

Velocity of sound measurements in gaseous per-fluorocarbons and their custom mixtures

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Abstract

An inexpensive sonar instrument was prepared for measurements of sound velocity in two fluorocarbon vapors; per-fluoro-n-propane (C_3F_8), per-fluoro-n-butane (C_4F_{10}), and their custom mixtures. The apparatus, measurement principle and instrument software are described.

All sound velocity measurements in per-fluorocarbons were made in the low pressure range between 0.01 and 0.4 MPa, and at temperatures between 253 and 303 K. The purity of the C_3F_8 and C_4F_{10} samples was checked using gas chromatography. Uncertainties in the speed of sound measurements were better than ± 0.1 %. Comparisons were made with theoretical predictions of sound velocity for the two individual components. The instrument was then used for concentration monitoring of custom C_3F_8/C_4F_{10} mixtures. This approach is based on the sensitivity of sound velocity to variations in the composition of binary mixtures of gases with disparate molecular weight. Verification of mixtures was made along the saturation line over a range of temperatures, and also over the P-T region where both components were superheated.

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The instrument was calibrated with sound velocity measurements in Xenon; a gas having the combination of a well-defined specific heat ratio and high molar mass. The temperature sensitivity of the instrument for the required mixture measurement precision of 1% was determined to be 0.9 °C; the measured temperature stability of the instrument was of this order.

Keywords: Experimental method, velocity of sound, perfluoro-carbons, mixtures

1. Introduction

As part of the development of evaporative fluorocarbon cooling for the silicon pixel and micro-strip tracking detectors [1, 2] of the ATLAS experiment at the future CERN Large Hadron Collider, we have studied perfluoro-n-propane (C_3F_8)², perfluoro-n-butane (C_4F_{10})³ and custom C_3F_8/C_4F_{10} mixtures. These fluids are suited to our cooling application due to their high dielectric constant, non-flammability and high expected radiation resistance [3].

Latent heat data for the refrigerants of interest are shown in Table 1, together with their molecular weights, saturated vapor pressures and the volume (cm^3) of vapor produced per cm^3 liquid evaporated at $-15^\circ C$. A target evaporation pressure close to 1 bar_{abs} at $-15^\circ C$ is attractive in our application, and this has motivated the study of custom C_3F_8/C_4F_{10} mixtures.

We have used the NIST REFPROP [4] database with added provisional data files for the C_3F_8 and C_4F_{10} components. The package was used to predict thermo-physical properties, including sound velocity, for the components and their binary mixtures, according to a modified Benedict-Webb-Rubin equation of state. The sonar was then used to verify the predictions of sound velocity and saturation pressure.

Table 1
Selected Refrigerant Properties for C_3F_8 , C_4F_{10} and 50/50 molar mixture
[-15°C Evaporation].

Fluid	Molecular Weight	Latent heat	Liquid-Gas Expansion Factor	S.V.P. at -15° C
		[kJ kg ⁻¹]		[bar _{abs}]
C_3F_8	188	97	71.4	2.46
C_4F_{10}	238	101.1	242.6	0.58
C_3F_8/C_4F_{10} (50/50, molar)	213	98.3	147.6	$1.01P_{SV} - 1.65 P_{SL}$

2. The sonar gas analyzer

In a binary mixture of gases, the sound velocity depends on the velocities in the individual components and their relative concentrations. Various formalisms have been developed to describe this variation, based [5] on Van der Waals and Benedict-Webb-Rubin equations of state, and [6] on a simplified formula for the case where the two gases differ widely in molecular weight. In this work we compare our measurements with the velocity predictions for C_3F_8/C_4F_{10} mixtures from the extended NIST REFPROP database [4], which uses a modified Benedict-Webb-Rubin equation of state.

² Mfr.: 3-M Corp. Specialty Chemicals Division, St. Paul, MN, USA PFG 5030, grade >99% purity

2.1 Present Apparatus

The sonar gas analyzer, based on an earlier development [5], is shown in Fig. 1. An aluminum tube contains a pair of ultrasonic transducers⁴ having a peak response at 45kHz, and separated by of (944.5 ± 1.0) mm. The tube is surrounded by a coiled copper pipe through which C_6F_{14} coolant⁵ was circulated over a temperature range from -20° to $30^\circ C$. The temperature of the vapor within the tube was sampled to a precision $\pm 0.1^\circ C$ by of pair of calibrated PT100 sensors. Pressure was monitored to ± 1 torr by an electronic pressure gauge⁶.

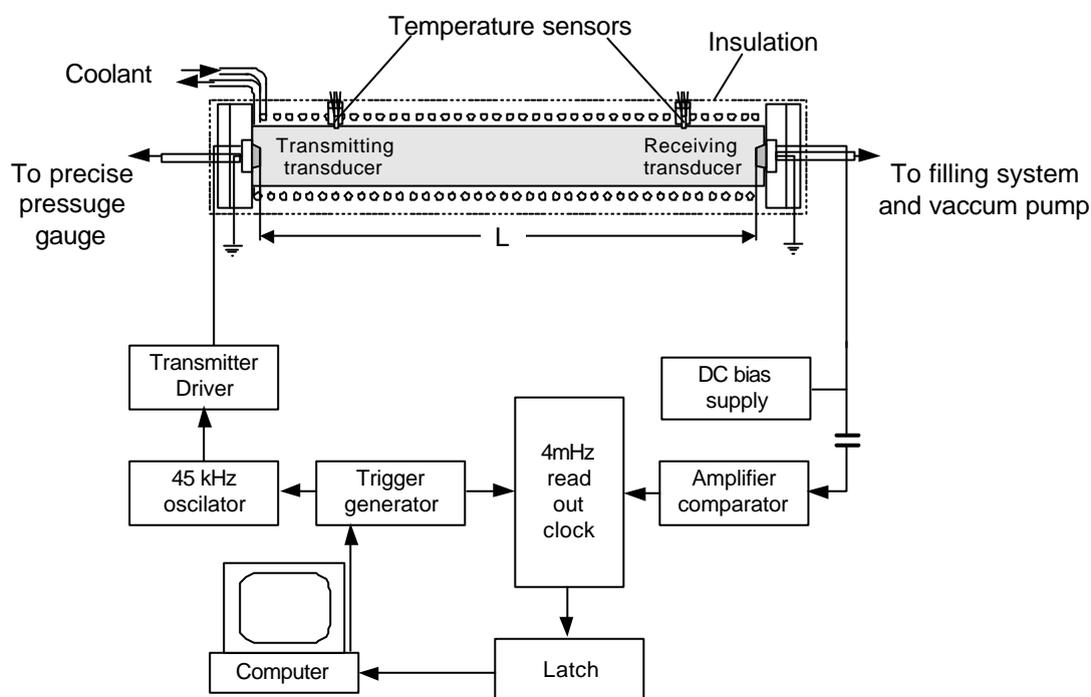


Fig. 1. Schematic of the sonar gas analyzer.

A photograph of the instrument and the analyzer timing sequence are shown in Fig 2. The sequencer is implemented on a custom clock generator card, which is triggered,

³ Mfr.: 3-M Corp. PFG 5040, grade >99% purity

⁴ Polaroid Corp. Instrument grade transducer, part no 604142

⁵ Mfr.: 3-M Corp. PFG 5060

⁶ MKS Corp. "Baratron" Model 122B read by MKS Corp. Model 600 Pressure Controller.

gated and interrogated by signals from a multifunction I/O board (MFB)⁷ in a PC. Gated packets of eight 45 kHz sound cycles are transmitted through the vapor in the tube. Synchronous with the leading edge of the first cycle (**A**), a fast (4 MHz) transit time clock is started.

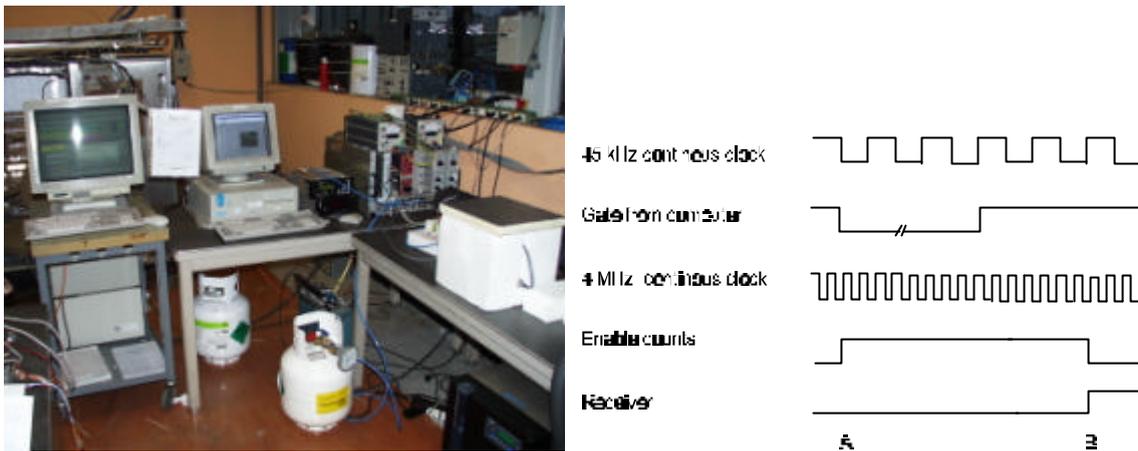


Fig. 2. Photograph of the sonar gas analyzer and instrument timing sequence.

This clock is stopped when an above-threshold sound signal is received (**B**), and the number of counted 4MHz pulses is used with the path length to calculate the sound velocity.

The instrument is controlled by a LabView program, which performs a cyclic series of operations:

- An output channel of the MFB is enabled (**A**) for a programmable time interval (usually the duration of eight 45 kHz pulses: 0.176 ms). This pulse gates a free-running 45 kHz oscillator, to pass a packet of eight 45 kHz pulses through to the emitting transducer
- An input counter is started (**A**) on a second channel of the MFB

⁷ National Instruments MOI-16-L9 multifunction I/O card.

- The program then enters a loop, polling the number of 4MHz pulses counted on the second channel. When this number does not change between iterations, the program assumes the receiving transducer has seen the sound packet and has stopped the 4MHz clock (**B**). The loop then terminates. It may also terminate if the number of pulses exceeds 65535, indicating the receiver has not seen the packet in a reasonable time. (This may occur if the gas is highly absorptive, or if the transmitter or receiver biases are insufficient)
- The sound velocity calculated from the number of counted 4MHz pulses is compared with the velocity curve as a function of C_4F_{10} in C_3F_8 predicted by the extended REFPROP database [4] at the measurement temperature. The user screen displays a real time cursor that projects the current mixture composition corresponding to the measured sound velocity. An example is shown in Fig.3 for a composition of 68.03% C_4F_{10} in C_3F_8 at 20°C and 0.1 MPa.

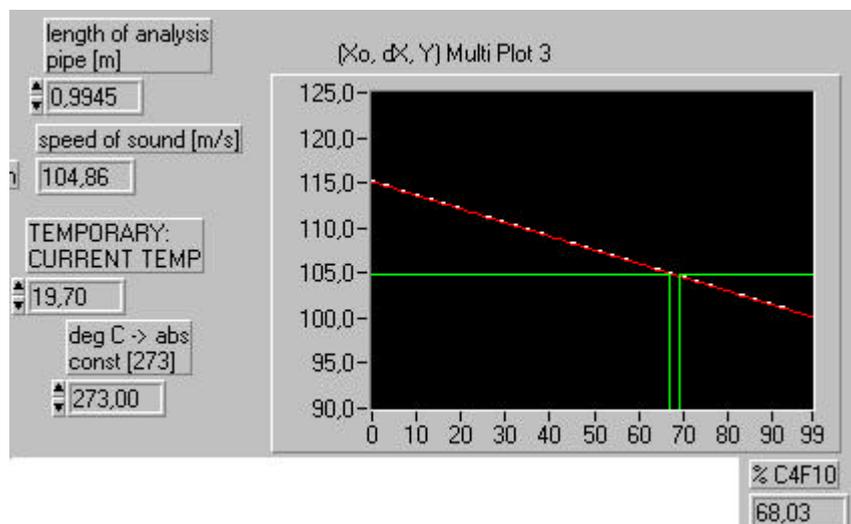


Fig. 3. Real time cursor display of mixture composition in the sonar gas analyzer

A maximum sampling speed of 10Hz is possible in the instrument, and simple statistical routines allow the average and standard deviation of the speed of sound to be determined over a series of measurements.

2.2. Calibration and Precision

The sonar analyzer was tested and calibrated with a range of gases, including nitrogen, helium and xenon, before being used with the refrigerants. The theoretical value of sound velocity, v_t , for an ideal gas is given by:

$$v_t = \sqrt{\frac{k RT}{m}}, \quad (1)$$

where k is the ratio of specific heats, R is the universal gas constant, T the absolute temperature and m the molar mass.

In nitrogen {helium} at 21.0 °C, the measured velocities were 349.7 {996.1} ms⁻¹: around 0.3% {0.2%} lower than the ideal gas predictions of 350.6 {998.0} ms⁻¹.

In mixture analysis, it is necessary to examine the level to which temperature fluctuations can mask changes in mixture composition. The variation of sound velocity with absolute temperature is given by

$$v_1^2 / v_2^2 = T_1 / T_2. \quad (2)$$

At a nominal temperature T_1 (K), the temperature change δT ($T_2 - T_1$) that can cause a velocity change δv ($v_2 - v_1$) is given by:

$$\delta T = T_1 (1 - v_1^2/v_2^2)(v_1^2/v_2^2)^{-1}. \quad (3)$$

Considering the example of C₃F₈/C₄F₁₀ mixtures at 20°C where v (C₃F₈) = 115.3 ms⁻¹ and v (C₄F₁₀) = 99.7 ms⁻¹ (see section 3), we find that for a specified 1% mixture resolution, the sonar instrument temperature is needed to a precision of 0.9°C.

To calibrate the instrument temperature, sound velocity measurements were made in Xenon. This was the most useful calibration gas, since it combines near ideal behavior with a molar mass (131.3 g) approaching those of the heavy refrigerants. A dense gas with lower sound velocity is a better calibrant than a lighter, faster gas such as Helium. Radon, the heaviest noble gas, would be ideally suited thermodynamically (molar mass 222 g, v = 135 ms⁻¹ at 20°C), but is hazardous.

Table 2 compares velocity measurements in xenon over a range of temperatures with ideal gas predictions at atmospheric pressure. The average difference in measured and predicted sound velocity of .0.2% is consistent with a temperature uncertainty of ~ 1°C.

Table 2

Velocity of sound in xenon: Ideal gas predictions and measurement

t _{tube}	P _{abs}	SOS	Theor. SOS	DIFF=M.-Th.	Rel._Err.
[C]	[MPa]	[ms ⁻¹]	[ms ⁻¹]	[ms ⁻¹]	[%]
0	0.107	169.22	169.44	-0.224	-0.1326
11.5	0.102	172.73	172.96	-0.232	-0.1346
19.3	0.108	175.67	175.34	0.330	0.1876
20	0.107	175.25	175.77	-0.516	-0.2942

3. Experimental results

The first tests were made with C_4F_{10} . A provisional data file was added to the NIST REFPROP package [4] for this fluid. Our measurements for the superheated region are shown in Table 3 and are on average $\sim -0.2\%$ lower than the NIST predictions at temperatures above $0^\circ C$, and lower by $\sim -1.2\%$ for predictions below $-10^\circ C$.

Table 3
Measured velocity of sound in C_4F_{10}

P _{abs} [MPa]	Temperature [C]											
	-17.9		-10.0		-0.1		10.0		20.0		30.0	
	SOS	STDV										
	[ms ⁻¹]	[-]										
0.010	95.10	0.06	96.57	0.07	99.26	0.05	101.05	0.08	103.02	0.10	104.78	0.10
0.020	94.56	0.04	96.22	0.04	98.71	0.05	100.64	0.07	102.70	0.08	104.57	0.08
0.030	93.98	0.04	95.70	0.05	98.33	0.04	100.23	0.06	102.37	0.10	104.25	0.07
0.050			94.78	0.04	97.39	0.04	99.38	0.06	101.71	0.12	103.35	0.12
0.070					96.39	0.07	98.40	0.05	100.86	0.05	103.06	0.05
0.100					94.79	0.10	97.04	0.05	99.66	0.05	103.05	0.08
0.150							95.08	0.05	97.68	0.05	99.91	0.05
0.200									95.63	0.05	98.41	0.07
0.250											96.50	0.05
0.300											94.89	0.05

More detailed measurements were performed at $20^\circ C$ with different samples of C_4F_{10} ; one of which was slightly polluted ($\sim 2\%$) by light impurities (mainly nitrogen).

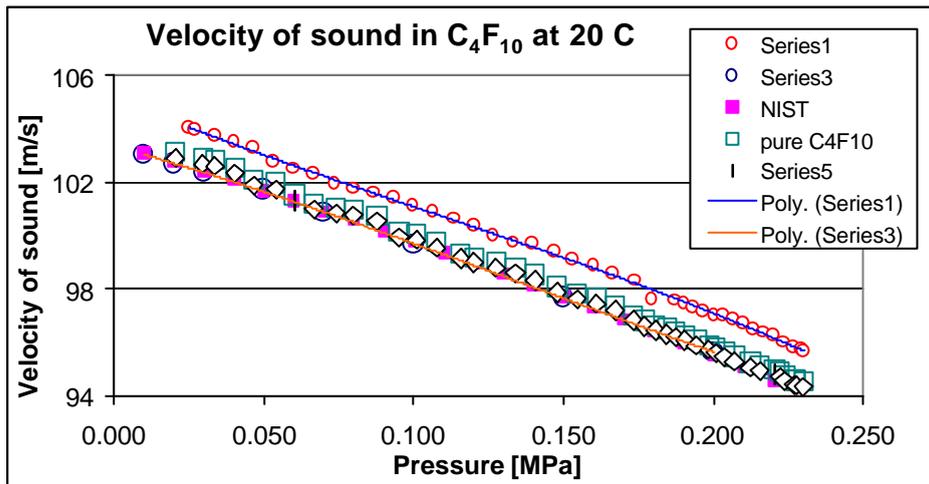


Fig. 4. Different series of measurement in C_4F_{10} . Series1 with slight impurities, Series 3 and 5 with standard purity compared with "fresh" sample of C_4F_{10} and REFPROP prediction

Measurements are compared with REFPROP predictions in Fig. 4. The significant shift in velocity due to the impurities is evident.

The next fluid under study was C_3F_8 . Our measurements for the superheated region are shown in Table 4.

Table 4

Measured velocity of sound in C_3F_8

P _{abs} [MPa]	Temperature [C]											
	-18.66		-10.19		-0.19		10.06		21.18		30.11	
	SOS	STDV										
	[ms ⁻¹]	[-]										
0.010	107.90	0.19	110.81	0.07	112.31	0.19	114.58	0.08	118.19	0.92	119.13	0.08
0.020	107.60	0.06	110.00	0.06	111.99	0.06	114.63	0.07	117.9	0.98	118.98	0.07
0.030	107.25	0.79	109.59	0.08	111.77	0.79	114.12	0.06	117.58	0.79	118.79	0.07
0.050	106.56	0.06	108.88	0.06	111.27	0.06	113.84	0.06	116.81	0.06	118.42	0.07
0.070	105.77	0.05	108.23	0.07	110.90	0.07	113.10	0.05	116.31	0.07	118.04	0.06
0.100	104.62	0.06	107.27	0.06	110.29	0.06	112.46	0.05	115.55	0.24	117.43	0.06
0.150	102.76	0.04	105.51	0.06	108.59	0.04	111.28	0.05	114.42	0.50	116.26	0.07
0.200			103.72	0.07	106.90	0.06	109.88	0.05	113.23	0.73	115.36	0.05
0.250			101.83	0.07	105.22	0.06	108.56	0.05	111.94	0.05	114.31	0.06
0.300					103.59	0.05	107.10	0.05	110.70	0.05	113.14	0.06
0.350					101.90	0.08	105.61	0.04	109.43	0.08	112.00	0.55
0.400					100.27	0.05	103.99	0.07	108.12	0.07	110.63	0.06

Measured velocities of sound are on average ~ 0.14% higher than the NIST predictions at temperatures above 0°C, and lower by ~ -0.78% for predictions below -10 °C.

Following these studies with the component gases, three different custom mixtures of C_4F_{10} and C_3F_8 were prepared via partial pressure mixing. The composition of these mixtures was checked using gas chromatography. Figure 5 is a sample chromatogram for a mixture with a target composition of 70% C_4F_{10} /30% C_3F_8 .

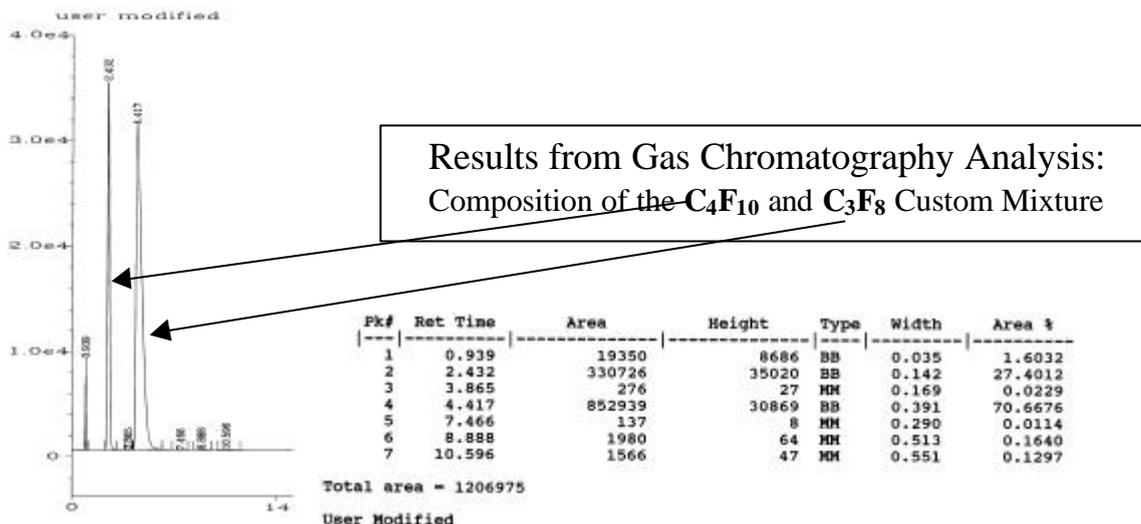


Fig. 5. Typical results from gas chromatography analysis

There is slight evidence for light impurities despite the sample having been prepared from the liquid phases of the two components. In Table 5, we present measurements for a custom mixture with target composition 20% C_4F_{10} /80% C_3F_8 . The composition of the mixture was checked by gas chromatography and found to be 17% C_4F_{10} /83% C_3F_8 .

Table 5

Sound velocity measurements in a custom 17% C_4F_{10} /83% C_3F_8 mixture.

Temperature [C]													
	-18.93			-10.01		-0.02		10.03		20.04		27.28	
P_{abs}	SOS	STDV	P_{abs}	SOS	STDV								
[MPa]	[ms^{-1}]	[-]	[MPa]	[ms^{-1}]	[-]								
0.01	105.12	0.12	0.01	107.40	0.15	109.48	0.08	112.12	0.15	114.96	0.11	116.15	0.14
0.01	105.03	0.11	0.02	107.18	0.07	109.17	0.07	111.72	0.07	114.62	0.07	116.05	0.07
0.02	104.84	0.06	0.03	106.95	0.07	108.78	0.07	111.47	0.07	114.35	0.06	115.78	0.08
0.03	104.58	0.06	0.05	106.30	0.07	108.25	0.05	111.19	0.07	113.75	0.07	115.29	0.09
0.03	104.45	0.06	0.07	105.81	0.07	107.66	0.07	110.59	0.07	113.21	0.05	114.72	0.07
0.03	104.36	0.05	0.10	104.56	0.08	106.40	0.05	109.75	0.05	112.30	0.05	114.03	0.07
0.04	104.12	0.05	0.15	102.68	0.05	104.90	0.04	108.40	0.05	111.00	0.05	112.72	0.07
0.05	103.84	0.05	0.20	101.95	0.05	103.44	0.05	106.92	0.05	109.85	0.05	111.59	0.05
0.05	103.75	0.07	0.25			102.59	0.04	105.34	0.05				
0.05	103.57	0.05	0.30			101.26	0.04	103.72	0.05				
0.06	103.27	0.06	0.35					101.99	0.05				
0.07	103.07	0.05	0.40					100.10	0.04				

The measurement data were quite close to the NIST REFPROP sound velocity predictions. For example, at 0.1 MPa and 20 C, the measured velocity is within 0.2% of

the REFPROP curve of predicted velocity. This curve is shown over the full mixture range in the real time display of Fig.3.

3.1 Measurement of saturation pressure

The precise pressure sensor enabled us to demonstrate the use of sound velocity to find the saturation line of single fluids, or of the lower boiling component in the binary mixture. The procedure is demonstrated in fig. 6 for a 60% C_4F_{10} /40% C_3F_8 mixture at -18C . The sound velocity falls as the pressure is increased to ~ 0.05 MPa, beyond which the C_4F_{10} condenses, leaving a mixture progressively enriched in C_3F_8 . The pressure of the saturation cusp at this temperature is in good agreement with the REFPROP prediction.

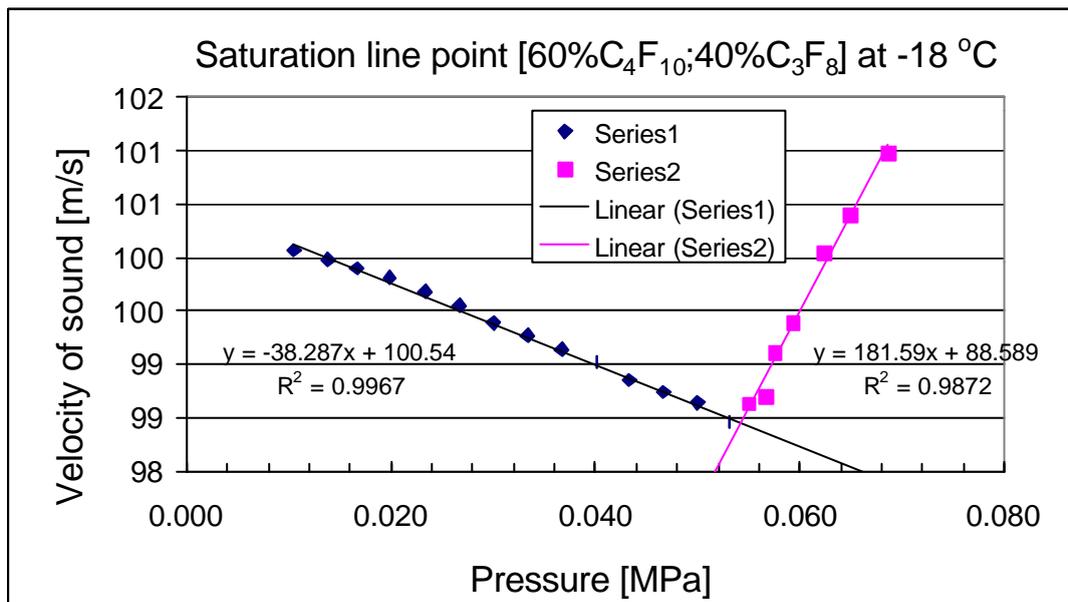


Fig. 6. Sound velocity determination of the saturation line point in a C_4F_{10}/C_3F_8 mixture.

4. Conclusions

A simple sonar gas analyzer has been constructed and verified using velocity of sound measurements made in light gases and xenon. Comparisons with ideal gas predictions

were satisfactory, and the instrument has been used for purity checking and mixture composition determination in C_4F_{10} and C_3F_8 per-fluorocarbon refrigerants and their mixtures in the pressure region (0.01 – 0.4 MPa) at temperatures ranging from $-20\text{ }^\circ\text{C}$ to $+30\text{ }^\circ\text{C}$. Informative comparisons with REFPROP values have been done with satisfactory agreement. The instrument has also been used to determine the saturation line point for single fluids and for mixtures. The present temperature uncertainty of $\sim 1\text{ }^\circ\text{C}$ in the instrument will be improved to allow more precise absolute superheated mixture determinations.

5. List of symbols

v_t theoretical (ideal gas) velocity of sound (ms^{-1})

v velocity of sound (ms^{-1})

P pressure (MPa)

R universal gas constant ($8.314\text{ J mol}^{-1}\text{ K}^{-1}$)

SOS measured velocity of sound (ms^{-1})

STDV standard deviation of the measured value

T temperature (K)

t temperature (C)

m molar mass (kg)

Greek letters

k ratio of specific heats

Subscripts

abs absolute (pressure)

SV saturated vapor

SL saturated liquid

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