CALDON

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October 16, 1998

Document Control Desk
U.S. Nuclear Regulatory Commission
Washington, DC 20555

Attention: Mr. Tim Polich

APPLICATION FOR WITHHOLDING PROPRIETARY
INFORMATION FROM PUBLIC DISCLOSURE

Subject: Responses to NRC Staff Questions Concerning Topical Report, "Improving Thermal Power Accuracy and Plant Safety While Increasing Operating Power Level Using the LEFM✓ System", Caldon, Inc. Engineering Power ER-80P (Proprietary), March 1997.

Dear Mr. Polich:

The proprietary information for which withholding is being requested in the above-referenced response is further identified in Affidavit CAW-98-02 signed by the owner of the proprietary information, Caldon, Inc. The affidavit, which accompanies this letter, sets forth the basis on which the information may be withheld from public disclosure by the Commission and addresses with specificity the considerations listed in paragraph (b)(4) of 10 CFR Section 2.790 of the Commission's regulations.

Accordingly, this letter authorizes the utilization of the accompanying Affidavit by TU Electric.

Correspondence with respect to the proprietary aspects of the application for withholding or the Caldon affidavit should reference this letter, CAW-98-02, and should be addressed to the undersigned.

Very truly yours,

CR Hastings

Calvin R. Hastings
President and CEO

CRH/ta
Enclosures

October 16, 1998

CAW-98-02

AFFIDAVIT

COMMONWEALTH OF PENNSYLVANIA:

ss

COUNTY OF ALLEGHENY:

Before me, the undersigned authority, personally appeared Calvin R. Hastings, who, being by me duly sworn according to law, deposes and says that he is authorized to execute this Affidavit on behalf of Caldon, Inc. ("Caldon") and that the averments of fact set forth in this Affidavit are true and correct to the best of his knowledge, information, and belief:

Calvin R Hastings

Calvin R. Hastings,
President and CEO
Caldon, Inc.

Sworn to and subscribed before me

this 16th day of

October, 1998

Antionette L. Herbst

Notarial Seal
Antionette L. Herbst, Notary Public
Pittsburgh, Allegheny County
My Commission Expires Mar. 11, 2002
Member, Pennsylvania Association of Notaries

1. I am the President and CEO of Caldon, Inc. and as such, I have been specifically delegated the function of reviewing the proprietary information sought to be withheld from public disclosure in connection with nuclear power plant licensing and rulemaking proceedings, and am authorized to apply for its withholding on behalf of Caldon.

2. I am making this Affidavit in conformance with the provisions of 10 CFR Section 2.790 of the Commission's regulations and in conjunction with the Caldon application for withholding accompanying this Affidavit.

3. I have personal knowledge of the criteria and procedures utilized by Caldon in designated information as a trade secret, privileged or as confidential commercial or financial information.

4. Pursuant to the provisions of paragraph (b) (4) of Section 2.790 of the Commission's regulations, the following is furnished for consideration by the Commission in determining whether the information sought to be withheld from public disclosure should be withheld.

   (i) The information sought to be withheld from public disclosure is owned and has been held in confidence by Caldon.

   (ii) The information is of a type customarily held in confidence by Caldon and not customarily disclosed to the public. Caldon has a rational basis for determining the types of information customarily held in confidence by it and, in that connection, utilizes a system to determine when and whether to hold certain types of information in confidence. The application of that system and the substance of that system constitutes Caldon policy and provides the rational basis required.

   Under that system, information is held in confidence if it falls in one or more of several types, the release of which might result in the loss of an existing or potential advantage, as follows:

(a) The information reveals the distinguishing aspects of a process (or component, structure, tool, method, etc.) where prevention of its use by any of Caldon's competitors without license from Caldon constitutes a competitive economic advantage over other companies.

(b) It consists of supporting data, including test data, relative to a process (or component, structure, tool, method, etc.), the application of which data secures a competitive economic advantage, e.g., by optimization or improved marketability.

(c) Its use by a competitor would reduce his expenditure of resources or improve his competitive position in the design, manufacture, shipment, installation, assurance of quality, or licensing a similar product.

(d) It reveals cost or price information, production capacities, budget levels, or commercial strategies of Caldon, its customer or suppliers.

(e) It reveals aspects of past, present or future Caldon or customer funded development plans and programs of potential customer value to Caldon.

(f) It contains patentable ideas, for which patent protection may be desirable.

There are sound policy reasons behind the Caldon system which include the following:

(a) The use of such information by Caldon gives Caldon a competitive advantage over its competitors. It is, therefore, withheld from disclosure to protect the Caldon competitive position.

(b) It is information which is marketable in many ways. The extent to which such information is available to competitors diminishes the Caldon ability to sell products or services involving the use of the information.

(c) Use by our competitor would put Caldon at a competitive disadvantage by reducing his expenditure of resources at our expense.

(d) Each component of proprietary information pertinent to a particular competitive advantage is potentially as valuable as the total competitive advantage. If competitors acquire components of proprietary information, any one component may be the key to the entire puzzle, thereby depriving Caldon of a competitive advantage.

(e) Unrestricted disclosure would jeopardize the position of prominence of Caldon in the world market, and thereby give a market advantage to the competition of those countries.

(f) The Caldon capacity to invest corporate assets in research and development depends upon the success in obtaining and maintaining a competitive advantage.

(iii) The information is being transmitted to the Commission in confidence, and, under the provisions of 10 CFR Section 2.790, it is to be received in confidence by the Commission.

(iv) The information sought to be protected is not available in public sources or available information has not been previously employed in the same manner or method to the best of our knowledge and belief.

(v) The proprietary information sought to be withheld in this submittal is that which is appropriately marked in the "Responses to NRC Staff Questions Concerning Topical Report, 'Improving Thermal Power Accuracy and Plant Safety While Increasing Operating Power Level Using the LEFM✓ System', as Applied to Comanche Peak, September 29, 1998, Proprietary Version" and is being transmitted by TU Electric letter and Application for Withholding Proprietary Information from Public Disclosure, to the Document Control Desk, Attention, Mr. Tim Polich. This proprietary information was initially distributed during the proprietary portion of the September 29, 1998, meeting between the NRC, TU Electric and Caldon. This information is submitted for use by TU Electric for the Comanche Peak Nuclear Plants and is expected to be applicable in other license submittals for justification of the use of the Caldon Leading Edge Flow Meter (LEFM✓) to increase reactor plants' thermal power. (A separate document "Responses to NRC Staff Questions Concerning Topical Report, 'Improving Thermal Power Accuracy and Plant Safety While Increasing Operating Power Level Using the

LEFM✓ System', as Applied to Comanche Peak, September 29, 1998, Non-Proprietary Version" is also being submitted which extracts the non-proprietary elements of the proprietary responses, and which non-proprietary document may be made publicly available. Note that the non-proprietary document contains the responses to questions 1, 2, 3, 5, 6, 9, 12, 14 (relevant portions), and 29.)

This information is part of that which will enable Caldon to:

(a) Demonstrate the design of the LEFM✓ and accuracy of the LEFM✓ flow and temperature measurements, as well as the improved calorimetric thermal power accuracy based on the LEFM✓ measurements.

(b) Demonstrate the reliability of the LEFM✓ based on design features and on compiled field experience data.

(c) Establish technical and licensing approaches for the application of the improved accuracy of this method toward increasing thermal power.

(d) Assist customers in obtaining NRC approval for increases in thermal power based on appropriate use of the LEFM✓ for calorimetric power measurement.

Further this information has substantial commercial value as follows:

(a) Caldon plans to sell the LEFM✓ and use of similar information to its customers for purposes of meeting NRC requirements for operation at increased thermal power.

(b) Caldon can sell support and defense of the technology to its customers in the licensing process.

Public disclosure of this proprietary information is likely to cause substantial harm to the competitive position of Caldon because it would enhance the ability of competitors to provide similar flow and temperature measurement systems and licensing defense services for commercial power reactors without commensurate expenses. Also, public disclosure of the information would enable others to use the information to meet NRC requirements for licensing documentation without the right to use the information.

The development of the technology described in part by the information is the result of applying the results of many years of experience in an intensive Caldon effort and the expenditure of a considerable sum of money.

In order for competitors of Caldon to duplicate this information, similar products would have to be developed, similar technical programs would have to be performed, and a significant manpower effort, having the requisite talent and experience, would have to be expended for developing analytical methods and receiving NRC approval for those methods.

Further the deponent sayeth not.

Responses to NRC Staff Questions Concerning

TOPICAL REPORT: Improving Thermal Power Accuracy and Plant Safety While Increasing Operating Power Level Using the LEFM√ System

as Applied to Comanche Peak

September 29, 1998

NON-PROPRIETARY VERSION

NRC Staff Questions

1. Describe Caldon's understanding of the background for 1.02 being ascribed just for instrument uncertainty in power determination
2. On page 5-2 of the Topical Report, explain the justification for the use of PTC-6.
3. Describe how the LEFM√ is used in calorimetric power determinations.
5. Who is responsible and how are Calibration, Maintenance, and Training performed and achieved?
6. How will monitoring, verification, and error reporting be handled?
9. Clarify that the 0.5% used in the Topical Report is 95% confidence level (2σ).
12. Does cross flow = transverse velocity?
14. Provide the references sited in the temperature correlation uncertainty and an explanation of the field data provided in this analysis. [Non-proprietary references provided here.]
29. How is the LEFM√ used currently to provide correction factors to the venturis? Is the correction determined on the basis of the absolute accuracy or the repeatability of the LEFM√?

Question 1:

Describe Caldon's understanding of the background for 1.02 being ascribed just for instrument uncertainty in power determination.

Answer:

Caldon proposes to increase current licensed power by 1% for plants using Appendix K evaluation models without any requirement to reanalyze ECCS performance if the plants utilize a new technology for determining thermal power. The new technology provides on-line verification of instrument accuracy and is capable of accuracies sufficient to ensure that there is a higher level of certainty that 1.02% of the current licensed power will not be exceeded than is currently being provided, and, hence, a higher level of certainty that the criteria of 10 CFR 50.46 (b) will not be exceeded.

As set forth in the Opinion of the Commission in the ECCS rulemaking proceeding, RM-50-1, December 28, 1973, Section I.A. of Part 50, Appendix K, specifies the following for the initial conditions to be used in Appendix K evaluation models:

> For the heat sources...it shall be assumed that the reactor has been operating continuously at a power level at least 1.02 times the licensed power level (to allow for such uncertainties as instrumentation error), with the maximum peaking factor allowed by the technical specifications. A range of power distribution shapes and peaking factors representing power distributions that may occur over the core lifetime shall be studied and the one selected should be that which results in the most severe calculated consequences for the spectrum of postulated breaks and single failures analyzed.

The question has been raised as to what the phrase "such uncertainties as" implies and whether operating at a power level 1% higher than the current licensed power could have any effect on the continued validity of the current Appendix K analyses of ECCS performance. A review of the regulatory history, including the interim acceptance criteria, the record of the ECCS rulemaking proceeding, implementation of Appendix K, and operating experience, has turned up nothing that would suggest that anything other than the need to account for the uncertainty of determining the thermal power at which the reactor is operating led to the adoption of 1.02 times the maximum licensed power for an initial condition for Appendix K ECCS evaluations.

The NRC staff, in its concluding statement, had recommended essentially the same initial conditions as were adopted by the Commission. However, the staff had recommended "that the reactor shall be assumed to have been operating continuously at a power level no lower than 1.02 times maximum licensed power level (to allow for instrument error),..." Concluding Statement of Position of the Regulatory Staff, RM-50-1, at 40, 109. Regulatory Guide 1.49, Rev. 1, issued in December 1973, concurrent with the issue of the Commission's opinion in RM-50-1, recommended the use of an assumed power level 1.02

times the proposed licensed power for analyses and evaluations of all normal, transient and accident conditions necessary to evaluate the adequacy of the facility. The staff explained the purpose of using 1.02 times the proposed licensed power as follows:

> ...analyses in support of the proposed licensed power are made for a slightly higher power to allow for possible instrument errors in determining the power level. The regulatory staff has concluded that a margin of 2% is adequate for this purpose.

Nowhere in the Commission's opinion is any reason given for the addition of the words "such uncertainties as."

The record shows that the initial conditions of Appendix K had their inception in the ECCS evaluation models approved with the issuance of the interim acceptance criteria. 36 Fed. Reg. 12247, June 1971. See for example WCAP-7422L, Westinghouse PWR Core Behavior Following a Loss-of-Coolant Accident. Id at Appendix A, Part 3. Here, 1.02 times the licensed power was used to account for uncertainties in determining the operating power level and the worst possible power distributions and maximum peaking factors were determined. The maximum peaking factors for which ECCS performance were found to be acceptable were placed in technical specifications for the plants.

The manner in which the initial conditions have been applied since the promulgation of Appendix K is also instructive. Initially, when Appendix K was issued, reactors then operating under the interim acceptance criteria were required to perform ECCS evaluations using approved Appendix K evaluation models. Since the worst possible power distributions and maximum peaking factors allowed by the then current technical specifications were used, unless, of course, the Appendix K evaluations supported different values. (As specified in 10 CFR 50.36, the technical specifications must be derived from the analyses and evaluations in the safety analyses reports and amendments thereto. Hence, the maximum peaking factors allowed by plant technical specifications must be consistent with the maximum peaking factors used in the ECCS evaluations which demonstrate that the ECCS performance satisfies the criteria of 10 CFR 50.46(b).

In general, in applying initial conditions for the interim acceptance criteria and those required by Appendix K, Section I.A., the following were incorporated in approved ECCS evaluation models:

1. Reactor power assumed to have been continuously at 1.02 times the licensed power (or proposed licensed power in case of amendments) to account for uncertainties in determining thermal power.

2. A cosine curve representing the power distribution shape resulting in the worst consequences (normally the highest calculated peak clad temperatures). The cosine curve is worse than any other power shape occurring at any time in core life. This shape can only occur during a return to power and for a

short time thereafter and is not possible in continuous power operation. Hence it is an extremely conservative assumption; and

3. The maximum peaking factor in the technical specifications (or proposed to be placed in the technical specifications);

These three assumptions have then been used in the Appendix K evaluation models as inputs to calculate the initial stored energy in the fuel, fission heat, and decay heat from actinides and fission products. None of these input assumptions are affected by increasing the operating power provided that the operating power does not exceed the 1.02 times maximum licensed power assumed in the evaluation of the ECCS performance showing that the criteria of 10 CFR 50.46(b) will not be exceeded. This is consistent with the objective stated in the opinion of the Commission in RM-50-46 dealing with conservatism:

> (1) Stored Heat. The assumption of 102% of maximum power, highest allowed peaking factor and the highest estimated thermal resistance between the UO_2 and the cladding [calculated using the above input assumptions] provides a calculated stored heat that is possible but unlikely to occur at the time of the hypothetical accident...Opinion of the Commission, RM-50-1, December 28, 1973 at 27, A-4.

Thus, it appears that the approval of the Caldon proposal resides solely in demonstrating that there is a sufficiently high probability that the power level assumed for evaluation of ECCS performance in existing Appendix K evaluations will not be exceeded in operation at a 1% increase in licensed power level with the proposed improved technology for determining plant operating power.

A review of the Standard Review Plan (SRP) was also conducted to identify references to application of the 2% margin to initial conditions for accidents. The results, summarized in Attachment 1, indicate that the 2% margin for initial conditions is required for analysis of 12 accidents in SRP Chapter 15. Of these 12 accidents, the license is permitted to use less than 2% margin in 9 cases provided the lower margin can be justified by the applicant.

Attachments:

1. Summary Table of Review of Chapter 15 of Standard Review Plan.

Attachment 1 to Question 1

Section of Chapter 15	Reference to 102% initial condition	Permission to use power level below 102% if justified
15.1-1 through 4: Decrease in Feed temp etc.	Yes	Yes
15.1.5 Steam sys piping failures in and out of containment	No	
15.1.5 A Rad Consequences	No	
15.2.1-5 Loss of Load etc	Yes	No
15.2.6 Loss of Emergency AC to Station Auxiliaries	Yes	Yes
15.2.7 Loss of Normal Feed Flow	Yes	Yes
15.2.8 Feed System Pipe Breaks – PWR	No	
15.3.1-2 Loss of forced reactor coolant Flow	Yes	Yes
15.3.3-4 Reactor coolant pump motor seizure	Yes	Yes
15.4.1 Uncontrolled Control rod withdrawal – subcritical/low power	No	
15.4.2Uncontrolled Withdrawal at Power	No	
15.4.3 Control Rod Malfunction	Yes	Yes
15.4.4-5 Startup of inactive loop and flow controller malfunction – BWR	Yes	No
15.4.6 CVCS reduces boron concentration PWR	Yes	No
15.4.7 Inadvertent Loading of fuel assembly	No	
15.4.8 Spectrum of rod ejection accidents – PWR	No	
15.4.8 A Rad Consequences of Ejection	No	
15.4.9 Spectrum of rod drop accidents – BWR	No	
15.4.9 A Rad consequences	No	
15.5.1-2 Inadvertent Operation of ECCS that increases inventory	Yes	Yes
15.6.1 Inadvertent opening of PWR or BWR pressure relief valve	Yes	Yes
15.6.2 Rad consequences of the failure of small lines carrying	No	

Attachment 1 to Question 1

Section of Chapter 15	Reference to 102% initial condition	Permission to use power level below 102% if justified
primary coolant outside containment		
15.6.3 Rad consequences of steam generator tube rupture – PWR	No	
15.6.4 Rad Consequences of Main Steam Line Failure Outside containment – BWR	No	
15.6.5 LOCA resulting from spectrum of pipe breaks within RC pressure boundary	Yes	Yes
15.6.5 Apps A, B, C, D: Various rad consequences of LOCA	No	
15.7.3 Rad releases due to liquid containing tank failures	No	
15.7.4 Rad consequences of fuel handling accidents	No	
15.7.5 Spent fuel cask drop accidents	No	

Question 2:

On page 5-2 of the Topical Report, explain the justification for the use of PTC-6.

Answer:

The context of the reference to PTC-6 is repeated here from page 5-2:

> "Immediately after it is calibrated, a flow nozzle is capable of providing measurement accuracies in the ±0.5% range, providing the differential pressure and fluid temperature measurements are made with laboratory grade, calibrated instruments (see for example the discussion of turbine heat rate testing in ASME-PTC-6, Reference 9)."

PTC-6 is referred to for purposes of illustration only and does not apply to the use of the LEFM✓ for thermal power measurement.

Attachments:

None.

Question 3:

Describe how the LEFM✓ is used in calorimetric power determinations.

Answer:

The proposed use of the LEFM✓ is for direct measurement of feedwater mass flow and temperature, and indirect measurement of feedwater enthalpy, for the thermal power determination. This determination would be used directly to calibrate the nuclear instruments in lieu of the existing instrumentation. At the discretion of the licensee, the LEFM✓ may also be used for calorimetric calculation of reactor coolant flow, and for setting non-safety-related setpoints for which thermal power is an input. The increased accuracy as compared to the existing instrumentation would be beneficial in these applications.

At Comanche Peak, the LEFM is currently used for the secondary calorimetric calculation only. The secondary calorimetric is used as input for the daily calibration of NIS and the cross-correlation N16 system.

In some plants, feedwater flow and/or temperature instruments are used as direct inputs to the reactor protection system or another automatic safety function. In these cases, those instruments are classified as safety-related, and would continue to be used for these functions. The LEFM✓ is not being proposed for these functions. Its use would be limited to power determination and the non-safety-related uses of calorimetric power discussed above.

Attachments:

None.

Question 5:

Who is responsible and how are Calibration, Maintenance, and Training performed and achieved?

Answer:

Calibration and Maintenance

Calibration and maintenance is performed by I&C using site procedures. The site procedures are developed using the CALDON technical manuals. All work is performed in accordance with site work control procedures.

Routine preventive maintenance procedures include physical inspections, power supply checks, back-up battery replacements, and internal oscillator frequency verification.

Ultrasonic signal verification and alignment procedures which involve digital oscilliscopes with the LEFM will be replaced by automatic set-up in the LEFM✓. Signal verification will still be possible by review of signal quality measurements performed and displayed by the LEFM✓.

Training

I&C personnel must be qualified per the I&C training program on the LEFM system before work or calibration may be performed. Formal training from Caldon was provided to site personnel. Formal training on the LEFM✓ system will be provided by Caldon.

Attachments:

None.

Question 6:

How will monitoring, verification, and error reporting be handled?

Answer:

Though this application is not safety-related, the LEFM✓ system is designed and manufactured under Caldon's Quality Control Program , which provides for configuration control, deficiency reporting and correction, and maintenance. Specific examples of quality measures undertaken in the design, fabrication and testing of the LEFM✓ system are provided in the Topical Report, Section 6.4 and Table 6.1. Table 6.1 lists the error bounding, validation and verification procedures planned for the LEFM✓ system.

At Comanche Peak, the LEFM system is included in the System Health Plan and the preventative maintenance program. The system is monitored by the System Engineer for reliability. As a plant system, all equipment problems fall under the site work control process. All conditions that are adverse to quality are documented under the ONE/SMART form program. The software falls under TU Electric's Appendix D QA program with a software QA plan in place. The current software was verified and validated and is under Caldon's Verification and Validation Program. Caldon's Verification and Validation Program provides procedures for deficiency reporting for engineering action and notification of holders of V&V software.

The Comanche Peak LEFM✓ System will likewise be under Caldon's V&V Program, and procedures will be maintained for user notification of important deficiencies.

Attachments:

None.

Question 9:

Clarify that the 0.5% used in the Topical Report is 95% confidence level (2σ).

Answer:

The 0.5% mass flow uncertainty stated for the chordal LEFM and the LEFM✓ is a 2 standard deviation (2σ) uncertainty; that is, it represents a 95% confidence interval. This is intended to be a bounding approximation. This subject is discussed further in response to Question 13.

Attachments:

None.

Question 12:

Does cross flow = transverse velocity?

Answer:

Yes. For the purposes of this report, the terms are used interchangeably.

Attachments:

None.

Question 14:

Provide the references sited in the temperature correlation uncertainty and an explanation of the field data provided in this analysis.

Journal of Research of the National Bureau of Standards Vol. 59, No. 4, October 1957 Research Paper 2795

Speed of Sound in Water by a Direct Method[1]

Martin Greenspan and Carroll E. Tschiegg

The speed of sound in distilled water was measured over the temperature range 0° to 100° C with an accuracy of 1 part in 30,000. The results are given as a fifth-degree polynomial and in tables. The water was contained in a cylindrical tank of fixed length, terminated at each end by a plane transducer, and the end-to-end time of flight of a pulse of sound was determined from a measurement of the pulse-repetition frequency required to set the successive echoes into time coincidence.

1. Introduction

The speed of sound in water, *c*, is a physical property of fundamental interest; it, together with the density, determines the adiabatic compressibility, and eventually the ratio of specific heats. The variation with temperature is anomalous; water is the only pure liquid for which it is known that the speed of sound does not decrease monotonically with temperature.

There is also a practical interest in *c* in that water is used as a standard liquid for the calibration of instruments that measure the speed of sound in liquids automatically, both in the laboratory and in the field. In fact, it was in connection with the calibration of such "velocimeters" [1][2] that our interest in this work was first aroused. In the first place, the available data scatter widely, as recent summaries [2, 3] clearly show. In many cases, the discrepancies far exceed the claimed accuracy or at least the precision of the methods, even when the methods compared are the same. In the second place, there exists no set of data that gives a smooth variation with temperature over any considerable range. In particular, the best of these data yield calibration curves for our velocimeters which are badly curved instead of straight (as they should be), and about which the data scatter irregularly, but reproducibly. The results here presented are free of these objections.

2. Method

At the top of figure 1 is a schematic of the apparatus. The sample is confined in a tube of which the ends are plane, parallel, electroacoustic transducers, quartz crystals in this case. If the left-hand crystal, say, is excited by a short pulse from the blocking oscillator, the oscilloscope, which measures the voltage on the right-hand crystal, will show a received pulse and a series of echoes, as indicated in idealized form on the line below (fig. 1). The pulse repetition frequency of the blocking oscillator is controlled by a sine-wave oscillator, and if this frequency were adjusted so that each blocking oscillator pulse coincided with the first received pulse of the next preceding cycle, then the oscillator period would equal the time of flight of the pulse. However, as the two pulses have different shapes, the accuracy with which the coincidence could be set would be very poor. Instead, the oscillator is run at about half this frequency and the coincidence to be set is that among the first received pulses corresponding to a particular electrical pulse, the first echo corresponding to the electrical pulse next preceding, and so on. Figure 1 illustrates the successive signals corresponding to three electrical input pulses. The input pulses fall halfway between the pulses for which the coincidence is set, so that they do not tend to overload the amplifier or distort the oscilloscope traces. The period of the oscillator, when properly set, multiplied by twice the length of the tank, is the speed of sound in the sample.

The oscilloscope trace actually looks like that shown in the inset (fig. 1). The first cycle corresponds to sound reflected from the inner faces only of the transducers, whereas the succeeding cycles correspond to sound reflected one or more times from an outer face. Therefore, the coincidence is set by maximizing the peak on either the first or second half-cycle; the same result is obtained in either case but the second half cycle is easier to use because it is bigger. What we are measuring here is the speed corresponding to the first arrival of the signal; in a nondispersive liquid this is the same as the phase velocity. It is true that the coincidence is made at a

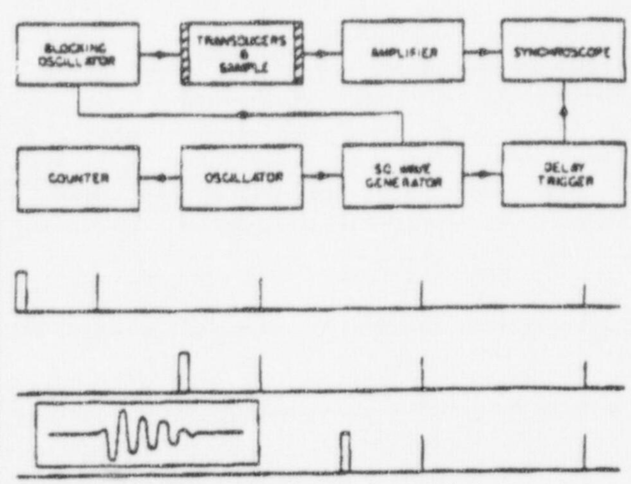

FIGURE 1. *Schematic of method.*

The three lower lines show in idealized form the events corresponding to three successive electrical pulses. The short, thick line represents the input pulse.

[1] This work was supported in part by the Office of Naval Research under contract NA-onr-70-48.

[2] Figures in brackets indicate the literature references at the end of this paper.

time one-fourth or three-quarters of the transducer period later than the time of first arrival, by which time there is opportunity for sound traveling by paths other than the shortest to affect the location of the maximum. However, the results are independent of whether the first or second half cycle is used; they are also not affected by substituting crystals of twice the thickness, or by changing the diameters of the tank, or of the hot electrodes. These results lead us to believe that the error introduced by this maximization technique is negligible.

The question has been examined also in another way. Suppose a coincidence to have been made at frequency f; others can then be made at submultiples of f. At the frequency $f/2$ for instance, the first received pulse corresponding to a particular input pulse coincides with the second echo (not the first, as before) corresponding to the electrical pulse next preceding, and so on. Effectively, the sound pulse is timed over a path twice as long as before. It is found that the measurements at f and near $f/2$ are substantially identical, so that the error in question is less than, or at most comparable to, the experimental error of the time measurement.

3. Apparatus

3.1. The Delay Line

The disassembled delay line is shown in the photograph, figure 2. The length of the tank is about 200 mm, and the bore about 13 mm. The filling holes are sealed by plugs having Teflon gaskets; a small hole in one plug provides pressure release.

The tank is of a chromium steel [3] which, after heat treatment, takes a good optical finish. Because this steel is not so corrosion resistant as the nickel-chromium stainless steels, the bore of the tank was heavily gold plated.

The ends of the tank are optically flat and parallel to within less than 1 μ. To these ends are carefully wrung the 0.8-mm thick x-cut quartz crystals, which also are optically flat. The caps, when bolted on, clamp the crystals through neoprene O-rings. A coaxial cable passes through a seal in each cap, and the center conductor makes contact with the outer (hot) electrode of the crystal through a light spring.

The outer electrode is a 9 mm circle of aluminum-backed pressure-sensitive adhesive tape. The inner (ground) electrode is of fired-on gold and is about 12 mm in diameter. Contact is made through a light gold-plated helical spring which touches the electrode around the edge and bears on a shoulder machined into the bore. The inner electrodes and springs are unnecessary if the sample has high conductivity or a high dielectric constant; they are usually omitted for water and aqueous solutions of salts. Figure 3 is a schematic drawing of one end of the assembly.

The length of the tank was measured at 20° C, and the coefficient of thermal expansion of the steel was measured on a sample cut from the same bar as

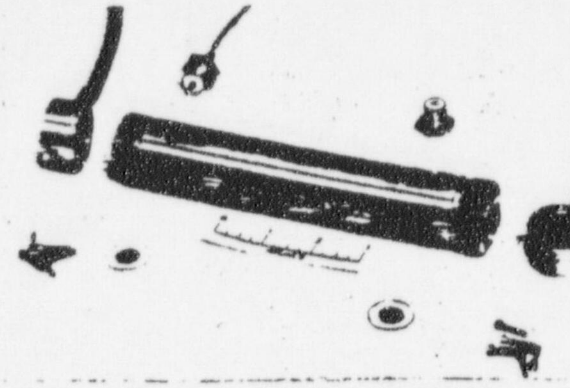

FIGURE 2. *Delay line, disassembled.*

Above the tank are the plugs which close the filling holes, and at the ends are the caps through which pass the electrical cables and which also clamp the crystals seen in the foreground.

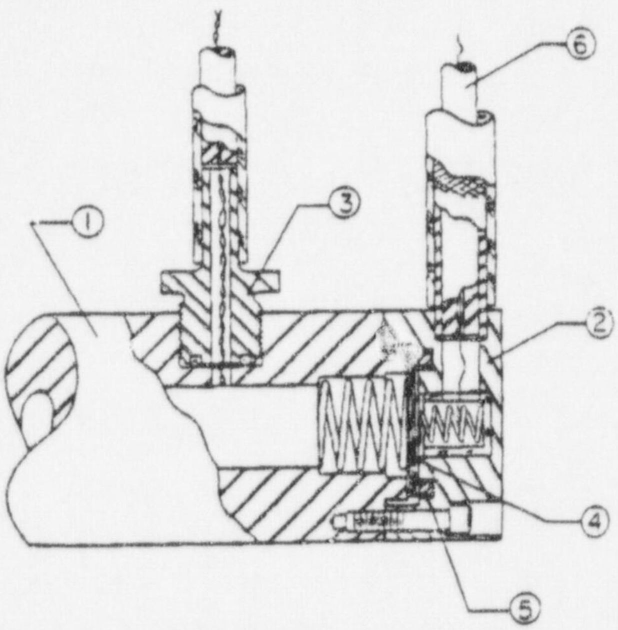

FIGURE 3. *Schematic of one end of the tank, showing the crystal and cap assembly.*

1, Tank; 2, cap; 3, plug sealed with Teflon O-ring (thermocouple passes through pressure relief tube); 4, quartz crystal wrung onto end of tank (springs make contact to electrodes); 5, neoprene O-ring; and 6, coaxial cable.

was the tank and heat-treated together with it. From these data, the length of the sound path is known to better than 2 parts in 10^5 at any temperature between 0° and 100° C. It is, of course, necessary that the crystals be wrung down with great care so that the fringes disappear all around the periphery, to achieve this accuracy. The clamping gaskets must bear directly over the contacting surface and not spread out over the unsupported area, else the crystal will bend. With these precautions, the delay line may be disassembled and reassembled repeatedly with reproducible results. If the crystals have been properly wrung on and clamped, they cannot be removed by hand after several days, but must be soaked off.

[3] Firth-Sterling type JB-440A.

3.2. The Electronics

The electronic circuits (fig. 1) are, for the most part, conventional. However, the oscillator and the pulse-forming circuits must be exceptionally free of jitter. In addition, the oscillator must be provided with fine frequency control, so that it can be set within the required sensitivity of measurement, and it must be so stable that the frequency does not change during the counting time by enough to alter the count by more than one.

The blocking oscillator produces a pulse about 100 v high and 0.05 to 0.25 μsec wide. It is best driven by a large, fast pulse such as is gotten by differentiation of a square wave derived, in turn, from the sine-wave generator.[4] The jitter may be reduced further by means of a narrow band filter after the oscillator.

The receiving circuit consists simply of a short length of low-capacitance cable, a wide band (5.5 Mc. in this case) amplifier of gain 100 to 1,000, and a high-frequency type oscilloscope equipped with fast sweeps. The sweep is triggered from the oscillator through a variable delay; the necessary delay time is about half the oscillator period.

3.3 Temperature Control and Measurement

The delay line, suspended from its cables, is deeply immersed in a 27 gal, well-insulated, water bath. The bath is provided with 2 pump-type stirrers, 3 heating coils, and a cooling coil connected to a small refrigeration unit. The temperature of the water adjusts itself so that the losses equal the power input to the heating coils, and various temperatures are obtained simply by varying the power input. The temperature is, by this means, easily held to within less than 0.005 deg C for the interval of time required for the measurements, except that above 75° C, or so, the variation may become 0.02° or 0.03° C; at the higher temperatures, however, the thermal coefficient of the speed of sound in water is rather low.

The temperature of the bath water is measured with a platinum resistance thermometer and Mueller Bridge. A differential thermocouple has one junction in the sample in the delay line, and one tied to the platinum thermometer; it passes through the pressure release tube (fig. 2). The thermocouple reading serves to indicate when the sample and bath water are substantially in thermal equilibrium, and measurements are made when the discrepancy is less than 0.01° C (somewhat greater at the high temperatures). The thermocouple and galvanometer combination was calibrated for small temperature differences against the platinum resistance thermometer so that small corrections to the temperature readings could be made.

3.4. Samples

The measurements here reported were made on three separate samples of water. One sample was ordinary laboratory distilled water. This was boiled and poured, while still hot, into the preheated tank. Although dissolved air has a negligible effect on the speed of sound in water [4], it is desirable to exclude air and so prevent possible bubble formation on the transducers.

The other two samples were vacuum distilled directly into the tank. The tank was placed in an ice bath and connected to a flask of distilled water. The system was then evacuated, and the water allowed to distill over at about 30° C.

The results of the three runs were the same within the errors of measurement; the data were, therefore, combined.

3.5. Technique

The water bath was cooled to just above 0° C, and the heaters were operated at low power to stabilize the temperature. (Below room temperature the refrigeration machine was run continuously.) After the readings were taken, the power input to the heaters was increased, and so on until the temperature was just below 100° C. When the temperature was stabilized, as indicated by the constancy of the Mueller bridge reading and the near zero reading of the thermocouple galvanometer, the coincidence was set on the oscilloscope by one observer and the frequency (doubled for convenience) was measured by counting cycles for 10 sec (about 75,000 counts) by means of an electronic counter. At the same time, another observer balanced and read the Mueller bridge and read the thermocouple galvanometer deflection.

While the temperature readings were being made, the coincidence was independently set and the resulting frequency measured three times or more. The various readings were always within the ±1 count inherent error (even for different observers) and the modal value was recorded. This, divided by 20 and multiplied by the length of the tank at the particular temperature, was taken as the speed of sound, c, corresponding to the temperature, T, obtained by calculation from the platinum thermometer and the thermocouple readings and the associated calibration data. All temperature calculations were made to the nearest 0.001° C and the final result was rounded off to the nearest 0.01° C.

In order to insure that the coincidence was set on the proper cycle, it was first set approximately, using the coarse frequency control, at a moderate sweep speed and low oscilloscope gain, so that the entire pulse was visible on the screen. The sweep speed was then increased while the delay was readjusted to keep the proper cycle centered. Next, the gain was increased while the base line was moved off the screen to keep the point of extreme deflection centered, and the amplitude was then adjusted to a maximum using the fine frequency control

4. Results

From readings taken at 83 temperatures between 0.14° and 99.06° C, the calculated values of the speed of sound were fitted by the electronic com-

[4] The square-wave generator must be of the type that amplifies and then clips the input sine wave. The free-running, synchronized type is not suitable.

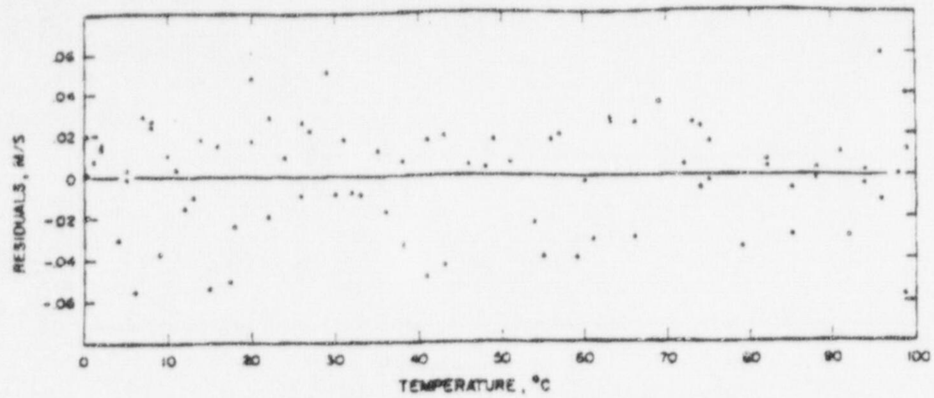

FIGURE 4. *Deviations, r, of equation 1 from the data.*

puter SEAC by the method of least squares, to a fifth-degree polynomial,

$$c=\sum_{i=0}^{5} a_i T^i. \qquad (1)$$

The reduction in the residual sum of squares over a fourth-degree polynomial, due to fitting the fifth-degree term, was statistically significant at a probability level less than 0.005, and the deviations of the data from the fifth-degree polynomial showed no statistically significant indication of lack of randomness. The deviations are plotted against temperature in figure 4.

The values of a_i in eq (1), for c in meters per second (m/s), and T in degrees C, are: $a_0=1{,}402.736$; $a_1=5.03358$; $a_2=-0.0579506$; $a_3=3.31636\times10^{-4}$; $a_4=-1.45262\times10^{-6}$; and $a_5=3.0449\times10^{-9}$. The standard deviation of the measurements is 0.0263 m/s, or about 17 ppm. Estimated standard deviations of the values of c predicted by eq (1) were calculated for five representative temperatures. The results are given in table 1.

TABLE 1. *Estimated standard deviation (s. d.) of values of c predicted by equation 1*

Temperature	s. d.	
°C	m/s	ppm
0	0.0114	8.1
10	.0063	4.5
40	.0058	3.5
70	.0062	4.0
100	.0145	9.4

Table 1 and figure 4 make it clear that eq (1), together with the listed constants, provides a satisfactory interpolation formula, and the errors introduced by its use are small relative to the possible systematic errors of measurement (see section 5). The values given in tables 2 and 3 were calculated from eq (1) by SEAC.

Table 2 gives the speed of sound in meters per second for each degree C from 0 to 100, and table 3 gives the speed of sound in feet per second at intervals of 2 deg F from 32° to 212°. In each case, the differences, which are listed for convenience in interpolation, were calculated from a table having more significant figures, so that on account of rounding-off errors, the tabulated differences in some cases differ by one unit in the last decimal place from the differences of the tabulated values of c. It is believed (see section 5) that the systematic errors do not exceed 1 part in 30,000. The tables should, therefore, be used in the following manner. In table 2, linear interpolation should be performed to the nearest 0.01 m/s and the final result rounded off to the nearest 0.1 m/s. The error will then not exceed one-half unit in the last place, i. e., 0.05 m/s. Linear interpolation in table 3 will yield errors that do not exceed 2 units (0.2 fps) in the last place.

5. Discussion

Following is a list of the known possible sources of error and an estimate of the upper limit of each error.

5.1. Frequency

As already stated, the frequency was measured by counting cycles for 10 sec; the total count was about 75,000. The inherent error is ±1 count, but in all cases the mode of at least three independent readings, of which, at worst, two were the same and the third different by one, was taken as the observed value. The counting error can thus be as great as 1 part in 75,000, but as it is random, the effect on the final results is negligible, as indicated in section 4. The 10-sec time base was obtained by division from a 1-Mc crystal oscillator which is stable to 2 parts in 10^7 per week, and which was compared with signals from WWV or from a local precision standard. The errors due to inaccuracies in the time base are therefore, also negligible.

5.2. Length of Path

The length of the tank across its polished ends at 20° C was determined within 1μ, i. e., 5 ppm. Thermal expansion measurements were made at 20°, 60° and 100° C; the lengths at intermediate temperatures were calculated by quadratic interpolation. The maximum absolute error in the thermal expansion coefficient is estimated at 0.2 ppm; this accumulates to 4 ppm at 0° C, and to 16 ppm at 100° C

TABLE 2. *Speed of sound in water, metric units*

T	c	Δ	T	c	Δ	T	c	Δ	T	c	Δ
°C	m/s 1,400+	m/s	°C	m/s 1,400+	m/s	°C	m/s 1,500+	m/s	°C	m/s 1,500+	m/s
0	2.71	....	25	97.00	2.71	50	42.87	1.12	75	55.45	−0.01
1	7.71	4.97	26	99.64	2.64	51	43.93	1.07	76	55.40	−.05
2	12.57	4.86	27	*2.20	2.56	52	44.95	1.02	77	55.31	−.09
3	17.32	4.75	28	4.68	2.49	53	45.92	0.97	78	55.18	−.13
4	21.98	4.66	29	7.10	2.41	54	46.83	.92	79	55.02	−.17
5	26.30	4.53	30	9.44	2.34	55	47.70	.87	80	54.81	−.20
6	30.92	4.43	31	11.71	2.27	56	48.51	.82	81	54.57	−.24
7	35.24	4.32	32	13.91	2.20	57	49.28	.77	82	54.30	−.28
8	39.46	4.22	33	16.05	2.14	58	50.00	.72	83	53.98	−.31
9	43.58	4.12	34	18.12	2.07	59	50.68	.67	84	53.63	−.35
10	47.59	4.02	35	20.12	2.00	60	51.30	.63	85	53.25	−.39
11	51.51	3.92	36	22.06	1.94	61	51.88	.58	86	52.82	−.42
12	55.34	3.82	37	23.93	1.87	62	52.42	.53	87	52.37	−.46
13	59.07	3.73	38	25.74	1.81	63	52.91	.49	88	51.88	−.49
14	62.70	3.64	39	27.49	1.75	64	53.35	.45	89	51.35	−.52
15	66.25	3.55	40	29.15	1.69	65	53.76	.40	90	50.79	−.56
16	69.70	3.46	41	30.80	1.63	66	54.11	.36	91	50.20	−.59
17	73.07	3.37	42	32.37	1.57	67	54.43	.31	92	49.58	−.63
18	76.35	3.28	43	33.88	1.51	68	54.70	.27	93	48.92	−.66
19	79.55	3.19	44	35.33	1.45	69	54.93	.23	94	48.23	−.69
20	82.66	3.11	45	36.72	1.39	70	55.12	.19	95	47.50	−.72
21	85.69	3.03	46	38.06	1.34	71	55.27	.15	96	46.75	−.76
22	88.63	2.95	47	39.34	1.28	72	55.37	.11	97	45.96	−.79
23	91.50	2.87	48	40.57	1.23	73	55.44	.07	98	45.14	−.82
24	94.29	2.79	49	41.74	1.17	74	55.47	.03	99	44.29	−.85
25	97.00 1,400+	2.71	50	42.87 1,500+	1.12	75	55.45 1,500+	−.01	100	43.41 1,500+	−.88

TABLE 3. *Speed of sound in water, English units*

T	c	Δ	T	c	Δ	T	c	Δ	T	c	Δ
°F	fps 4,600+	fps	°F	fps 4,900+	fps	°F	fps 5,000+	fps	°F	fps 5,000+	fps
30	....	....	80	25.7	9.4	130	76.2	3.1	180	99.2	−1.0
32	2.1	....	82	34.8	9.1	132	79.2	3.1	182	98.0	−1.2
34	20.3	18.2	84	43.7	8.9	134	82.1	2.9	184	96.7	−1.3
36	37.9	17.7	86	52.2	8.5	136	84.8	2.7	186	95.2	−1.5
38	55.1	17.2	88	60.5	8.3	138	87.3	2.5	188	93.6	−1.6
40	71.9	16.8	90	68.5	8.0	140	89.6	2.3	190	91.8	−1.8
42	88.2	16.3	92	76.2	7.7	142	91.7	2.1	192	89.9	−1.9
44	104.1	15.9	94	83.6	7.4	144	93.6	1.9	194	87.9	−2.1
46	119.6	15.5	96	90.8	7.2	146	95.3	1.7	196	85.7	−2.2
48	134.6	15.1	98	97.7	6.9	148	96.9	1.6	198	83.4	−2.3
50	149.3	14.7	100	*4.4	6.7	150	98.3	1.4	200	81.0	−2.5
52	163.6	14.3	102	10.8	6.4	152	99.5	1.2	202	78.4	−2.6
54	177.5	13.9	104	17.0	6.2	154	100.5	1.0	204	75.7	−2.7
56	191.0	13.5	106	22.9	5.9	156	101.4	0.9	206	72.9	−2.8
58	*4.1	13.1	108	28.6	5.7	158	102.1	.7	208	70.0	−3.0
60	16.9	12.8	110	34.0	5.4	160	102.6	.6	210	66.9	−3.1
62	29.3	12.4	112	39.2	5.2	162	103.0	.4	212	63.7	−3.2
64	41.3	12.0	114	44.2	5.0	164	103.2	.2	....	....	....
66	53.0	11.7	116	48.9	4.8	166	103.2	.0	....	....	....
68	64.4	11.4	118	53.3	4.5	168	103.1	−.1	....	....	....
70	75.4	11.0	120	57.8	4.3	170	102.8	−.3	....	....	....
72	86.1	10.7	122	61.9	4.1	172	102.4	−.4	....	....	....
74	96.4	10.4	124	65.8	3.9	174	101.8	−.6	....	....	....
76	106.5	10.1	126	68.4	3.7	176	101.1	−.8	....	....	....
78	116.2	9.8	128	72.9	3.5	178	100.2	−.9	....	....	....
80	125.7 4,800+	9.4	130	76.2 5,000+	3.3	180	99.2 5,000+	−1.0	....	.... 5,000+	....

Thus, the total uncertainty in the length of the tank is about 5 ppm at 20° C, and increases with temperature both ways; at 0° C it becomes about 9 ppm and at 100° C, about 21 ppm.

The question arises as to how closely the length of the sound path in the sample, i. e., the distance between the inner faces of the transducers, approximates to the length of the tank across the ends to which the crystals are wrung. Experience with developmental models showed that unless the assembly were very carefully made, with particular attention to avoidance of clamping pressure too near the unsupported areas of the crystals, the crystals might deflect enough to cause very sizable errors. The present design makes it possible to disassemble and reassemble the delay line repeatedly without affecting the result by a detectable amount; this holds true when the crystals normally used, which are 0.8 mm thick, are replaced by crystals 1.6 mm thick. It, therefore, appears that errors produced by misplacement or deformation of the crystals are insignificant.

5.3. Setting the Coincidence

As explained in section 2, it is believed that no measurable error is introduced by the technique of maximization of the second half cycle of the received pulse. However, a word should be said about the effect of personal bias on the part of the operator. The operators report, to varying degrees, tendencies to adjust not only for maximum height of peak, but also for maximum symmetry and sharpness of peak. Long experiment has convinced us that any of the three criteria lead to sensibly the same result, so that although different operators weigh the three criteria differently, they reproduce each other's settings so well that the discrepancies are negligible relative to other sources of error. The assumption is implicit that the errors of bias do not much exceed the discrepancies among individuals.

5.4. Temperature

The Mueller bridge with which the resistance of the platinum thermometer was measured has a least count of 0.0001 ohm corresponding, for a 25-ohm thermometer, to about 0.001° C. The bridge was calibrated internally so that the indicated resistance in terms of the internal standard is correct to about 0.0002 ohm aside from temperature effects and slow drifts in the arm ratio and in the zero. Allowing for these, it is estimated that the bridge error does not exceed 0.005° C; errors in the calibration of the platinum thermometer itself and those due to heating by the bridge current are much smaller. More important is the error that arises from thermal gradients in the bath. On the assumption that this does not exceed half the reading of the differential thermocouple which, it will be recalled, measures the difference between the temperature of the platinum element and that of the sample, an upper limit to the corresponding uncertainty in the speed of sound, c, was calculated at various temperatures from the known thermal coefficient of c. This upper limit is zero at 74° C, where c is stationary and increases steadily in both directions, reaching about 25 ppm at 0° C, and about 14 ppm at 100° C.

5.5. Purity of Sample

Because the results obtained on ordinary laboratory distilled water were indistinguishable from those obtained on the same water redistilled in vacuum directly into the apparatus, it is felt that the remaining impurities do not have a measurable effect. Several measurements made on local tap water gave results about 30 ppm higher than for distilled water.

5.6. Over-all Accuracy

From the foregoing discussion it appears that the major sources of error are the uncertainties in the length of the path and in the temperature. Both of these are temperature dependent; their sum is an upper limit to the total error. This is about 35 ppm at 0° C; it falls to 15 ppm at 40° C and is almost constant at this value out to 70° C, and rises to about 35 ppm at 100° C. It is upon these considerations that the recommendations for the use of the tables in section 4 are based.

The values of c here reported are lower than those of most other workers, in particular the value at 30° C is about 0.4 m/s below that of Del Grosso, Smura, and Fougere [3], whose work with the ultrasonic interferometer is perhaps the most carefully planned, executed, and analyzed work of this type to date. It was, therefore, felt desirable to perform an independent experiment using an apparatus and a method as different as possible from those of both Del Grosso, et al., and ourselves. An apparatus was constructed with which it is possible to measure, as a function of distance, the phase on the axis of a beam of progressive waves emitted by a small piston-like radiator. If the wave were plane, the phase φ would vary linearly with distance x, and the phase speed c would be $2\pi fx/\varphi$ where f is frequency. In the present case, the wave is not plane and the slope of the curve $2\pi fx$ versus φ depends on x and on the geometry of the arrangement. However, the theory enables us to select a distance x_0 of the receiver from the source such that for $x > x_0$ the departure of $2\pi f dx/d\varphi$ from c is as small as desired.

Five runs were made in distilled water at temperatures between 15° and 25° C. The principal uncertainties are thought to be first, one of about 40 ppm corresponding to a possible error of 0.01° C in the temperature, and second, one of about 56 ppm related directly to the inaccuracies of the screw with which the receiver displacement was measured. These are independent. However, in the worst case of the 5, the result differed from the value gotten from table 2 by only 27 ppm. The value of Del Grosso, et al. [3] disagrees with that of table 2 by 272 ppm.

This work will be reported in detail elsewhere.

The authors are grateful to the personnel of the Engineering Metrology Section and of the Length Section, in whose Laboratories the length of the tank and its thermal expansion, respectively, were measured. Thanks are particularly due to Joseph M. Cameron of the Statistical Engineering Section who advised the authors on problems of data processing, and who performed the curve-fitting computations on SEAC.

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Speed of Sound in Distilled Water as a Function of Temperature and Pressure

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An ultrasonic pulse type apparatus was used to measure the speed of sound in distilled water over the pressure range 14.7 to 14 000 psia and the temperature range 0.9 to 91.2°C. The temperature where the maximum sound speed occurs shifts to a higher temperature when the pressure is increased. At atmospheric pressure the computed maximum speed was 1555.36 m/sec and occurred at a temperature of 74.164°C. The isotherms of sound speed, plotted as a function of pressure, are concave upward below 20°C, concave downward above 20°C, and are approximately linear near 20°C for the pressure range of 14.7 to 14 000 psia. These curvatures have a maximum value of 1 part in 300 compared to the estimated accuracy of measurement which is 1 part in 10 000. The results are presented in tables and also in the form of a fourth degree equation fitted to the experimental data by the method of least squares.

I. INTRODUCTION

A PRECISE knowledge of the speed of sound in distilled water is important for the computation of many thermodynamic quantities. Numerous measurements have been made of the speed of sound but only a few measurements have been made of sound speeds as a function of temperature and pressure. Greenspan and Tschiegg[1] and also Del Grosso[2] have published accurate tables of sound speed as a function of temperature at atmospheric pressure. The effect of pressure on sound speeds have been explored by Holton,[3] Smith and Lawson,[4] and by Litovitz and Carnevale,[5] and others; however, differences exist between these data. Consequently, measurements have been made at the Naval Ordnance Laboratory (NOL) to determine sound speeds in water within the temperature range $0°C<T<100°C$ and the pressure range 14.7 psia$\leq P\leq$14 000 psia. The present paper is concerned with measurements in distilled water. Numerous systems have been designed for sound speed measurements but the fixed-path double crystal "velocimeter" was selected by NOL as most suitable for measurements under pressure.

II. EXPERIMENTAL ARRANGEMENT

The method used in this work is similar in principle to that developed by Greenspan and Tschiegg at the National Bureau of Standards. The water sample is contained in a tubular housing, each end of which is terminated by a 5-Mc quartz crystal for the transmission and reception of sound pulses. A knowledge of the repetition rate of the pulses when echoes are superimposed is sufficient to determine the time required for a sound pulse to traverse the length of the velocimeter. An accurate determination of this length then allows the velocity of sound to be computed.

The main differences between the velocimeter used

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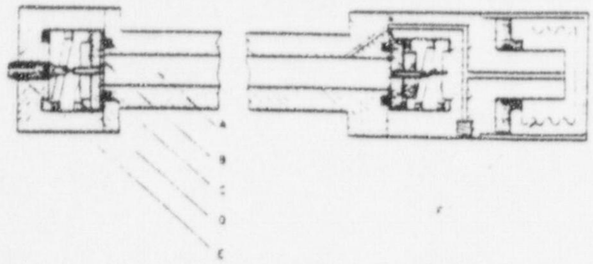

FIG. 1. Schematic of velocimeter: *A*, test chamber; *B*, quartz crystal; *C*, O-ring seal; *D*, compression spring; *E*, electrical lead; *F*, bellows.

by Greenspan and Tschiegg and the velocimeter used at NOL are as follows: (a) the National Bureau of Standards (NBS) instrument was 20 cm in length as compared to 12.7 cm for the NOL instrument; (b) the NBS instrument used 3.5-Mc crystals and the NOL instrument used 5.0-Mc crystals; and (c) the NBS instrument used crystals which were wrung to the ends of the tube without electrode plating at the contact area while the NOL instrument used gold plated crystals. The NOL velocimeter, shown in Fig. 1, is a stainless steel tube with a ½-in. bore approximately 5 in. long. The two ends of the tube were machined plane parallel and perpendicular to the axis of the tube to an accuracy of 0.00005 in. To each end of the tube is attached a cap containing a 5-Mc gold-plated X-cut crystal backed up by a Mycalex insulator and a compression spring. The springs are used to force the crystals against the ends of the tube when assembled. A neoprene O-ring located between each crystal and the tube provide leakage seals. This O-ring is designed to compress fully under the force of the spring and allow the crystal to make uniform contact with the ends of the tube. One end cap contains the electrical leads for the communication of sound pulses between the crystals and the external electronics, and the second end cap has a bellows attached for the purpose of transmitting the pressure to the water sample inside the tube. The bellows was carefully designed to insure a negligible pressure differential between the hydrostatic pressure field outside and the pressure inside the velocimeter. The velocimeter is placed inside a heat treated steel pressure vessel capable of withstanding 100 000 psia. This vessel has steel end plugs, one of which is used to transmit pressure to the inside of the vessel and the other to bring out the electrical leads. A medium grade oil is used to convey pressure from the pressure generator to the pressure vessel.

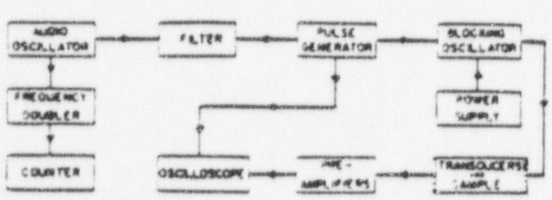

FIG. 2. Block diagram of instrumentation.

Figure 2 presents a block diagram of the electronic instrumentation required for the sound speed measurements. An interpolation oscillator equipped with a fine frequency control is filtered electronically and used to control a pulse generator. The pulse from this generator is shaped by a blocking oscillator to furnish a pulse of 180-v amplitude with a duration of 0.05 μsec to one crystal in the velocimeter. The second crystal receives the pulse after it has traversed the water sample and feeds it into preamplifiers prior to displaying the signal on an oscilloscope. Coincidence of the sound pulses in the velocimeter is adjusted by observing the signal trace on the oscilloscope while varying the oscillator frequency. It is this frequency which determines the time required for the pulse to traverse the liquid in the velocimeter. The pulse repetition frequency is doubled and displayed on a frequency counter with an accuracy of 1 part in 100 000 for the computation of sound velocity.

Figure 3 shows the general arrangement of the complete instrumentation for monitoring and accurate control of the physical environment of the velocimeter. The pressure vessel containing the velocimeter is placed in a 110-gallon constant temperature bath regulated by a mercury thermoregulator. Three stirring pumps are used to circulate the water in the bath to assure a constant and uniform temperature. The absolute temperature of the bath is measured by a platinum resistance thermometer to the nearest 0.001°C. Temperature variations and temperature gradients are recorded by the action of a thermistor placed in the bath near the pressure vessel. The thermistor acts as the resistance in one leg of a Wheatstone bridge; the unbalance of this bridge is observed on a recording potentiometer and variations in temperature of 0.0005°C are easily detected.

In Fig. 3 a single meter is shown as the device used to measure pressure. Actually, a manganin resistance gauge, a sensitive Heise gauge, and a dead weight tester were used to determine the absolute pressure. Greatest reliance was placed on the dead weight tester since the manganin cell was unstable at low pressures; this cell was used however to detect changes in pressure as small as 4 psi for higher pressures. It is estimated that the absolute pressures were known to within 7 psi or, when referred to velocity coordinates, the pressure was known approximately to 1 part in 20 000.

III. METHOD OF MEASUREMENT

Sound speeds were measured by first adjusting the bath to a particular temperature and then by varying the pressure over the desired range. Since an adiabatic increase in pressure of 2000 psi will change the temperature inside the velocimeter nearly 1°C it was necessary to wait until thermal equilibrium was reestablished before a measurement was made. The thermistor used to measure temperature was located outside the pressure vessel and was not sensitive to changes inside the

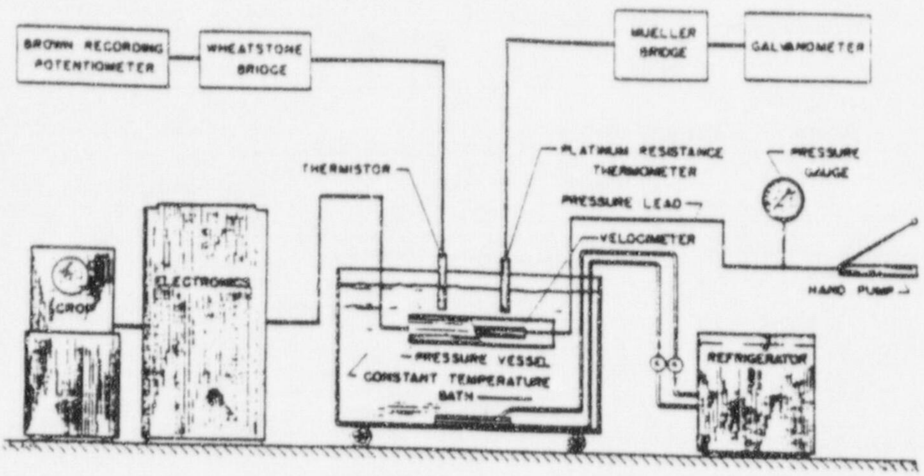

FIG. 3. Schematic of experimental setup.

velocimeter. Hence the sound speed measurement itself was used to determine when thermal equilibrium existed. That is, the measurement of sound speed over a period of time (approx 1 hr) was used as a thermometer to determine when thermal equilibrium was established. After thermal equilibrium was reached ten measurements of the pulse repetition frequency were recorded and averaged to give the time required by the pulse to traverse the velocimeter. The pulse repetition frequency is obtained by superimposing on the oscilloscope the peaks of the first half-cycle of all echoes in the velocimeter.

IV. RESULTS

The measured values for the speed of sound as a function of temperature and pressure are presented in Table I. These values are plotted in Fig. 4 with temperature as the abscissa and in Fig. 5 with pressure as the abscissa. In the determination of the sound speeds recorded in Table I, corrections for the change of length of the velocimeter due to changes in temperature and pressure have been applied. The results of Table I were used to obtain empirical equations for the speed of sound as a function of temperature and pressure. Equation (1), a fourth degree equation, was first obtained by the method of least squares for each of the eight curves shown in Fig. 4. The coefficients of the eight equations were tabulated and a third degree equation obtained to describe the coefficients of Eq. (1). The speed of sound in distilled water is therefore given by

$$C=a_0+a_1T+a_2T^2+a_3T^3+a_4T^4, \qquad (1)$$

where

$$a_i=\sum_{j=0}^{3}(b_i)_jP^j.$$

T is the temperature (°C), P is the absolute pressure (psia), and the computed $(b_i)_j$ values are given in Table II. The parentheses indicate a set of b_i values associated with each a_i; for example, Table II gives

$$a_0=1402.859+1.050469\times10^{-2}P+1.633786\times10^{-7}P^2-3.889257\times10^{-12}P^3, \text{etc.}$$

An IBM computer was used to compute sound speeds from these equations and the results are tabulated in Table III. The standard deviations of the differences between the computed curves and the measured curves for four pressures are given in Table IV.

V. DISCUSSION OF RESULTS

It may be noted in Fig. 4 that the maximum sound speed shifts toward higher temperatures as higher pressures are considered. This behavior agrees with the results obtained by Smith and Lawson, and also by Litovitz and Carnevale.[5] The temperature for the peak

TABLE I. Measured values of the speed of sound in distilled water.

Pressure psia	Temperature °C 0.91°	2.77°	10.20°	19.66°	29.95°	39.42°	49.57°	59.59°	69.66°	78.70°	91.27°
14.7	1407.41	1416.35	1449.05[a]	1481.63	1509.37	1528.36	1542.60	1551.01	1555.02	1554.90	1549.80
2000	1429.25	1438.06	1471.46	1504.34	1532.67	1552.03	1567.11	1576.21	1581.13	1581.83	1578.03
4000	1451.66	1460.83	1494.17	1527.38	1555.87	1575.72	1591.22	1600.96	1606.58	1607.97	1605.31
6000	1475.37	1484.42	1517.28	1550.49	1579.04	1599.16	1614.92	1625.21	1631.44	1633.35	1631.75
8000	1499.72	1508.50	1540.99	1573.79	1602.12	1622.17	1638.22	1648.91	1655.69	1657.95	1657.36
10 000	1524.61	1533.29	1564.78	1596.90	1625.06	1645.14	1661.28	1672.30	1679.34	1682.13	1682.18
12 000	1549.93	1558.09	1588.75	1620.25	1647.88	1667.72	1684.00	1695.13	1702.55	1705.65	1706.39
14 000	1575.22	1583.15	1612.66	1643.41	1670.58	1690.41	1706.51	1717.68	1725.28	1728.69	1730.02

[a] It is believed that this point is in error by +0.6 m/sec.

TABLE II. Coefficients in the sound velocity equations for distilled water.

a_i	$(b_i)_{j=0}$	$(b_i)_{j=1}$	$(b_i)_{j=2}$	$(b_i)_{j=3}$
a_0	1402.859	1.050469×10^{-2}	1.633786×10^{-7}	-3.889257×10^{-12}
a_1	5.023859	6.138077×10^{-4}	-1.080177×10^{-8}	2.477679×10^{-13}
a_2	-5.690577×10^{-2}	-1.071154×10^{-6}	2.215786×10^{-10}	-5.088886×10^{-15}
a_3	2.884942×10^{-4}	1.582394×10^{-8}	-2.420956×10^{-13}	5.086237×10^{-17}
a_4	-8.238863×10^{-7}	-6.839540×10^{-11}	9.711687×10^{-15}	-1.345198×10^{-19}

TABLE III. Sound velocity in distilled water computed from Eq. (1).[a]

Pressure psia	Temperature °C 0.00°	10.00°	20.00°	30.00°	40.00°	50.00°	60.00°	70.00°	80.00°	90.00°	100.00°
14.7	1403.01	1447.85	1482.92	1509.66	1529.30	1542.88	1551.26	1555.06	1554.74	1550.54	1542.51
2000	1424.49	1470.03	1505.66	1532.92	1553.11	1567.34	1576.47	1581.14	1581.77	1578.58	1571.54
4000	1447.24	1492.88	1528.68	1556.21	1576.79	1591.51	1601.25	1606.65	1608.10	1605.80	1599.70
6000	1470.93	1516.15	1551.79	1579.37	1600.17	1615.26	1625.49	1631.47	1633.62	1632.10	1626.88
8000	1495.36	1539.76	1574.97	1602.41	1623.30	1638.63	1649.23	1655.68	1658.40	1657.57	1653.20
10 000	1520.36	1563.60	1598.17	1625.33	1646.19	1661.68	1672.54	1679.36	1682.54	1682.33	1678.78
12 000	1545.72	1587.60	1621.38	1648.15	1668.90	1684.44	1695.48	1702.56	1706.13	1706.47	1703.73
14 000	1571.28	1611.66	1644.56	1670.88	1691.44	1706.96	1718.10	1725.38	1729.26	1730.10	1728.17

[a] Velocity given in m/sec.

atmospheric velocity can be obtained by differentiating Eq. (1) and equating the resulting cubic equation to zero. When this is done it is found that the peak sound speed at atmospheric pressure occurs at a temperature of 74.164°C. Linear interpolation of the results of Greenspan and Tschiegg yields a corresponding temperature of 74.178°C. Later work by Greenspan and Tschiegg[6] with the sing-around system placed this maximum speed at 73.95°C. The sound speeds measured at NOL at atmospheric pressure agree well with the results of Greenspan and Tschiegg. The standard deviation of the difference between the NBS and the NOL results for all of the atmospheric pressure data is 0.15 m/sec.

The characteristics of the isotherms shown in Fig. 5 require comment. At high temperatures it is seen that some curves intersect; this is to be expected, however, since the sound speeds at low pressures decrease for

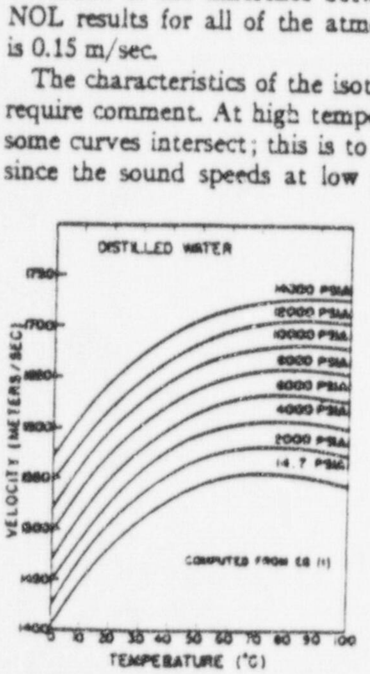

FIG. 4. Velocity of sound in distilled water as a function of temperature.

temperature exceeding 74.17°C (see Fig. 4). A change in curvature of the isotherms in the vicinity of 20°C has been observed. Below 20°C the isotherms are concave upward, above 20°C they are concave downward, and in the vicinity of 20°C they are nearly linear. Additional measurements at NOL on sea water show that the general effect of pressure on sound speed is essentially the same as that for distilled water. This behavior is in contrast with the results predicted by Kuwahara[7] in his sea water table and by Matthews[8] in tables of pure water and sea water which show the isotherms plotted against pressure to be concave downward at all temperatures. The sound speeds computed by these authors depend on an empirical equation developed by Ekman[9] for the mean compressibility of sea water. This equation was derived from Ekman's measurements on sea water and from Amagat's[10] specific volume measurements on distilled water. Ekman has suggested that Amagat's specific volume data is in error below 150 atmos and he applied a correction factor to Amagat's data in this range. A descriptive analysis of Kuwahara's computation is given by Beyer.[11] It is shown here that the corrections Ekman applied to Amagat's data were in the correct direction although, as Beyer points out, a more accurate expression for compressibility is still desired. Ekman's equation is accurate to 1 part in 500 and this is what limits the accuracy of Kuwahara's

[6] M. Greenspan and C. Tschiegg, J. Acoust. Soc. Am. 28, 500 (1956).

[7] S. Kuwahara, Hydrographic Rev. 16, 126 (1939).

[8] D. J. Matthews, Hydrographic Department Rept. HD 282, (London, 1939).

[9] V. W. Ekman, Pubis. circ. cons. perm. internat. l'explor. la mar. No. 43, 3–47 (1910).

[10] E. H. Amagat, Ann. chim. et phys. 29, 68–138, 504–574 (1893).

[11] R. T. Beyer, J. Marine Research (Sears Foundation) 13, 113–121 (1954).

work. Del Grosso[13] has called attention to an error in Ekman's pressure determination which is of sufficient magnitude to explain the 3.0 m/sec difference which exists between the predicted and the measured sound speeds at atmospheric pressure. Ekman did not measure pressure himself; instead he used his compressibility measurements to compute his operating pressures from an empirical formula which was made to agree with Amagat's data for 0°C. The error in Ekman's equation for mean compressibility is only 0.25%, but it is sufficient to explain the 3.0 m/sec discrepancy in sound speed. A comparison of the sound speeds computed by Matthews for distilled water and the sound speeds measured at NOL is shown in Fig. 6. It is seen that the predicted speeds are remarkably accurate in spite of the complexity of the computation. In particular, it

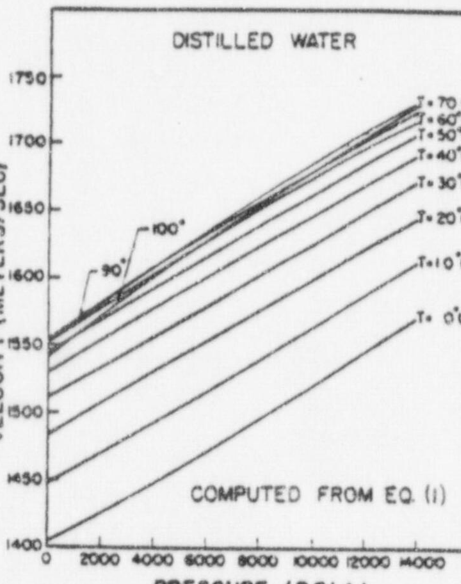

FIG. 5. Velocity of sound in distilled water as a function of pressure.

may be noted that the present measurements are nearly 3.0 m/sec higher than the predicted sound speeds at atmospheric pressure, as first noted by Del Grosso. Although the second derivatives of Amagat's distilled water data are unsatisfactory for the direct computation os sound speed, it is interesting to note that sound speeds computed in this manner and plotted against pressure are concave upward for Amagat's temperature range of 0 to 40°C. The curvature (concave downward) noted in Kuwahara's and Matthew's work must result then from the inclusion of Ekman's work. Although the majority of data referred to above pertains to sea water, the same arguments hold true for distilled water and can be used when speaking of general features such as curvature. It is hoped that theoretical predictions, or subsequent measurements, will be available in the future to explain this interesting behavior.

TABLE IV. Standard deviation of the differences between a computed curve and a corresponding measured curve of sound speed.

Pressure psia	σ_s m/sec	Parts per 10 000
14.7	0.16	1.0
4000	0.23	1.4
8000	0.20	1.3
12000	0.19	1.2

VI. DISCUSSION OF ERRORS

An estimate of the accuracy of the sound speed measurements is obtained from a summation of the individual errors. Assuming a random distribution, the experimental error σ_e in sound speed that may occur for any one measurement is given by

$$\sigma_e^2 = \alpha^2\sigma_f^2 + \beta^2\sigma_L^2 + \gamma^2\sigma_T^2 + \delta^2\sigma_P^2,$$

where α, β, γ, and δ are representative constants for the change in velocity with frequency, length, temperature, and pressure. σ_f, σ_L, σ_T, and σ_P represent the standard deviation of frequency, length, temperature, and pressure from the measured value. Thus, from Table V, the maximum experimental error in the measurements is computed to be 0.093 m/sec. It should be pointed out that the "constants" α, β, γ, and δ are not actually constants, however, the deviation from linearity of these functions is small except for γ. In Fig. 4 it is seen that γ varies from 4.97 m/sec/°C at 1°C to 0.00

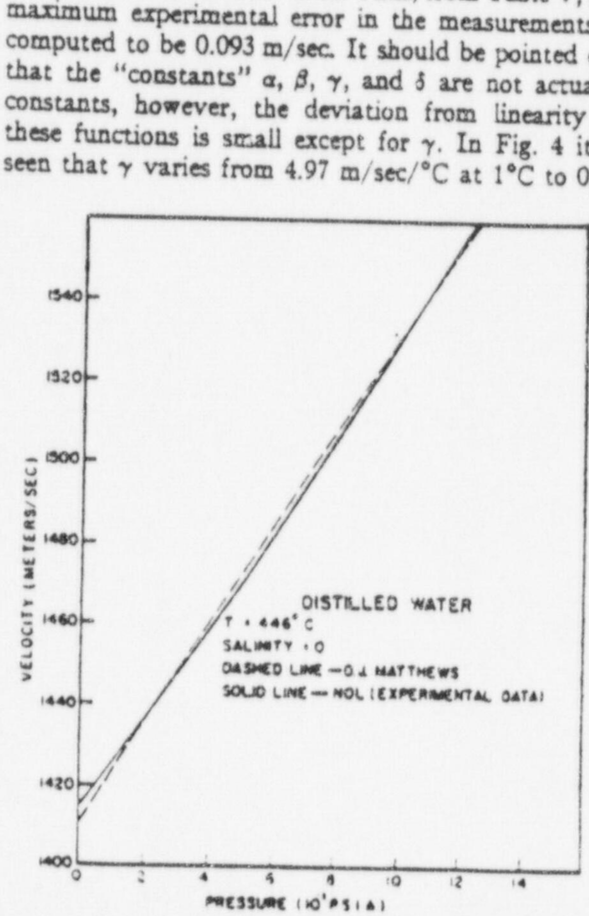

FIG. 6. Comparison of velocities predicted by D. J. Matthews and measured at NOL.

[13] V. A. Del Grosso, Natl. Acad. Sci., Natl. Research Council, Publ. 600 (1959).

Table V.

Individual error	Coefficient
$\sigma_F = 0.2$ cps	$\alpha = 0.127$ m/sec/cps
$\sigma_L = 1.27 \times 10^{-4}$ m	$\beta = 304.8$ m/sec/m
$\sigma_T = 0.007$°C	$\gamma = 4.97$ m/sec/°C
$\sigma_P = 7.5$ psia	$\delta = 0.011$ m/sec/psia

m/sec/°C at 74.164°C. The above error was computed at a temperature where γ is greatest, i.e., at 1°C. σ_F, the error in the frequency measurement, includes the error due to the accuracy of the counter and the error which results from the ability of the operator to set coincidence. Each value for the velocity in Table I was obtained from the average of ten measurements of frequency at each temperature and pressure. The standard deviation from the mean of these ten readings is 0.2 cps and it includes a ±0.1 cps variation which is characteristic of the counter.

In addition to the random errors discussed above, systematic errors resulting from actual physical phenomena must be added to obtain the over-all accuracy of the measurements. Corrections may be made for systematic errors when they are known, however, since the tables of sound speed have not been corrected for such errors, they are treated here like random errors. A complete review of systematic errors is beyond the intended scope of this paper; a summary of these errors is given however in Table VI for reference. The errors in Table VI have been computed to the first three significant figures and errors which are less than 0.001 m/sec are considered as negligible in this report.

The pressure differential error is an error which results from the force required to compress the bellows of the velocimeter. This force causes the pressure inside the velocimeter to be less than the pressure outside where the pressure is measured. The error due to the small pressure differential listed in Table V is the maximum error expected. This error will decrease approximately linearly to zero as the pressure goes to atmospheric pressure. It is also conceivable that this pressure difference may cause a deflection in the crystal transducers in the NOL velocimeter. If this should occur, the maximum error in sound speed produced by the distortion would be −0.030 m/sec at 14 000 psia and would decrease linearly to zero as the pressure is made to approach its atmospheric value. The third error listed in Table VI is due to the time delay that occurs during reflection of the sound wave at the transducers. This additional time delay has been computed by treating the transducer as a damped mechanical system which responds to a transient force. Only the first half-cycle of the incident wave train was considered in this analysis since this is the portion used to measure sound speeds. The error in sound speed due to a time delay during reflection in the NOL velocimeter computed in this manner was found to be 0.0001 m/sec and it is considered negligible for the purpose of this work.

The remaining errors in Table V are computed directly from the references given. The term "shear viscosity" refers to the viscous absorption which occurs at the tube walls. The effect of bulk viscosity, radial and lateral heat conduction, scattering, and molecular and chemical absorption are all absorption phenomena which are computed easily from the references cited.

The arithmetic sum of the systematic errors is seen from Table V to be +0.027 m/sec at atmospheric pressure and −0.013 m/sec at a pressure of 14 000 psia. The total error, which is the sum of the random errors and the systematic errors, is then −0.106 m/sec or +0.120 m/sec depending on what pressure is considered. The over-all accuracy is then at least 1 part in 10 000.

Table VI. Systematic errors.

Type of error	Magnitude of error	Reference
Pressure differential	(at 14 000 psia) −0.010	
Crystal deflection	(at 14 000 psia) −0.030	
Reflection (time delay)	Negligible	a, b
Finite pulse height	−0.002	c, d
Shear viscosity	+0.029	d
Bulk viscosity	Negligible	e
Radial heat conduction	Negligible	d, f
Lateral heat conduction	Negligible	g
Molecular scattering	Negligible	g
Chemical absorption	Negligible	e
Dispersion	Negligible	h

[a] W. W. Soroka, Prod. Eng. 26, 150 (1955).
[b] W. W. Soroka, Prod. Eng. 26, 167 (1955).
[c] See reference 11.
[d] L. E. Kinsley and A. B. Fry, *Fundamentals of Acoustics* (John Wiley & Sons Inc., New York, 1950).
[e] K. Herzberg and T. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, Inc., New York) (to be published).
[f] Lord Rayleigh, *Theory of Sound* (MacMillan and Company, Ltd., London, 1929).
[g] P. Vigoureux, *Ultrasonics* (John Wiley & Sons, Inc., New York, 1951).
[h] F. Fox and T. Marion, J. Acoust. Soc. Am. 25, 661 (1953).

VII. ACKNOWLEDGMENTS

The author is deeply indebted to Mr. Dudley Taylor for the design and construction of the velocimeter, for the pressure vessel, and for the frequent consultation on the numerous problems encountered in this work. Equally important has been the work of Mr. Walter Madigosky who contributed much thought and effort to the choice and assembly of the necessary instrumentation for the measurement of sound velocities. The author would also like to express his gratitude to the IBM computer staff at NOL for their participation in the derivation of the velocity equations expressed herein, and to Dr. T. A. Litovitz, Dr. H. E. Ellingson, and Mr. A. T. Jaques for their frequent aid and encouragement of this work.

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Resonance Absorption and Molecular Crystals. II. Benzene†

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(Received March 24, 1959)

Thermal oscillations in molecular solids are of two distinct classes: lattice vibrations and atomic vibrations within each molecule. These two vibrational modes can overlap in frequency and "resonate." This resonance leads to lengthy relaxation times manifested as unusually high acoustic absorption, a phenomenon termed resonance absorption. In order to study resonance absorption in solid benzene a method was developed for growing single benzene crystals of average linear dimension, 10 cm. At the acoustical frequency 10 mc, absorption in single benzene crystals is found to be 0.24 cm^{-1}; at 6.4 mc the value is 0.09 cm^{-1}. This excessively high absorption (10^4 higher than in crystalline quartz) was quantitatively predicted from available molecular constants by a theory given previously. A partial list of compounds is given in which resonance absorption is predicted to be the dominant absorption mechanism.

INTRODUCTION

A MOLECULAR crystal exhibits two classes of thermal oscillation: those in which each molecule vibrates as a whole about its lattice position, termed the acoustical branch, and the internal vibrations of the atoms comprising a molecule, termed the optical branch. In many crystals these two vibrational modes overlap in frequency, leading to resonance.

Previous work,[1] hereafter referred to by the designation I, has shown that resonance can result in unusually high acoustic absorption. High absorption results from the relatively slow transfer or exchange of energy between lattice and internal vibrations. Just as in weakly coupled mechanically resonant systems, the transfer energy at resonance is large, but the rate of transfer is slow, particularly close to resonance. The phenomenon is some respects resembles the familiar relaxation absorption observed in gases and liquids, but the latter arises from transfer of energy by collision, whereas the present phenomenon requires near frequency coincidence of two vibrational states; hence the term, *resonance absorption*. It should be emphasized that this resonance phenomenon is not associated with acoustical frequencies but rather with the extremely high frequency thermally excited vibrational modes within the crystal.

It was shown in I that the rate with which energy oscillates between the two vibrational systems determines the acoustical absorption; a low transfer frequency leads to large acoustic absorption. Stated in another manner, whenever the oscillator coupling is small, or the intermolecular binding forces weak, absorption will be high. Conversely, in highly absorbing crystals the Lennard-Jones molecular constants, ϵ and r_0, will be found to be small and the intermolecular spacing large.

Tables of the Lennard-Jones constants suggest that many organic compounds should exhibit resonance absorption in the solid state. One of these, benzene, was selected for initial study because of the wide variety of thermodynamic data available for this compound. Although benzene is a liquid at room temperature it has a relatively high melting point (5.5°C) which makes its study in the solid state possible without unusual techniques. However, it is necessary for acoustic observations to be made on a single crystal rather than on the polycrystalline state, in order to eliminate contributions to absorption from friction and scattering at crystal boundaries, fractures, and at other imperfections. For this reason a large single crystal of benzene was grown for the purpose of the acoustic observations. The following sections describe the method of preparation of the crystal and observations of the acoustic absorption.

GROWTH OF MONOCRYSTALLINE BENZENE

As in the case of nearly all organic compounds, molecular binding forces in benzene are relatively weak (its binding forces are largely van der Waals' forces). Consequently crystalline benzene is a fragile substance incapable of supporting severe thermal stresses. The conventional technique for crystal growth in which heat flows through the external crystal surface introduces far too many stresses and could not be utilized for benzene.

The schematic diagram given in Fig. 1 illustrates the method whereby unsupported thermal strains were avoided in crystal growth. Instead of the usual method of crystallization from the liquid, whereby heat is extracted from the external surfaces, heat is extracted from within. The coldest exposed region is the tip of a heavy copper rod on which the seed is placed. Hence the exterior growing surface is always warmer than the central region and thermal stresses are compressive rather than in tension. In practice the copper tip was attached directly to the refrigeration coils and operated in the vicinity of 0°C. The air temperature in the refrigerator was accurately controlled by means of heaters and thermostats at a constant temperature in the vicinity of 5°C. In addition a small amount of

† This work received support from the Bureau of Ships, Navy Department. Contribution from the Scripps Institution of Oceanography, New Series.
[1] L. Liebermann, Phys. Rev. 113, 1052 (1959).

Sustaining Members *(continued from page ix)*

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Pressure dependence of the velocity of sound in water as a function of temperature

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MS. received 28th June 1966, in revised form 28th November 1966

Abstract. Measurements of the velocity of sound in doubly distilled water have been made at pressures up to 11 600 lb in^{-2} in the temperature range 16–94°C. The basic experimental technique and the theory of measurement have been described in detail in a previous paper by Barlow and Yazgan. The results are believed to be accurate to within $\pm 0{\cdot}30$ m sec^{-1} at 16°C, the error decreasing to $\pm 0{\cdot}20$ m sec^{-1} at about 74°C. A polynomial has been fitted to the data to permit calculation of the velocity at any temperature and pressure in the range investigated. The results at high pressure are generally in agreement with those obtained by Wilson, although substantial differences at atmospheric and low pressures indicate some systematic error in Wilson's results. The factors involved in making definitive measurements of higher accuracy are discussed.

1. Introduction

Several measurements of the variation of the velocity of sound in water as a function of pressure and temperature have been made in recent years. Up to 1959 the accuracy of such measurements was rather limited, few investigators claiming a maximum error of less than $\pm 0{\cdot}1\%$ (Holton 1951, Smith and Lawson 1954, Litovitz and Carnevale 1955, Tait 1957). Comparison of the values obtained at the same temperatures and pressures shows discrepancies exceeding this limit. In order to obtain more reliable values, Wilson (1959) carried out an extensive series of measurements of the velocity of sound in distilled water at pressures up to 14 000 lb in^{-2} in the temperature range 0–100°C. A maximum error of $\pm 0{\cdot}01\%$ is claimed for these results.

The acoustic system used by Wilson (1959) was similar to that developed by Greenspan and Tschiegg (1957) and used for the determination of the velocity of sound in water as a function of temperature at atmospheric pressure. Essentially their method involved a measurement of the transit time of a short transient sound pulse through a known liquid path length, the pulse being generated by shock excitation of a piezoelectric transducer.

Recent measurements by Barlow and Yazgan (1966) have shown that although the variation of velocity with temperature found by Greenspan and Tschiegg (1957) is substantially correct, their absolute values are high by approximately $0{\cdot}40$ m sec^{-1}. The technique developed by Barlow and Yazgan (1966) is based upon measurement of the total phase shift experienced by a modulated high-frequency pulse propagated through a known liquid path. This method is capable of high accuracy and, under suitable conditions, absolute accuracies to within $\pm 0{\cdot}003\%$ are attainable. The results obtained over the temperature range 23–80°C are in agreement with those of McSkimin (1965), Ilgunas, Kubilyunene and Yapertas (1964) and others. In particular, the value of $1496{\cdot}58 \pm 0{\cdot}04$ m sec^{-1} obtained at 25·000°C is in close agreement with the value of 1496·55 m sec^{-1} recently found by Gucker, Chernick and Roy-Chowdhury (1966), using a different experimental technique of comparable accuracy.

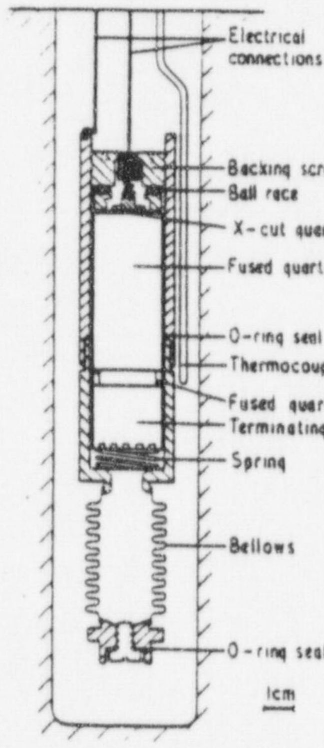
The values of velocity obtained at atmospheric pressure by Wilson (1959) are consistently higher than those found by Barlow and Yazgan (1966). The difference increases from a value of $0{\cdot}34$ m sec^{-1} at about 74°C, where the velocity of sound in water passes through a maximum, to approximately $0{\cdot}65$ m sec^{-1} at 25·000°C. For comparison, the absolute accuracy claimed by Wilson (1959) corresponds to a maximum error of $0{\cdot}15$ m sec^{-1}

In view of the evidence for a systematic error in the results given by Wilson (1959), possibly inherent in the type of acoustic system employed, there is a need for a definitive series of measurements of the velocity of sound in water over wide ranges of temperature and pressure. As a step towards this objective, measurements have been made over the temperature range 16–94°C at pressures from atmospheric to 11 000 lb in^{-2}.

2. Experimental

2.1. *Acoustic system and velocity measurement*

The fixed path acoustic system used to obtain the results given in §3 is similar to that developed by McSkimin (1957). The electronic system and method of velocity measurement are considerably different, and have been described in detail in a previous publication (Barlow and Yazgan 1966). A diagram of the acoustic system is given in the figure.



Acoustic system for measurement of velocity under high pressure.

The length of the liquid path is defined by a fused quartz ring spacer. The end surfaces of the buffer rod are optically flat to 0·1 μm and parallel to 5 seconds of angle. The faces of the ring spacer are similarly optically flat and parallel, and one end of the terminating rod is also optically flat. By wringing the cylinders to the faces of the ring spacer, a known and reproducible separation of the cylinders is obtained. Small radial grooves on opposite sides of the spacer allow the liquid to fill the space between the faces of the fused quartz rods. The effective separation of the two quartz cylinders was determined by making an extensive series of measurements of the velocity of sound in water at atmospheric pressure and comparing the results obtained with those using precision gauge blocks in place of the ring spacer (Barlow and Yazgan 1966). Thus, although the limited space in the high-pressure vessel precluded the direct use of gauge blocks to define the liquid path, the effective length of the ring spacer at atmospheric pressure was determined by reference to the previous measurements. By this method the separation was found to be 0·304 588 in., giving an acoustic path length of 1·547 307 cm. This value is in excellent agreement with the results of a series of measurements which have been made by the Metrology Division of the

National Engineering Laboratory, of the thickness of the spacer at several points. These measurements gave an average thickness of 0·304 580 ± 0·000 010 in.

As shown in the figure, the acoustic system was mounted vertically in a holder inside the pressure vessel. A light spring was used to apply a slight axial force to the terminating rod, chiefly to prevent damage should the parts of the acoustic system become separated. This spring was not such as to cause appreciable compression of the fused quartz ring spacer. The water sample was separated from the pressure transmitting fluid by means of 'O'-rings, and a bellows allowed compression of the sample.

2.2. *High-pressure apparatus and temperature measurement*

A conventional arrangement of the high-pressure system was employed. The pressure was generated by a hand pump and monitored by a Bourdon gauge. The pressure vessel had an internal working space $1\frac{1}{4}$ in. diameter by 10 in. long, which was sufficient to contain the acoustic system and a special thermocouple. Pressure measurements were made by means of a dead-weight tester (Barnet Instruments Ltd. type 4540), for which a maximum error of ± 3 parts in 10^4 is claimed. This instrument was correctly calibrated for the local gravitational factor of 981·55 cm sec^{-2}, and the readings in bars were converted to lb in^{-2} using the relation 1 bar = 14·504 lb in^{-2}. A silicone liquid was used as the pressure transmitting fluid.

The pressure vessel was fitted with a heating jacket, and the temperature was stabilized by a sensitive controller based upon a design by Tempest (1963). A thermistor in the inner shell of the heating jacket was used as the sensing element.

The temperature in the pressure vessel was determined by the use of an iron–constantan thermocouple arranged so that the thermocouple junction was as near as possible to the fused quartz ring spacer, although outside the water sample. This thermocouple was calibrated in the open pressure vessel directly against a platinum resistance thermometer certified by the National Physical Laboratory. Measurements were made at a number of points in the range 20–100°c. Checks were made of the temperature variation with thermocouple position inside the vessel and it was found that the variations were insignificant. It is estimated that the overall accuracy of temperature measurement was such that a maximum error of $\pm$ 0·03 degc was possible. For measurements made under pressure, the readings of the potentiometer used to determine the thermocouple e.m.f. were corrected for the pressure dependence of the e.m.f. The results of Bridgman (1918) for an iron-constantan thermocouple were used to make these corrections: in general the corrections were small or insignificant.

2.3. *Water sample*

Doubly distilled water was used throughout. This degree of purification was considered adequate in view of the negligible effect of small quantities of impurities on velocity (Weissler and Del Grosso 1951, Del Grosso, Smura and Fougere 1954). No attempt was made to free the water of dissolved air, since the effect on velocity is probably less than 1 part in 10^5 at atmospheric pressure (Greenspan and Tschiegg 1956). However, care was taken to prevent the inclusion of air bubbles when filling the sample container, so that the sample measured was saturated with air at atmospheric pressure.

2.4. *Experimental procedure*

Measurements were first made of the velocity of sound in water at atmospheric pressure and a temperature of about 20°c, with the sample in the pressure vessel and using the associated temperature measurement and control apparatus. The results at nominal operating frequencies of 10 and 30 Mc/s were in agreement to within 0·06 m sec^{-1}, after applying a correction for the effects of diffraction. The value at 30 Mc/s was found to be only 0·02 m sec^{-1} less than the value obtained by extrapolation of the results of Barlow and Yazgan (1966) which were obtained over the temperature range 23–80°c. At about

20°c an error of 0·03 degc corresponds to an error in velocity of about 0·10 m sec⁻¹, the estimated limit of temperature error given in § 2.2 is therefore substantiated.

A series of velocity measurements was then obtained at a temperature of about 16·6°c over the pressure range from atmospheric to 1000 bars, using a nominal operating frequency of 30 Mc/s. Measurements were made at intervals of 100 bars for increasing and decreasing pressures. Although pressure changes were made very slowly, about one hour was required for the restoration of thermal equilibrium after each pressure change. Slight pressure readjustments were made during this time to confine readings to exact 100 bar intervals and to allow for the very slight leakage in the dead-weight tester. This leakage was greater at the higher pressures and some instability at 900 and 1000 bars was found. Accordingly, the pressure range was restricted to 800 bars. Only the results of a series of measurements in which velocity values for increasing and decreasing pressures agreed to within 0·20 m sec⁻¹ were regarded as acceptable, and the average value was taken at each pressure.

For temperatures above about 30°c it was thought undesirable to make measurements at atmospheric pressure since the expansion of the enclosed water sample could distort the bellows and a slight excess pressure may have given unreliable values of velocity. A pressure of 100 bars was therefore applied before increasing the temperature above about 30°c and all initial readings were obtained at this pressure.

3. Results

The experimental results are given in table 1. Except for the six values given for temperatures above about 30°c at atmospheric pressure, each value of velocity is the average of readings taken with increasing and decreasing pressure obtained at a nominal frequency of 30 Mc/s.

A small correction, equivalent to a maximum of 0·05 m sec⁻¹, has been applied to account for the change in length of the fused quartz ring spacer with temperature. Since the spacer is compressed by the hydrostatic pressure, a correction amounting to a maximum of 1·24 m sec⁻¹ at 800 bars has also been applied to reduce the apparent velocity to the true value. This correction has been based upon a value of $5{\cdot}35 \times 10^6$ lb in⁻² for the bulk modulus of fused quartz obtained from published elastic constants (American Institute of Physics Handbook 1957) and from data given by McSkimin (1957). This value has been taken to apply over the temperature and pressure range of measurement, the amount of the correction is correct to better than ±2% over the range (McSkimin 1957).

A correction of 0·02 m sec⁻¹ for diffraction effects has also been applied to the data, following the theoretical results of Bass and Williams (quoted by McSkimin 1961), which have been confirmed experimentally by Barlow and Yazgan (1966). Errors arising from other sources, for example the differential pressure across the bellows, are negligible, and corrections are therefore unnecessary.

4. Analysis of experimental results

Following the procedure adopted by Wilson (1959) an equation of the form

$$V = a_0 - a_1T - a_2T^2 - a_3T^3 - a_4T^4 - a_5T^5 \text{ m sec}^{-1} \qquad (1)$$

where

$$a_i = b_{i0} - b_{i1}P - b_{i2}P^2 - b_{i3}P^3 - b_{i4}P^4 \qquad (2)$$

has been fitted to the results. The coefficients of equation (2) are given in table 2. In these equations T is the temperature in °c and P is the absolute pressure in units of 10^4 lb in⁻². The coefficients are valid over the range of measurement 15–95°c, and from atmospheric pressure to just over 10^4 lb in⁻².

As a check on the fitting of these equations, recalculated values of the velocity at the temperatures and pressures of measurement have been obtained and compared with the original data. The greatest deviation was found to be 0·19 m sec⁻¹ with an average of 0·065 m sec⁻¹, the deviations being randomly distributed throughout the temperature and pressure range.

Table 1. Experimental values of the velocity of sound ($m\ sec^{-1}$) in water as a function of temperature and pressure

Temperature (°C) / Pressure ($lb\ in^{-2}$)	16·565	30·680	39·930	47·990	60·590	71·350	78·850	93·370
14·7	1471·19	1510·58	1528·66	1540·16	1551·24	1554·91	1554·64	1548·26
1450·4	1487·79	1527·81	1546·04	1557·93	1569·83	1574·02	1574·27	1569·01
2900·8	1504·25	1544·52	1563·32	1575·42	1587·92	1592·88	1593·45	1589·12
4351·2	1520·73	1561·58	1580·60	1593·05	1605·83	1611·44	1612·41	1609·20
5801·6	1537·78	1578·37	1597·51	1610·07	1623·37	1629·54	1631·03	1628·23
7252·0	1554·64	1595·30	1614·61	1627·21	1640·87	1647·08	1648·99	1647·18
8702·4	1571·82	1611·78	1631·22	1644·31	1657·96	1664·66	1666·75	1665·92
10152·8	1589·13	1628·82	1647·94	1660·86	1675·03	1681·99	1684·40	1683·93
11603·2	1605·82	1645·35	1664·43	1677·46	1691·75	1699·06	1701·55	1702·40

Table 2. Coefficients of the equations $a_i = b_{i0} + b_{i1}P + b_{i2}P^2 + b_{i3}P^3 + b_{i4}P^4$†

i	b_{i0}	b_{i1}	b_{i2}	b_{i3}	b_{i4}
0	1401·968	+83·73652	+49·69035	+20·51695	−33·83572
1	+5·051718	+4·325934	−10·00579	+3·787598	+1·452633
2	5·848526 $\times 10^{-2}$	−2·029127 $\times 10^{-1}$	+5·478028 $\times 10^{-1}$	−3·373606 $\times 10^{-1}$	+7·830629 $\times 10^{-3}$
3	+3·381084 $\times 10^{-4}$	+4·493318 $\times 10^{-3}$	1·290872 $\times 10^{-2}$	+9·460639 $\times 10^{-3}$	1·245880 $\times 10^{-3}$
4	1·484859 $\times 10^{-6}$	−4·498863 $\times 10^{-5}$	+1·357265 $\times 10^{-4}$	−1·090535 $\times 10^{-4}$	1·984527 $\times 10^{-5}$
5	+3·091069 $\times 10^{-9}$	+1·674962 $\times 10^{-7}$	5·229535 $\times 10^{-7}$	+4·441468 $\times 10^{-7}$	9·317469 $\times 10^{-8}$

† $V = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5$ $m\ sec^{-1}$, where T is in °C and P in units of 10^4 $lb\ in^{-2}$ absolute.

5. Discussion

The main errors in the results given arise from the uncertainties in absolute pressure and temperature measurement. The possible error of $\pm 0 \cdot 03$ degc in temperature measurement corresponds to an error of $\pm 0 \cdot 10$ m sec^{-1} at about 16°c, decreasing to zero at about 74°c, where the velocity passes through a maximum. Although the dead-weight tester used is capable of absolute pressure determination to ± 3 parts in 10^4, a realistic estimate of the precision obtained indicates that it is reasonable to allow limits of ± 10 lb in^{-2} on pressure readings throughout the range. This uncertainty arises from the difficulty found in maintaining constancy of pressure at the limit of sensitivity of the instrument. The absolute pressure is then accurate to ± 13 lb in^{-2} overall, corresponding to a possible error in velocity of $\pm 0 \cdot 13$ m sec^{-1}.

As described in the previous account of the experimental technique for velocity measurement (Barlow and Yazgan 1966), random errors in velocity arising from the electrical measurements are small and have a maximum of $\pm 0 \cdot 04$ m sec^{-1} with a standard deviation of $0 \cdot 02$ m sec^{-1}. The sum of the random errors is therefore $\pm 0 \cdot 24$ m sec^{-1} at room temperature, decreasing to $\pm 0 \cdot 14$ m sec^{-1} at about 74°c. Examination of the experimental data shows that the values obtained deviate from smooth curves by random amounts which are less than these estimates. Except for a possible uncertainty of about 1 part in 10^5 in the length of the liquid path defined by the fused quartz ring spacer and possibly slight errors in the variation of this length with pressure, systematic errors are, by comparison, negligible. The results given are therefore estimated to be accurate to within $\pm 0 \cdot 30$ m sec^{-1} around 15°c and to within $\pm 0 \cdot 20$ m sec^{-1} around 74°c. A comparison of the results with those obtained by Wilson (1959) shows significant differences between the values obtained at atmospheric pressure, and differences in the variation with pressure at constant temperature. At atmospheric pressure, the present results are some $0 \cdot 65$ m sec^{-1} lower around 20°c and $0 \cdot 34$ m sec^{-1} around 70°c. These differences become gradually less with increasing pressund are change sign at about 10 000 lb in^{-2} at 20°c and 5000 lb in^{-2} at 90°c. Thus, although the values at atmospheric pressure indicate a systematic error in Wilson's results, over most of the pressure range there is agreement within the combined experimental error limits between the two sets of values. It is possible that the systematic error is reduced by increase of temperature and pressure, or that the differences are reduced by small unsuspected temperature or pressure dependent errors in either the present results or those of Wilson.

In order to obtain definitive values of the velocity of sound in water as a function of pressure and temperature, significantly better than the existing data, further experimental work is required. Absolute velocity measurements accurate to about 3 parts in 10^5 are now possible without undue difficulty. The reduction of errors arising from inaccuracies in pressure and temperature measurement to this level or less would involve considerable experimental problems. It is preferable to define the liquid path by precision gauge blocks; the resulting increase in the diameter of the acoustic system would entail a larger pressure vessel. Absolute measurement and stabilization of the temperature of the water sample to $\pm 0 \cdot 001$ degc is desirable, and can only be achieved by immersion of the vessel in a large constant temperature bath and by the use of a platinum resistance thermometer in conjunction with a Smith bridge or similar instrument. The greatest problem arises in absolute pressure measurement. Direct use of a dead-weight tester is undesirable since, although the time required for the measurement of velocity is only a few minutes, the slight leakage in this time may give some uncertainty in pressure readings. A sensitive secondary gauge is preferable, but reduction of the absolute error in pressure to a maximum of 1 or 2 lb in^{-2} at about 10^4 lb in^{-2} is extremely difficult and is close to the limit attainable at the present stage of development of high-pressure measurement.

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Phase change method for the measurement of ultrasonic wave velocity and a determination of the speed of sound in water

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Abstract. A description is given of a technique for measuring the ultrasonic wave velocity in liquids, based upon the measurement of the total phase shift through a liquid path at frequencies in the region of 10 Mc/s. A fixed-path acoustic system is employed and the method is suitable for use over wide ranges of temperature and hydrostatic pressure.

The phase difference between a modulated r.f. pulse propagated through the known liquid path and the incident pulse reflected from a solid–liquid interface is determined by cancelling each pulse separately against a continuous-wave signal adjustable in phase and amplitude. From two such measurements at slightly different frequencies the total phase shift in the liquid may be calculated.

The technique is capable of very high accuracy and under suitable conditions an absolute accuracy to better than 3 parts in 10^6 in velocity is obtainable.

Measurements of the velocity of sound in water have been made over the temperature range 23–80°C and the results are presented as a fifth-degree polynomial. A value of 1496·58 ± 0·04 m sec^{-1} at 25·000°C is obtained.

1. Introduction

Any study of experimental methods for the determination of the velocity of sound in liquids leads inevitably to a comparison of the values obtained for water in view of the many measurements of this basic reference value made during the past thirty years. A summary of results reported up to 1954 is given by Del Grosso, Smura and Fougere (1954). The results show considerable scatter, and more recent measurements made by means of experimental techniques apparently capable of high accuracy have not fully resolved the discrepancies. The present situation is shown in table 1. Only those results are given for which an accuracy to better than ±0·03% is claimed. Four of these values are in

Table 1. Values of the velocity of sound in water at 25·00°C

Reference	Experimental technique	Velocity (m sec^{-1})	Limit of error claimed (m sec^{-1})
Barthel and Nolle (1952)	Double crystal interferometer, 5–25 Mc/s, variable path of a few cm	1496·2*	±0·20
Del Grosso *et al.* (1954)	Single crystal interferometer, 1 Mc/s, variable path of a few cm	1497·41‡	±0·05
Greenspan and Tschiegg (1957)	Time delay, fixed path 20 cm	1497·00	±0·05
Brooks (1960)	Time delay, variable path 1–2 m	1496·52	±0·34
Neubauer and Dragonette (1964)	Time delay, differential path about 1 m	1496·60	±0·20
Ilgunas *et al.*	Single crystal interferometer, 1–12 Mc/s, variable path of a few cm	1496·59§	±0·15
McSkimin (1965)	Modulated pulse cancellation, 60 Mc/s, fixed path of less than 1 cm	1496·65	±0·10

* Extrapolated from 24·76°C; ‡ extrapolated from 20·00°C; § extrapolated from 17·50°C, using data of Greenspan and Tschiegg (1957) in each case.

agreement within the limits of stated error, those of Brooks (1960), Neubauer and Dragonette (1964), Ilgunas, Kubilyunene and Yapertas (1964) and McSkimin (1965). Two other results, for which the highest accuracies are claimed, those of Del Grosso *et al.* (1954) and Greenspan and Tschiegg (1957) differ considerably.

Several factors may be readily excluded as possible reasons for these differences. The variation of velocity with temperature around 25°C is 2·7 m sec^{-1} degc^{-1} (Greenspan and Tschiegg 1957), thus the variations in the values are too large to be explicable as temperature errors. Deviations from absolute purity of the samples of water used are unlikely to be sources of substantial errors. Dissolved air has been found (Greenspan and Tschiegg 1956) to increase the velocity of sound in water by less than a few parts per million. Small quantities of other impurities have been shown to have negligible effect (Del Grosso *et al.* 1954, Weissler and Del Grosso 1951).

On the evidence available it therefore seems probable that certain experimental techniques, including those of Del Grosso *et al.* (1954) and Greenspan and Tschiegg (1957), are not suitable for absolute measurements of high precision. Systems involving steady-state sinusoidal wave propagation are preferable to those involving the propagation of transient waveforms, or step functions, over distances appreciably less than 1 metre. Error estimation in the latter systems is difficult since pulses may be distorted by resonances in transducers and by different absorptions applying to each Fourier component of the transient waveforms.

In view of the importance of diffraction of the acoustic wave on observed velocities, the frequency of operation and dimensions of the acoustic system should be so chosen that diffraction effects are small or negligible. Calculations of diffraction corrections have been given by McSkimin (1960), Bass and Williams (reported by McSkimin 1961) and Del Grosso (1964). Furthermore, experimental techniques requiring only small quantities of liquid are preferable since temperature stabilization is simplified and measurements under high hydrostatic pressure are possible. The choice of a fixed-path acoustic system reduces the problems of mechanical alignment and further facilitates the study of velocity as a function of pressure.

A fixed-path acoustic system based on the design of Schulz (1955), as developed by McSkimin (1957), fulfils the foregoing conditions and has been taken as the basis of the experimental technique used in the present work. However, a new method of measurement based upon a determination of the total phase shift in the liquid path has been devised. This method gives a differential accuracy comparable with that of the 'sing-around' technique used by Greenspan and Tschiegg (1957) together with a high absolute accuracy.

The method uses a continuous sinusoidal waveform gated to provide a pulse of r.f. oscillations, which is propagated as an acoustic wave through the liquid path. The pulse duration is sufficient for steady-state conditions to be attained after the decay of the initial transients. The time taken for the acoustic pulse to travel through the liquid path is determined by phase comparison with the original continuous waveform. Essentially, the method combines the high resolution and accuracy of a continuous-wave interference measurement with the advantages of a pulse propagation technique. A detailed description of the system is given in the following section.

2. Experimental system

2.1. *Mode of operation*

A schematic diagram of the experimental system is given in figure 1. A continuous-wave signal from the crystal-controlled oscillator a_1 is passed through a buffer amplifier b to a diode gating circuit c. The gate is opened by a pulse of a few microseconds duration to produce a short wavetrain which, after further amplification (d), is used to excite the X-cut quartz crystal transducer of the acoustic system. Longitudinal waves generated by the transducer propagate in the fused quartz rod and are partly reflected at the quartz-liquid interface. Part of the incident wave propagates through the liquid and, after reflection from the boundary between the liquid and the terminating fused quartz rod, follows the

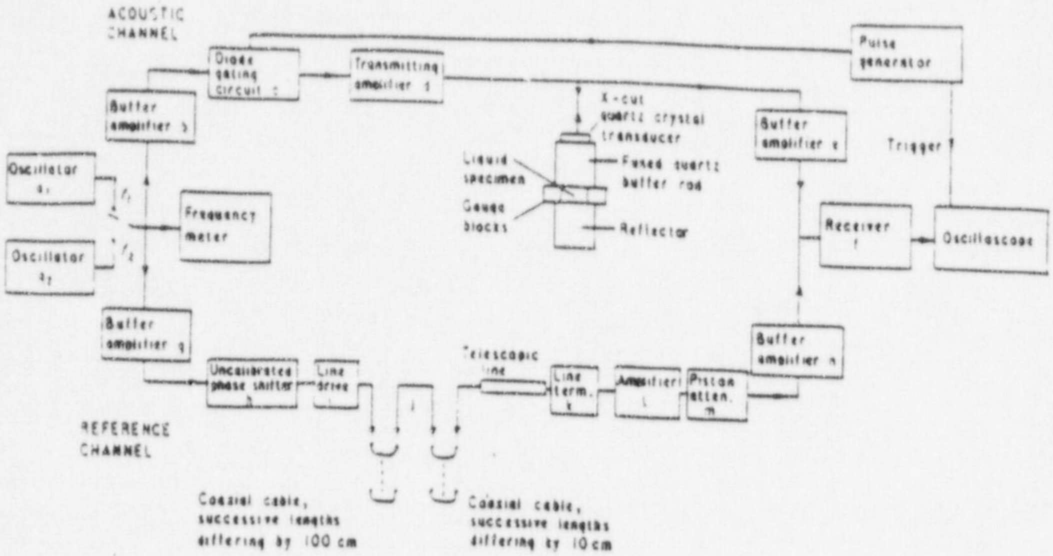

Figure 1. Schematic diagram of experimental system.

first reflected wave in re-exciting the transducer. The output from the acoustic system is passed through a buffer amplifier e and into the receiver f. The received pulse train is displayed on the oscilloscope. Apart from the transmitter pulse, the display shows two main pulses, the first from the fused-quartz–liquid interface and the second resulting from one double transit of the liquid path by the sound wave. The total phase difference between the high-frequency content of these two pulses is a function of the velocity of sound in the liquid. In addition, the display will contain subsequent pulses which have made further transits of the liquid path or the buffer rod. In the present system these pulses are irrelevant.

The remaining part of the system provides a reference signal for measuring the phase difference due to the liquid path. A signal from the oscillator a_1 passes through a buffer amplifier g to a simple uncalibrated phase shifting network h. This is followed by a precision adjustable delay line j capable of providing a known and continuously variable phase shift. Accurately matched source and load impedances are used to minimize standing waves on the delay line. The output from the line is further amplified (l), controlled in amplitude by a piston attenuator m, and passed through a buffer amplifier n into the receiver.

2.2. *Measurement procedure*

The phase difference between the waveform of the pulse reflected from the interface and that which has made one double transit of the liquid path is determined by cancelling each separately against the reference signal. Initially, the uncalibrated phase shifter and the attenuator are adjusted to give cancellation of the interface pulse. The calibrated delay line and the attenuator are then adjusted to give cancellation of the second pulse. The change in setting of the delay line gives the fractional part of a cycle or wavelength difference between the two pulses, but does not indicate the number of complete cycles forming the major part of the total phase difference. This number may be evaluated if the measurement is repeated at a slightly different frequency, obtained from a second oscillator a_2. The two oscillators generate frequencies f_1 and f_2, differing in frequency only by a few parts in a thousand. Thus a principal advantage of the system is that it is essentially a narrow-band technique. The electronic circuits can therefore be designed so that the variation in overall phase shift on changing frequency is negligible, eliminating the possibility of errors arising on this account. Furthermore, the mean frequency of operation can be chosen to coincide with the resonant frequency of the transducer, or with odd harmonics of this frequency, ensuring a high signal-to-noise ratio in the received pulses. Previously developed systems using pulse cancellation techniques generally involve determination of several cancellation frequencies over a comparatively wide bandwidth. The present system avoids the experimental difficulties inherent in this procedure and virtually eliminates the possibility of errors arising from frequency-dependent phase shifts in the electronic apparatus. In addition, the need for the sound wave to make only one double transit of a short liquid path makes this system particularly suitable for the measurement of highly attenuating liquids.

The high precision of the technique arises from the separate evaluation of the number of complete wavelengths in the liquid path and of the remaining fractional part of a wavelength. The former, typically 50–300 with the frequencies and liquid paths used in the present work, is determined exactly. The fractional part of a wavelength is determined to an accuracy governed by the measurement of the phase shift, given in turn by the change in the delay line setting. This measurement can be made with an accuracy to better than $\pm 3°$, giving approximately 3 parts in 10^5 overall.

Changes in velocity of this magnitude can therefore be detected; the absolute accuracy depends also on other factors discussed in §6.

3. Description of apparatus

Two completely separate sets of apparatus have been constructed and used in the measurement of the velocity of sound in water. One of these sets operates at frequencies of 30·000280 and 29·932800 Mc/s, the other at 10·011780 and 9·912014 Mc/s. These frequencies are measured by an electronic counter checked against standard frequency transmissions. The use of a continuous-wave reference signal, controllable in phase and amplitude, necessitates particularly thorough screening of the basic oscillators and of all units preceding the receiver. In addition, stability is of prime importance. The following descriptions give the relevant details of each unit.

3.1. *Oscillators*

Standard circuits have been used for the two crystal-controlled oscillators required in each frequency range. Colpitts circuits using resonant quartz crystals operating in the fundamental mode are satisfactory at 10 Mc/s; at 30 Mc/s third-overtone crystals operating in a Butler circuit are preferable. The crystals used are AT-cut quartz, designed for zero temperature coefficient around 25°C, and temperature stabilization is therefore not required. Each oscillator provides an output of approximately 1 v r.m.s.

3.2. *Buffer amplifiers b and g*

These buffers eliminate any possibility of interaction between the 'acoustic' and reference signal channels. Each consists of a single broad-band stage with tuned output, having a voltage gain of about 3 and a bandwidth of at least 25% of operating frequency.

3.3. *Diode gating circuit c*

This unit consists of a balanced four-diode switching network and is operated by a positive pulse of 100 v amplitude. During the application of the pulse, typically of 5 μsec duration, an output of 0·6 v peak-to-peak is obtained. In the 'off' condition the output is less than 10^{-4} of this value. This rejection ratio in the gating unit is sufficient since the overall rejection ratio of the transmitter channel is improved by class C operation of the following amplifier.

3.4. *Transmitting amplifier d*

The transmitting amplifier consists of two broad-band class A stages followed by a class C push–pull output stage. The circuit is aligned to give a substantially flat response around the nominal operating frequency, to ensure negligible variation in the overall phase shift between the two slightly differing actual operating frequencies. In the 'on' state of the gating unit a minimum of 25 v r.m.s. is generated across the transducer crystal, in the 'off' state the output is less than 2μv.

3.5. *Buffer amplifier e*

This buffer serves to isolate the acoustic system from the continuous-wave signal present at the receiver input. A single untuned pentode stage is used and the gain of the circuit is approximately unity.

3.6. *Phase shift channel*

The uncalibrated phase shifter h consists of a conventional series RC circuit supplied from a low-impedance balanced transformer of 1 : 1 : 1 ratio. A switch preceding the transformer permits 180° phase change, and adequate variation of phase within this limit is given by values of $R = 0$–5kΩ and $C = 5$–100 pF.

This circuit is followed by a single-stage amplifier, the primary function of which is to provide a source impedance equal to the characteristic impedance of the calibrated delay line. Since the impedance of the delay cable is almost entirely resistive (71·7Ω) a 'wire-in' triode of very low output capacitance is used with a non-inductive anode load resistor of 72Ω. The cable is connected directly to the anode lead of the valve in order to minimize wiring capacitances. Series capacitors of appreciable reactance in the line are avoided by supplying the line drive circuit from a negative h.t. supply.

The delay line consists of precision coaxial cable (Uniradio 21) with the lengths in circuit joined by s.h.f. connectors (Plessey CZ70157 and CZ70159). By arranging the cable in two series of lengths, successive lengths in the first decade differing by 100 cm and in the second by 10 cm, only four pairs of connectors are in circuit for any setting. The design of these connectors makes it possible to adjust the length of each cable to $\pm$ 0·1 cm. A constant-impedance telescopic line, having the same characteristic impedance as the cable, is used for fine adjustment of the overall delay. This line has a maximum variation equivalent to 12 cm length of the cable.

The line is terminated by a matched resistance at the input of a single-stage wide-band amplifier with a gain of approximately unity. As in the line drive circuit, considerable care is necessary to minimize stray capacitance and inductance; a 'wire-in' pentode of very low input capacitance is used.

3.7. *Piston attenuator m and compensating amplifier l*

The line termination stage is followed by a wide-band amplifier having a gain of some 40 dB. This amplifier compensates part of the insertion loss of the piston attenuator. The second stage of the amplifier is tuned, the coil forming the launching coil of the attenuator. The attenuator is a circular tube of 0·750 in. internal diameter; operation is in the H_{11} (least attenuation) mode. A Faraday screen is fitted to eliminate other modes and to assist in ensuring the absence of phase shift along the waveguide. This essential requirement is also ensured by maintaining sufficient spacing between the launching and pickup coils to give a minimum insertion loss of 50 dB.

The signal from the attenuator is passed through the buffer amplifier n and added to the output of buffer e at the input of the receiver. These two buffer amplifiers are the only active circuits in the system in which the signal level varies between initial and final measurements. By making them identical any variation of overall phase shift with signal level is automatically balanced since the signal levels in each are identical at cancellation.

3.8. *Receiver f*

The receiver is a conventional fixed frequency-tuned amplifier having a variable gain of 80 dB maximum and a bandwidth of 1 Mc/s. The circuit is designed for rapid recovery from overload so that maximum sensitivity is restored less than 10 μsec after the high-voltage transmitter pulse. The receiver output is displayed without demodulation on a wide-band oscilloscope (Tektronix 545A).

Table 2. Specification of gauge blocks

Type	Supplier	Thickness (20°c)	Stated max. error (parts in 10^6)	Exp. coeff. × 10^6 (degc^{-1})
Chromium carbide	C. E. Johansson Ltd.	0·200000 in.	±1·0	7·5
Quality AA		0·300000 in.	±0·67	7·5
Fused quartz	E. Leitz Ltd.	3·00000 mm	±3·53	0·43
Class O		5·50000 mm	±2·02	0·43
		6·50000 mm	±1·74	0·43

The length of the liquid path was defined by precision gauge blocks. Table 2 gives the specifications of these blocks. Three identical blocks were optically wrung on to the buffer rod, well clear of the path of the ultrasonic beam, and the surface of the termination rod was in turn wrung on to the blocks. This process required considerable care, but was found to give values of velocity repeatable within experimental error, although the system was assembled and dismantled several times. Only a slight axial pressure was applied to the assembly, chiefly to prevent damage in the event of the system coming apart. Errors arising from compression of the blocks are therefore negligible.

The acoustic system was placed horizontally in the liquid sample to permit free circulation through the gap between buffer and termination rods. A holder similar to that described by McSkimin (1965) was used to support the system and to enclose the transducer end of the buffer rod. The axis of the acoustic path was approximately 10 cm below the water level.

4.2. *Water sample and temperature measurement*

Doubly distilled water was used throughout the measurements, this degree of purification being considered adequate in view of the negligible effects of dissolved air (Greenspan and Tschiegg 1956) and of very small amounts of impurity (Weissler and Del Grosso 1951, Del Grosso *et al.* 1954). The specimen was contained in a small tank surrounded by a large bath. Conventional controls were used to stabilize the temperature of the water bath to a few millidegrees. The specimen was gently stirred and precautions were taken to minimize cooling by evaporation. The temperature of the specimen was determined by a platinum resistance thermometer situated close to the acoustic path. This thermometer was calibrated, by the National Physical Laboratory, shortly before making the series of measurements. Resistances were determined by means of a Smith Bridge to a precision corresponding to ± 0·001 degc. No variations in temperature around the acoustic path could be detected and the temperature of the specimen remained constant to better than 0·002 degc during a velocity measurement at a given temperature. The average of initial and final readings was taken as the temperature of measurement. As a check on the thermometer calibration, a second platinum resistance thermometer was used, the temperatures given by the two thermometers being equal within the accuracy of measurement. The absolute accuracy of temperature measurement is estimated to be better than ± 0·003 degc. This figure corresponds to a velocity error of ± 0·8 cm sec^{-1} around 25°c, reducing to zero at 74°c where the velocity in water passes through a maximum.

4.3. *Effect of diffraction on observed velocities*

The excess velocity due to diffraction has been calculated, for each frequency and liquid path length, by three distinct methods. These calculations are based upon the empirical curve given by McSkimin (1960), the theoretical results of Bass and Williams quoted by McSkimin (1961) and the tabulated phase errors given by Del Grosso (1964). The results are shown in table 3.

Del Grosso has computed phase errors as a function of $z\lambda/a^2$, where z is the path length and a is the source radius, for values of $2\pi a/\lambda$ up to 100π. For the source radius of 0·625 cm

Table 3. Excess velocity resulting from diffraction

Values calculated for a beam diameter of 12·5 mm

Frequency	Liquid path	Calculated excess velocity (m sec^{-1}) Bass and Williams, see McSkimin (1961)	McSkimin (1960)	Del Grosso (1964)
30	13 mm	0·019	0·020	0·028
30	11 mm	0·021	0·021	0·030
30	6 mm	0·028	0·028	0·044
30	0·6 in.	0·017	0·019	0·026
30	0·4 in.	0·021	0·022	0·031
10	13 mm	0·101	0·143	0·144

used in the present work, the values of $2\pi a/\lambda$ are 133π and 249π for frequencies of 10 and 30 Mc/s respectively. Although Del Grosso (1964), confirming the earlier work of Williams (1951), states that for $2\pi a/\lambda > 50$ the phase error is substantially independent of this parameter, there is some indication that for values of $z\lambda/a^2 < 0{\cdot}1$ the phase error decreases slightly for values of $2\pi a/\lambda$ exceeding 100π. The results in table 3 have been calculated assuming $2\pi a/\lambda = 100\pi$; it is therefore probable that the true values are slightly less than those given in the table. Accordingly, in the present work the excess velocity caused by diffraction has been calculated using the theoretical results of Bass and Williams, quoted by McSkimin (1961). Table 3 shows that at 30 Mc/s the differences between the correction calculated from the experimental results obtained by McSkimin (1960) and the corrections calculated using Bass and Williams' theory are negligible.

4.4. *Errors arising from phase change measurements*

Errors in the measurement of the fractional part of a wavelength in the acoustic path may arise in three ways: from the uncertainty in the lengths of cable, from the setting of cancellation points, and by deviations from linearity of the phase characteristic of the line.

The length of each cable was adjusted to $\pm 0{\cdot}1$ cm; the maximum possible error on changing from one pair of cables to a second pair is therefore $\pm 0{\cdot}4$ cm. At 30 Mc/s the corresponding phase error is $\pm 0{\cdot}22°$. It was found possible to determine cancellation points to about $\pm \frac{1}{3}°$ of phase angle; the maximum possible error between two settings is therefore $\pm \frac{2}{3}°$.

Deviations from linearity of phase change on varying the length of the line arise from standing-wave effects caused by mismatching at the termination and source of the line. To a first approximation, the error ϵ associated with a phase change θ is given by (A. J. Barlow 1959 Ph.D. Thesis, London University)

$$\epsilon = \pm 2 r_s r_l \theta \tag{14}$$

where r_s and r_l are the magnitudes of the reflection coefficients at the source and load respectively. Reflection occurs mainly as a result of reactive mismatch. The maximum error occurs when $\theta = 180°$. For the delay system used (Barlow 1959 Ph.D. Thesis), $2r_s r_l < 0{\cdot}01$ at 30 Mc/s; the maximum phase error is then less than $\pm 1{\cdot}8°$.

The total maximum possible error in a particular determination of θ is therefore approximately $\pm 2{\cdot}7°$. For the three longest liquid paths and a frequency of 30 Mc/s this figure corresponds to a maximum possible error in velocity of about $\pm 0{\cdot}05$ m sec^{-1}.

Errors in the determination of the length of cable equivalent to one wavelength are negligible, since several measurements were taken at each frequency f_1 and f_2 using different pairs of cables, and the average value was calculated.

4.5. *Experimental results*

Typical results for the values of the velocity of sound in twice distilled water are given in table 4. Each value represents the average, given to the nearest 0·01 m sec^{-1}, of the two results obtained from measurements made at the slightly differing frequencies f_1 and f_2. In general, the two results differed by less than 0·03 m sec^{-1}. The values shown have been

Table 4. Experimental values of the velocity of sound in distilled water

(*a*) Frequency 30 Mc/s, 6·5 mm gauge blocks

Temperature (°C)	Velocity (m sec⁻¹)	Δ (m sec⁻¹)	Average Δ (m sec⁻¹)
23·503	1492·49	0·41	
24·037	1493·94	0·46	
24·905	1496·34	0·40	
25·125	1496·90	0·40	
25·380	1497·59	0·43	
25·707	1498·43	0·43	
25·812	1498·73	0·41	
25·910	1498·99	0·40	
			0·42
27·570	1503·24	0·37	
27·935	1504·10	0·40	
29·920	1508·84	0·41	
29·323	1507·49	0·39	
29·985	1509·02	0·38	
35·020	1519·72	0·44	
39·990	1528·78	0·38	

Temperature (°C)	Velocity (m sec⁻¹)	Δ (m sec⁻¹)	Average Δ (m sec⁻¹)
45·127	1536·46	0·43	
49·966	1542·43	0·40	
55·105	1547·36	0·43	
64·980	1553·35	0·40	
70·050	1554·75	0·38	
			0·40
71·160	1554·89	0·40	
72·080	1554·98	0·39	
73·050	1555·02	0·42	
73·900	1555·07	0·40	
74·200	1555·09	0·38	
75·040	1555·02	0·43	
76·220	1555·00	0·41	
77·030	1554·92	0·39	
8·310	1554·70	0·42	
/9·115	1554·61	0·39	
80·045	1554·39	0·41	
			0·40

(*b*) Frequency 10 Mc/s, 6·5 mm gauge blocks

Temperature (°C)	Velocity (m sec⁻¹)	Δ (m sec⁻¹)	Average Δ (m sec⁻¹)
23·340	1492·00	0·44	
25·307	1497·37	0·44	
25·425	1497·72	0·40	
25·562	1498·03	0·45	
25·705	1498·45	0·41	
			0·43
34·990	1519·73	0·37	
46·131	1537·77	0·46	

Temperature (°C)	Velocity (m sec⁻¹)	Δ (m sec⁻¹)	Average Δ (m sec⁻¹)
55·046	1547·36	0·39	
62·780	1552·33	0·47	
			0·42
70·950	1554·88	0·38	
74·220	1555·08	0·39	
78·130	1554·73	0·43	
			0·40

corrected for the effect of diffraction, and the expansion of the gauge blocks with increasing temperature has also been taken into account. Table 4 also shows the amount Δ m sec^{-1} by which these values are lower than those calculated from the results obtained by Greenspan and Tschiegg (1957). The rate of variation with temperature found by Greenspan and Tschiegg is generally regarded as being substantially correct (McSkimin 1965). The average values of Δ for temperature around 25 and 74°c and for the intermediate range are also given.

5. Analysis of experimental results

In an analysis of the experimental results it is convenient to distinguish between three groups of variables which may give rise to errors. The first group consists of those factors which either give constant errors throughout the whole series of measurements or cause random variations which are negligible compared with other random errors. This group includes temperature, specimen purity, pressure and frequency. The second group comprises those variables purposely changed during the measurements; these include differences between acoustic path length, operating frequency and diffraction corrections. In the third group are the main random errors.

For the present measurements the spread of random errors in velocity should result entirely from the uncertainties of phase measurement and therefore be a maximum of $\pm$ 0·05 m sec^{-1}. This is confirmed by the experimental results, the values of Δ varying by not more than this amount for a given frequency and path length.

The results obtained using the 6·5 mm gauge blocks at frequencies of 10 and 30 Mc/s are in good agreement, as may be seen by a comparison of the average Δ figures for corresponding temperature regions. Essentially this agreement substantiates the diffraction theory, since the diffraction correction of 0·101 m sec^{-1} at 10 Mc/s is appreciable. It can therefore be assumed that any errors in the diffraction corrections applied at 30 Mc/s are negligible.

The average Δ figures in the region around 74°C show that the results at 30 Mc/s obtained with the 6·5 mm, 0·3 and 0·2 in. gauge blocks, for which the highest accuracy is claimed, are in precise agreement, with $\Delta_{av} = 0{\cdot}40$ m sec^{-1}. The 5·5 mm blocks give $\Delta_{av} = 0{\cdot}42$ m sec^{-1} and the 3·0 mm blocks give $\Delta_{av} = 0{\cdot}39$ m sec^{-1}. These averages are correct to the nearest 0·01 m sec^{-1}. These differences have been confirmed by an extensive series of measurements made using a sample of water taken directly, without purification, from the public supply. An average velocity consistently 0·05 m sec^{-1} higher than that for distilled water was obtained over the range 23–80°C, but the relative differences between the five sets of blocks remained the same. It follows that the average thicknesses, taken over each set of three blocks of the 6·5 mm, 0·3 and 0·2 in. blocks are within $\pm$ 0·7 parts in 10^6 of their nominal values, since this is the stated accuracy of the 0·3 in. blocks. The average deviation from the nominal value for the 5·5 mm block is then probably between $-$ 0·6 and $-$ 2·0 parts in 10^6, the corresponding figures for the 3·0 mm blocks being $-$ 0·7 and $-$ 1·4 parts in 10^6. These deviations are well within the limits specified by the manufacturers.

Considering only the results obtained in the region of 74°C at 30 Mc/s, the average value of Δ for the 6·5 mm, 0·3 and 0·2 in. sets of gauge blocks is 0·403 m sec^{-1}. This figure is unchanged if the results obtained with the other two sets of blocks are included, the value of Δ being decreased by 0·02 m sec^{-1} for the 5·5 mm blocks and increased by 0·01 m sec^{-1} for the 3·0 mm blocks. The standard deviation is 0·014 m sec^{-1} and the distribution of the Δ-values around the mean is very close to a normal distribution, as may be expected from the random nature of the phase measurement errors.

Applying the same procedure to the results obtained at 30 Mc/s around 25°C, the average value of Δ is found to be 0·412 m sec^{-1}, with a standard deviation of 0·020 m sec^{-1}. The slight increase in standard deviation is probably partly due to the uncertainty in temperature measurement.

The small difference in Δ_{av} between c. 74°C and c. 25°C is somewhat larger than could be expected from the estimated possible error in absolute temperature measurement. It is probable that this discrepancy represents a slight difference between the variation of velocity with temperature found by Greenspan and Tschiegg (1957) and that found in the present work, but it would be unrealistic to regard the difference as significant. In general it is seen that the present measurements confirm the variation of velocity with temperature found by Greenspan and Tschiegg (1957), but the actual values of velocity are approximately 0·40 m sec^{-1} lower.

A fifth-degree polynomial has been fitted to the experimental results by means of a computer, the fit being such as to give a minimum mean-square error. The data for all five sets of blocks were used, those for the 5·5 mm and 3·0 mm blocks being modified as indicated previously. The resulting equation is

$$V = 1400{\cdot}7873 + 5{\cdot}189939T - 6{\cdot}394257 \times 10^{-2}T^2 - 4{\cdot}4060241 \times 10^{-4}T^3 - 2{\cdot}399801 \times 10^{-6}T^4 - 6{\cdot}214865 \times 10^{-9}T^5 \text{ m sec}^{-1} \quad (15)$$

where T is the temperature in °C.

The standard deviation of the data from this curve is less than 0·018 m sec^{-1}. The maximum deviation of any single measurement from the curve is 0·041 m sec^{-1}, and the deviations of the data from the curve are apparently random and are substantially in accordance with a normal distribution. This scatter is adequately accounted for by the possible errors in phase measurement; the extent of the scatter is approximately two-thirds of that obtained by Greenspan and Tschiegg (1957) using the 'sing-around' technique. No significant reduction of these values is obtained by using a polynomial of higher order.

Equation (15) has been used to calculate the velocity of sound in water at 1 degC intervals from 23 to 80°C, the range over which this equation is valid, and the results are given in table 5. Following Greenspan and Tschiegg (1957), the increase for each 1 degC interval is also given to facilitate interpolation.

Table 5. Velocity of sound in water, values calculated using equation (15), together with the increase in velocity per deg C

T (°C)	V (m sec^{-1})	Increase (m sec^{-1})	T (°C)	V (m sec^{-1})	Increase (m sec^{-1})	T (°C)	V (m sec^{-1})	Increase (m sec^{-1})
23·0	1491·06	—	43·0	1533·47	1·51	63·0	1552·50	0·49
24·0	1493·86	2·80	44·0	1534·91	1·45	64·0	1552·95	0·45
25·0	1496·58	2·72	45·0	1536·31	1·39	65·0	1553·35	0·40
26·0	1499·22	2·64	46·0	1537·64	1·34	66·0	1553·71	0·36
27·0	1501·79	2·57	47·0	1538·93	1·28	67·0	1554·02	0·32
28·0	1504·28	2·49	48·0	1540·15	1·23	68·0	1554·30	0·27
29·0	1506·70	2·42	49·0	1541·33	1·17	69·0	1554·53	0·23
30·0	1509·04	2·34	50·0	1542·45	1·12	70·0	1554·72	0·19
31·0	1511·31	2·27	51·0	1543·52	1·07	71·0	1554·87	0·15
32·0	1513·52	2·20	52·0	1544·53	1·02	72·0	1554·97	0·11
33·0	1515·65	2·13	53·0	1545·50	0·97	73·0	1555·04	0·07
34·0	1517·72	2·07	54·0	1546·42	0·92	74·0	1555·07	0·03
35·0	1519·72	2·00	55·0	1547·28	0·87	75·0	1555·05	−0·01
36·0	1521·66	1·94	56·0	1548·10	0·82	76·0	1555·00	−0·05
37·0	1523·53	1·87	57·0	1548·87	0·77	77·0	1554·91	−0·09
38·0	1525·34	1·81	58·0	1549·59	0·72	78·0	1554·78	−0·13
39·0	1527·08	1·75	59·0	1550·26	0·67	79·0	1554·61	−0·17
40·0	1528·77	1·69	60·0	1550·89	0·63	80·0	1554·41	−0·20
41·0	1530·39	1·62	61·0	1551·47	0·58			
42·0	1531·96	1·57	62·0	1552·01	0·54			

6. Discussion

Measurements of the velocity of sound in water show that the experimental system described here is capable of extremely consistent results. The scatter of the data is small and follows a normal distribution. Since most of the scatter can be attributed to imperfect matching of the delay line, further development of the system could probably reduce the scatter by a factor of two. There is no evidence of any systematic errors arising from the use of different acoustic path lengths or different operating frequencies. During a separate series of measurements investigations were made into the effects of varying the amplitude and duration of the transmitted pulse and of changing certain critical components of the system, including the buffer amplifiers and piston attenuator. Such changes gave no differences in the measured velocities. Results were also obtained, using the 3 mm blocks at a frequency of 30 Mc/s, on pulses which had made two and three double transits of the liquid path. Again no variations in the values of velocity were found.

It follows that the results obtained represent true values of the velocity of sound in the liquid measured. In relating such values to the absolute value for the velocity of sound in water those factors which may give errors constant throughout the whole series of measurements must be considered. At 25°C the possible error of ± 0·003 degC in absolute temperature measurement gives a possible error of ± 0·008 m sec^{-1} in velocity. At 74°C, where the velocity passes through a maximum, the error is negligible. The effect of hydrostatic pressure on velocity causes the values obtained to be high by 0·002 m sec^{-1}, due to the head of water above the acoustic path. Errors resulting from the variation of atmospheric pressure are negligible. The attenuation in water gives errors of less than 1 part in 10^6; errors in the determination of operating frequencies are also negligible.

Dissolved air was probably the principal impurity in the sample of water investigated.

Greenspan and Tschiegg (1956) conclude that dissolved air increases the velocity in water by less than 1 part in 10^5, and around 30°C the increase is possibly of the order of 1 part in 10^6. This latter figure is negligible; even if the difference is significant, it would seem preferable to regard the velocity of sound in water saturated with air as a standard for reference, since this is the normal state of water in contact with air.

It may therefore be deduced that the only significant sources of possible error in the results are the uncertainties in acoustic path length, in the determination of temperature, and the standard error of the data. The sum of these possible errors is $\pm$ 0·024 m sec^{-1} at 74°C and $\pm$ 0·038 m sec^{-1} at 25°C. From the present measurements, the velocity of sound in water to the nearest 0·01 m sec^{-1} is found to be 1496·58 $\pm$ 0·04 m sec^{-1} at 25·000°C and 1555·07 $\pm$ 0·03 m sec^{-1} at 74·00°C. The accuracy of these values is believed to be the highest yet attained. The results are in close agreement with the values found by McSkimin (1965), Ilgunas *et al.* (1964), Neubauer and Dragonette (1964) and Brooks (1960).

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Speed of Sound in Pure Water

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A sound-speed equation of fifth order in temperature is fit with a standard deviation of 0.0028 m/sec to 148 observations between 0.001°C and 95.126°C on the T_{68} scale. The accuracy is believed to be 0.015 m/sec, and the reproducibility over replications is 0.005 m/sec.

Subject Classification: 13.3.

INTRODUCTION

In the course of obtaining a satisfactory sea-water sound-speed equation based on laboratory measurements,[1] data were obtained in pure water[2] with an apparent reproducibility of better than 4 ppm. In this latter reference, it was demonstrated that by comparison of results of reputable observers, the speed of sound in pure water could be specified to better than 0.05 m/sec. Mention was also made therein of indications of an anomaly near 4°C. These measurements, with emphasis about this temperature but extending the total range closer to both 0° and 100°C, are now reported.

I. EXPERIMENTAL METHOD

Sound-speed measurements were made indirectly by means of the ultrasonic interferometer whose construction and operation have been discussed earlier.[1,2] Briefly, acoustic wavelengths are measured by electronically noting some characteristic of a quartz crystal

Table I. Sound speeds measured in pure water for temperatures on T_{68} scale.

Temperature (°C)	Sound speed (m/sec)	Temperature (°C)	Sound speed (m/sec)	Temperature (°C)	Sound speed (m/sec)	Temperature (°C)	Sound speed (m/sec)
0.0010	1402.395	3.4933	1419.287	1.0035	1407.384	7.9894	1439.089
0.0020	1402.398	3.7972	1420.702	1.0035	1407.384	7.9904	1439.094
0.0030	1402.404	3.7982	1420.694	1.0045	1407.392	7.9904	1439.096
0.0030	1402.406	3.7992	1420.700	1.0045	1407.386	7.9904	1439.094
0.0110	1402.445	3.8002	1420.707	1.0055	1407.391	7.9914	1439.102
0.0120	1402.448	3.8002	1420.707	1.0095	1407.412	9.9537	1447.087
0.0130	1402.456	3.9911	1421.584	1.0175	1407.451	9.9537	1447.087
0.0130	1402.453	3.9911	1421.587	1.0235	1407.482	9.9547	1447.094
0.0140	1402.459	3.9921	1421.590	1.0305	1407.516	9.9547	1447.091
0.0520	1402.649	3.9921	1421.589	2.0490	1412.468	9.9547	1447.089
0.0520	1402.652	3.9931	1421.595	2.0560	1412.501	39.9657	1528.809
0.0520	1402.649	4.2160	1422.620	2.0620	1412.527	39.9777	1528.831
0.0530	1402.654	4.2170	1422.624	2.0650	1412.543	39.9887	1528.847
0.0530	1402.654	4.2170	1422.622	2.0680	1412.554	59.9924	1550.980
0.1979	1403.383	4.2170	1422.622	2.0720	1412.574	60.0034	1550.986
0.1979	1403.383	4.5269	1424.032	2.4868	1414.553	60.0124	1550.994
0.1989	1403.390	4.5279	1424.039	2.4868	1414.556	60.0204	1550.998
0.1989	1403.388	4.5279	1424.040	2.4898	1414.573	60.0294	1551.004
0.1989	1403.388	4.5279	1424.039	2.4918	1414.582	70.1190	1554.819
0.4878	1404.829	5.4935	1428.364	2.4928	1414.585	70.1210	1554.819
0.4898	1404.843	5.4935	1428.365	2.9736	1416.861	70.1240	1554.819
0.4908	1404.848	5.4945	1428.367	2.9746	1416.864	70.1340	1554.824
0.4988	1404.888	5.4965	1428.378	2.9766	1416.875	70.1500	1554.824
0.5008	1404.894	5.9892	1430.543	2.9766	1416.876	90.0858	1550.430
0.5018	1404.901	5.9902	1430.548	3.4913	1419.279	90.0868	1550.430
1.0005	1407.365	5.9902	1430.551	3.4913	1419.277	95.1214	1547.096
1.0025	1407.377	5.9922	1430.559	3.4923	1419.277	95.1224	1547.100
1.0025	1407.382	5.9952	1430.572	3.4923	1419.280	95.1264	1547.095

TABLE II. Previous sound-speed measurements in pure water with temperatures converted to T_{68} scale

Temperature (°C)	Sound speed (m/sec)	Temperature (°C)	Sound speed (m/sec)	Temperature (°C)	Sound speed (m/sec)	Temperature (°C)	Sound speed (m/sec)
0.0560	1402.673	29.9816	1509.081	9.9917	1447.234	49.9956	1542.543
0.0610	1402.695	29.9836	1509.089	9.9957	1447.249	50.0126	1542.563
0.0640	1402.705	34.9710	1519.752	10.0027	1447.276	50.0366	1542.591
0.0680	1402.726	34.9810	1519.768	10.0117	1447.307	50.0466	1542.602
0.0720	1402.747	34.9870	1519.781	19.9196	1482.091	60.0194	1550.999
4.9887	1426.115	39.9727	1528.82[illegible]	19.9206	1482.096	60.0124	1550.999
4.9917	1426.126	39.9747	1528.823	19.9216	1482.102	73.9957	1555.144
4.9927	1426.129	39.9777	1528.827	24.9815	1496.636	74.0117	1555.144
4.9937	1426.131	39.9847	1528.837	24.9855	1496.646	74.0218	1555.145

TABLE III. Coefficients for Eq. 1 for sound speed in m/sec.

k	Table I fit	Table II fit	Combined fit
0	0.140238689×10^{4}	0.140238749×10^{4}	0.140238754×10^{4}
1	0.503686088×10^{1}	0.503699148×10^{1}	0.503711129×10^{1}
2	$-0.580858499\times10^{-1}$	$-0.580268889\times10^{-1}$	$-0.580852166\times10^{-1}$
3	0.334817140×10^{-3}	0.331767408×10^{-3}	0.334198834×10^{-3}
4	$-0.149252527\times10^{-5}$	$-0.144373838\times10^{-5}$	$-0.147800417\times10^{-5}$
5	0.323913472×10^{-8}	0.298841057×10^{-8}	0.314643091×10^{-8}

TABLE IV. Speed of sound in pure water in m/sec. Calculations from equation fit to 148 measurements between 0.001°C and 95.128°C on T_{68} scale with standard deviation of 0.003 m/sec.

T_{68} °C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1402.388	1402.891	1403.393	1403.893	1404.393	1404.892	1405.389	1405.885	1406.380	1406.874
1	1407.367	1407.859	1408.349	1408.838	1409.327	1409.814	1410.300	1410.784	1411.268	1411.751
2	1412.232	1412.712	1413.192	1413.670	1414.147	1414.622	1415.097	1415.571	1416.043	1416.515
3	1416.985	1417.454	1417.922	1418.389	1418.855	1419.320	1419.784	1420.246	1420.708	1421.168
4	1421.628	1422.086	1422.543	1422.999	1423.454	1423.908	1424.361	1424.813	1425.264	1425.713
5	1426.162	1426.609	1427.056	1427.501	1427.946	1428.389	1428.831	1429.272	1429.712	1430.151
6	1430.589	1431.026	1431.462	1431.897	1432.331	1432.764	1433.196	1433.626	1434.056	1434.485
7	1434.912	1435.339	1435.764	1436.189	1436.612	1437.035	1437.456	1437.877	1438.296	1438.715
8	1439.132	1439.549	1439.964	1440.378	1440.792	1441.204	1441.615	1442.026	1442.435	1442.843
9	1443.251	1443.657	1444.062	1444.467	1444.870	1445.273	1445.674	1446.074	1446.474	1446.872
10	1447.270	1447.666	1448.062	1448.456	1448.850	1449.243	1449.634	1450.025	1450.415	1450.803
11	1451.191	1451.578	1451.964	1452.349	1452.733	1453.116	1453.498	1453.879	1454.259	1454.638
12	1455.016	1455.394	1455.770	1456.145	1456.520	1456.893	1457.266	1457.637	1458.008	1458.378
13	1458.747	1459.115	1459.482	1459.848	1460.213	1460.577	1460.940	1461.303	1461.664	1462.025
14	1462.384	1462.743	1463.101	1463.458	1463.814	1464.169	1464.523	1464.876	1465.229	1465.580
15	1465.931	1466.280	1466.629	1466.977	1467.324	1467.670	1468.015	1468.359	1468.703	1469.045
16	1469.387	1469.728	1470.067	1470.406	1470.745	1471.082	1471.418	1471.754	1472.088	1472.422
17	1472.755	1473.087	1473.418	1473.748	1474.078	1474.406	1474.734	1475.061	1475.386	1475.712
18	1476.036	1476.359	1476.682	1477.003	1477.324	1477.644	1477.963	1478.282	1478.599	1478.916
19	1479.231	1479.546	1479.860	1480.174	1480.4[illegible]5	1480.798	1481.108	1481.418	1481.727	1482.035
20	1482.343	1482.649	1482.955	1483.260	1483.564	1483.868	1484.170	1484.472	1484.772	1485.073
21	1485.372	1485.670	1485.968	1486.264	1486.560	1486.856	1487.150	1487.443	1487.736	1488.028
22	1488.319	1488.610	1488.899	1489.188	1489.476	1489.763	1490.049	1490.335	1490.620	1490.804
23	1491.187	1491.469	1491.751	1492.032	1492.312	1492.591	1492.870	1493.147	1493.424	1493.700
24	1493.976	1494.250	1494.524	1494.797	1495.070	1495.341	1495.612	1495.882	1496.151	1496.420
25	1496.687	1496.954	1497.220	1497.486	1497.751	1498.014	1498.278	1498.540	1498.802	1499.063
26	1499.323	1499.582	1499.841	1500.099	1500.356	1500.612	1500.868	1501.123	1501.377	1501.630
27	1501.883	1502.135	1502.386	1502.637	1502.887	1503.136	1503.384	1503.632	1503.878	1504.124
28	1504.370	1504.615	1504.858	1505.102	1505.344	1505.586	1505.827	1506.067	1506.307	1506.546
29	1506.784	1507.022	1507.258	1507.494	1507.730	1507.964	1508.198	1508.431	1508.664	1508.896
30	1509.127	1509.357	1509.587	1509.816	1510.044	1510.272	1510.499	1510.725	1510.950	1511.175
31	1511.399	1511.623	1511.845	1512.068	1512.289	1512.510	1512.730	1512.949	1513.167	1513.385
32	1513.603	1513.819	1514.035	1514.250	1514.465	1514.679	1514.892	1515.104	1515.316	1515.527
33	1515.738	1515.948	1516.157	1516.365	1516.573	1516.780	1516.987	1517.193	1517.398	1517.602
34	1517.806	1518.009	1518.212	1518.414	1518.615	1518.815	1519.015	1519.214	1519.413	1519.611
35	1519.808	1520.005	1520.201	1520.396	1520.591	1520.785	1520.978	1521.171	1521.363	1521.554
36	1521.745	1521.935	1522.125	1522.314	1522.502	1522.690	1522.877	1523.063	1523.249	1523.434
37	1523.618	1523.802	1523.985	1524.168	1524.350	1524.531	1524.712	1524.892	1525.071	1525.250
38	1525.428	1525.606	1525.783	1525.959	1526.135	1526.310	1526.484	1526.658	1526.832	1527.004
39	1527.176	1527.348	1527.518	1527.689	1527.858	1528.027	1528.195	1528.363	1528.530	1528.697

TABLE IV. (continued)

T_{∞} °C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
40	1528.863	1529.028	1529.193	1529.357	1529.521	1529.684	1529.846	1530.008	1530.169	1530.329
41	1530.489	1530.649	1530.807	1530.965	1531.123	1531.280	1531.436	1531.592	1531.747	1531.902
42	1532.056	1532.210	1532.362	1532.515	1532.666	1532.818	1532.968	1533.118	1533.267	1533.416
43	1533.564	1533.712	1533.859	1534.006	1534.152	1534.297	1534.442	1534.586	1534.730	1534.873
44	1535.015	1535.157	1535.298	1535.439	1535.579	1535.719	1535.858	1535.997	1536.134	1536.272
45	1536.409	1536.545	1536.681	1536.816	1536.950	1537.084	1527.218	1537.351	1537.483	1537.615
46	1537.746	1537.877	1538.007	1538.137	1538.266	1538.394	1538.522	1538.650	1538.776	1538.903
47	1539.028	1539.154	1539.278	1539.402	1539.526	1539.649	1539.772	1539.894	1540.015	1540.136
48	1540.256	1540.376	1540.495	1540.614	1540.732	1540.850	1540.967	1541.083	1541.199	1541.315
49	1541.430	1541.544	1541.658	1541.772	1541.885	1541.997	1542.109	1542.220	1542.331	1542.441
50	1542.551	1542.660	1542.768	1542.877	1542.984	1543.091	1543.198	1543.304	1543.409	1543.514
51	1543.619	1543.723	1543.826	1543.929	1544.032	1544.134	1544.235	1544.336	1544.436	1544.536
52	1544.636	1544.734	1544.833	1544.931	1545.028	1545.125	1545.221	1545.317	1545.412	1545.507
53	1545.601	1545.695	1545.788	1545.881	1545.973	1546.065	1546.156	1546.247	1546.337	1546.427
54	1546.517	1546.605	1546.694	1546.781	1546.869	1546.955	1547.042	1547.128	1547.213	1547.298
55	1547.382	1547.466	1547.549	1547.632	1547.715	1547.796	1547.878	1547.959	1548.039	1548.119
56	1548.199	1548.278	1548.356	1548.434	1548.512	1548.589	1548.665	1548.741	1548.717	1548.892
57	1548.967	1549.041	1549.115	1549.188	1549.260	1549.333	1549.405	1549.476	1549.547	1549.617
58	1549.687	1549.756	1549.825	1549.894	1549.962	1550.029	1550.096	1550.163	1550.229	1550.295
59	1550.360	1550.425	1550.489	1550.553	1550.616	1550.679	1550.741	1550.803	1550.865	1550.926
60	1550.986	1551.046	1551.106	1551.165	1551.224	1551.282	1551.340	1551.397	1551.454	1551.510
61	1551.566	1551.622	1551.677	1551.731	1551.786	1551.839	1551.892	1551.945	1551.998	1552.049
62	1552.101	1552.152	1552.202	1552.252	1552.302	1552.351	1552.400	1552.448	1552.496	1552.543
63	1552.590	1552.637	1552.683	1552.729	1552.774	1552.818	1552.863	1552.907	1552.950	1552.993
64	1553.035	1553.078	1553.119	1553.160	1553.201	1553.241	1553.281	1553.321	1553.360	1553.398
65	1553.437	1553.474	1553.512	1553.548	1553.585	1553.621	1553.656	1553.691	1553.726	1553.760
66	1553.794	1553.828	1553.860	1553.893	1553.925	1553.957	1553.988	1554.019	1554.049	1554.079
67	1554.109	1554.138	1554.167	1554.195	1554.223	1554.250	1554.277	1554.304	1554.330	1554.356
68	1554.381	1554.406	1554.430	1554.454	1554.478	1554.501	1554.524	1554.546	1554.568	1554.590
69	1554.611	1554.632	1554.652	1554.672	1554.691	1554.710	1554.729	1554.747	1554.765	1554.782
70	1554.799	1554.816	1554.832	1554.848	1554.863	1554.878	1554.893	1554.907	1554.920	1554.934
71	1554.947	1554.959	1554.971	1554.983	1554.994	1555.005	1555.015	1555.026	1555.035	1555.044
72	1555.053	1555.062	1555.070	1555.077	1555.085	1555.091	1555.098	1555.104	1555.110	1555.115
73	1555.120	1555.124	1555.128	1555.132	1555.135	1555.138	1555.140	1555.142	1555.144	1555.145
74	1555.146	1555.147	1555.147	1555.146	1555.146	1555.145	1555.143	1555.141	1555.139	1555.136
75	1555.133	1555.130	1555.126	1555.122	1555.117	1555.112	1555.107	1555.101	1555.095	1555.088
76	1555.081	1555.074	1555.066	1555.058	1555.050	1555.041	1555.032	1555.022	1555.012	1555.002
77	1554.991	1554.980	1554.968	1554.956	1554.944	1554.931	1554.918	1554.905	1554.891	1554.877
78	1554.862	1554.847	1554.832	1554.816	1554.800	1554.784	1554.767	1554.750	1554.732	1554.714
79	1554.696	1554.677	1554.658	1554.639	1554.619	1554.599	1554.578	1554.557	1554.536	1554.514
80	1554.492	1554.470	1554.447	1554.424	1554.400	1554.376	1554.352	1554.327	1554.302	1554.277
81	1554.251	1554.225	1554.199	1554.172	1554.144	1554.117	1554.089	1554.061	1554.032	1554.003
82	1553.974	1553.944	1553.914	1553.883	1553.852	1553.821	1553.789	1553.758	1553.725	1553.693
83	1553.660	1553.626	1553.592	1553.558	1553.524	1553.489	1553.454	1553.418	1553.383	1553.346
84	1553.310	1553.273	1553.235	1553.198	1553.160	1553.121	1553.083	1553.044	1553.004	1552.964
85	1552.924	1552.884	1552.843	1552.802	1552.760	1552.718	1552.676	1552.634	1552.591	1552.547
86	1552.504	1552.460	1552.415	1552.371	1552.326	1552.280	1552.234	1552.188	1552.142	1552.095
87	1552.048	1552.001	1551.953	1551.905	1551.856	1551.807	1551.758	1551.709	1551.659	1551.609
88	1551.558	1551.507	1551.456	1551.404	1551.352	1551.300	1551.248	1551.195	1551.141	1551.088
89	1551.034	1550.980	1550.925	1550.870	1550.815	1550.759	1550.703	1550.647	1550.590	1550.533
90	1550.476	1550.418	1550.360	1550.302	1550.243	1550.184	1550.125	1550.065	1550.005	1549.945
91	1549.884	1549.823	1549.762	1549.700	1549.638	1549.576	1549.513	1549.450	1549.387	1549.323
92	1549.259	1549.195	1549.131	1549.066	1549.000	1548.935	1548.869	1548.803	1548.736	1548.669
93	1548.602	1548.534	1548.467	1548.398	1548.330	1548.261	1548.192	1548.122	1548.053	1547.983
94	1547.912	1547.841	1547.770	1547.699	1547.627	1547.555	1547.483	1547.410	1547.337	1547.264
95	1547.190	1547.116	1547.042	1546.967	1546.892	1546.817	1546.741	1546.665	1546.589	1546.513
96	1546.436	1546.359	1546.281	1546.204	1546.126	1546.047	1545.969	1545.890	1545.810	1545.731
97	1545.651	1545.570	1545.490	1545.409	1545.328	1545.246	1545.164	1545.082	1545.000	1544.917
98	1544.834	1544.751	1544.667	1544.583	1544.499	1544.414	1544.329	1544.244	1544.159	1544.073
99	1543.987	1543.900	1543.814	1543.727	1543.639	1543.552	1543.464	1543.376	1543.287	1543.198
100	1543.109									

operated in a continuous wave iterative-reflection technique and counting these imposed characteristics as the reflector–source separation is varied. The path change for some 300 acoustic fringes at 5 MHz is measured by a laser interferometer. Consideration of all sources of error, including theoretical predictions[3,4] leads to a specification of accuracy of 10 ppm or 0.015 m/sec.

II. DATA

Some 112 new data points for the speed of sound in pure water were taken in 1970 and are reported in

Table I, with temperatures on the T_{68} scale. In Table II, the previous measurements[2] are repeated with temperatures converted to the same scale. The results of these calculations are given to the nearest 0.0001°C, although the measurements were made to only 0.001°C, to facilitate conversion.

III. EQUATION DEVELOPMENT

To ascertain whether these two data sets are compatible, separate least-squares fits were made[5] at the Naval Undersea Research and Development Center (NAVUSEARANDCEN). A fifth-degree polynomial was found satisfactory for both, viz:

$$C=\sum_{i=0}^{5} k_i T^i. \tag{1}$$

The 36 earlier observations in Table II over the temperature range $0.056°C \leq T_{68} \leq 74.022°C$ were fit with a standard deviation of 0.0025 m/sec and coefficients as given in the third column of Table III.

The least-squares fit to the 112 data points of Table I over the larger temperature range $0.001°C \leq T_{68} \leq 95.126°C$, but with emphasis between 0° and 10°C has a standard deviation of 0.0026 m/sec and comparable coefficients as given in column two of Table III.

Because of the close agreement between these expressions, Tables I and II were combined, and a least-squares fit was obtained to all 148 observations with a standard deviation of 0.0029 m/sec and coefficients as given in the last column of Table III.

TABLE V. Regression curve deviation average and scatter for nominal experimental temperatures.

Nominal T (°C)	Average (m/sec)	Scatter (m/sec)
Second data set		
0.01	−0.002	0.003
0.05	0.000	0.000
0.2	−0.001	0.000
0.5	−0.001	0.004
1.0	+0.001	0.006
2.0	+0.002	0.004
2.5	+0.004	0.006
3.0	0.000	0.002
3.5	+0.004	0.006
3.8	+0.003	0.004
4.0	+0.002	0.002
4.2	−0.002	0.002
4.5	−0.004	0.002
5.5	−0.004	0.002
6.0	−0.003	0.004
8.0	−0.003	0.004
10.0	−0.001	0.004
40.0	−0.004	0.002
60.0	+0.001	0.002
70.0	0.000	0.004
90.0	−0.004	0.000
95.0	+0.002	0.004
First data set		
0.06	+0.001	0.006
5.0	−0.001	0.006
10.0	+0.005	0.006
20.0	+0.003	0.002
25.0	+0.002	0.000
30.0	+0.002	0.003
35.0	+0.001	0.004
40.0	−0.001	0.002
50.0	0.000	0.002
60.0	0.000	0.001
74.0	+0.002	0.001

TABLE VI. Temperature scale conversion.

T_{48} (°C)	T_{68} (°C)	$T_{48}-T_{68}$ (°C)	T_{48} (°C)	T_{68} (°C)	$T_{48}-T_{68}$ (°C)	T_{48} (°C)	T_{68} (°C)	$T_{48}-T_{68}$ (°C)	T_{48} (°C)	T_{68} (°C)	$T_{48}-T_{68}$ (°C)
0	0	0	26	25.9913	0.0087	51	50.9897	0.0103	76	75.9932	0.0068
1	0.9995	0.0005	27	26.9911	0.0089	52	51.9897	0.0103	77	76.9934	0.0066
2	1.9990	0.0010	28	27.9909	0.0091	53	52.9898	0.0102	78	77.9937	0.0063
3	2.9986	0.0014	29	28.9908	0.0092	54	53.9899	0.0101	79	78.9939	0.0061
4	3.9981	0.0019	30	29.9907	0.0093	55	54.9899	0.0101	80	79.9941	0.0059
5	4.9977	0.0023	31	30.9905	0.0095	56	55.9900	0.0100	81	80.9944	0.0056
6	5.9973	0.0027	32	31.9904	0.0096	57	56.9901	0.0099	82	81.9946	0.0054
7	6.9969	0.0031	33	32.9902	0.0098	58	57.9902	0.0098	83	82.9949	0.0051
8	7.9965	0.0035	34	33.9901	0.0099	59	58.9903	0.0097	84	83.9952	0.0048
9	8.9961	0.0039	35	34.9900	0.0100	60	59.9904	0.0096	85	84.9954	0.0046
10	9.9957	0.0043	36	35.9899	0.0101	61	60.9906	0.0094	86	85.9957	0.0043
11	10.9953	0.0047	37	36.9898	0.0102	62	61.9907	0.0093	87	86.9960	0.0040
12	11.9950	0.0050	38	37.9898	0.0102	63	62.9908	0.0092	88	87.9963	0.0037
13	12.9946	0.0054	39	38.9897	0.0103	64	63.9910	0.0090	89	88.9965	0.0035
14	13.9943	0.0057	40	39.9897	0.0103	65	64.9911	0.0089	90	89.9968	0.0032
15	14.9940	0.0060	41	40.9896	0.0104	66	65.9913	0.0087	91	90.9971	0.0029
16	15.9937	0.0063	42	41.9896	0.0104	67	66.9914	0.0086	92	91.9974	0.0026
17	16.9934	0.0066	43	42.9896	0.0104	68	67.9916	0.0084	93	92.9977	0.0023
18	17.9931	0.0069	44	43.9895	0.0105	69	68.9918	0.0082	94	93.9981	0.0019
19	18.9929	0.0071	45	44.9895	0.0105	70	69.9920	0.0080	95	94.9984	0.0016
20	19.9926	0.0074	46	45.9895	0.0105	71	70.9922	0.0078	96	95.9987	0.0013
21	20.9924	0.0076	47	46.9895	0.0105	72	71.9923	0.0077	97	96.9990	0.0010
22	21.9921	0.0079	48	47.9986	0.0104	73	72.9925	0.0075	98	97.9993	0.0007
23	22.9919	0.0081	49	48.9896	0.0104	74	73.9928	0.0072	99	98.9997	0.0003
24	23.9917	0.0083	50	49.9896	0.0104	75	74.9930	0.0070	100	100.0000	0
25	24.9915	0.0085									

This equation fit to the combined data predicts a sound-speed maximum of 1555.147 m/sec at a temperature of 74.172°C on the T_{48} scale. Sound speeds calculated with these coefficients are given in Table IV for tenth-degree celsius intervals. A rounding off of these coefficients is employed at NAVUSEARANDCEN for velocimeter calibrations.[6]

IV. DISCUSSION OF RESULTS

The standard deviation of the equation fit to the data is 0.003 m/sec or 2 ppm. As stated, the measurements are most probably accurate to 0.015 m/sec. Another measure of the precision of the data (apart from accuracy) in the form of reproducibility over replications can be obtained from Table V, which lists the average regression deviation and scatter thereof, for nominal experimental temperatures. It is tempting to postulate the existence of anomalies not only about 4°C but also at 40° and 90°C, but such an assertion is strongly resisted since the deviations are of the order of the scatter and standard deviation. Comparison of the present results may be made to other work[7] of lesser precision (standard deviation five times larger) and greater scatter (twenty times larger) where relative measurements over a smaller temperature range ($6°C \leq T \leq 81°C$) showed "no significant discontinuities or other anomalous behavior." These latter authors found an eighth-order polynomial was required to fit their data, and they ignored a deviation three times greater than their scatter.

In light of the above, this present data is presented simply as the most precise and hopefully accurate values of sound speed in pure water.

A temperature scale conversion table is presented in Table VI to assist those still operating on the T_{48} scale.

[1] V. A. Del Grosso and C. W. Mader, J. Acoust. Soc. Amer. (in press, 1972).
[2] V. A. Del Grosso, J. Acoust. Soc. Amer. 47, 947–949 (1970).
[3] V. A. Del Grosso, J. Acoust. Soc. Amer. 48, 770–771 (1970).
[4] V. A. Del Grosso, Acustica 24, 299–311 (1971).
[5] K. V. Mackenzie, private comunication (January 1971).
[6] K. V. Mackenzie, private communication (February 1971). Also, see J. Acoust. Soc. Amer. 50, 1321–1333 (1971).
[7] W. Senghaphram, G. O. Zimmerman, and C. E. Chase, J. Chem. Phys. 51, 2543–2545 (1969).

Bubble Growth by Diffusion in an 11-kHz Sound Field

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Bubble growth by rectified diffusion of gas was measured for single bubbles in an 11-kHz underwater sound field. Observed results are compared to calculated results for assumed isothermal or adiabatic pulsations of the bubbles. The calculated threshold for growth is consistent with observations, but the calculated times of growth exceed the observed times by factors of about 10–100.

SUBJECT CLASSIFICATION: 13.8.

This paper reports measurements of bubble growth by rectified diffusion in an 11-kHz underwater sound field. Bubble radii ranged from about 50 μ to greater than 200 μ, and peak acoustic pressures ranged up to about 0.3 bar. The results are compared to predictions of theory.

Threshold conditions for growth, and the subsequent rates of growth, were previously reported for a sound frequency of 26.6 kHz.[1] The present results extend the previous study to a lower frequency and were obtained by a procedure similar to that described in Ref. 1.

The experiments were conducted with air bubbles in air-saturated water in a vertical 6-in.-diam Pyrex pipe, driven by a transducer at the bottom. The water column was 43 cm high and resonated at 11.08 kHz. The water surface at the top and the glass walls were approximate pressure-release surfaces. Individual air bubbles were acoustically trapped near a pressure antinode located one quarter wavelength, about 4.6 cm, below the surface. Bubble size was monitored by means of rise-time measurements at regular time intervals. The acoustic pressure was monitored with a calibrated hydrophone.

After each set of measurements, the pressure amplitude at the bubble was calculated through knowledge of the bubble and hydrophone locations and the geometry of the sound field. The bubble radius R was computed from the rise velocity u by iterating the following approximate equation from Langmuir and Blodgett[2–4]:

$$R^2 = (9\nu/2g)u[1+0.197(2Ru/\nu)^{0.63}], \qquad (1)$$

where ν is the kinematic viscosity of water at the appropriate temperature, and g is the gravitational acceleration.

During one series of experimental runs, the sound pressure was continually adjusted to bring it close to the threshold for growth of the bubble present. The results are presented in Fig. 1. The symbol × indicates the values of peak sound pressure amplitude and bubble radius for bubbles that grew smaller and, hence, were below threshold. The symbol ○ indicates bubbles that grew larger; they were above the threshold. The solid curves are calculated thresholds for isothermal and adiabatic pulsations of the bubble. These curves were calculated from Eq. 8, which is derived later. The adiabatic threshold curve is consistent with the observations, and, with a few exceptions, this curve separates the conditions for growing and dissolving bubbles.

In a review of the thermal properties of pulsating gas bubbles, Devin[5] defines a parameter α that indicates the proximity of the bubble motion to isothermal or adiabatic behavior. Values of γ/α range from 1, for an isothermal process, to 1.4, for an adiabatic process in which the ratio of specific heats γ is 1.4. For the experimental conditions, computed values of γ/α range from 1.07, for a bubble radius of 50 μ, to 1.27, for a bubble radius of 150 μ. Thus, Devin's parameter indicates that the experimental bubbles fall between isothermal and adiabatic behavior, with smaller bubbles closer to isothermal conditions and larger bubbles closer to adiabatic.

In a second series of experiments, the acoustic pressure amplitude was held constant at 0.25 bar. The growth of a single bubble located near the pressure antinode was monitored by means of frequent rise-time measurements. Seventeen different bubbles were observed, and the data were used to compute the average time required for a bubble to grow from selected values of initial and final radius. The observed average times of growth are presented in Table I and compared to calculated times of growth during isothermal and adiabatic pulsations. The observed times are considerably shorter than the calculated times. Bubble radii were observed to increase from 120 to 180 μ, for example, in

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Echo Phase-Comparison Technique and Measurement of Sound Velocity in Water

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A technique is described in which the ultrasonic time delay between successive echoes in an echo train is determined by phase comparison of the echoes with a coherent continuous signal. Corrections for phase shift of an echo upon reflection from the face of a transducer and for diffraction effects are discussed. The velocity of sound at 1 MHz in distilled water from 23° to 75°C has been measured with this technique. Measurements of time delay are accurate to 20 ppm while the over-all accuracy is 127 ppm or ±0.20 m/sec. Excellent agreement with values in the literature is found.

I. INTRODUCTION

Ultrasonic pulse techniques for the measurement of sound velocity in solids and fluids have become well developed in recent years. For ultimate accuracy and sensitivity, these techniques must measure time delays with a resolution much smaller than one cycle of the carrier frequency. This usually involves some type of phase comparison. Ultrasonic delays are determined by comparing the phase of an echo in an echo train with that of another echo[1–5] or with a coherent continuous wave at the carrier frequency.[6–10] It is the purpose of this paper to present an application of a standard phase-comparison technique of the latter type (phase-sensitive detection or homodyne technique) to measurement of the absolute velocity of sound. The necessary corrections for diffraction and for phase shift of a pulse on reflection are discussed. Data on sound velocity in distilled water are given and compared in detail with similar measurements by McSkimmin[12] and other authors who used different techniques.

[1] H. J. McSkimmin, J. Acoust. Soc. Amer. 33, 12–16 (1961).
[2] E. P. Papadakis, J. Acoust. Soc. Amer. 42, 1045–1051 (1967).
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[8] R. J. Blume, Rev. Sci. Instrum. 34, 1400–1407 (1963).
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[10] W. M. Whitney and C. E. Chase, Phys. Rev. 158, 200–214 (1967).
[11] R. C. Williamson and C. E. Chase, Phys. Rev. 176, 285–294 (1968).

I. METHOD

A. Standard Phase-Comparison Technique

Before describing the manner in which the phase-comparison technique can be applied to measurements of absolute velocity, a general description of the technique in its usual form is in order. A block diagram of the circuitry is shown in Fig. 1. The output of a signal generator is fed through a gated amplifier to provide a burst, which excites the transmitting transducer. The signal generated in the receiving transducer (or in the dual purpose transmitting transducer) by the train of echoes bouncing back and forth between the transducers is amplified and mixed in the phase detector (mixer) with a continuous reference signal from the signal generator.

By means of a variable delay line, the phase of the reference signal can be placed in quadrature with the received signal of a chosen echo thus giving a null output from the phase detector during the receipt of that echo. As the ultrasonic delay changes, the setting of the delay line can be changed to maintain the null condition. Changes of delay-line settings are thus equal to changes in delay of the ultrasonic signal.[9–11] Alternately, the frequency of the signal generator can be varied to maintain a null condition.[7] Because these are null techniques, they can be made extremely sensitive

[12] H. J. McSkimmin, J. Acoust. Soc. Amer. 37, 325–328 (1965).

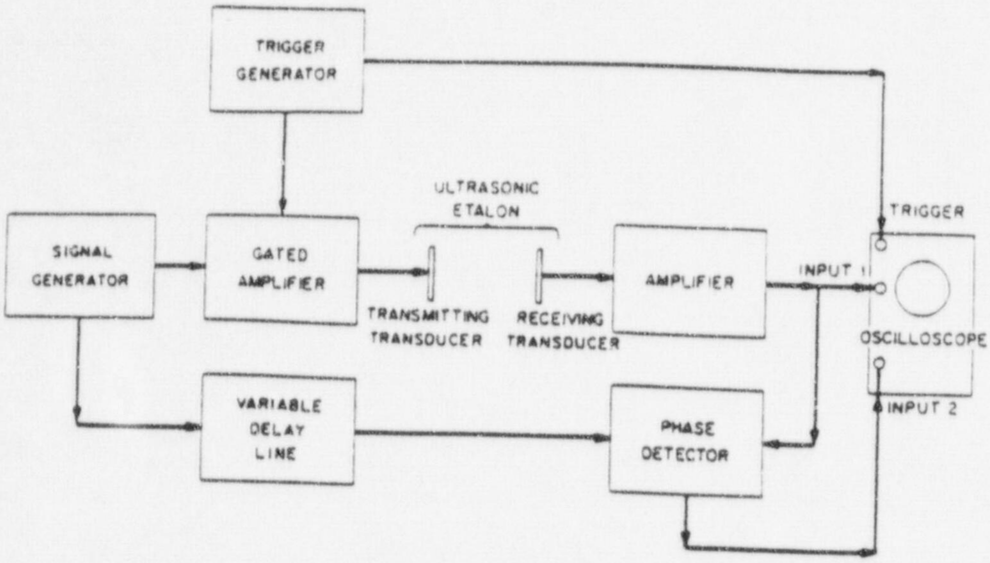

FIG. 1. Schematic diagram of ultrasonic phase-comparison circuitry.

to small phase shifts. Sensitivities of 10^{-3} signal periods are routinely obtainable and, with an ultrasonic path containing 10^3 wavelengths, this results in an over-all sensitivity of 1 ppm.

In situations where high attenuation exists, phase-comparison techniques have another distinct advantage over other velocity-measurement schemes. The circuit shown in Fig. 1 is essentially that of a phase-sensitive coherent detector. By using a boxcar integrator at the phase-detector output gated on a particular echo (usually the first when high attenuation exists), it is possible to measure ultrasonic delay and attenuation even when the signal is buried in receiver noise.[13]

With all the advantages of the phase-comparison technique enumerated above, the standard application of the technique has been of limited usefulness because it is capable of measuring only changes in ultrasonic delay caused by *in situ* changes in experimental parameters, e.g. temperature or pressure. With the technique described above, it is not possible to measure the total ultrasonic delay across a fixed path and thereby determine the absolute sound velocity.

The technique described in this paper is a means of using the standard circuit shown in Fig. 1 to measure the velocity of sound to high accuracy. As is shown, the technique is competitive with any existing means for the accurate measurements of absolute sound velocity and is simultaneously able to exploit the unique capabilities of phase-sensitive detection for measurement of small velocity changes and highly attenuated signals.

B. Echo Phase Comparison Technique

Consider the arrangement of transducers and specimen shown in Fig. 2. When a short burst gated from the signal generator (Fig. 1) is applied to the transmitting transducer, a series of echoes will be detected by the receiving transducer. The frequency of the signal generator and the phase of the reference can be adjusted until the reference signal is simultaneously in quadrature with the received signal during all of the echoes. This condition is shown in Fig. 2. When the reference and received signals are mixed in the phase detector, a null output will result for every echo, and for this "null condition" we can say

$$T = n\tau = \frac{n}{f}, \tag{1}$$

where T is the time delay between echoes; n, an integer; and $\tau = 1/f$, the period of carrier frequency. The values of f that satisfy Eq. 1 are referred to as "null frequencies."

By obtaining this null condition for a series of values of n, it is possible to determine the value for n for any given null frequency and thus to determine T.[14] From the value of T and the path length between the transducer faces d, the ultrasonic velocity u can be determined:

$$u = 2d/T' \approx 2df/n,$$
$$T' = \text{ULTRASONIC DELAY} \approx T. \tag{2}$$

The small corrections, which are applied to the measured delay T in order to obtain the ultrasonic delay T', are discussed later.

Let us examine, more generally, the form of the phase-detector output for arbitrary frequencies. The output E of a balanced mixer (phase detector) is pro-

[13] R. C. Williamson, "Measurement of the Velocity and Attenuation of Ultrasonic Pulses in the Presence of Noise," Rev. Sci. Instrum. 40, 670–674 (1969).

[14] In situations where it is not possible to make measurements over a sufficiently wide range of frequencies to determine n, a less accurate value for the sound velocity may be obtained from $u = 2d\Delta f/\Delta n$.

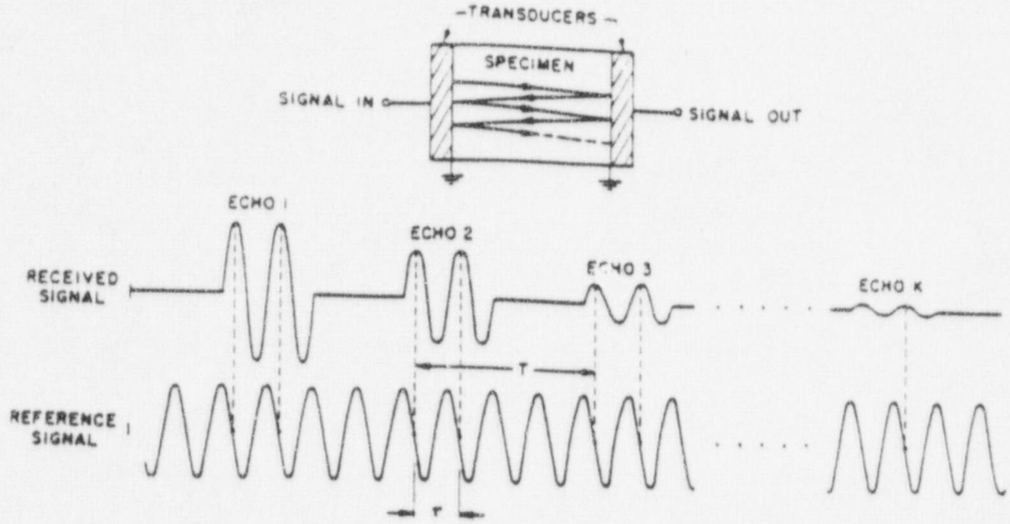

FIG. 2. Schematic diagram illustrating the phase relationships of the received and reference signals for a null condition.

portional to the amplitude of the received signal and a sinusoidal function of the phase difference θ between the references and the received signals. For the kth received echo with amplitude A_k,

$$E_k = A_k \sin\theta_k. \qquad (3)$$

The time delay and amplitude of the kth echo are given by[15]

$$T_k = (k-\tfrac{1}{2})T = (k-\tfrac{1}{2})/f_0, \qquad (4)$$

$$A_k = A_0 e^{-2\alpha d(k-\frac{1}{2})}, \qquad (5)$$

where α is the attenuation constant, and k the echo number. Therefore,

$$E_k = A_0 e^{-2\alpha d(k-\frac{1}{2})} \sin(2\Pi(k-\tfrac{1}{2})f/f_0+\phi). \qquad (6)$$

The difference in electrical delay between the reference and signal paths (Fig. 1), including delay in the delay line, is absorbed in the phase angle ϕ.

When ϕ is adjusted to 0° or 180° (with the variable delay-line), E_k is zero for all echoes (all k's), whenever $f = nf_0$ and n an integer. This is the null condition. In practice, the delay line must be adjusted slightly to obtain nulls at different values of n because phase shifts that occur in the electronics and in the acoustical coupling change with frequency.

When f is not an integer multiple of f_0, we can write

$$f = (n+x)f_0, \quad |x| < \tfrac{1}{2} \qquad (7)$$

and

$$E_k = A_0 e^{-2\alpha(k-\frac{1}{2})d} \sin(2\Pi(k-\tfrac{1}{2})x+\phi). \qquad (8)$$

In this case, the phase-detector output is a damped sinusoidal function of the echo number k with period equal to $1/x$. Figure 3 shows the phase-detector output for ultrasonic transmission through water at $f \approx 1$ MHz for various values of f and ϕ. The damped sinusoidal form of the output predicted by Eq. 8 is evident.

The accuracy with which null frequencies can be determined depends on the precision with which the phase of echoes far out in the echo train can be resolved. This in turn depends on the attenuation constant α, the noise level in the system, how well the phase within each echo is defined, the capabilities of the phase detector, and the number of wavelengths in the ultrasonic path. As a result, the precision varies considerably from one experiment to another. However, a general idea of the considerations involved can be obtained from the following example, which approximately corresponds to the measurements in distilled water that are discussed later.

Consider the situation in which the phase difference between the 11th echo in an echo train and the reference signal can be resolved to within 10^{-2} signal periods τ. Further echoes are discarded since the resolution of their phase rapidly deteriorates owing to increased attenuation. If the round trip delay between successive echoes is $10^2\ \tau$, the delay between the first and 11th echo is $10^3\ \tau$. Therefore, the over-all time (or frequency) resolution is $10^{-2}\ \tau$ out of $10^3\ \tau$ or 10 ppm.

Although the time delay between any two selected echoes in an echo train can be measured as described above, the null frequencies are actually determined by viewing an over-all scope display described by Eq. 8, not by careful attention to any given pair of echoes. It is, therefore, instructive to view, in an alternate way, the precision with which the null frequencies can be determined. The smallest value of x that can be resolved, δx, is reached when x, the frequency of the damped oscillation, becomes small compared to the damping rate $2\alpha d$. The fractional resolution in null frequency or time delay is $\delta x/n$ (see Eq. 7). Note that at the crossover point where $\delta x = 2\alpha d$, the resolution $= 2\alpha d/n = \alpha\lambda = \Pi/Q$, where $\alpha\lambda$ is the attenuation per

[15] For the situation in which only one transducer is used as both transmitter and receiver, k should be substituted for $(k-\frac{1}{2})$ in these equations.

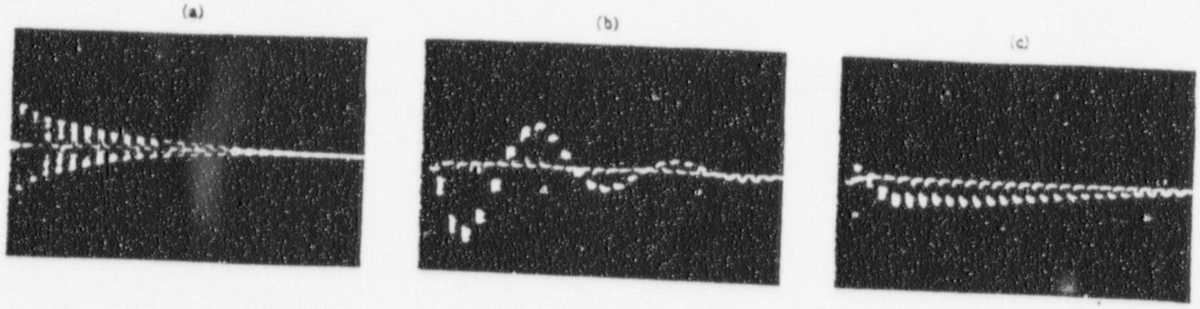
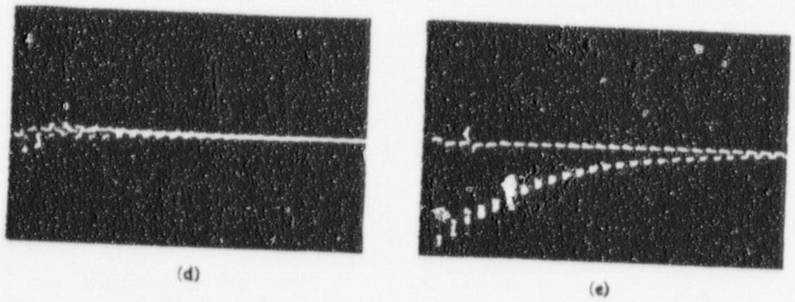

FIG. 3. (a) Unrectified echo train transmitted through water; (b) phase detector output for $f=70.100\ f_s$, $\phi=180°$ in Eq. 6 of the text; (c) same for $f=70.010\ f_s$, $\phi=180°$; (d) same for $f=70.000\ f_s$, $\phi=180°$; (e) same for $f=70.000\ f_s$, $\phi=-90°$. Total sweep length is 2 msec in all cases.

wavelength in the sample and Q, the mechanical quality of the sample. In our example, $2\alpha d \approx 10^{-1}$ and therefore, resolution is limited to values of x of the order of 10^{-4}. The value of n in Eq. 7 is about 100 (number of signal periods in one round trip delay) and the over-all frequency resolution is therefore 10 ppm, as obtained previously.

C. Corrections for Phase Shift upon Reflection

The time-delay T between successive echoes in an echo train differs from the ultrasonic delay $T'=2d/u$, whenever a nonzero phase shift, γ, occurs upon reflection at a transducer–sample interface. For a two-transducer arrangement (two identical reflections in each round trip)

$$T'-T=2(\gamma/2\Pi)(1/f),$$

or

$$fT'-n=2(\gamma/2\Pi). \tag{9}$$

Therefore, in order to obtain T' from the measured T, it is necessary to calculate γ accurately or to arrange the experimental apparatus to make γ as close to 0° or 180° as possible. In practice, the latter course is usually chosen.

The reflection coefficient r at a transducer–sample interface is given by

$$r=|r|e^{i\gamma}=(Z-Z_s)/(Z+Z_s) \quad \text{(for pressures)}, \tag{10}$$

where Z is the acoustic input impedance to the transducer assembly (including effects of electrical loading, bonding materials and backings, when present) and Z_s is the acoustic impedance of the specimen (usually assumed to be pure real). According to Eq. 10, $\gamma \approx 0°$ or 180°, whenever (a) $|Z| \ll |Z_s|$; (b) $|Z| \gg |Z_s|$; or (c) Z a real number.

The technique for minimizing γ for measurements in solids has been discussed by several authors.[1–4] For solids, the characteristic impedance of the transducer material Z_T is often close to Z_S. In this case, the object is to approach Condition a by operating the transducers at resonance since in the ideal case where effects of bonds and electrical loading are neglected,

$$Z=iZ_T \tan \Pi f/f_r, \tag{11}$$

and Z goes to zero when the signal frequency f is equal to the resonant frequency f_r.

For measurements in fluids, Condition c can be obtained by the use of buffer rods.[12] This technique has the disadvantage of limiting the length of the echo train, which may be examined before unwanted echoes interfere.

A simple alternate to the use of buffer rods is described here. Since Z_S for most fluid–transducer combinations is smaller than Z_T, the attainment of Condition b is suggested. Consider an open-circuited, lossless transducer with resonant frequency f_r immersed in a fluid medium of impedance Z_S. In this case, the input impedance Z for a planar acoustic wave incident on the transducer is

$$Z=Z_T\left[\frac{iZ_T \sin \Pi f/f_r + Z_s \cos \Pi f/f_r}{Z_T \cos \Pi f/f_r + iZ_S \sin \Pi f/f_r}\right]. \tag{12}$$

Under the assumptions $Z_S \ll Z_T$ and $\Delta f/f' \ll 1$, where $f'=f_r/2$ and $\Delta f=f-f'$, γ in Eq. 10 is given by:

$$\gamma/2\Pi=-(\tfrac{1}{2})(\Delta f/f')(Z_S/Z_T). \tag{13}$$

At $\Delta f=0$, $\gamma=0°$, and the transducer is operating as a quarter-wave termination with infinite input impedance. This is the technique that was used in the measurements of sound velocity in distilled water, which are described in this paper.

II. SOUND VELOCITY IN DISTILLED WATER

A. Introduction

Distilled water provides a good specimen for testing and comparison of different sound velocity measurement techniques. Water is stable, readily available, has fairly constant acoustic properties and is relatively unaffected by impurities, particularly dissolved air.[16]

Many measurements of sound velocity in water have been made and good data exist in the literature with which to make comparisons. However, as Greenspan[17] and McSkimmin[12] have pointed out, considerable disagreement exists between quoted values of absolute velocity. McSkimmin has made a study of the absolute sound velocity with a technique of high absolute accuracy and his values therefore provide a good standard of comparison. As is shown later, our values for sound velocity agree quite well with those of McSkimmin.

B. Experimental Apparatus

The electronic circuit used is basically the same as that shown in Fig. 1. For ease in setting and measuring frequency, a frequency synthesizer was used as the signal generator. The phase detector was a modified AC–DC converter.[18] A diode switch followed by a power amplifier served as the gated amplifier. The remainder of the circuit was composed of standard commercial components.

The ultrasonic transducers were two 1-in. diam x-cut, quartz crystals, resonant at 2 MHz. These crystals were fully plated on both sides and spring loaded against opposite ends of an accurately machined brass spacer. The length of the spacer at room temperature ($\approx 25°C$) was measured with a micrometer. Several measurements were made around the circumference of the spacer, and were averaged to compute the path length $d=5.1517\pm0.0004$ cm. The spacer was constructed such that the region surrounding the ultrasonic path contained no solid material except for two narrow brass posts, which supported the opposing transducer holders with respect to each other. By placing these supporting posts about 1 cm beyond the outside edges of the transducers, the ultrasonic path was essentially free of obstructions and the sound propagation was free field.

The transducer assembly was directly immersed in a temperature-controlled water bath filled with the distilled water specimen. The temperature of the bath was read on a $-1°$ to 101°C (0.1°C division) mercury in glass thermometer supplied with the National Bureau of Standards certification. When fully immersed, the indicated thermometer corrections usually amounted to less than 0.03°C. At the higher temperatures, emergent stem corrections of as much as 0.2°C were required.

[16] M. Greenspan and C. E. Tschiegg, J. Acoust. Soc. Amer. 28, 501 (1956).
[17] M. Greenspan, J. Acoust. Soc. Amer. 31, 847(A) (1959).
[18] Pacific Measurements model 1008.

C. Method

At a few temperatures, null conditions were obtained for a series of frequencies above and below 1 MHz. By making such measurements over a sufficiently wide range of frequencies, it was possible to determine unambiguously the proper value of n for each null frequency (Eq. 2). At each temperature, the delay T was calculated for each of the null frequencies (Eq. 1). The values of T obtained in this way differed by a small amount due to the frequency-dependent phase shift γ predicted by Eq. 9. The value of T at 1 MHz, half the resonant frequency, was assumed to be equal to the ultrasonic delay T' since Eq. 13 implies $\gamma=0$ at this frequency. Representative data at a temperature of 25°C are presented in Table I.

The third column of Table I represents the phase shift upon reflection as obtained from Eq. 9, where T' is the ultrasonic delay computed for $f=1$ MHz by interpolation between the values of T computed at the null frequencies. The quantity $\gamma/2\Pi$ should vary according to Eq. 13. However, the data in Column 3 have a slope versus frequency approximately twice as large as the predicted value. This result is probably due to electrical and mechanical loading effects on the transducer, which are not accounted for in Eq. 9. More important, such effects may cause the frequency at which $\gamma=0$ to shift away from 1 MHz. If we make the assumption that the frequency at which $\gamma=0$ is within $\pm2\%$ of 1 MHz, we can use the slope of the data in Column 3 to estimate the possible error intro-

TABLE I. Null frequencies and phase-shift upon reflection in water at 25.00°C.

Frequency (MHz)	Number of wavelengths per round trip	$fT'-n$ (Ref. a) (% of a cycle)
0.90105	62	1.9
0.91555	63	1.7
0.93004	64	1.5
0.94453	65	1.2
0.95900	66	0.8
0.97348	67	0.5
0.98798	68	0.3
1.00246	69	−0.1
1.01696	70	−0.3
1.03142	71	−0.7
1.04589	72	−1.1
1.06037	73	−1.5
1.07487	74	−1.7
1.08939	75	−1.7

a See text.

TABLE II. Uncertainties.

Quantity	Uncertainty	Uncertainty in velocity (%)
Temperature	±0.03°C (25°C)	±0.0053
	±0.04°C (50°C)	±0.0032
	±0.05°C (75°C)	±0.0000
Path length	±0.0004 cm	±0.0080
Thermal expansion	±0.0000 cm (25°C)	±0.0000
	±0.0001 cm (50°C)	±0.0025
	±0.0002 cm (75°C)	±0.0059
Frequency	±20 Hz at 1 MHz	±0.0020
Phase shift upon reflection	±0.004 cycles	±0.0057
Diffraction	...	±0.0050
Over-all	±0.20 m/sec (all T)	±0.0127

duced by a nonzero γ at 1 MHz. The resulting uncertainty is ±0.004 cycles.

Once n for each null frequency has been determined at a given temperature, it is not necessary to repeat the whole procedure at nearby temperatures if the change in sound velocity is sufficiently small. Over most of the temperature range, measurements were made only for a small range of frequencies close to 1 MHz and the value of the ultrasonic delay and sound velocity at 1 MHz were interpolated from these measurements.

The final value for the sound velocity was obtained by applying a correction for the thermal expansion of brass (17 ppm/°C) and for effects of diffraction. The magnitude of the diffraction correction for each echo was computed from the equations and empirical study by McSkimmin.[19] Beyond the third echo, this correction was relatively constant at $-(1.8\pm0.5)\times10^{-4}$ for all visible echoes. Therefore, when determining the frequencies for the best null conditions, the first two or three echoes were ignored and a constant correction was applied for all the remaining echoes.

D. Uncertainties

The major sources of possible error in this experiment are listed in Table II. As can be seen from the Table, the largest source of error is uncertainty in the path length and in the correction for thermal expansion. The values listed for thermal expansion and diffraction in Table II are the uncertainties in the magnitude of the correction to the measured sound velocity and are not equal to the magnitude of the corrections themselves. The fact that the uncertainty in frequency is among the smallest in Table II indicates that the echo phase-comparison technique has capabilities for measuring time delays that have not been fully exploited in these measurements. The over-all uncertainty of ±0.013% or ±0.20 m/sec is computed by treating all values in Table II as random errors.

[19] H. J. McSkimmin, J. Acoust. Soc. Amer. 32, 1401–1404 (1960).

TABLE III. Velocity of sound in distilled water as a function of temperature.

Temperature (°C)	Velocity (m/sec)	Δ (Ref. a) (m/sec)
22.97	1491.07	0.03
23.98	1493.87	0.01
25.00	1496.65	0.00
26.01	1499.29	0.06
26.97	1501.70	0.03
28.00	1504.31	0.02
29.00	1506.71	−0.01
30.00	1509.10	−0.07
35.00	1519.85	0.03
40.00	1528.92	0.09
45.00	1536.42	0.05
50.00	1542.56	−0.01
55.00	1547.41	0.05
60.00	1551.13	0.17
65.04	1553.61	0.19
70.00	1554.90	0.09
73.00	1555.22	0.15
74.00	1555.30	0.21
75.00	1555.30	0.22

a Comparison with Ref. 12. See text.

It should be noted that the frequency of 1 MHz used in these measurements is much lower than the frequencies normally used in ultrasonic pulse measurements. If, for example, a frequency of 30 MHz were used, the number of wavelengths in a round trip (n in Eq. 7) would be 30 times as large and the corresponding accuracy would be 30 times greater. In addition, diffraction effects would be much smaller. However, the increased accuracy obtainable by going to higher frequencies is limited by the correspondingly higher attenuation, which limits the number of usable echoes. More fundamentally, it is difficult with any technique at any frequency to obtain a velocity resolution much less than the inverse of the mechanical quality of the sample.

E. Results

Table III shows the data obtained in this experiment over the temperature range from 23° to 75°C. These data are compared with the values obtained by interpolation from the data of McSkimmin,[12] whose values are lower than those listed by Δ. Excellent agreement is obtained up to 55°C. Above this temperature, the agreement is not as good, but Δ remains within the combined uncertainties of our measurements (McSkimmin[12]: ±0.10 m/sec, this work: ±0.20 m/sec). These measurements confirm the accuracy of McSkimmin's results and indicate the accuracy and usefulness of the echo phase-comparison technique.

Recently, very accurate measurements of sound velocity in water have been made by Carnvale *et al.* at the Naval Oceanographic Office.[20] Our data overlap

[20] A. Carnvale, P. Bowen, M. Basileo, and J. Sprenke, J. Acoust. Soc. Amer. 44, 1098–1102 (1968).

theirs at four points, 25°, 30°, 35° and 40°C. The differences in the sound velocities that we measure are (this work—NAVOCEANO): −0.04, +0.04, +0.10, and +0.10 m/sec, respectively. Again, agreement within the stated accuracy is obtained.

A comprehensive comparison with other data in the literature can be made by referring to Refs. 12 and 21. Our data agree quite well with all of the most accurate measurements except those of Greenspan and Tschiegg[22] and Wilson,[23] whose values for velocity lie consistently higher than ours.

[21] R. A. McConnell and W. F. Mruk, J. Acoust. Soc. Amer. 27, 672–676 (1955).

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[22] M. Greenspan and C. E. Tschiegg, J. Acoust. Soc. Amer. 31, 75–76 (1959).

[23] W. D. Wilson, J. Acoust. Soc. Amer. 31, 1067–1072 (1959).

Question 29:

How is the LEFM used currently to provide correction factors to the venturis? Is the correction determined on the basis of the absolute accuracy or the repeatability of the LEFM?

Answer:

The LEFM is used at Comanche Peak to directly calibrate the nuclear instrumentation. The correction factor is used only to keep the venturi calibration contemporary for use in the event that the LEFM is unavailable.

A correction factor is calculated in accordance with a plant procedure which has its methodology based on approved calculation. A minimum of 50 separate two hour data sets of FW mass flow rate from the LEFM and venturis are recorded in a spreadsheet. The percent difference of each data set, the average percent difference of all data sets, and the standard deviation of all data sets is calculated. The correction factor is calculated from the average percent difference plus the two standard deviation margin. The spreadsheet calculation is independently reviewed, documented by a TE, and given to the System Engineering Computer Group to implement in the appropriate plant computer software under an approved change process.

The Plant Computer multiplies the feedwater flow rate as determined by the venturis by the correction factor. This correction is displayed on the plant computer as "NET LEFM CORRECTED POWER" and is available for use when the LEFM is out of service. The LEFM is used directly when it is in service. The 2 standard deviation margin used in the correction factor calculation prevents this corrected MWth from being equal to the MWth calorimetric power determined directly from the LEFM.

The correction is based on the absolute accuracy of the LEFM but a high degree of repeatability is also required.

Attachments:

None.