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Towards the validation of ultrasonic flowmeters operating in hydrogen-enriched natural gas mixtures through speed of sound measurements obtained by a clamp-on meter

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ABSTRACT

New flow metering challenges are presented by the energy transition program since the available and new infrastructures might be used to transport energy using energy vectors, such as hydrogen-enriched natural gas mixtures, including blends never adopted before in current distribution lines. In this framework, it is necessary to have the possibility to verify the performance of flowmeters, which are currently calibrated using natural gas and nitrogen as reference fluids, even when operating with fluids that are not yet in use. For this reason, a commercial clamp-on ultrasonic flowmeter was used to measure the speed of sound in a mixture of hydrogen and iso-butane after being calibrated using helium as reference fluid. Helium is actually much more expensive than nitrogen, but in our case it is advantageous because, in the temperature and pressure ranges considered in this work, the speeds of sound of helium are more comparable with those of the binary mixture of hydrogen and isobutane than the speeds of sound of nitrogen under the same thermodynamic conditions. A specifically developed control apparatus was designed to adjust the temperature and the pressure of the gas filling a DN50-PN100 spool where the ultrasonic meter was mounted on. The instrument was calibrated for temperatures between (270 and 320) K and for pressures up to 3 MPa by using the prediction of the reference equation of state for helium of Ortiz-Vega et al. The measurements of the speed of sound were obtained in a binary mixture containing mainly hydrogen with a small content of iso-butane since, for these compounds, new results are necessary to validate and improve the predictions of thermodynamic models installed in flowmeters and in flow computers. The expanded relative uncertainty was evaluated to be of 0.09% ($k = 2$) that was estimated by considering the contributions of the main influence quantities, repeatability and reproducibility of the measurements. The obtained results were compared with the AGA-8-92DC and GERG-2008 equations of state and found to be consistent with the values predicted by both models, demonstrating the feasibility of using a clamp-on ultrasonic flowmeter to determine the speed of sound and possibility to verify the performance of flowmeter installed on the gas networks using the speed of sound as transfer quantity.

1. Introduction

The reduction of carbon dioxide and polluting gases emissions in the atmosphere has become an increasingly central concern in the environmental and industrial policies of the world's most important economies. Furthermore, the European Green Deal [1] sets an ambitious goal of achieving carbon neutrality in the entire European Union by 2050. In this framework of energy transition, the adoption of hydrogen as a carbon-free vector is increasingly recognized as a pivotal strategy for achieving global decarbonization goals [2–5] however, a realistic first step, towards the carbon-free energy distribution, is to introduce mixtures of hydrogen and natural gas to reduce significantly the carbon footprint and to meet the targets of the Green Deal [3,6–8].

Unfortunately, blending the natural gas with increasingly higher content of hydrogen can deteriorate and corrode pipeline as well as storage materials. For this reason a 5 mol% limit is imposed for many end-user applications [9], while for Power-to-Gas applications the amount of H_2 in the gas grid is limited by country specific standards and regulations to a maximum of 12 mol% [10]. Finally, several studies on the hydrogen tolerance of various appliances with combustion processes identify a limit of 25 mol% for the hydrogen content [11–13]. Considering that the content of hydrogen in the gas grid is expected to increase in the coming decades, an growing heterogeneity in the thermodynamic properties of hydrogen enriched mixtures is expected. In this context, technical guidelines and new standards are expected to

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be reviewed in terms of possible hydrogen applications and limitations, when necessary.

Today, the standard models for describing the properties of hydrogen blends are SGERG-88 [14] and AGA-8-92DC [15] equations of state, here referred to as AGA-8. The first is older and does not consider the full composition of the mixture but only its calorific value and the content of CO_2 and H_2. For SGERG-88, the formulation has a limitation of 10 mol% with respect to H_2 concentration and when the hydrogen content approach the 15 %, the formulation does not converge and density cannot be calculated. AGA-8 calculations converge even when the content of hydrogen is close to 100 % however the equation is not validated for a hydrogen content higher than 30 %. Nevertheless, the AGA-8 model is prescribed as the standard for the calculation of natural gas and similar mixtures in the gaseous state in the standard ISO 12213-2 [16], where the content of hydrogen is limited to 10 mol%. Moreover, GERG-2008 standard model [17], which is also an ISO standard (20765-2) [18], has been shown to provide reliable results for hydrogen concentrations up to 30 mol% in typical pipeline conditions [19]. Considering the diffusion of SGERG-88 model in flow computers, the equation has been modified to calculate the compression factor of mixtures with hydrogen concentrations up to 100 mol% [20], although the improved version showed to deviate up to 0.3% for temperatures below 293 K and for pressure higher than 5 MPa.

Considering that international standards are used by flowmeters and by flow computer for billing, for simulations and for operations in many engineering processes, it is urgent to validate the models by measuring accurately the thermodynamic properties of mixtures with high hydrogen content. However, it is to be expected that, in the near future, new thermodynamic models will be implemented specially designed to adapt to the presence of elevated and variable hydrogen contents in gas grids.

Among the properties suitable for the validation of standard models, the measurement of the speed of sound of hydrogen-enriched gas blends can be particularly suitable since it is one of the most useful properties needed to implement accurate equations of state along with density, vapor pressure and specific heat.

The step from the improvement of thermodynamic models to the meters calibration is straightforward however the latter reserves some peculiarities. For example, meters may work with a gas which composition changes significantly before the gas-chromatographs can provide the new composition. In this case, the possibility to timely reveal the variations by speed of sound, in combination with a validated model for predicting the properties of the gas, allows to correct the apparent measurement of flow.

Furthermore, current state-of-the-art flow measurement techniques, including traditional methods such as orifice meters and turbine meters, often face challenges when applied to hydrogen-enriched mixtures due to hydrogen's low density and high diffusivity [21–23]. These limitations can lead to inaccurate flow readings, which pose risks in safety, efficiency, and regulatory compliance. Consequently, there is a growing interest in non-invasive flow measurement methods, such as ultrasonic flowmeters, which offer advantages in terms of reduced pressure drop and the ability to measure flow without interrupting the pipeline, with the additional advantage of requiring minimal maintenance and having high flexibility [24].

This enforces the need to use specific facilities and instruments, or to modify existing ones, that are compatible with the use of hydrogen [25].

The need for effective calibration techniques tailored to the specific properties of these mixtures remains a critical research area. Being able to perform new experimental measurements of the speed of sound in hydrogen-enriched gas mixtures can have an impact on the accuracy of the calibration of industrial ultrasonic flowmeters. These sensors, often used as fiscal instruments for measuring volumetric flow rates, are based on the measurements of the time-of-flight of acoustic tone-burst propagating within the flowing fluid. Moreover, all of them are already able to provide additional information and directly measure the speed of sound that, unfortunately, is not used for improving the accuracy of the flow measurements because the meter is calibrated only for flow measurements and not for speed of sound measurements.

Exploiting the measurement of the speed of sound in a gas opens up possibilities that are not yet deeply explored. One of the most interesting is the possibility to verify the meter on-site by comparing the measured speed of sound with that of a calibrated reference instrument. In particular, one class of ultrasonic flowmeters that look very promising in terms of on-site verification are the clamp-on ultrasonic flow meters, of which recent studies have proven the potential of accurate flow measurement in a variety of gas mixtures, including those containing hydrogen [26–28], and of which this work aims to demonstrate the possibility of their use also as accurate speed of sound meters in the same mixtures. In this context, it is therefore useful to explore the potential of using clamp-on flowmeters characterized in the laboratory, directly in-line alongside ultrasonic flowmeters, so as to increase the latter's flow measurement accuracy by comparing the speeds of sound obtained from the two types of meters.

In this work, we discuss the possibility of using a commercial clamp-on flow meter that was installed on a DN50-PN100 spool equipped with sensors and actuators needed to control the temperature and the pressure of the gas filling the pipe. To calibrate the meter, pure helium was used for which a well established reference equation of state is available [29].

Using the reference values and the apparent speed of sound measured by the meter, the calibration curve has been obtained in a wide range of temperatures and pressures. The clamp-on flow meter was then used again to measure the speed of sound of a blend of hydrogen and isobutane. The experimental values of the obtained speed of sound were then compared with the expected values and found to be consistent with the values predicted by both AGA-8 model and GERG-2008.

By proving the effectiveness of speed of sound measurements using a calibrated ultrasonic flow meters, this study aims to contribute to investigate the possibility of alternative procedures for the on-site verification and, possibly in the future, the calibration of ultrasonic flow meters installed on pipe lines carrying hydrogen both pure or blended.

2. Description of the ultrasonic flowmeter

A fresh view for measuring the speed of sound in gasses is presented in this paper. In fact, among all the different existing methods and approaches normally used to determine the speed of sound by laboratory instruments, here we chose to investigate the feasibility of using an ultrasonic flowmeter specifically modified and characterized under laboratory conditions. The chosen device is a clamp-on meter designed for noise-free, reliable readings and will be optimized specifically for industrial applications. Ultrasonic clamp-on flowmeters are able to measure the flow rate of a fluid inside a pipe by using sound waves to determine the transit time of a gas or liquid. Compared to industrial fixed ultrasonic flowmeters, which are semi-permanently mounted along the distribution lines, clamp-on flowmeters are easy to install without interrupting the process and are quite accurate and versatile for a variety of industrial applications, fluids and pipe thicknesses. On the other hand, the behavior of the clamp-on flowmeter and its performance strongly depend on the conditions under which it is assembled, mounted, configured and characterized. For example, the distance between the ultrasonic transducers, their coupling with the pipe walls, the geometry that defines the acoustic paths, and the dimensions of the pipe are crucial parameters for accurate and repeatable volumetric flow rate measurements, because they influence the transit time between the two transducers, which mount to the outside of the pipe working as transmitter and receiver. By knowing the pipe size and measuring the difference in the transit time of an ultrasonic wave traveling within the

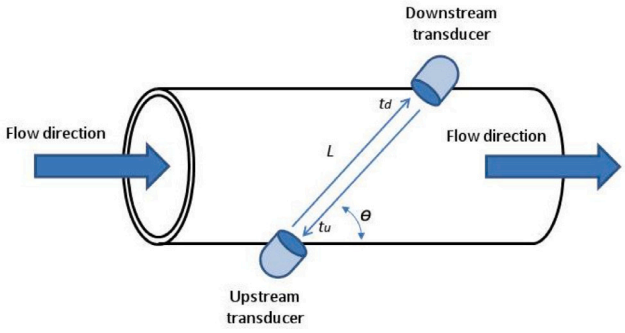

Fig. 1. Scheme of an ultrasonic flowmeter. L is acoustic transit path, θ is the angle of incidence of the acoustic wave at the interface between the pipe wall and the fluid, and t_u and t_d are the upstream and downstream transit time respectively.

flowing fluid both upstream and downstream, the meter determines the fluid speed, v, and calculates its flow rate, using the Eq. (1).

$$v = \frac{L}{2\cos\theta}\frac{t_u - t_d}{t_u t_d} \tag{1}$$

where L is acoustic transit path, θ is the angle of incidence of the acoustic wave at the interface between the pipe wall and the fluid, while t_u and t_d are the upstream and downstream transit time respectively. On the other hand, the geometric properties of the system composed of the flowmeter and the pipe, which is shown in a simplified scheme in Fig. 1, enables the relationship between the fluid speed, v, and the speed of sound, w, to be described through the following system of equations:

$$w - v\cos\theta = \frac{L}{t_u} \tag{2}$$

$$w + v\cos\theta = \frac{L}{t_d} \tag{3}$$

From these relationships, the speed of sound can be calculated from the simple measurement of transit times, as:

$$w = \frac{L}{2}\frac{t_u + t_d}{t_u t_d} \tag{4}$$

In the case of moving fluid, the transit time difference $t_u - t_d$ is measured. A flow profile correction is then performed in order to obtain the area averaged flow velocity, which is proportional to the volumetric flow rate. In the case of zero flow, $t_u = t_d$. The transit time is the same in both directions and can be used to measure the speed of sound at a given temperature and pressure.

Therefore, in principle, it is possible to use an ultrasonic flowmeter that has been appropriately configured and characterized to be able to measure the speed of sound instead of the flow rate. The purpose of this work is therefore to investigate the viability of obtaining accurate speed of sound measurements using a clamp-on flowmeter in a reference fluid and to use these results to calibrate the instrument. Specifically, helium was used as the calibration fluid. Then, using the resulting calibration curve, the same clamp-on flowmeter was used to carry out speed of sound measurements in a mixture of hydrogen and isobutane.

Among several clamp-on ultrasonic flowmeters available on the market, the clamp-on device chosen to perform these measurements is the commercial instrument FLUXUS® G721, manufactured and distributed by Emerson's Flexim. This specific model was selected because it provides stable, drift-free flow measurements for pressures starting from 3 bar in gases. Furthermore, besides being an ATEX-certified instrument (zone 1 and 2), it enables transit times and speed of sound measurements to be downloaded in addition to flow data.

In order to characterize the new experimental apparatus, it was required to determine the best possible configuration, namely the best signal-to-noise ratio at laboratory temperature and atmospheric pressure. The instrument set-up can have several different configurations

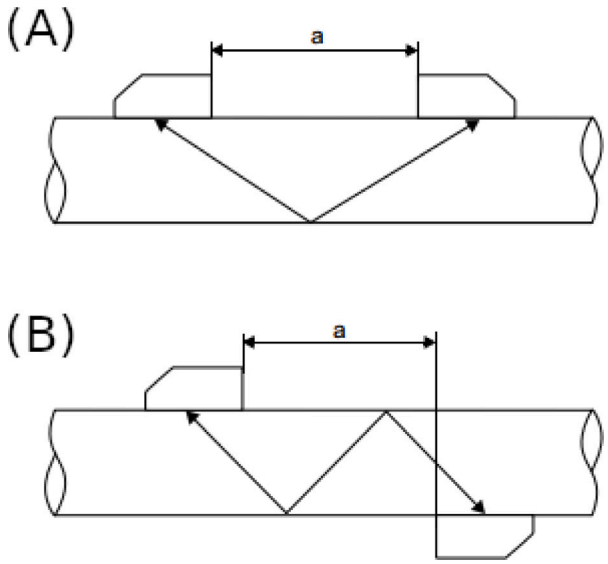

Fig. 2. Example of two possible configurations. (A) reflection arrangement; (B) diagonal arrangement.

from which it is necessary to select the one which maximizes the quality of the acoustic signal received by the transducers. These configurations depend not only on the fluid contained in the pipeline, but above all on the thickness and material of the pipe walls.

Fig. 2 shows the main features that define the possible transducer mountings on the pipe. There are two main possible arrangements: reflection arrangement (A), where the number of sound paths is even and the transducers are mounted on the same side of the pipe, and the diagonal arrangement (B), where the number of sound paths is odd and the transducers are mounted on opposite sides of the pipe. Another crucial parameter for identifying the best device configuration is the distance between the two transducers, a. It depends on the angle of incidence of the ultrasonic wave, then on the fluid, the temperature and pressure involved during the measurement. Finally, the number of acoustic paths, i.e. the number of reflections on the walls of the acoustic wave, must also be defined. As a general principle, increasing the number of sound paths increases the accuracy of the measurement but at the same time, signal attenuation increases as well. It is therefore crucial to determine the optimal number of acoustic paths that best achieve the signal-to-noise ratio.

After a trial-and-error process, a series of tests to find the best configuration has been carried out. Then, it was decided to mount the transducers on the same side of the pipe (reflection arrangement), at about 36.8 mm from each other, so that there would be 4 acoustic paths, which means three reflections on the walls before the acoustic wave, emitted by the first transducer, is received by the second transducer.

Then, a specially developed experimental apparatus has been used, that could maintain stable and controllable thermodynamic conditions, in particular temperature and pressure, throughout the process, in order to obtain accurate measurements from a metrological point of view. This system has also been developed, built and tested in order to be vacuum-proof and, at the same time, pressure-tested. The gas injection and storage system was also built in such a way as to keep the composition of the mixture constant throughout the measurements, which lasted about a month. Fig. 3 shows the schematic diagram of the experimental apparatus designed and built to carry out speed of sound measurements under controlled conditions of temperature and pressure; while Fig. 4 shows two pictures of the actual experimental apparatus used. Since one of the objectives of this work is to investigate the possibility of calibrating industrial flowmeters installed directly

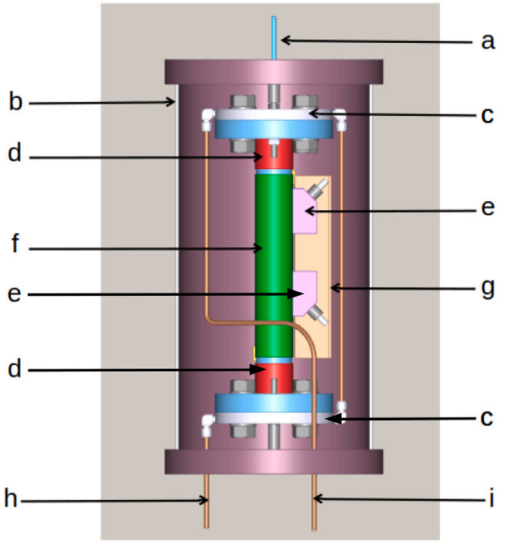

Fig. 3. Schematic diagram of the experimental apparatus. (a) inlet tube; (b) vacuum chamber; (c) DN 50 flange; (d) heat exchanger; (e) ultrasonic transducer; (f) damping mat; (g) Metric-referenced rail; (h) inlet tube for thermal fluid; (i) outlet tube for thermal fluid.

along gas or liquid distribution lines by means of speed of sound measurements, a perfect reproduction of a DN 50 PN 100 spool was realized, which is the industry standard for delivering gas up to 100 bar. This stainless steel tube, with a nominal inner diameter of 50 mm and a wall thickness of 3.5 mm, is used as a pressure vessel and is closed on both sides by two custom-made flanges. These flanges, (c) in Fig. 3, are designed to work as both vessel stoppers and heat exchangers, providing the best configuration to simultaneously allow the flow of a thermal fluid and preserve the structural integrity of the flange as well as the pressure sealing when the vessel is pressurized. To do this, a channel grid inside the flange, shown in Fig. 5, was realized and special Teflon® gaskets were used to seal the flanges. The sample gas is injected into the vessel through an inlet tube, (a) in Fig. 3, while the system temperature is controlled through a thermal fluid flowing through the two flanges, which are connected through an inlet and outlet line, (h) and (i) in Fig. 3, to an external thermal bath. A finer temperature control is possible due to the presence of two independently operating electrical heaters, (d) in Fig. 3, namely two manganin copper wires wrapped in aluminum foil applied to the tube walls. The temperature stability achieved during measurements is better than 10 mK, and the thermal gradient between the top and bottom of the vessel never exceeded 50 mK. Finally, two transducers, (e) in Fig. 3, both used as emitters and receivers of ultrasound waves are clinging through a metric-referenced rail, (g) in Fig. 3, on the tube walls. These are two Lamb wave transducers (ATEX - zone 2 certified), which are specially designed to work with gasses with a carrier frequency of 1MHz. Both are coupled to the walls of the pipe through a viscoelastic polymer layer damping materials, (f) in Fig. 3, used for the gas measurement to reduce acoustic noise influences on the measurement. Temperature is measured with an uncertainty of ±0.02 K by means of two PT100 thermometers placed at the top and bottom of the tube walls. The pressure measurements are obtained by a temperature controlled pressure transducer (Honeywell Super TJE), placed on the hydraulic inlet line of measuring fluid, with an accuracy of ±0.025 MPa and a working range up to 52 MPa.

3. Calibration procedure

Since the aim of this work is to use an instrument, originally designed for flow measurement, to measure the speed of sound instead, it is essential from a metrological point of view to characterize and calibrate it. To do this, it is necessary to compare the measurements performed with a reference fluid whose thermodynamic properties, such as the speed of sound, are very well known. For this reason, we carried out speed of sound measurements in helium before measuring the enriched-hydrogen mixture, so as to obtain a calibration curve for the instrument. Conversely, directly measuring the speed of sound of the mixture with hydrogen, we could not compare them to any reference values, since the GERG-2008 and AGA-8 equations of state, were developed in the absence of experimental speed of sound measurements for mixtures with high hydrogen content. Thus, the developed prototype was first validated under controlled laboratory conditions with accurate speed of sound measurements in helium. These experimental measurements were carried out over six isotherms from (270 to 320) K and for pressures up to 3 MPa. The results thus obtained were compared with reference values calculated using the equation of Ortiz-Vega et *al.* [29], and from the analysis of the deviations between the experimental measurements and the expected values, the calibration curve of the instrument was determined. Table 1 contains the helium speed of sound measurements, w_{He}, obtained by the instrument without correction. Furthermore, the measured speeds of sound versus pressure along six isotherms are plotted in Fig. 6. Each measurement corresponding to a given temperature, T, and pressure, p, was obtained as the average of about 50 consecutive measurements at the same thermodynamic point. Then a standard deviation value was also calculated for each measurement point, which can be used as an indicator of the typical measurement noise of the instrument, i.e., the statistically calculated repeatability value of the measurement, due to the instrument stability. In this way, an average value of the standard deviation of each measurement point of 217 ppm was estimated. Despite this, repeated measurements were still carried out for the isotherms at (300 and 310) K in order to define the experimental repeatability of the measurements. To include this contribution, the final repeatability value was calculated as the squared sum of the mean standard deviation and the experimental repeatability, reaching the value of 319 ppm.

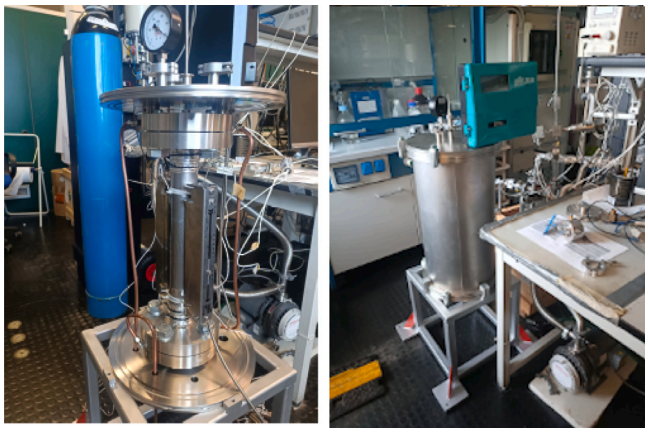

Fig. 4. Experimental apparatus used for the speed of sound measurements.

The uncertainty $u(w_{\mathrm{He}})$ associated with the speed of sound measurements obtained for helium was calculated through the following equation:

$$u(w_{He}) = \sqrt{\left(\frac{u(p)}{w_{He}}\frac{\delta w_{He}}{\delta p}\right)^2 + \left(\frac{u(T)}{w_{He}}\frac{\delta w_{He}}{\delta T}\right)^2 + R^2} \quad (5)$$

where $u(p)$ and $u(T)$ are the uncertainties associated with the pressure and temperature measurements, respectively, $\frac{\delta w_{He}}{\delta p}$ and $\frac{\delta w_{He}}{\delta T}$ are the sensitivity coefficients of the speed of sound with respect to pressure and temperature, calculated from the values of the experimental measurements, and R is the repeatability of the measurements. Table 2

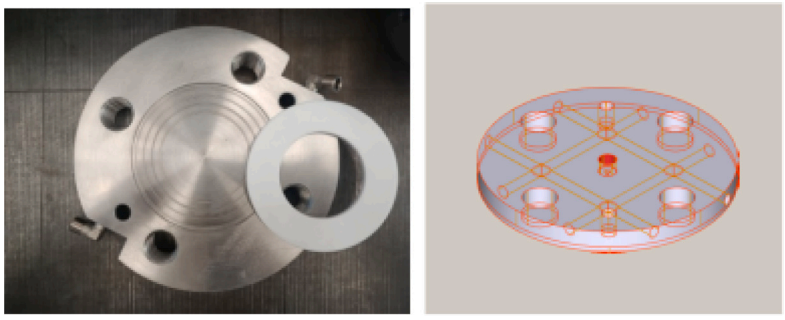

Fig. 5. DN 50 flange with the Teflon® gasket. The image on the right shows the channel grid inside the flange.

Table 1
Experimental speed of sound in helium.

T/K	p/MPa	w_{He}/m/s	T/K	p/MPa	w_{He}/m/s
319.977	3.096	1066.046	290.018	3.066	1015.151
319.845	2.547	1062.608	290.007	2.543	1013.027
319.903	2.047	1061.508	290.005	2.046	1010.562
319.760	1.555	1058.783	290.051	1.551	1008.945
319.836	1.043	1056.802	290.006	1.048	1006.502
T/K	p/MPa	w_{He}/m/s	T/K	p/MPa	w_{He}/m/s
310.027	3.068	1048.815	280.031	3.042	997.788
310.037	2.555	1047.155	280.039	2.542	995.479
310.034	2.048	1044.022	280.059	2.043	993.378
309.998	1.546	1043.164	280.079	1.547	991.095
309.970	1.042	1038.863	280.028	1.041	988.825
T/K	p/MPa	w_{He}/m/s	T/K	p/MPa	w_{He}/m/s
300.021	3.058	1032.298	270.008	3.052	980.293
299.998	2.555	1030.145	270.041	2.541	978.020
300.032	2.043	1027.717	270.050	2.044	975.601
299.978	1.547	1026.058	270.099	1.542	973.475
300.022	1.042	1023.371	270.128	1.041	971.165

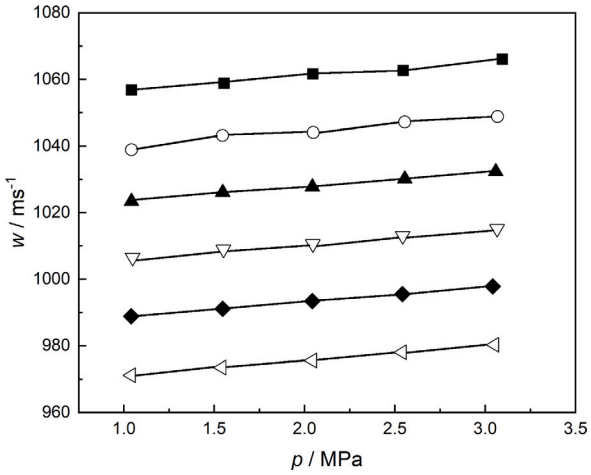

Fig. 6. Experimental speed of sound in helium along six isotherms. ■ 320 K; ○ 310 K; ▲ 300 K; ▽ 290 K; ♦ 280 K; ◁ 270 K.

lists the main contributions to uncertainty for speed of sound measurements in helium. The adopted helium was 6.0, so the uncertainty contribution related to its purity, which is mainly due to 0.1 ppm of oxygen, 0.1 ppm of nitrogen, 0.2 ppm of hydrogen, 0.5 ppm of water, 0.1 ppm of methane, typically produces deviations in speed of sound below 10 ppm, that is negligible with respect to the other sources of uncertainties.

Table 2
Contributions to uncertainty of the speeds of sound of helium.

Contributions to uncertainty	Relative magnitude/%
Pressure	0.011
Temperature	0.004
Repeatability	0.032

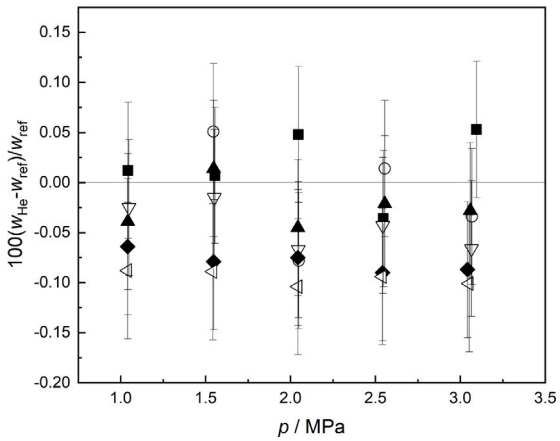

Fig. 7. Deviations of the experimental speed of sound in helium, w_{He}, *from the reference values,* w_{ref}. ■ 320 K; ○ 310 K; ▲ 300 K; ▽ 290 K; ♦ 280 K; ◁ 270 K.

Thus, the overall expanded relative uncertainty, with coverage factor ($k = 2$), of the speed of sound measurements in helium obtained in this work is $u(w_{He}) = 0.068\%$.

The experimental values of speed of sound obtained in helium were then compared with the expected values, w_{ref}, given by the Helmholtz Equation of state of Ortiz-Vega et *al* [29]. This model claims uncertainties in the speed of sound, $u(w_{ref})$, of 0.02 % for the vapor phase and 0.2% for the liquid phase. The deviations that were calculated between the experimental measurements and the reference values of the speeds of sound are shown in Fig. 7. These deviations, which are below 0.1%, show the good agreement between the measured and the predicted speeds of sound. From these results, the calibration curve of the instrument was calculated as the temperature dependent only equation, given below.

$$w_c(w_{exp}, T) = w_{exp} \cdot [1 - Y(T)] \tag{6}$$

where w_c is the corrected speed of sound, w_{exp} is the experimental measurement and $Y(T)$ is a temperature-dependent term that has the following form:

$$Y(T) = 2.11828 \cdot 10^{-5} T - 0.00652626 \tag{7}$$

where T is the temperature in Kelvin.

Residues between corrected speeds of sound coming from the calibration curve and the reference speed of sound values for the same

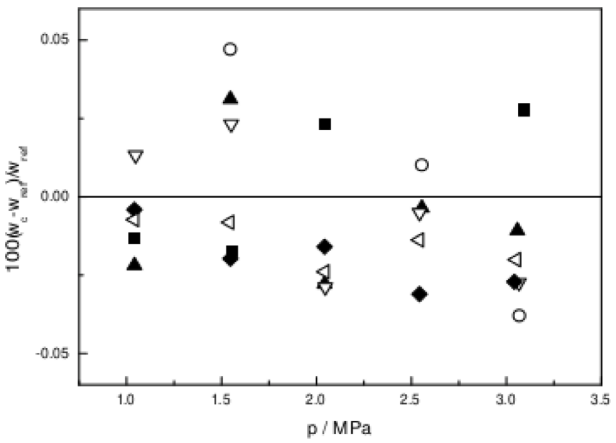

Fig. 8. Residuals between speed of sound corrected by the calibration curve,w_c, *and expected values,* w_{ref}. ■ 320 K; ○ 310 K; ▲ 300 K;▽ 290 K; ♦ 280 K; ◁ 270 K.

thermodynamic points are plotted in Fig. 8. The average value of these residuals is 0.016%.

4. Speed of sound results in H_2+iC_4H_{10}

Using the same clamp-on flowmeter described above, keeping the same settings and not modifying its configuration, speed of sound measurements have been carried out in a binary mixture of hydrogen and isobutane, with a mole composition $x(iC_4H_{10})$ = 0.05 mol (94.991 mol% hydrogen + 5.009 mol% isobutane). The binary mixture was prepared gravimetrically by Nippon Gases Industrial S.r.l. The uncertainty stated in the calibration certificate of the mixture for the molar concentration of isobutane is, $u(x[C_4H_{10}])$ = 0.05%. The speed of sound measurements have been carried out at temperatures between (270 and 320) K and for pressure up to 3 MPa. For the isotherms at 270 K and 280 K, it was chosen not to exceed the maximum pressures of 1.8 MPa and 2.1 MPa, respectively. This precaution was taken because at those temperatures and for higher pressures, partial condensation of the mixture was experienced, resulting in decomposition of the fluid leading to the two-phase region. The measured values of speed of sound, w_{exp}, have been corrected by using Eq. (6). The obtained values, w_c, alongside the experimental values before they were corrected, w_{exp}, are listed in Table 3. Deviations between experimental and corrected speeds of sound, calculated using Eq. (6), were found to be less than 800 ppm. Specifically, they range from a minimum value of 40 ppm at a temperature of 310 K to a maximum of 800 ppm at a temperature of 270 K. For this reason, since the differences would not be graphically appreciable, only the corrected values of speed of sound were shown in Fig. 9.

5. Uncertainty analysis

The uncertainty associated with the measurements of the speed of sound in the mixture was calculated by taking into account not only the repeatability of the measurements and the contributions associated with the temperature and pressure measurements, but also the uncertainty associated with the composition of the binary mixture and the uncertainty resulting from the correction of the experimental values using Eq. (6). More specifically, the uncertainty associated with the mole fraction $x(C_4H_{10})$ is stated by the calibration certificate as $u(x[C_4H_{10}])$ = 0.05%. Thus, the uncertainty contribution of the speed of sound related to the composition of the binary mixture, $u(x)$ is estimated as:

$$u(x) = \frac{u(x[C_4H_{10}])}{w_c} \cdot \frac{\partial w_c}{\partial x} \tag{8}$$

Table 3
Experimental, w_{exp}, and corrected speed of sound, w_c, in the binary mixture H_2+C_4H_{10}.

T/K	p/MPa	w_c/m/s	T/K	p/MPa	w_c/m/s
320.021	3.050	875.929	289.982	3.133	839.571
319.982	2.546	873.085	289.982	2.551	836.102
319.949	2.042	869.733	289.996	2.047	833.469
320.012	2.043	869.879	290.023	1.549	830.846
319.968	1.541	867.018	290.033	1.048	828.394
319.965	1.045	864.297			
T/K	p/MPa	w_c/m/s	T/K	p/MPa	w_c/m/s
310.010	3.048	863.565	279.985	2.119	820.676
309.974	2.540	860.684	279.973	1.793	818.854
309.935	2.039	857.677	279.949	1.543	817.317
309.990	1.542	855.091	280.015	1.284	815.953
309.872	1.042	852.466	280.030	1.041	814.759
T/K	p/MPa	w_c/m/s	T/K	p/MPa	w_c/m/s
300.039	3.051	850.864	269.942	1.795	805.476
300.068	2.558	848.209	269.992	1.546	804.204
300.069	2.050	845.625	270.024	1.293	802.759
300.074	1.548	842.792	270.064	1.042	801.301
300.101	1.044	839.956			

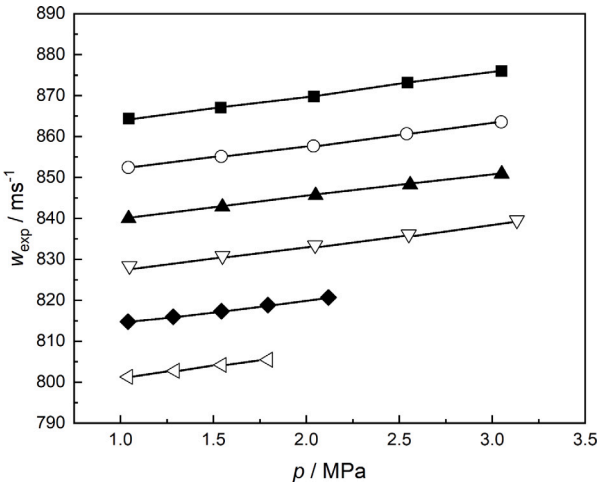

Fig. 9. Corrected speed of sound in the binary mixture H_2+C_4H_{10}*along six isotherms.* ■ 320 K; ○ 310 K; ▲ 300 K; ▽ 290 K; ♦ 280 K; ◁ 270 K.

where $\frac{\partial w_c}{\partial x}$ is the sensitivity coefficient of the speed of sound with respect to composition, which was calculated as 0.31 $ms^{-1}mol\%^{-1}$ was estimated by evaluating the change in the speed of sound, calculated using GERG-2008, after slightly varying the composition of the mixture. The contribution to the uncertainty due to the calibration correction was calculated as the root-mean-square sum of the uncertainty stated in Ortiz-Vega [29], $u(w_{ref})$ = 0.02%, for the reference speeds of sound in helium, and the mean value of the residuals between the corrected and reference speeds of sound, res_{mean} = 0.016%. Table 4 then lists the contributions to the overall expanded relative uncertainty (k = 2), $U_r(w_c)$, that is calculated with Eq. (9) and is equal to 0.089%.

$$u(w_c) = \sqrt{\left(\frac{u(p)}{w_c}\frac{\delta w_c}{\delta p}\right)^2 + \left(\frac{u(T)}{w_c}\frac{\delta w_c}{\delta T}\right)^2 + u(x)^2 + u_{cal}^2 + R^2} \tag{9}$$

where $u_{cal} = \sqrt{u(w_{ref})^2 + res_{mean}^2}$ is the calibration contribution to the uncertainty of the measured speeds of sound.

6. Comparison of the results with AGA-8 and GERG-2008

The measured experimental values of sound speed for the binary hydrogen-isobutane mixture, with $x(C_4H_{10})$=0.05 mol, were compared

Table 4
Contributions to uncertainty of the speeds of sound of the binary mixture H_2+C_4H_{10}.

Contributions to uncertainty	Relative magnitude/%
Pressure	0.017
Temperature	0.003
Repeatability	0.032
Calibration	0.019
Composition	0.002

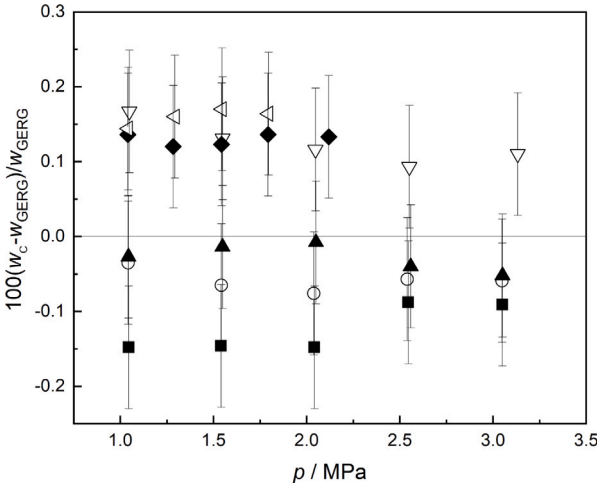

Fig. 10. Deviations of the corrected experimental speed of sound in the binary mixture H_2+C_4H_{10}, w_c, *from the reference values,* w_{GERG}, *provided by GERG-2008 model.* ■ 320 K; ○ 310 K; ▲ 300 K;▽ 290 K; ♦ 280 K; ◁ 270 K.

with the expected values provided by the thermodynamic model GERG-2008 [17], which is the equation of state for the thermodynamic properties of natural gasses, similar gasses, and other mixtures explicit in the Helmholtz free energy, and by the AGA-8 model [15], which is the widely used equation of state for the compressibility factor of natural gas.

Figs. 10 and 11 plot the deviations calculated between the experimental speeds of sound and the reference speeds of sound provided by GERG-2008, w_{GERG}, and AGA-8, w_{AGA-8}. These deviations are found to be within (−0.148 and 0.17) % when compared to GERG-2008 and within (−0.108 and 0.312) % when compared to AGA-8. These two models, whose stated expanded (k = 2) uncertainties for speed of sound are $U_r(w_{AGA-8})$ = 0.2%, for AGA-8 and $U_r(w_{GERG})$ = 0.5%. Thus, considering that relative deviations of experimental data from model estimations are within the experimental uncertainty, it can be concluded that all the measurements of speed of sound performed for the hydrogen-isobutane binary mixture using the clamp-on flowmeter are consistent with the reference values predicted by both the GERG-2008 and AGA-8 models.

7. Results and comments

In this work accurate speed of sound measurements in pure helium has been carried out along seven isotherms from T = (270 to 320) K at pressures up to about 3 MPa, using a commercially available clamp-on ultrasonic flowmeter, specifically customized to operate as a speed of sound meter under controlled temperature and pressure with fluid at rest. The instrument was calibrated using helium as a reference fluid, and showed deviations below 0.068% when compared with the prediction of the Ortiz-Vega equation of state. Analyzing the residues, the calibration curve of the clamp-on meter was formulated for the temperature and pressure range in which the measurements were carried out. Using the same flowmeter, and keeping the same

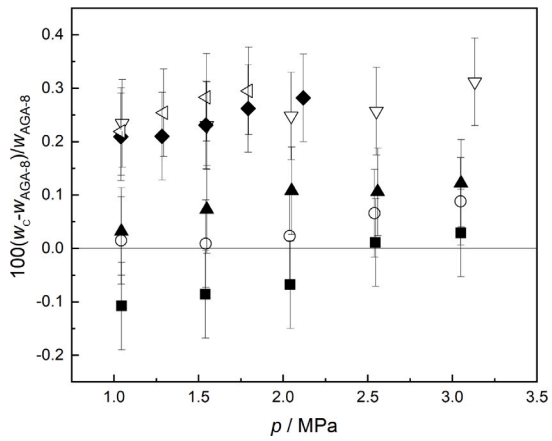

Fig. 11. Deviations of the corrected experimental speed of sound in the binary mixture H_2+C_4H_{10}, w_c, *from the reference values,* w_{AGA-8}, *provided by AGA-8 model.* ■ 320 K; ○ 310 K; ▲ 300 K;▽ 290 K; ♦ 280 K; ◁ 270 K.

configuration, additional speed of sound measurements were carried out, in a mixture of hydrogen and isobutane (94.991 mol% hydrogen + 5.009 mol% isobutane) along seven isotherms, from 270 K to 320 K, at pressures up to 3 MPa. The overall expanded relative uncertainty (k = 2) of these measurements was estimated to be 0.089%. The experimental results have been corrected according to the obtained calibration curve and then compared with the AGA-8 and GERG-2008 equations of state. Therefore, it was verified that the speeds of sound measured in the hydrogen-isobutane mixture using the clamp-on flowmeter are consistent with the reference values predicted by both models.

CRediT authorship contribution statement

G. Cavuoto: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **R. Romeo:** Visualization, Validation, Investigation, Conceptualization. **S. Lago:** Supervision. **P.A. Giuliano Albo:** Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Paolo Alberto Giuliano Albo reports financial support was provided by EURAMET European Metrology Programme for Innovation and Research. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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