

Sample Purity and the N.Q.R. of Cl^{35} in KClO_3 at 0°C

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It is shown that careful preparation is necessary to achieve a consistent value for the Cl^{35} nuclear quadrupole resonance frequency in KClO_3 samples at 273.16°K (the triple point of water). This is illustrated by measurements on a number of samples. It is suggested that the N.Q.R. frequency of Cl^{35} in KClO_3 at 273.16°K and atmospheric pressure is $28,213,372 \pm 2$ Hz. This value is compared with measurements made by previous workers which show a considerable spread.

Key Words: Measurements at 0°C , nuclear quadrupole resonance thermometry, potassium chlorate.

For some time there has been interest in the use of the Cl^{35} nuclear quadrupole resonance (N.Q.R.) frequency in KClO_3 as a thermometer [1–5].¹ In references [1–4] the line center could be measured to within an experimental accuracy of $\sim \pm 10$ Hz corresponding to $\pm 0.002^\circ\text{K}$ at room temperatures. More recently Volpicelli et al. [6], and Vanier [5] have described arrangements in which the spectrometer frequency is locked to the line center and Vanier [5] has made measurements at 77°K to an experimental accuracy of order ± 2 Hz.

We have used a Pound, Knight, Watkins [7, 8] marginal oscillator, with frequency modulation, locked to the resonance using an arrangement similar to that of Volpicelli et al., [6]. The specimen coil was connected to the oscillator by means of a 20 in length of rigid stainless steel coaxial cable; the earth's magnetic field was shielded by a μ -metal can.

It was established that the resonance frequency was independent of the detection system by observing the N.Q.R. signal from one sample (later referred to as #8) using a modified Knight oscillator [9]. The resonance frequency was also found to be independent of the oscillation level, if the rf voltage across the tuned circuit was in the range 0.05 to 0.5 V. (At higher levels not only is it difficult to eliminate incidental amplitude modulation effects but sample heating is also observed.)

In order to obtain an accurate value for the N.Q.R. frequency of a particular substance the crystals must possess a high degree of physical perfection and chemical purity. Crystal imperfections will broaden the resonance line if they are random in nature but may also lead to a shift in the line center if one particular type of imperfection predominates. Chemical impurities, introducing a distribution in nuclear environ-

ments, may cause line broadening which can also be accompanied by a shift in the center frequency [10]. Chemical purity can be approached by starting from "pure" supply materials and recrystallizing. Physical perfection is more difficult to achieve but certainly requires slow steady growth and careful subsequent handling. The former is subject to check by quantitative analysis; it seems reasonable to accept as a relative measure of physical perfection, at least, narrowness of lines and intensity of the signal. That is to say, the different possible origins of a given line breadth cannot be separated readily, but among different samples of comparable chemical purity, those exhibiting the narrowest lines are surely the most nearly characteristic of the pure material.

Vanier [5] has shown that recrystallization in 30 to 60 min produces samples with resonance frequencies consistent to within ± 2 Hz at 77°K . We have made measurements at the triple point of water (273.16°K), using the type of cell developed for precision thermometric calibration, and find that greater care must be taken to obtain samples with consistent resonance frequencies at this temperature. The specimen, in a sealed Pyrex tube, was placed within the rf coil which in turn was immersed in oil contained by a brass extension of the rf coaxial outer conductor. Water provided thermal contact between the outer conductor and the triple point cell. To check that the specimen attained the triple point equilibrium temperature of 273.16°K the sample holder was raised 3 in from its usual position at the bottom of the central well (total depth $12\frac{1}{2}$ in). The observed change in N.Q.R. frequency was equivalent to 0.1 ± 0.7 mdeg indicating that the specimen had indeed attained the equilibrium temperature.

Table 1 lists measurements made on various powder samples at 273.16°K . Sample 1 is Fisher Reagent

¹ Figures in brackets indicate the literature references at the end of this paper.

Grade, Catalog No. P-212; sample 7 was kindly loaned by Dr. Vanier and is his sample P-212 [5]. Samples 2 to 4 were recrystallized in a period of 1 to 24 hr, many others prepared in the same way gave frequencies within the same range. This includes samples doubly and triply recrystallized [11]. Note that the frequency range is greater than the experimental uncertainty of the individual measurements. Samples 5, 6, and 9 were recrystallized by slow evaporation (> 14 days) in a temperature controlled room (72 °F). A wide range of crystal sizes were obtained but only the smaller ones were used in order to achieve a reasonable filling factor in the rf coil. Even so, the filling factor for sample 5 was smaller than for the others. Sample 8 is, unfortunately, of unknown origin. The mean values for the resonance frequencies can be reproduced on different occasions within the limits quoted.

TABLE 1. Comparison of various KClO₃ samples

Sample	Frequency ^a	Linewidth ^b	Signal amplitude arbitrary units	Water ^c content
	Hz	Hz		%
1	28,213,352.2 ± 4.2	520 ± 21	1.0	0
2	28,213,371.4 ± 4.5	517 ± 36	0.77	0.2
3	28,213,366.3 ± 3.3	504 ± 13	1.1	.08
4 ^d	28,213,362.1 ± 1.8			
5	28,213,372.0 ± 3.0	465 ± 29	1.2	.07
6	28,213,372.4 ± 2.9	467 ± 30	1.4	.05
7	28,213,354.8 ± 3.7	540 ± 40	0.94	
8	28,213,372.8 ± 1.1	435 ± 27	3.3	.56 ^e
9	28,213,371.8 ± 2.2			.14

^a Mean of 20 one second counts, uncertainties are rms deviations.

^b Distance between 1st deviative extrema.

^c Limit of detection 0.04 percent.

^d Sample not available when linewidth determinations made.

^e It is suspected that there is some organic material present. The sample had been contaminated with oil. Initial analysis showed 2.2 percent water (hydrogen), 1 percent carbon. After a wash in ether the hydrogen content was equivalent to 0.56 percent water whilst the carbon dropped to 0.01 percent.

We note that slow recrystallization results in a consistent value for the N.Q.R. frequency i.e., the difference in mean values is small compared with the experimental uncertainties and that the resonance is also narrower and more intense. (Sample 6 was recrystallized in a polyethylene beaker to determine if any impurities are introduced by the Pyrex glassware.) Chemical analysis [11] was unable to distinguish between samples 2 to 4 (in fact the impurity levels were below the detection threshold), whilst the N.Q.R. frequencies differed significantly, hence it was assumed that further chemical analysis of the other samples would not be worthwhile. The results of analysis for water content [12] are given in table 1. We note that whilst the samples contain detectable quantities of water there is no obvious correlation between N.Q.R. frequency and water content. From the foregoing discussion concerning resonance line characteristics and sample purity, we suggest that, to within present experimental accuracy samples 5, 6, 8, and 9 are most likely to be representative of KClO₃, and therefore propose 28,213,372 Hz ± 2 Hz as a best

value for the N.Q.R. frequency of Cl³⁵ in KClO₃ at 273.16 °K (≡ 0.01 °C) and atmospheric pressure.

Table 2 shows the frequency determinations made by various workers at 0 °C. The wide discrepancies are rather surprising. The ice point should be reproducible to within 0.002° (≡ 10 Hz) if reasonable experimental care is taken. Brodskii and Solov'ev [4] controlled the temperature with platinum resistance thermometers calibrated at the triple point of water, however, they did not investigate sample impurity effects. The triple point of water is easily reproduced to within 0.0002 °C.

Using a calibrated platinum resistance thermometer, work is now in progress on the accurate measurement (to within 1 mdeg and ± 3Hz) of the frequency-temperature characteristic of Cl³⁵ in KClO₃ over the range 15 to 300 °K. Other possible thermometric substances are also under investigation.

It is a pleasure to acknowledge the continuing interest and encouragement of R. P. Hudson.

TABLE 2. N.Q.R. frequency of Cl³⁵ in KClO₃ at 0 °C from the literature

Frequency Hz	Reference
28,213,470 ± 25	4
28,213,420 ± 20	7
28,213,421 ± 2 ^a	Present work
28,213,345 ± 10	2
28,213,270 ± 11	3

^a From triple point of water determination and using

$$\left(\frac{d\nu}{dt}\right)_{0^\circ\text{C}} = 4.9\text{kHz}/^\circ\text{C}.$$

References and Notes

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- [11] Spectrochemical analysis of samples 2-4 revealed the impurity level of Na, Rb and Cs to be less than 0.001% whilst polarographic analysis showed the bromate and iodate content also to be less than 0.001% by weight. Sample 2 contained between 0.001 and 0.01% Al.
- [12] The water content was determined using an F&M C-H-N Analyzer. All hydrogen present has been calculated as water.

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