Thermochimica Acta, 5 (1972) 129–132

THE INFLUENCE OF TEMPERATURE ON WEIGHING WITH QUARTZ OSCILLATORS AND ITS COMPENSATION

F. J. VAN EMPEL, E. C. BALLEGOOYEN, F. BOERSMA, J. A. POULIS,
and C. H. MASSEN
Physics Department, Eindhoven University of Technology, Eindhoven (The Netherlands)
(Received April 3rd, 1972)

ABSTRACT

The use of resonating quartz crystals for mass determination is very attractive because a sensitivity of about 10^{-12} g is possible. For technical reasons the application has so far been restricted to room temperature. In the present paper it will be discussed how these technical problems can be coped with by using a quartz crystal with two electrode sets. The result is that the high sensitive resonating quartz crystal method can become of interest in instrumentation design for thermogravimetry.

INTRODUCTION

The application of resonating quartz crystals has introduced the possibility of measuring mass variations as small as 10^{-12} g. This development is based upon the relation between the variation Δf of the resonant frequency, f, and the mass, Δm, added to the electrode:

$$\frac{\Delta f}{f} = -\frac{\Delta m}{m} \qquad (1)$$

where m stands for the effective mass of the quartz between the electrodes.

For the crystal used in the experiments described in this paper the following values were relevant: $f = 10^7$ Hz, and $m = 4 \times 10^{-3}$ g, so that Eqn. (1) reads:

$$\Delta f = -2.5 \times 10^9 \, \Delta m \qquad (2)$$

It is evident that in these measurements frequency variations due to environmental influences should be reduced as much as possible. The influence of temperature variations upon the frequency is usually reduced, therefore, by choosing a special crystalline cut[2]. Fig. 1 shows that the temperatures near 27 °C, the frequency is independent of temperature. Therefore, the resonating quartz crystals used in the immediate vicinity of 27 °C have found a use in those experiments which can be carried out at this temperature. At first sight this temperature restriction excludes resonating quartz crystals from application in thermogravimetry. From a second look at Fig. 1,

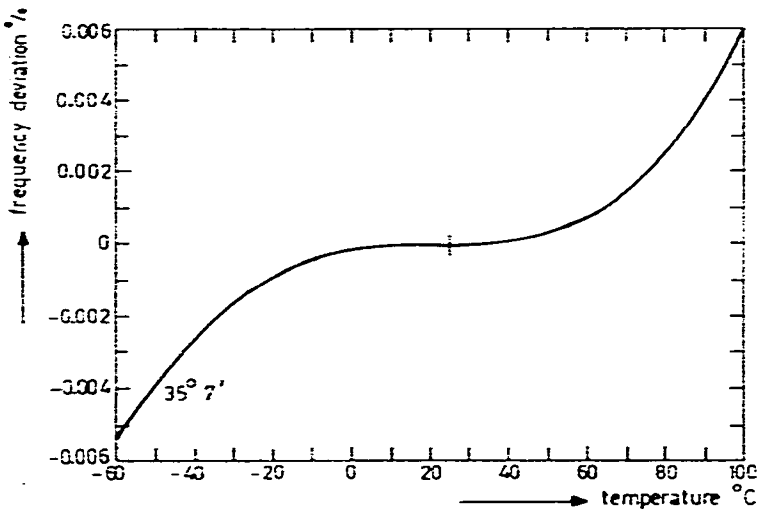

Fig. 1. The temperature dependency of the resonance frequency at cut (YXI 35°7').

we learn that, at higher temperatures, a temperature variation of 1 °C corresponds to a relative frequency change of 2 × 10^{-6}, which results in an apparent mass change of 8 × 10^{-9} g. This could be coped with by a correction, but would involve the use of an extremely sensitive thermometer. In the method presented here this temperature information is obtained from the quartz crystal itself. The crystal is supplied with two electrode systems (see Fig. 2), one of them is submitted to the mass variations and the other serves as a temperature sensing unit.

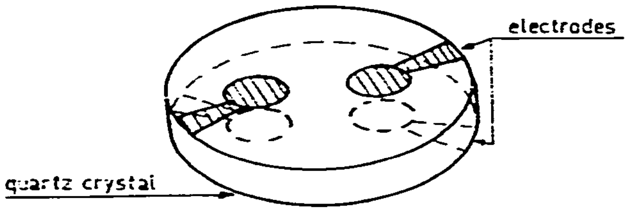

Fig. 2. Configuration of the electrodes.

EXPERIMENTAL

For the realisation of the procedure discussed above, three requirements must be fulfilled. First, the two electrode systems must act independently from one another Secondly, the temperatures of the electrode systems must be equal. Thirdly, the temperature coefficients of the two resonance frequencies must be equal.

The first requirement has been dealt with in former papers[3,4]. The following experiments were carried out. The mass of one of the electrode systems was increased by evaporating onto it a metal film, the other electrode system was shielded from the evaporation source. The results are shown in Fig. 3. The electrode system onto which metal is evaporated shows a shift of the resonating frequency at each mass increase, while the other, the reference frequency, remains constant. Actually, the reference frequency shift is not exactly zero but about 1000 times smaller than the main effect, On the scale of Fig. 3 this is not visible. This small shift is probably due to a temperature variation accompanying the evaporation.

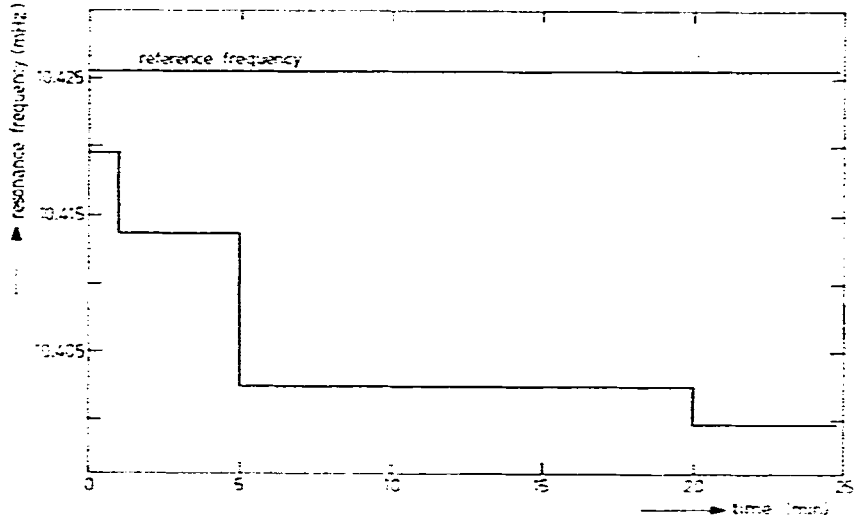

Fig. 3. Response of the resonance frequency of both electrode systems to a mass increase of one of them. The evaporations were carried out at 1, 5 and 20 min.

The second and third requirements have been checked simultaneously in the following way. The crystal with the two electrode systems was mounted in a thermostat, the temperature of which was varied. The response of the resonance frequencies of the two electrode systems is shown in Fig. 4. We can see that the two responses are, though very similar, not completely equal. One of the reasons for the remaining discrepancy could well be the fact that the planes of the electrodes are not completely parallel. An orientation difference of only 4×10^{-3} rad could account for the measured discrepancy.

DISCUSSION

The fact that the two electrode systems have not completely equal responses excludes the set up from application without corrections for temperature differences. However, the set up still has advantages, as it can reduce the consequences of temperature variations which are too small to be detected by other thermometers. The similarity of their responses ensures that the errors caused by such small temperature variations can be reduced by a factor of 20. A thermostat with temperature variations of 10^{-2} °C would, for a single electrode system, involve a spurious mass change of 10^{-10} g. With the double electrode system these changes would be as small as $5 \times$

10^{-12} g, and so become of the order of magnitude corresponding to spurious mass changes which accompany even advanced electronic circuitry.

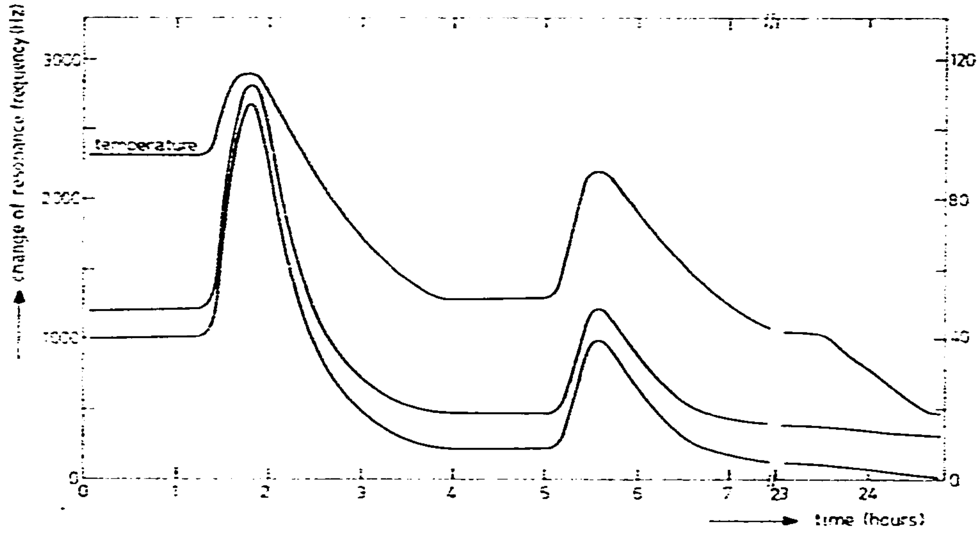

Fig. 4. Response of the resonance frequencies of the two electrode pairs to temperature variations.

ACKNOWLEDGEMENTS

Thanks are due to Miss M. C. K. Gruyters and Miss M. A. van Basten for preparing the manuscript.

REFERENCES

1 A. W. Warner, in S. P. Wolsky and E. J. Zdanuk (Eds.), *Ultra Microweight Determination in Controlled Environments*, Wiley, New York, 1969, p. 37.
2 A. W. Warner and C. D. Stockbridge, *Vac. Microbalance Tech.*, 2 (1962) 71; *ibid.*, 3 (1963) 55.
3 J. Ph. Termeulen, F. J. van Empel, C. H. Massen, and J. A. Poulis, *Vac. Microbalance Tech.*, in press.
4 F. J. van Empel, C. H. Massen, H. J. J. M. Arts, and J. A. Poulis, *J. Acoust. Soc. Am.*, 50 (1971) 1386.