposed outside, but in well protected environments, e.g. under a loggia or a shielded window facing north. Indoors, there was negligible UV radiation, and in the case of loggias it was much less than in open outdoor envirnments. However, even in the theoretical case of fully unshielded thermometers exposed to open sky, it should be considered that glass is partially transparent to UVA but is opaque to shorter wavelengths, i.e. UVB and UVC, passing about 90% of the light above 350 nm, but blocking over 90% of the radiation below 300 nm. The conclusion is that photochemical transformation of winespirit is theoretically possible, but it is highly unlikely for the protection of glass, and especially in the 18th century when thermometers were mainly kept indoors.

Another popular claim is the oxidation of ethyl alcohol for the air pocket left on the top of the tube. In order to give a quantitative evaluation of the problem, the number of molecules of ethyl alcohol that may be oxidized by the air pocket is here evaluated. Reference is made to the accurate original drawing of the big Réaumur (1730) thermometer (*étalon*) (**Fig.ESM3**) that was employed for calibration of smaller thermometers for common use.



Fig.ESM3 The big Réaumur (1730) thermometer (étalon). Colours have been added. See text.

The drawing (Réaumur 1730) reports the level reached by wine-spirit at ebullition, i.e. the level marked 1080-80. The violet part of the thermometer is filled of wine-spirit (WS), and the cyan is

filled of air (A). At this stage, the top of the bulb is sealed. The ratio of the two filled volumes, i.e.

$V_{\rm A}/V_{\rm WS} = 0.0030$

The two molar masses are similar, i.e. ethyl alcohol 28.05 g mol^{-1} and air $28.996 \text{ g mol}^{-1}$, but the used quantities are different. Ethyl alcohol is liquid, while air is at the gaseous state. At standard conditions, every mole of liquid that passes to the gaseous state will expand to 22.4 litres. However, the oxidation may occur with oxygen only, that in air constitutes the 20.95% molar fraction. Therefore, even if all the oxygen molecules of the air pocket will combine with ethyl alcohol, the maximum fractional number of molecules of wine-spirit that could be oxidized is 2.8×10^{-5} , i.e. less than 30 molecules oxidized for every million of wine-spirit molecules.

The above calculations may be expressed in terms of temperature bias. In the volumetric calibration of the *"True"* Réaumur thermometer the range is from the initial 1000 to the final 1080 volumes that correspond to $80^{\circ}R_{T}$, i.e. 1 R_{T} is related to a fractional value the order of 10^{-3} . Here the problem concerns a potential transformation of physical properties of wine-spirit for a molecular fraction of the order of 3×10^{-5} . Therefore, the largest potential impact cannot exceed 3×10^{-2} ° R_{T} , i.e. the maximum reachable bias may be of the order of $0.03 \, {}^{\circ}R_{T}$.

In conclusion, even if the above calculation has been made with crude, most pessimistic assumption, the drift derived from the claimed oxidation is absolutely irrelevant and not detectable.

3.2. Stability of glass

Similarly, changes of the volume of the bulb may cause a drift of the zero point of historical thermometers. Bellani (1808) recognized that the freezing point is liable to vary, and raised the problem whether this was due to a change of volume of water, or glass, or both. Some years later, Bellani (1822, 1823, 1841) returned to the topic, reporting that after the first year of life, the zero point of a thermometer may rise by 1 or 2°C. He interpreted the shift of the ice point because glass has not a crystalline lattice structure, and may remain partially plastic for one year or so after it was built, if it had not been adequately annealed. Flaugergues (1822) too noted that in the first 6 months of life a thermometer may raise its zero point up to 0.5°C, but he disagreed on the Bellani's interpretation. His explanation was that glass is elastic, and is deformed under the weight of the atmospheric pressure. To avoid the problem, he recommended to leave a small opening on the top of the tube, thus avoiding the difference of pressure inside and outside the tube. The suggestion to leave a small opening was bad, but the most likely explanation is that the glass may require some time to reach the final structure, and at ambient temperature the glasswork is subject to high pressure, e.g. 931 hPa at 20°C, as discussed in the text.

Yelin (1824) performed some laboratory tests by using 21 thermometers with and without air inside in order to consider the potential influence of atmospheric pressure and found that the large majority of thermometers had variations of the freezing point similar to those detected by Bellani and Flaugergues, but some had lower. The same information was reported by Gmelin (1828) and Peixotto (1829). In the same issue of the journal in which Yelin published the above contribution, he also reported (page 373-377) the second part of his experiment with a table reporting the boiling points of alcohol at various strengths (i.e. % ABV). However, his experiments had a sharp comment: «I am persuaded that these results of Yelin are inaccurate» (Thomson 1831).

3.3. Stability of mercury

Mercury thermometers suffered the zero shift all the same, and this should exclude that the drawback was due to wine-spirit transformations. Flauguergues (1822) reported the error for ageing of six old

Error (°C)	Instrument maker	Thermometer age
+0.1	Jesse Ramsden, London	>40 years
+1.1	Paul son	20 years
+2.1	Paul father	40 years
+2.2	Betalli, Paris	15 years
+0.9	Gourdon, Geneva	2 years
+0.3	Gourdon, Geneva	8 months

mercury thermometer of famous instrument makers, as reported in Table ESM1.

Table ESM1. Zero-shift of mercury thermometers reported by Flauguergues (1822)

As the bias of mercury thermometers was similar to wine-spirit thermometers, the most obvious conclusion is that the bias was mostly due to glass, that may need months or even years to stabilize its amorphous structure, as suggested by Bellani.

3.4. Combined stability of wine-spirit, mercury and glass

At mid-19th century, Adie (1850) repeated the tests with wine-spirit and mercury thermometers, with the upper space of the column empty or with an air pocket inside, to investigate the general problem and the Flaugergues hypothesis of the external pressure. He excluded that wine-spirit thermometers suffered the shift of the ice point. He tried to explain the contradiction, considering that whine-spirit had a large expansion coefficient compared to mercury and especially to glass, so that small change in the glass bulb might pass unobserved. As opposed, mercury thermometers had a small drift, but without difference between those with vacuum or an air pocket, demonstrating that the Flaugergues (1822) hypothesis of the atmospheric pressure was untenable.

Several years later, with more advanced knowledge and technology, Chappuis (1888) and Guillaume (1889) returned to the same topic and evaluated the estimated error for various types of glass (e.g. Jena, English glass, hard-glass, soft-glass) and the correction formulae. The departures were very small, i.e. generally smaller than 0.1 °C. As opposed, the experience with common thermometers reported by Ganot (1860) was more negative, i.e.: «Regnault has found that some mercury thermometers, which agree at 0° and at 100°C, differ in the interval between these points, and that the departures frequently amount to several degrees. Regnault thinks that this is due to the unequal expansion of different kinds of glass» (Camuffo and della Valle 2016).

The Little Florentine Thermometers gave an excellent opportunity to test the drift. They were built in the 1641-1670 period and were used in the international Medici Network (1654-70). Some of them are still kept at the Museo Galileo, Institute of the History of Science, Florence. Unfortunately, the instruments are vulnerable and cannot be used to test their calibration and their drift after 350 years. However, Camuffo and Bertolin (2012) considered the historical calibrations published by Martine (1740), Cotte (1774), Libri (1830) and Meucci (1873) and the last one made 40 years ago by Vittori and Mestitz (1981). There was not significant difference, i.e. $\pm 2.3\%$, that is very small considering that the tested instruments were of the same type, but not the same instruments. They were produced individually, trying to make them identical, as far as possible, so that the scatter may be likely due to small individual differences when they have been built. This was a unique opportunity to test the overall drift, i.e. wine-spirit and glasswork, over a so long time period. In particular, these thermometers had not wooden frame, but were completely made of glass and were weatherproof (they were nicknamed *weather glass*) and could be exposed outdoors, receiving UV radiation.

3.1. When thermometric drifts became detectable

It must be said that, except the Little Florentine Thermometers that had the scale incorporated into the glasswork, the problem of drift makes sense only since the late 18th century, i.e. starting with the *Societas Meteorologica Palatina*, Mannheim, when the thermometers became resistant to outdoor exposure. At this point the capillary tube was in some way fixed to the scale and it was possible to recognize drifts.

As opposed, for most of the 18th century, thermometers were composed of a glasswork attached with iron wires to the wooden tablet with scale painted or glued on it (see **Fig.1e** of the article, reported here). In general, thermometers had the glasswork (i.e. bulb and tube) gently fixed to the tablets with two iron wires i.e. L1 and L2 in the figure and only exceptionally on the top too (i.e. L3). Therefore, in the case of vibrations, or shrinkage-swelling cycles of the wooden tablet in response to temperature and relative humidity cycles, the glasswork could slip down along the scale, and needed frequent adjustments. It was thus impossible to recognize drifts, except after they generated macroscopic changes as explained elsewhere (Camuffo and Bertolin 2012; Camuffo et al. 2016; Camuffo 2019).



Fig.1e

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ESM 4. Supplement to Section 1: List of Réaumur papers concerning observations with the "True Réaumur" thermometer

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Réaumur, alias Ferchaud de, RA (1741) Observations du thermomètre faites en MDCCXL à Paris et dans d'autres endroits, soit du Royaume, soit des pays étrangers. Histoire et Mémoires de l'Académie royale des sciences, 539-566.

ESM 5 Supplement to Section 1: Maraldi's comparisons between thermometers

Gauvin (2012, Fig.6 p. 543 of his paper) presented an interesting case study. From 23rd February to 8th March 1741, at the Observatory of Paris, Jean-Dominique Maraldi took a series of observations with four thermometers: two novel "*Universal Thermometers*" built by du Crest with highly purified wine-spirit, a big reference Réaumur thermometer (*étalon*) calibrated volumetrically with glass phials, and a small normal Réaumur thermometer built by Nollet and calibrated by comparison with the big reference. Both were "*True*" Réaumur. Two thermometers were located on a terrace (**Fig.ESM4**), and two on windows.





Fig.ESM4. Paris Observatory. (a) A view of the terrace one century later, with small turrets and windows, as well as meteorological instruments, screens and shields of various types (From Flammarion 1872). On the right-side window, a hutshaped metal screen is attached at some distance from the wall to get better ventilation in the free air. (b) The terraces today, viewed from north-west. The arrow shows the point of view of the Flammarion drawing (picture Rui Ornelas CC-BY-2.0 reworked).

Maraldi presented his readings in tabular form with columns (here transformed in rows) headed as reported in **Table ESM2**. These headings are fundamental to interpret the data.

Table ESM2. Headings of the Table made by Maraldi at the Paris Observatory from 23rd February to 8th March 1741, to compare four thermometers between them.

Date	
Micheli [du Crest] thermometer located on the	Readings in his [i.e. Micheli du Crest] scale
terrace	Readings transformed to ["True"**] Réaumur
Big Réaumur thermometer located on the terrace	
Small thermometer of Abbot Nollet located on the wa	indow of the [?]* terrace
Another Micheli thermometer located on the [?]*	Readings in its own scale [i.e. Micheli du Crest]
window	According to ["True"**] Réaumur
Difference between the last two	

Notes. (*) in the handwriting, the obscure word here reported as $[?]^*$ is an abbreviation, likely lad^e . (**) The specification "*True*" is missing because in February 1741 the novel Réaumur type, i.e. the so-called "*False*" was just born and still unknown.

Headings include the obscure abbreviation «*lad*^e"». The meaning is uncertain, probably: article *la* (i.e. "the"), followed by the first and last letter of the word, i.e. *d* and *e*. The interpretation is unclear, e.g. "the second" (*la deuxième*)?; "the last" (*la dernière*) possibly because it was at the top floor called "the upper" terrace?; "on the right" (*la droite*) because it was on the right side? In conclusion, we must forcedly follow Gauvin (2012) who neglected it.

Gauvin was unable to understand how the conversion of scale was made, and commented: «Note that Micheli du Crest's scale is different from Réaumur's. A straightforward mathematical conversion was required to compare the two scales». However, he did not consider that Maraldi used the novel *Universal Thermometer* built by du Crest, which had parallel scales, e.g.: du Crest, Delisle, "*True*" Réaumur and Fahrenheit, reported with their calibration points. Consequently, the observer could read the preferred scale without need to transform readings. This is the reason why it was named "*Universal*". In the Maraldi log, the two columns with the different scales report the values directly read on the *Universal thermometer*, without conversion.

A conversion table from the du Crest scale to the "*True*" Réaumur, and vice-versa, was published by van Swinden (1778) and is reported in **Fig.ESM5**.

On the bottom of this Table there is a note, indicated (106). The translation is: «This table refers to the "*True*" (*vrai*) Réaumur thermometer. For a comparison with the "*False*" (*faux*) Réaumur thermometer almost universally used today, one should add 0.8 [°R] to **all** degrees of the Réaumur thermometer on this Table». This note considers the difference between the two zero points: 0 °R_T was -1 °C, i.e. -0.8 °R, while 0 °R was 0 °C. However, van Swinden (1778) did not consider that the difference 0.8 decreases at increasing temperatures and the scale is not liner. Consequently, the addition of 0.8°R is good in close proximity of the zero, probably reasonable in winter, but should be revised in the other seasons.

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	5	_	14.67	30	-	16.77			
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Fig.ESM5. Title: Table for the conversion from the du Crest (D.C.) scale to the *"True"* Réaumur (R.) thermometer and vice-versa. Selected reference points. Note: negative values. Negative values follow the positive ones, after 0. For readers not used to the old style, negative values are highlighted in cyan.

It is now possible to return to Maraldi, on the terrace of the Paris Observatory, in winter 1741, as reported by Gauvin (2012). The big Réaumur thermometer and the two du Crest thermometers were wine-spirit; Réaumur refined around 75% ABV, du Crest around 95% ABV, and their difference is expected to be maximum in summer, when high temperatures are reached. However, this is known today (Camuffo and della Valle 2016), but not in the 18th century, and for his field test Maraldi selected the wrong season, at the height of winter, when the thermometric departures for different ABV values are smallest, and null at 0°C. During this winter test, the temperature ranged from around 2° to 7°C, and in this interval the departure of purified wine-spirit from mercury is from 0.5°C at 2°C to 1.6°C at 7°C. However, the difference for different ABV values is a fraction of the above values and is very small (i.e. <0.2°C), so that it is not surprising that Maraldi found differences generally lower than 0.5°C between the two instruments on the terrace. The du Crest thermometer on the window was also consistent with those on the terrace. The Nollet thermometer on the window recorded some 2°C less, and this was interpreted as a bad calibration, as explained later.

As usual, Maraldi did not specify how the thermometers were exposed or shielded. In another paper, De Luc (1784) gave a better idea about the general problem of exposure and representativeness, i.e.: «I have already explained that the normal thermometers are not precise when measuring the air

temperature, because their wooden frame constitutes an obstacle: the free air enters in contact with this object [i.e. the bulb], is heated by the solar beams, and heated again or cooled by the wind. Such causes that determine the air temperature operate from different directions, and the thermometric bulb fixed on a tablet, from one hemispheric side is affected by the [atmospheric] factors active in front of it, and does not reach the same temperature as the air». This means that these thermometers were unshielded and were affected by atmospheric disturbances in uncontrolled way.

Gaussen (1789) returned to other, more extensive tests that Maraldi performed at the Paris Observatory. He reported some key information missed by Gauvin. In February 1731, Réaumur placed **inside** the eastern tower of the Observatory his novel big thermometer used as a reference (i.e. *étalon*), and this thermometer was used to read the most extreme summer and winter temperatures published on the *Mémoires de l'Académie* until 1754; after, it was abandoned. In 1736, Maraldi added another Réaumur thermometer outside a window facing north of the same tower of the Observatory. This second Réaumur thermometer was much smaller for field surveys, i.e. the Nollet type calibrated after comparison with the reference. Maraldi noted that over the whole summer the small external thermometer recorded a lower temperature in comparison with the big thermometer kept inside. As in 1742 the opposite was observed, the small thermometer was considered bad, was broken and substituted with another one. Gaussen commented that possibly the temperature difference was due to the different size of the two thermometers, but this is not tenable. Nobody suspected that the temperatures inside the turret, on the terrace and the window could be different. Today, this would be the most obvious explanation, but not in the 18th century.

Van Swinden commented: «all thermometers named *Réaumur thermometers* don't speak the same language, but may differ by 0.8° (i.e. 1°C)» for a number of reasons including the particularities of the lower point with artificial or natural ice, the upper point and the ambiguity between the boiling of spirit and water, the difficulties in making the volumetric calibration with phials, and so on (van Swinden 1778).

As another example, Lambert complained: «the du Crest scale, between the point of temperature of the Earth [i.e. the *Temperate*] and the boiling water has 100 degrees; Mr. de Reaumur only 69 3/4 degrees. In the transmitted scale, however, approximately 95 Reaumur coincides with 100 degrees from du Crest. A noticeable error must have occurred in the graduation of one or the other thermometer» (Lambert 1782). Therefore, not all thermometers were good and well calibrated; not all observers followed a correct sampling protocol, especially concerning the exposure and to avoid disturbances from the solar radiation or other atmospheric variables. Who analyses early data must consider, case-by-case, the reliability of the observer, the observation protocol, and the instrument.

Maraldi made the test described by Gauvin (2012) in 1741, when Jacques Barthélemy Micheli du Crest produced the novel *Universal thermometer* tested by Maraldi and published anonymously in French his book on this thermometer, with the synthetic title: *«Description of the method for a Universal Thermometer»* (du Crest, 1741). This thermometer was innovative for the very accurate construction, the highly-purified wine-spirit, and for having several scales simultaneously, so that anybody could read the preferred scale, or find the transformation from one scale to another. Probably the idea of using a multiple scale was derived after Martine (1740) (see **ESM 11**) but this was not acknowledged. The publication appeared anonymously because du Crest was condemned for political reasons and his name could be dangerous for the book printer, his sellers and the book dissemination. Du Crest continued to work although from 1749 to 1765 he was imprisoned in Aarburg Castle, and was pardoned when his life was approaching its end (Wolf 1858). Du Crest needed an

assistant and instrument maker, and since 1755 he worked with the mechanist George Friedrich Brander. Du Crest was French speaking but understood German, and vice-versa Brander. For this reason, du Crest agreed that Brander translated into German his book. Du Crest died in 1766, and Brander published the German translation in 1770, with a longer and detailed title, i.e. *«News of the Universal Thermometer, which is made from the spirit-of-wine which ignites the powder, and which must show a hundred degrees from the Temperate (i.e. the average temperature) of the Earth to the violently boiling water»* (Brander 1770). The author name is only Brander, not du Crest, who lost this second opportunity. The translation includes some additional explanations by Brander, but not always correct, as already commented concerning the positive effects of the higher pressure in the tube.

Du Crest (1741) was willing to ascertain the Earth's *Temperate* i.e. the temperature of the terrestrial globe, that he thought to be constant and uniform, and obtainable as the average of the temperature read at the bottom of deep cellars and mines. He charged Brander for this task and Brander performed several measurements. However, at the end, du Crest and Brander used as a fixed point the temperature measured inside the cellar of the Paris Observatory, like Réaumur. Brander made some comparisons with thermometers manufactured in France and The Netherlands to improve his technology. Thermometers du Crest - Brander were used in Switzerland and sometimes around Europe until the 19th century. Brander hosted Lambert from 1759 till 1761, and had the opportunity of exchanging ideas and expertise. However, Lambert was more interested in optics and published an article on the glass micrometer built by Brander (Lambert1769).

Johann Heinrich Lambert, in his book *Pyrometry*, appeared posthumous (Lambert 1779), gave a fundamental contribution on the knowledge of the dynamics of heat, its transmission by conduction and radiative dispersion, and discovered important physical laws concerning radiant heat. In the first chapters, he reported an extensive overview of various thermometers, hypotheses and discussions, like the commented overviews by Martine (1740), Nollet (1748), De Luc (1772; 1784), Cotte (1774), van Swinden (1778), and many others. Although his overview is not innovative, it may be useful to add something to the context. For instance, Lambert wrote about the intuition that du Crest had to explain between the difference between wine-spirit kept in an open or a closed capillary tube dipped in a calibration bath. Lambert wrote that De Crest was inspired by Denis Papin (1707) and his steamengine to reach the temperatures of boiling spirit and boiling water. Du Crest thought that in the steam engine water reached higher temperatures and the steam higher pressures, i.e. the higher pressure was the key. Therefore, he concluded that the only way that wine-spirit had to reach the boiling temperature of water was to close it inside a sealed glass tube, like the Papin's steam engine. The explanation was not rigorous, but was helpful. This shows that Martine in Scotland and du Crest in Switzerland and had the same intuition, but Martine had it one year earlier.

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ESM 6. Supplement to Section 1: Volumetric method used by Réaumur to calibrate his thermometers



Fig.ESM6. The original big Réaumur thermometer (the so-called *étalon*) and the phials used to fill the thermometer with selected volumes of wine-spirit (from Réaumur 1730)

Reference

Réaumur, alias Ferchaud de, RA (1730) Règles pour construire des thermomètres dont les degrés soient comparables et qui donnent des idées d'un chaud et d'un froid qui puissent être rapportés à des mesures connues, Mem Acad r Sci Paris, pp. 452–457

ESM 7. Supplement to Section 1: Origin of the nicknames "*True*" and "*False*" Réaumur, & Nollet or De Luc style

Réaumur (1730, 1731) in his early calibration dipped the glassware containing WS in a water bath over the fire. The glassware, i.e. bulb and tube had the top open, so that WS boiled remaining at the same temperature when the water bath exceeded the boiling temperature of WS and finally reached the boiling point of water. His 80° correspond to the WS boiling point even if the water was boiling on the calibration pot.

George Martine (1740) stated that there was no difference between the melting and freezing points except when the freezing point was made with artificial ice, and that most thermometers of the Royal Society had this point «very erroneously graduated». In addition, Martine criticized the method of calibrating thermometers volumetrically, i.e. adding with phials known volumes of liquid at the same temperature because this method does not consider that glass and wine-spirit had different expansions. Finally, he wrote that «Réaumur was in the wrong» when he evaluated the boiling point. Although Martine published his book in 1740, the print of the chapter concerning the thermometers was dated August 1738, and certainly Réaumur read it. From this date, Réaumur abandoned thermometers.

Around 1739, Nollet started producing new thermometers with 0° corresponding to the melting point and 80° corresponding to the boiling point of water, without acknowledging the misinterpretation, giving explanations or even publishing anything. As Réaumur was very renown, these thermometers and this second scale were also named Réaumur, generating confusion. The new generation of *"False"* Réaumur thermometers was born in 1739 because in 1740 Giovanni Battista Morgagni started a series of observations in Padua, with the new Réaumur thermometer (Camuffo 2002b). There is no doubt about the scale used by Morgagni because his readings continued till 1768, when he died, and were very close to the contemporary records taken by Giovanni Poleni (who used a modified Amontons air thermometer) and Giuseppe Toaldo (who used the Réaumur thermometer of the second generation), also in Padua.

Some 30 years later, De Luc (1772) made precise experiments, understood that the boiling point of water was reached only if the tube in the bath had the top sealed and named "*False*" (*faux* in French) Réaumur this second generation, in contrast with the early type that he called "*True*" (*vrai* in French) Réaumur. These nicknames became popularly adopted when there was need to distinguish the two types. For instance, in the previous **Fig.ESM5**, the title and the note, and later in **Fig.ESM10**, the title and the third column heading report «*Vrai Thermomètre*», i.e. "*True*" Thermometer.

Another nickname that van Swinden (1778) and Gaussen (1789) gave to the two types of Réaumur thermometers was: "*Nollet style*" for the "*True*" Réaumur because Nollet was the instrument maker, and the "*False*" Réaumur was nicknamed "*De Luc style*" because De Luc (1772) published a clear theoretical explanation of the difference; another nickname could be "*Delisle style*" because Joseph Nicholas Delisle (1738) proposed a similar scale when he was in St Petersburg (Middleton 1966). De Luc was disappointed that the scale from the ice to the boiling point of water divided into 80 degrees was indicated with the Réaumur name, because Réaumur used it by mistake, and never published a paper explaining this scale.

A list of selected papers where the specification "True" or "False" Réaumur thermometer is made:

- De Luc JA (1772) Récherches sur les modifications de l'atmosphère: contenant l'histoire critique du baromètre et du thermomètre. Tome I. Printed by the Author, Geneva
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ESM 8. Supplement to Section 3.1: The gunpowder test and the boiling point of wine-spirit

8.1. The "*gunpowder test*" consisted in putting on a spoon some gunpowder and some wine-spirit to test. After, a flame was approached. If the water content was too high, the gunpowder was soaked and could not burn. If the wine-spirit had low water content, the gunpowder could burn (du Crest 1741). The test, however, gave a crude indication. No better tests were in use in that period.

8.2. The different mole fractions of the binary mixture of ethyl alcohol and water that constitutes wine-spirit are expressed in terms % ABV (alcohol-by-volume), and in the 18th century they were described in terms of refinement, simple distillation (around 40-50% ABV) or double distillation (around 90-95% ABV), or obtained with a mixture ow water and refined wine-spirit. In the binary mixture of ethyl alcohol and water (**Fig.ESM7**), the Azeotropic Point is at 95.6% ABV, i.e. it is positioned inside the interval 80% - 100% ABV where the boiling temperature is almost constant. At higher mole fractions of water, the boiling temperature slightly increases. However, in the 70% - 95% ABV interval, typically used by wine-spirit thermometers, the difference is small.



Fig. ESM7 Boiling point and vapor-liquid equilibrium of the binary mixture of ethyl alcohol and water (from Wilfried Cordes - Dortmund Data Bank, Wikipedia, CC-BY-SA 3.0).

The particular mixture of ethanol and water that is reached at the azeotropic point boils as if it were a pure liquid. The azeotropic mixture has a constant boiling point, and the vapor composition is exactly the same as the liquid. The azeotropic mixture, i.e. 95.6% ABV, is the highest level of winespirit refinement obtainable by distillation. Therefore, <u>all thermometers had a spirit concentration below this threshold</u>.

Reference

du Crest, alias Micheli JB (1741) Description de la méthode d'un thermomètre universel. Valleyre, Paris

ESM 9 Supplement to Section 3.1: The letter by Voltaire

Excerpt from the letter by François-Marie Arouet nicknamed Voltaire to abbot Moussinot, dated 17 August 1737: «If you will meet [Nollet?] who supplied you with our thermometers, please tell him that the boiling oil caused one of these instruments to burst, not because the ball was broken, but because, while boiling, the liquor of the thermometer rose to the top of the tube and broke it. Tell him that it is sad that with these wine-spirit thermometers one cannot know the boiling points of the different liquors and that he should make mercury thermometers like those of Fahrenheit. I can only with great difficulty make my experiences with those of Mr de Réaumur. [...] If this person can make Fahrenheit thermometers, he will do a great service to physics». (Translation made with corrected name spelling)

Reference

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ESM 10 Supplement to Section 4.1: Historical Tables illustrating wine-spirit departures

Carlo Taglini was the first to consider the quality of wine-spirit. He advised that thermometers built with highly refined wine-spirit, i.e. purified from air and water, provide more exactly the degrees of het and cold, other things being equal (Taglini 1725). The real problem was not dissolved air, but the water content. However, Réaumur and many other instrument makers disregarded this advice, while du Crest followed it and built thermometers with wine-spirit refined at the gun-powder level. The result was that readings taken with different wine-spirit thermometers, built with different ABV values, were not comparable between them.

The departure between wine-spirit thermometers was complained by several authors. The most extensive and accurate study was made by De Luc (1772) who made a comparison between several kinds of thermometers at different mole fractions of ethyl alcohol and water, i.e. at different ABV values. The De Luc Table is reported in **Fig.ESM8**.

The Table by De Luc is composed of 12 columns \times 17 rows, in total 204 values. The column of the mercury thermometer has been highlighted with a blue label; the column of the wine-spirit passing the gunpowder test (i.e. 90-95% ABV), used by du Crest, has been highlighted with a red label; and the column of Réaumur, indicated with 5 volumes of wine-spirit and 1 of water (i.e. 83% ABV), with a green label. Camuffo and della Valle (2016) relied on these original calibrations to study how wine-spirit deviates from linearity with temperature and alcohol refinement. The transformation from empirical tests to ABV may be found there.

IA De Luc. Recherches sur les Modifications... Tome I - 1772 326 II. PART. CONST. ET USAGE DU BAROM. TABLE des degrés correspondans, de dix Thermomètres faits de liqueurs différemment spiritueuses & des Thermomètres d'eau & de mercure. Mercu- Efp.d.v. Efp.d. Efp. de Efp. de 3 Part. Eau-d. Efp. d. 1 part. re. diftillé v. qui v. reft. v. de M. d'efp.de vie. v. aff. d'ef. de Via I part. East vieux de d'espritparl'6- v. & I brul.la de la difd. v. & 3 au bain de Réau- v.& 1p. Languede sable poud. till. au mur , 5 doc, p. d'eau. vapor. partie d'eau. après ap. d'el.d. bain de tion. d'eau. voir bru fable. v. & 1 lé la poupartie dre. d'ean. 80,0 80,0 80,0 80,0 80,0 80,0 80,0 80,0 80,0 80,0 80,0 80 73,8 71,4 71,6 73,8 74,0 73,9 73,2 71,0 73.7 73-4 73,4 75 67,8 67,9 67,8 66,7 64,3 62,9 62,0 67,6 67,5 67,4 66,9 70 62,1 8,10 61,5 61,5 61,9 61,4 61,0 60,6 56,6 55,2 65 53,5 56,2 56,4 56,2 55,8 55,6 \$5,0 54,8 49,5 47,7 45,8 60 55,5 50,8 50,5 50,2 49,8 40,6 \$8,5 50,3 50,7 49,3 49,I 42,5 55 43,6 36,3 32,0 45,I 45.3 45,5 45,0 44,9 44,4 44,0 34,4 50 28,4 26, I 38,9 38,4 40,2 40,8 39,8 39,7 39,2 30,1 45 40,0 34,8 24,6 23,0 20,5 15,1 35,2 35,0 34,2 34,0 33,3 35,0 40 30,0 30,1 28,4 18,0 **2**9,8 15,9 29,4 29,2 19,9 30,1 30,3 35 25,6 25,2 25,5 25,2 24,7 13.5 11,2 24,6 23,9 15,3 25,5 30 9,4 11,0 20,6 20,8 20,7 20,3 20,2 19,4 11,2 7.3 20,9 25 16,5 16,5 16,3 16,3 16,2 15,9 10,0 15,3 7.7 6, I 4,I 20 11,8 1,6 13,3 11,9 9ر11 11,8 11,6 11,5 12,0 4,9 3,4 15 7,6 7,9 7,9 7.7 7.7 7,1 2,3 1,4 0,2 7,9 7,9 10 3,8 3,8 3,8 3,9 3,4 0,**9** 5 3,9 3,9 3,9 0,1 - .0,4 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0

Fig.ESM8 Table title: «Table of correspondent degrees, of ten thermometers with different proportion of spirit, and a thermometer with mercury, and another with water».

Translation of column headings in Fig. ESM5: « Mercury | Wine-spirit distilled in a sand bath after having burned the powder | Wine-spirit that burns the [gun] powder | Distilled wine-spirit rectified from sand bath distillation | Wine-spirit of Mr de Réaumur, 5 parts of wine-spirit & 1 part of water | 3 parts of wine-spirit & 1 part of water | Water-of-life | wine-spirit refined by evaporation | 1 part of wine-spirit & 1 part of water | Old wine from Languedoc | 1 part of wine-spirit & 3 parts of water | Water |»

The De Luc Table (1772) became famous and excerpts of it were published by several authors, e.g. Goubert (1789) as shown in **Fig.ESM9**. This is a good example of how second-hand information may degrade. Goubert reported only two columns: *«Mercury thermometer»* and *«Wine-spirit thermometer»*. The refinement level of wine-spirit was not specified but, after comparison with the original, one can recognize that it is identical to the gunpowder refinement column (red dot) except for a misprint in correspondence with the 40°R of the mercury thermometer: the correct value is 35.1 instead of 33.1. The Goubert Table is composed of only 2 columns × 17 rows = 34 values from 204 of the original, i.e. it misses 83% of the information. This shows how misleading may be to rely on overview papers instead of the original.

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Fig.ESM9 Table title: «Table of the difference between two thermometers, each divided into 80 degrees [°R] ». Column headings: «Mercury thermometer | Wine-spirit thermometer». The right-hand columns represent degrees and decimals (dix^{e}).

8	degrés corresp. entre Therm. de même lique 10 part. entre la glace	le vrai The eur que le e qui fond o	rm. de M. de Re fien & de mercu が l'eau bouill.	eaumur; & i are, divisés
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		75	73,9	92,8
		7 0	67,8	85, 2
(b) ⁷	erme fixe supérieur du Therm.	\$ 66,6	63 , 7	8 0 , 0
(-)	ue pris de Accaumar.	5 65	61,8	77,8
		60	56,2	70,8
		55	50,5	63,7
		50	45,0	56,8
		45	39,8	50,4
		40	35,0	44,2
		35	30, 1	38, 3
		20	25,5	32,6
(c) T	empérature du corps humain ; par des observations immé-	· `	21 3	32,5
(C)	diates sur les trois Therm.	J ²⁵ , y	20,8	25,7
		20	16,3	21, 1
		10	11,9	15,6
т	empér. des caves de l'Obser	·)	7.9	10,6
(1)	vatoire de Paris, par Obier vation immédiate sur le Th		7,6	10, 15
(a)	de mercure & fur celui de M. de Reaumur.		3,9	5,7
(a)	Class ani ford	, ,	0.0	0,8
(e)	france qui jona		0, 7	0,0
(1)	Reaumur , ou fon zero.	<u>ζ</u> °, 8	2.8	3.9
		5	7.5	8.5
-	Tom Arainra du mélanza da i	10	/,)	12.1
1	parties de glace qui fond, 8	15	11, 2	AC 1 0
(g)	d'i partie de fel marin par observation immédiat	17.	11 , 7	

Fig.ESM10. Table title: «Table of the degrees that correspond to the "*True*" Thermometer of Mr de Réaumur; & les Thermometers made with the same liquid as him (i.e. wine-spirit) and mercury, divided in 80 intervals between melting ice & boiling water». For readers not used to the old style, negative values have been highlighted in cyan.

Translation of headings in Fig.ESM10.

Column headings: «| Mercury thermometer | Thermometer made with the same liquor as Mr de Réaumur: the scale is the same as the mercury thermometer | *True* thermometer of Mr de Réaumur».

Row headings: (a) «boiling water»; (b) «upper fixed point of the thermometer of Mr de Réaumur [i.e. boiling wine-spirit]»; (c) «temperature of the human body by direct observation of the three thermometers»; (d) «temperature of the cellars of the Paris Observatory, by direct observations of the mercury thermometer & that of Mr de Réaumur»; (e) «melting ice»; (f) «lower fixed point of Mr de Réaumur, i.e. his zero»; (g) «Temperature of the mixture composed of 2 parts of melting ice & 1 part of marine salt, by direct observation of the three thermometers». Red letters (a) to (g) have been added to the original Table.

Another fundamental Table published by De Luc (1772) concerns the various reference points originally used by Réaumur (**Fig.ESM10**), including the cellar temperature assumed as *Temperate*. The Table is composed of 3 columns $\times 25$ rows = 75 values. Please note that all the values below the zero point, i.e. 0 at level (e) in the first two columns, and level (f) in the third column, are negative even if the sign minus has been omitted. This was a common practice, often misleading when early data are recovered. It was considered obvious that, in a series of decreasing values, all those after having passed 0 should be intended negative, and vice-versa in the warming phase. Sometimes the very first value after the sign change was indicated, i.e. only the first "-" and the first "+". This requires particular attention when early instrumental data are recovered.

This Table is here compared with the overview (**Fig.ESM11**) made by Lambert (1779) who summarized De Luc (1772). The Lambert's Table is composed of only 2 columns \times 6 rows = 12 values from 75 of De Luc, i.e. it misses 84% of the information. This is normal for an overview.



Fig.ESM11. Table title is missing, but the context explains that this Table reports the results of the tests made by De Luc (1772), i.e. a summary of the previous Table. The legends on the right side are the same as in De Luc, but shortened, i.e. (a) «boiling water»; (b) «wine-spirit stops boiling»; (c) «body temperature»; (d) «cellars of the Paris Observatory»; (f) «freezing water»; (g) «ice from salts». Please note that the item (e), i.e. melting ice, has been omitted. Here negative values had been highlighted with a big "-". We have added red legends for easier reading and comparison.

Lambert commented that at ordinary weather conditions, in the lower part of the scale, the wine-spirit thermometer almost agrees with a mercury thermometer calibrated between 0° and 80°R.

The conclusion of this section is that the progress of science required several efforts, either theoretical thoughts or experiments, some of which wrong, some other good, and a few genial intuitions. The science proceeds progressing in cumulative way, so that theories built up on unstable grounds soon or later fall, while those well grounded will develop.

From the historical and cultural point of view, every idea or experiment is interesting. However, if one is interested in extracting sound practical results, e.g. climate data, metadata and useful formulae, it is necessary to skim misguiding attempts and concentrate on the best experiments, like De Luc, and the related information to correctly interpret them.

Let us return to the basic De Luc Table in **Fig.ESM8.** At 50°C, when the error is maximum, the under-estimation of readings is represented in **Fig.ESM12.** It may be recognized that, in the ABV interval from highly refined wine-spirit 95% ABV to 50% ABV, the bias increases almost linearly from 12 to 17% of the value. The turning point is around 50% ABV, when the mole fraction of ethyl alcohol equals water. When water becomes dominant over alcohol, the bias sharply increases.



Fig.ESM12. Maximum underestimation (at 50°C) of readings taken with wine-spirit thermometers at different ABV values.

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ESM 11 Supplement to Section 4.2: the Celsius Scale

Fig.ESM13a. Overview of different thermometric scales published by Martine (1740), i.e. Fahrenheit, Florence, Paris, De la Hire, Amontons, Poleni, du Réaumur, De l'Isle, Crucquius, Royal Society, Newton, Fowler, Hales, Edinburgh, Fahrenheit (repeated without heading), and Celsius. The Celsius scale has been repeated below because the sheet folding makes it hardly readable



"ne Haussard Sculp.

Fig.ESM13b. Overview of different thermometric scales published by Cotte (1774), Plate VII, i.e. Fahrenheit, Florence, Paris, la Hire, Amontons, Poleni, Réaumur, de l'Isle, Crucquius, Royal Society, Newton, Fowler, Hales, Edinburgh and Fahrenheit (repeated). Celsius scale is missing. (Source: gallica.bnf.fr / Bibliothèque nationale de France)

George Martine (1740) published an overview of the main thermometric scales (**Fig ESM12a**). This Table was reprinted 34 years later by Cotte (1774), with minor changes made by the engraver C^{ne} Haussard (**Fig ESM12b**). The Cotte Table (Plate VII) reports the same content except for the last reference scale on the extreme right-hand side, i.e. Celsius, disregarded because considered irrelevant, and some decorative details, e.g. volumetric bulbs, and the apparently random Latin numbering used as a reference to match the presentation order in the text. In literature, this Table is found quoted Cotte without considering that it had been plagiarized. In addition, it is representative of the situation at the end of the 1730s, not at mid 1770s, which explains the particular Réaumur scale.

The original table by Martine (1740) is remarkably important for three intriguing items:

(i) Martine reported the original scale devised by Réaumur for his big reference (*étalon*) thermometer, where the freezing point is indicated 1000 and the upper point 1080 (making reference to the boiling spirit temperature), although in the drawing the scale is interrupted at mid level, i.e. 45. From the publication date, 1740, it is obvious that this scale, i.e. the "*True*" Réaumur scale, was the only known Réaumur scale, because the new scale with reference to the boiling point of water was born while the Martine publication was in print.

(ii) It is very surprising to find the Celsius scale, with 0° at ice melting point and 100° at boiling water, published in 1740, i.e. a very revolutionary date, as the early original reversed scale (i.e. decreasing) is generally quoted "Celsius (1742)" and the increasing scale after his colleague Carl von Linné in 1747. The Martine publication comments all thermometers, except Celsius, which leads to suppose that Martine was just in time to add it in the table, but not in the text. The conclusion of the Martine overview was: «We have heard of many other Thermometers, and the observations and registers of weather kept by them. But they have been generally so ill limited and described, that they are of no manner of use; and to whatever purpose they might serve their authors, as to us if they never had been» (Martine 1740). This conclusion is very general and does not explicitly mention Celsius. However, it is undoubtable that the increasing Celsius scale, as we use it today, was included in the 1740 paper and the page number (i.e. 217) is correct, so that the suspect of a page added later, after the book was bound is not justified.

Martine died in 1741, and the chapter on thermometers was published again as independent publication, i.e. Martine (1780). This posthumous reprint reports the same text but does not include the above table, nor other figures, possibly to reduce publication costs or because it could seem a duplicate of the Table plagiarized by Cotte (1774), i.e. Plate VII.

(iii) The Martine table, with the scales of the most important thermometers reported side-by-side on the same frame, might have inspired du Crest (1741) to produce his *Universal Thermometer*, that appeared one year later. In the *Universal Thermometer*, the wooden frame reported side-by-side different scales, e.g. du Crest, Delisle, *"True"* Réaumur and Fahrenheit, together with their reference points. Of course, the number of scales was necessarily limited, e.g. two on the right and two on the left of the tube, to keep the scale close to the liquid column and avoid parallax errors when reading heights.

Martine gave several relevant inputs in this field, e.g. having clearly outlined all the weaknesses of the *"True"* Réaumur thermometer and having devised the principle of differential thermal analysis.

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