ARCHIVES OF ACOUSTICS
18, 4, 539–551 (1993)

PRACTICAL POSSIBILITIES OF MORE ACCURATE VELOCITY MEASUREMENTS OF ULTRASONIC WAVES IN LIQUIDS BY MEANS OF THE RESONATOR METHOD

A. BALCERZAK, Z. BAZIOR, Z. KOZŁOWSKI AND R. PŁOWIEC

Institute of Fundamental Technological Research
Polish Academy of Sciences
(00-049 Warszawa, Swiętokrzyska 21)

A precise investigation of the dependence between the resonance frequencies and the frequency for the real resonator cell was carried out using automatic measurement equipment which works in the range of frequency 0.5–10 MHz. This experimental dependence was compared with the theoretical one for the ideal resonator cell. As a result, regularities were found which are important for more accurate velocity measurements in liquids in the whole frequency range used in the resonator method. It was pointed out how on the basis of these results the method of calculating the propagation velocity in the resonator method can be improved and its accuracy increased.

1. Introduction

Physico-chemical investigations of liquid and solution properties using ultrasonic spectroscopy methods require measurements of the propagation parameters of the compression waves (attenuation and velocity) in tested liquids at a wide frequency range. Depending on the tested liquid and investigated phenomena, this range may cover the frequency from several hundreds kilocycles/s up to several gigacycles/s. As a rule it is impossible to make measurements at such a wide range using only one measurement method. The biggest obstacles occur at the beginning and at the end of the mentioned range. Wave-guide effects are an obstacle at low frequencies. At high frequencies piezoelectric transducers and electronic equipment are the main problem.

To avoid these wave-guide effects, the so-called resonator method proposed by Eggers [1–4] and, next, used and developed by other investigators [5–15] for measurements below 10 MHz has been commonly applied in the last years. This method allows to measure the attenuation of a tested liquid as well as the propagation velocity of an ultrasonic wave as a function of the frequency. The attenuation coefficient is determined by the measurement of the quality factor of the resonator cell with the tested liquid inside. The ultrasonic velocity is calculated from the frequency distance between the subsequent resonance frequencies of the resonator cell (filled up with the tested liquid). A theory about this method can be found in the literature [1, 2, 6, 9–11].

The measurements of attenuation do not cause particular difficulties, but those of velocity are more controversial.

From the theoretical point of view, the principle of velocity measurement is very simple. In accordance with [1, 2], in the ideal resonator cell the frequency intervals between subsequent resonances Δf_n, should be the same and equal to the first basic resonance frequency of that system, f_1:

$$\Delta f_n = f_{n+1} - f_n = f_1 = \frac{c}{2l}, \qquad n=1,2,... \tag{1}$$

where c is the wave velocity in the liquid, l is the distance between the internal surfaces of the transducers, n is the integer, a number of the resonance.

Thus when the distance l is known and the interval Δf_n is measured, one can find velocity c from Eq. (1).

In practice, the relationship between Δf_n and f_1 is complicated and direct use of Eq. (1) to determine the velocity causes significant errors. Indeed, many investigators [1, 2, 6, 10, 11] noticed that resonance frequencies are not to be situated in the equal frequency distances in the real made resonator cell. Especially at frequencies close to f_q (where f_q is the fundamental resonance frequency of the transducers) and odd harmonic, e.g. $3 f_q$, $5 f_q$ etc. Δf_n are smaller than f_1 in a significant manner.

EGGERS [1, 2] presented the formula for calculating the direct value of velocity from measurements of the frequency intervals between subsequent resonances (Δf_n) but that may be used only in the frequency range that is close to the anti-resonance frequencies of the transducers of the resonator cell, e.g. $\frac{1}{2} f_q$, $\frac{3}{2} f_q$ etc. without a definition of the applicability range.

SARVAZAN [9] also considered the velocity measurements but limited his considerations only to relative measurements. LABHARDT [6] obtained an analytical relationship for the direct calculation of velocity from the measurements of Δf_n; however, it requires some of the values of the resonator cell parameters, the determination of which, mostly in the experimental way, introduce additional errors.

Thus, as one can notice, in the literature no precise investigations of the dependence between Δf_n and the frequency f for the real resonator cells can be found. Such investigations are fundamental for accurate velocity measurements and, what is very important, they enable to employ the whole frequency range used in the resonator method not only at the anti-resonance frequencies like in [1, 21].

The aim of this work was to study the dependence between Δf_n and the frequency f for the resonance cells and as a result of this investigation, determine the consequences for the velocity measurements and their accuracy.

2. Formulation of the problem

The solutions mentioned by EGGERS [2] were the starting point for the study. According to those, the first resonance frequency f_1 for the liquid layer in the resonator cell can be determined with great accuracy by measuring f_n and Δf_n at a frequency close to $\frac{f_q}{2}$ (where f_q is the fundamental resonance frequency of the transducers used in the resonance cell) and, subsequently, by introducing the correction which accounts for the influence of the transducers on the measured frequency of the resonance. Under these conditions

$$f_1 = \frac{f_n}{n}\left[1 + \frac{R}{n}\left(\frac{2f_n}{f_q} - 1\right)\right], \tag{2}$$

where R is the ratio of acoustical impedances of the tested liquid and the quartz (the material of the transducers), n is the number of resonance.

For the frequency f close to $\frac{f_q}{2}$, n is calculated from Eq. (3)

$$n \cong \frac{f_n}{\Delta f_n} \tag{3}$$

making the result even to an integral.

After calculating f_1, one can find the velocity from the relationship (4)

$$c = 2\,l f_1. \tag{4}$$

However, in [2] there was no information as to what range of frequency the correction introduced in Eq. (2) allows to get the value of f_1 and, consequently, to get the value of c, with order of the accuracy of about 0.1%. Such an exactness is regarded to be the minimum accuracy required in physico-chemical investigations.

In the frequency range distant to the anti-resonance frequency of the tranducers, the values of $\frac{f_n}{n}$ are different in a significant manner from f_1 and the correction introduced in Eq. (2) is not sufficient. On the other hand, when n is determined from the relationship (3) a significant error is also involved.

The experimental investigations carried out and described below allow to determine the range of applicability of the calculation procedure based on Eqs. (2) and (3). These measurements enable to calculate f_1 in a different, more accurate way in the whole measurement frequency range.

3. Measuring system

When the method described above is used in measurements, the transducer of the resonator must have electric signals from frequency source that can supply stable frequency and have the possibility of frequency change in the range defined by the resonator. The output signal, sometimes on the millivolts level, is very sensitive to disturbances. In the article [14] the authors describe a set-up for ultrasonic measurements using the resonator method with a manually operated frequency synthesizer as the supply source of the resonator cell. The output signal was amplified in the selective amplifier especially designed for this purpose and was indicated on a typical oscilloscope. However, measurements in this set-up were time-consuming, the amplification of the receiving channel was not sufficient for frequency distant from the resonance frequency of the resonator transducers and the determination of the signal level of the output signal from the oscilloscope was not so accurate.

To eliminate these inconveniences, a new equipment was constructed [15], which is shown in the block diagram in Fig. 1. This equipment automatically changes the frequency of the supplying signal. Disturbances of the received signal are eliminated by using a superheterodyne circuit in the receiving channel. The electronic part of the equipment may work in the frequency range 20 kHz–10 MHz. However, the measurement possibilities of the resonators limit the lower range of the frequencies to 0.5 MHz.

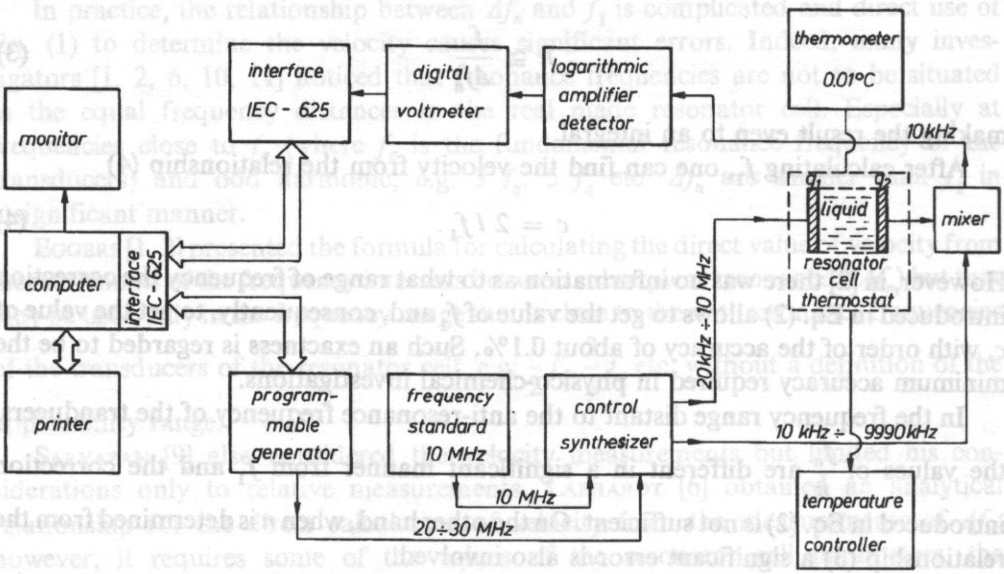

Fig. 1. The block diagram of the overall set-up.

The Hewlett-Packard mod. 3324A generator with a minimal step 1 mHz and range from 1 mHz to 60 MHz was used as the programmable source of the variable frequency. It supplied the synthesizer which controlled the resonator and delivered voltage to the mixer. The synthesizer, the mixer and the amplifier were made to be used in this measuring equipment. The digital voltmeter Meratronik mod. V553 was used as A/D converter from which data were transmitted to an IBM PC/AT computer. It gave 0.01 dB resolution in this equipment.

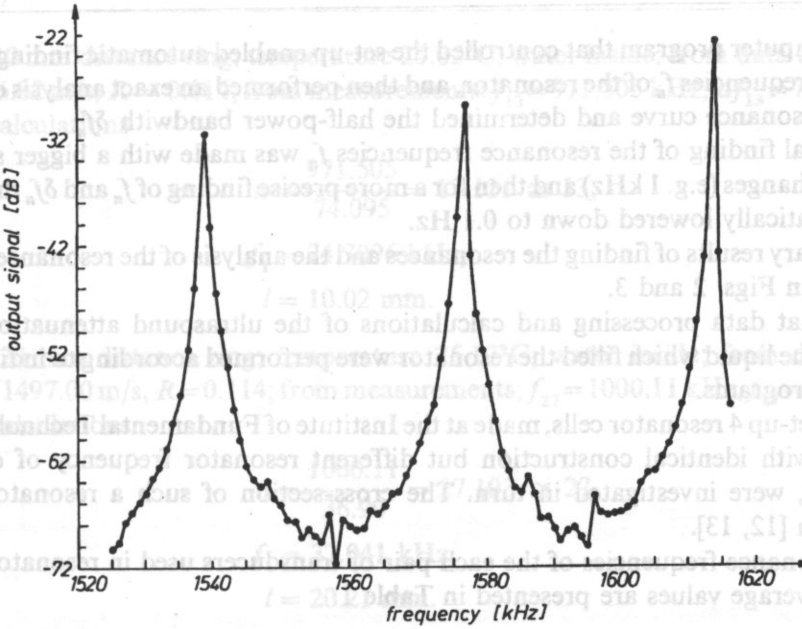

Fig. 2. The resonance peaks of the resonator.

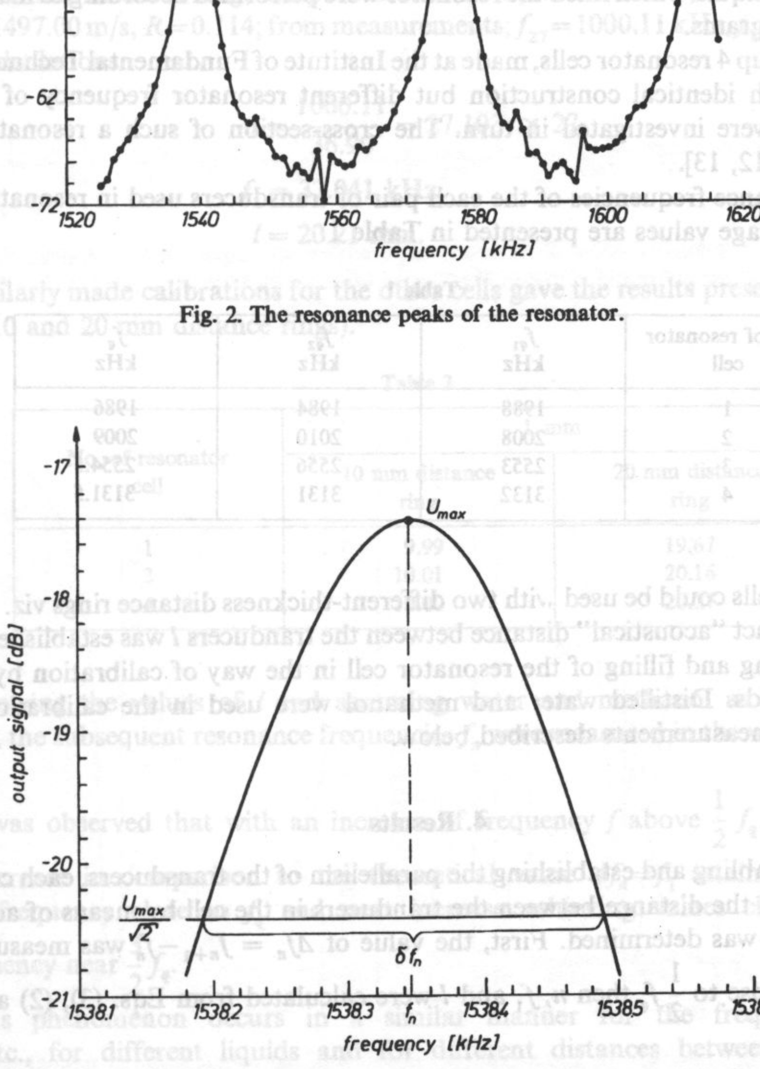

Fig. 3. The resonance curve for the frequency f_n = 1538,342 kHz.

The computer program that controlled the set-up enabled automatic finding of the resonance frequencies f_n of the resonator, and then performed an exact analysis of each obtained resonance curve and determined the half-power bandwith δf_n.

An initial finding of the resonance frequencies f_n was made with a bigger step of frequency changes (e.g. 1 kHz) and then for a more precise finding of f_n and δf_n this step was automatically lowered down to 0.1 Hz.

Exemplary results of finding the resonances and the analysis of the resonance curve are shown in Figs. 2 and 3.

After that data processing and calculations of the ultrasound attenuation and velocity in the liquid which filled the resonator were performed according to individual computer programs.

In this set-up 4 resonator cells, made at the Institute of Fundamental Technological Research, with identical construction but different resonator frequency of quartz transducers, were investigated in turn. The cross-section of such a resonator was presented in [12, 13].

The resonance frequencies of the each pair of transducers used in resonator cells and their average values are presented in Table 1.

Table 1

No. of resonator cell	f_{q1} kHz	f_{q2} kHz	f_q kHz
1	1988	1984	1986
2	2008	2010	2009
3	2553	2556	2554.5
4	3132	3131	3131.5

All these cells could be used with two different-thickness distance rings viz. 10 and 20 mm. An exact "acoustical" distance between the tranducers l was established after each assembling and filling of the resonator cell in the way of calibration by using reference liquids. Distilled water and methanol were used in the calibration and investigation measurements described below.

4. Results

After assembling and establishing the parallelism of the transducers, each cell was calibrated, i.e., the distance between the tranducers in the cell by means of acoustic measurements was determined. First, the value of $\Delta f_n = f_{n+1} - f_n$ was measured at a frequency close to $\frac{1}{2} f_q$ then n, f_1 and l were calculated from Eqs. (3), (2) and (4) respectively.

As an example the results of the measurements and calculations for the cell No. 2 (f_q = 2009 kHz) are mentioned below:

1) 10 mm distance ring; temperature 25.05°C; water inside; from data tables: c_{water} = 1496.82 m/s, R = 0.114; from measurements: $f_{13}=971.505$ kHz, $\Delta f_{13}=74.095$ kHz; from calculations

$$n = \frac{971.505}{74.095} = 13.111 \cong 13,$$

$$f_1 = 74.7096 \text{ kHz},$$

$$l = 10.02 \text{ mm}.$$

2) 20 mm distance ring; temperature 25.17°C; water inside; from data tables: $c_{water}=1497.00$ m/s, $R=0.114$; from measurements; $f_{27}=1000.11$ kHz, $f_{27}=36.90$ kHz; from calculations

$$n = \frac{1000.11}{36.90} = 27.103 \cong 27,$$

$$f_1 = 37.041 \text{ kHz},$$

$$l = 20.21 \text{ mm}.$$

Similarly made calibrations for the other cells gave the results presented in Table 2 (for 10 and 20 mm distance rings).

Table 2

No. of resonator cell	l, mm	
	10 mm distance ring	20 mm distance ring
1	9.99	19.67
3	10.01	20.16
4	10.00	20.27

Knowing the values of l and assuming water and methanol as nondispersive liquids, the subsequent resonance frequencies f_n were measured in the wide frequency range.

It was observed that with an increase of frequency f above $\frac{1}{2} f_q$, the intervals Δf_n decrease in comparison to the theoretical value $\Delta f_n = f_1$ attaining minimum for a frequency close to f_q and next increase achieving values close to f_1 for a frequency near $\frac{3}{2} f_q$.

This phenomenon occurs in a similar manner for the frequencies 3 f_q, 5 f_q etc., for different liquids and for different distances between transducers with very small quantity differences. Some results are presented in Figs. 4–7 as examples.

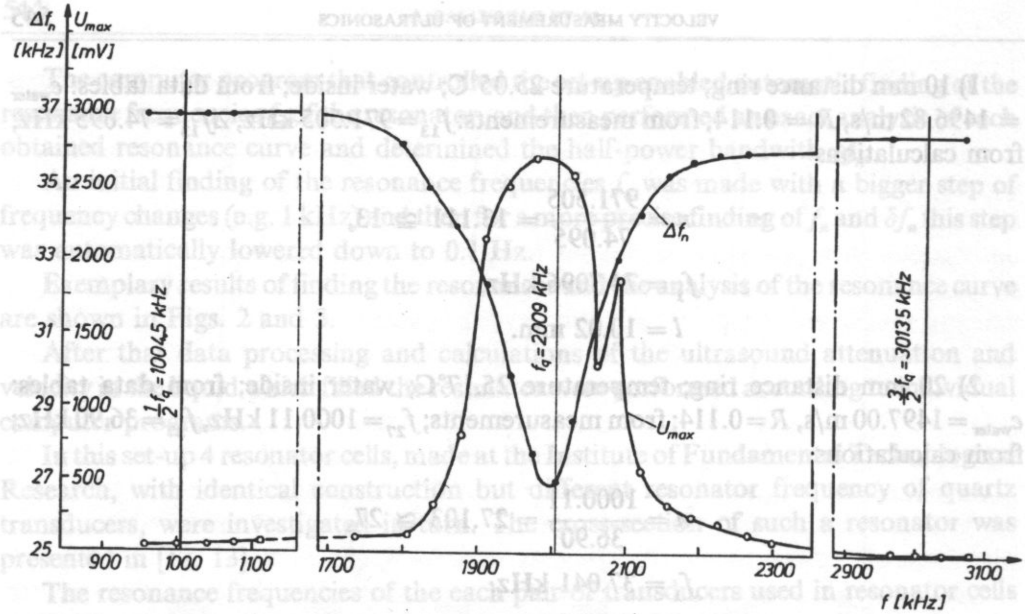

Fig. 4. The frequency interval Δf_n and maximum amplitude of the output signal at resonances U_{max} as a function of the frequency f for the cell No. 2. The 20 mm distance ring. Water. $f_q = 2009$ kHz, $l = 20.21$ mm, $f_1 = 37.041$ kHz, $U_{input} = 5.8$ V.

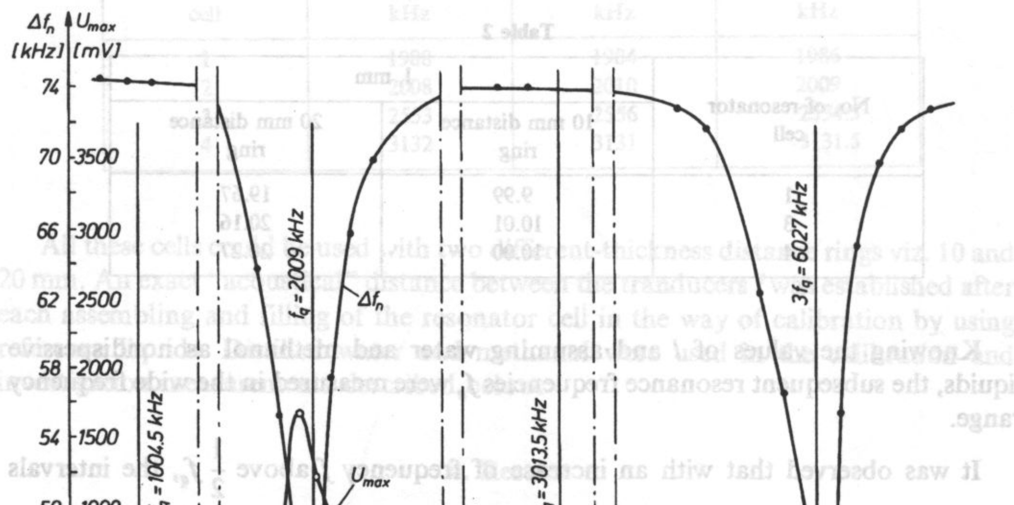

Fig. 5. The frequency intervals Δf_n and maximum amplitude of the output signal at resonances U_{max} as a function of the frequency f for the cell No. 2. The 10 mm distance ring. Water. $f_q = 2009$ kHz, $l = 10.02$ mm, $f_1 = 74.7096$ kHz, $U_{input} = 5.8$ V.

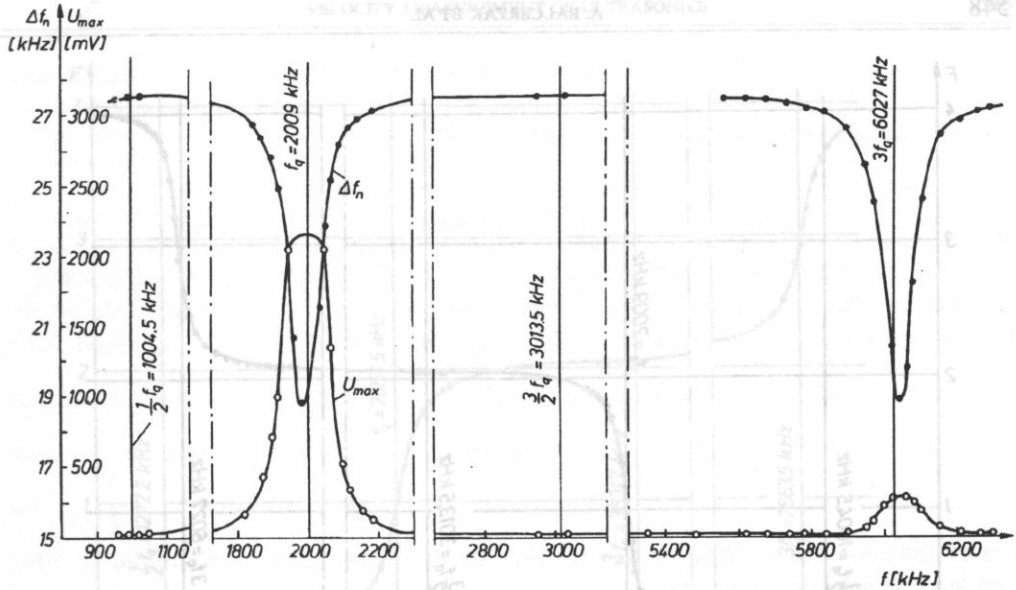

Fig. 6. The frequency intervals Δf_n and maximum amplitude of the output signal at resonances U_{max} as a function of the frequency f for the cell No. 2. The 20 mm distance ring. Methanol. $f_q = 2009$ kHz, $l = 20.06$ mm, $f_1 = 27.571$ kHz, $U_{input} = 5.8$ V.

Fig. 7. The frequency intervals Δf_n and maximum amplitude of the output signal at resonances U_{max} as a function of the frequency f for the cell No. 3. The 20 mm distance ring. Water. $f_q = 2554.5$ kHz, $l = 20.16$ mm, $f_1 = 37.121$ kHz, $U_{input} = 5.8$ V.

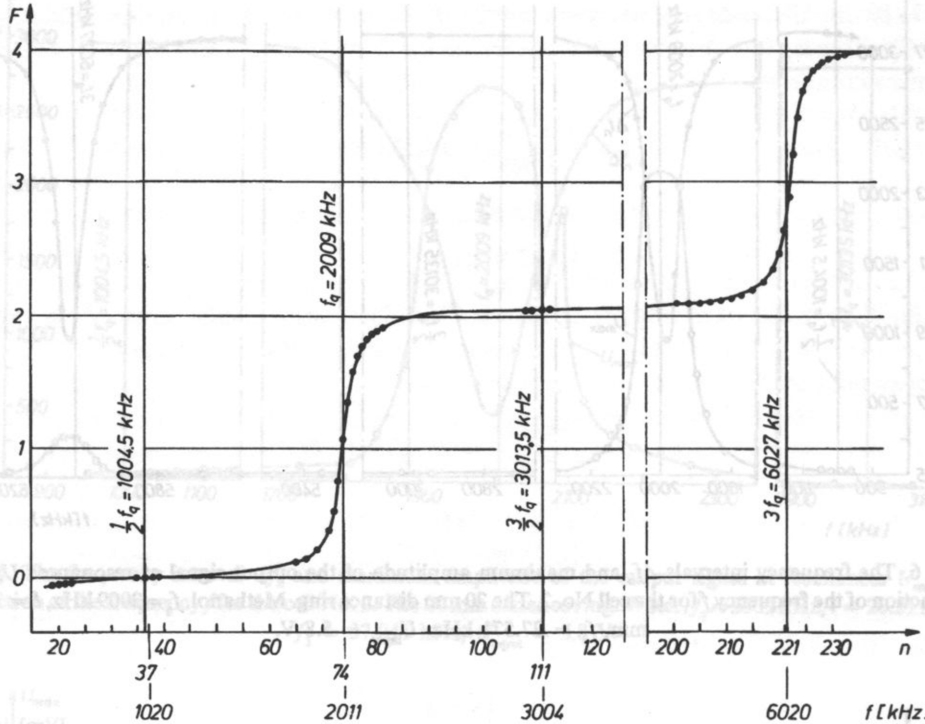

Fig. 8. *F* as a function of the frequency *f* and the number of resonances *n* for the cell No. 2. The 20 mm distance ring. Methanol.

Another interesting regularity can be noticed from the analysis of the measurements carried out. Namely, as a result of contracting of frequency intervals between subsequent cell resonances, the number of recorded resonances is bigger than for an ideal resonator cell (than $f_n = \text{const} = f_1$) exactly by one among the frequencies $\frac{1}{2} f_q$ and f_q. This regularity occurs independently of the kind of liquid the distance ring thickness and resonance frequency of the cell transducers. Figures 8 and 9 present examples of experimental observations which visualize this regularity. *n* is the number of the resonance for a real cell at frequency f_n, *F* is the difference between *n* and $\frac{f_n}{f_1}$, i.e.,:

$$F = n - \frac{f_n}{f_1}. \tag{5}$$

The ratio $\frac{f_n}{f_1}$ is the number of resonances for an ideal resonator cell; this is a real number. Thus, as it was mentioned above, the value of *F* equals 1 at $f = f_q$. At frequencies close

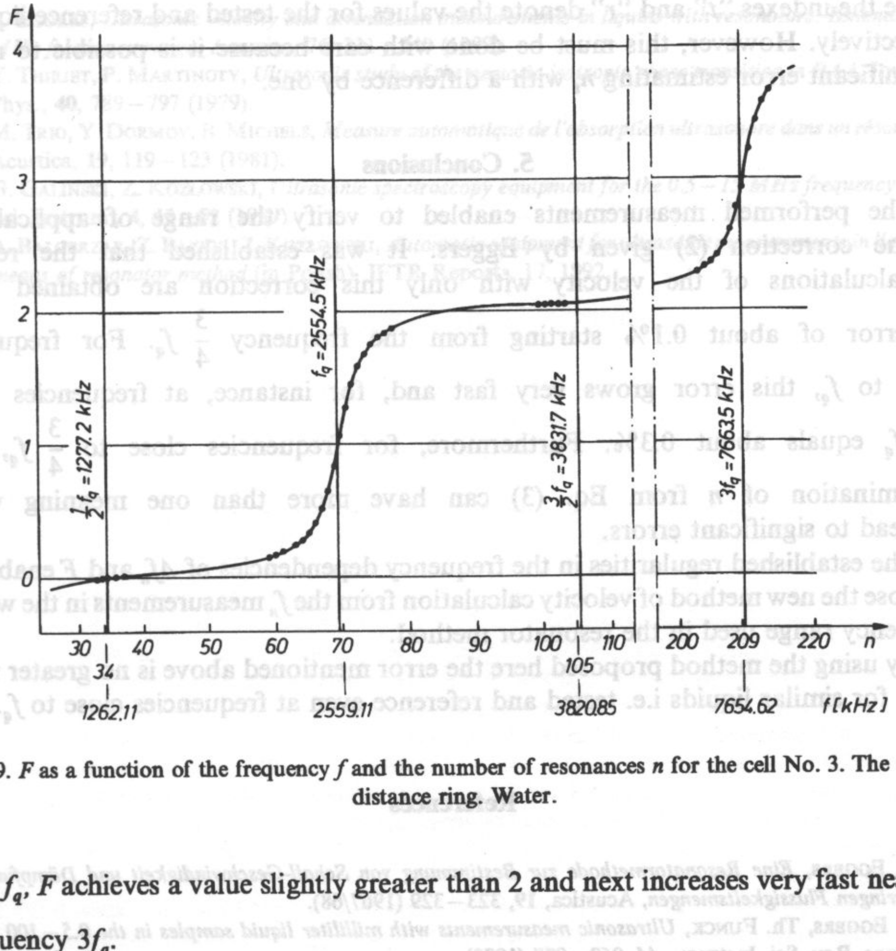

Fig. 9. F as a function of the frequency f and the number of resonances n for the cell No. 3. The 20 mm distance ring. Water.

to $\frac{3}{2}f_q$, F achieves a value slightly greater than 2 and next increases very fast near the frequency $3f_q$.

The regularity described above of increasing F makes it possible to determine the propagation velocity in a tested liquid at frequencies far to $\frac{1}{2}f_q$ from Eq. (6).

$$f_1 = \frac{f_n}{n-F} \tag{6}$$

Knowing f_1, the velocity c is calculated from the relationship (4). The value of F is found from the calibration curve for the reference liquid (for instance, Figs. 8 and 9 for the cell No. 2 with a 20 mm distance ring and cell No. 3 with the same ring respectively) at the frequency of that measurement. One can encounter difficulties when determining the number of real resonance for the tested liquid n_t, which should be estimated from Eq. (7)

$$n_t \cong \frac{(f_n)_t}{(f_1)_r} \tag{7}$$

where the indexes "t" and "r" denote the values for the tested and reference liquids, respectively. However, this must be done with care because it is possible to make a significant error estimating n_t with a difference by one.

5. Conclusions

The performed measurements enabled to verify the range of applicability of the correction (2) given by Eggers. It was established that the results of calculations of the velocity with only this correction are obtained with an error of about 0.1% starting from the frequency $\frac{3}{4} f_q$. For frequency close to f_q, this error grows very fast and, for instance, at frequencies near 0.9 f_q equals about 0.3%. Furthermore, for frequencies close to $\frac{3}{4} f_q$, the determination of n from Eq. (3) can have more than one meaning what can lead to significant errors.

The established regularities in the frequency dependencies of Δf_n and F enable to propose the new method of velocity calculation from the f_n measurements in the whole frequency range used in the resonator method.

By using the method proposed here the error mentioned above is no greater than 0.1% for similar liquids i.e. tested and reference even at frequencies close to f_q.

References

[1] F. Eggers, *Eine Resonatormethode zur Bestimmung von Schall-Geschwindigkeit und Dämpfung an geringen Flussigkeitsmengen,* Acustica, **19**, 323–329 (1967/68).

[2] F. Eggers, Th. Funck, *Ultrasonic measurements with milliliter liquid samples in the 0.5–100 MHz range,* Rev. Sci. Instrum., **44**, 969–977 (1973).

[3] F. Eggers, Th. Funck, *New acoustic resonator for liquids in the 0.2 to 2 MHz range,* J. Acoust. Soc. Am., **57**, 331–333 (1975).

[4] F. Eggers, Th. Funck, K.H. Richmann, *High Q ultrasonic liquid resonators with concave transducers,* Rev. Sci. Instrum., **47**, 361–379 (1976).

[5] U. Kaatze, B. Wehrmann, R. Pottel, *Acoustical absorption spectroscopy of liquids between 0.15 and 3000 MHz: High resolution ultrasonic resonator method,* J. Phys. E: Sci. Instrum., **20**, 1025–1030 (1987).

[6] A. Labhardt, G. Schwarz, *A high resolution and low volume ultrasonic resonator method for fast chemical relaxation measurements,* Berichte der Bunsen-Gesellschaft, **80**, 83–92 (1976).

[7] Y. Naito, P. Choi, K. Takagi, *A plano-concave resonator for ultrasonic absorption measurements,* J. Phys. E: Sci. Instrum., **17**, 13–16 (1984).

[8] Y. Naito, P. Choi, K. Takagi, *High-Q ultrasonic resonator for absorption measurements in liquid,* Jap. Journ. of Appl. Phys., **23**, 45–47 (1984).

[9] A.P. Sarvazyan, *Development of methods of precise ultrasonic measurements in small volumes of liquids,* Ultrasonics, **20**, 151–154 (1982).

[10] I. Alig, G. Hempel, W. Lebek, *Application of the Fourier transform technique to an ultrasonic resonator,* Acustica, **68**, 40–45 (1989).

[11] F. Eggers, *Ultrasonic velocity and attenuation measurements in liquids with resonators, Extending the MHz frequency range*, Acustica, **76**, 231–240 (1992).

[12] Y. Thiriet, P. Martinoty, *Ultrasonic study of the nematic-isotropic phase transition in PAA*, Journ. de Phys., **40**, 789–797 (1979).

[13] M. Trio, Y. Dormoy, B. Michels, *Measure automatique de l'absorption ultrasonore dans un résonateur*, Acustica, **19**, 119–123 (1981).

[14] G. Galiński, Z. Kozłowski, *Ultrasonic spectroscopy equipment for the 0.5–15 MHz frequency range*, Sci. Instrum., **4**, 43–52 (1989).

[15] A. Balcerzak, Z. Bazior, Z. Kozłowski, *Automatic equipment for ultrasonic measurements in liquids by means of resonator method* (in Polish), IFTR Reports, 17, 1992.