

THE DENSITY OF RICH NATURAL GAS MIXTURES

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Abstract

A major programme of work is being undertaken at NEL to establish reference-quality measurements of density for ten natural gas mixtures typical of those recovered from North Sea condensate fields. The measurements are being made using the UK's primary standard densitometer for gases over a range of pressures and temperatures commensurate with typical metering conditions. A description of the modified apparatus is presented together with preliminary findings for the first three mixtures.

This Joint Industry Project, being undertaken in collaboration with the Gas Research Institute and major oil and gas companies, will lead to a revision of the AGA8 equation allowing calculations to be made of the density of rich natural gas mixtures, at typical metering conditions, with a target uncertainty commensurate with fiscal-quality requirements.

1. INTRODUCTION

As a result of difficulties in the use of commercial densitometers for the metering of natural gas mixtures, many operators have opted to determine the density of the gas flows indirectly by gas chromatography. Density, in this instance, is derived from an equation of state and a knowledge of the temperature, pressure and composition of the gas. The equation of state most widely used with the gas chromatographic technique is the Detail Characterization Method or AGA8 equation developed by the American Gas Association^[1]. This equation is valid for lean natural gas mixtures over a wide range of conditions but its application to rich natural gases (some 60 % mole fraction of methane), as encountered in gas condensate fields, is untested.

In principle, the gas chromatographic technique for the determination of density should be as effective as that using fully calibrated and traceable densitometers. This assumes that a valid equation of state is employed for the gas mixture and that measurements of temperature, pressure and composition are made to a sufficiently high standard. However, indications are that for gases from condensate fields, at metering conditions of between 80 and 180 bar pressure and 40 to 80°C, differences of some 2.0 to 2.5% are regularly being observed between density values determined from the AGA8 equation and those monitored by gas densitometer.

There are a number of possible sources of error which could give rise to differences in density of this magnitude. The major causes were considered to be:-

- residual installation effects on the gas densitometer;
- errors in the analysis of composition possibly resulting from poor sampling techniques; and
- the suitability of the AGA8 equation for use with rich natural gas mixtures.

A Joint Industry Project (JIP) was established, in conjunction with the Gas Research Institute, a number of major oil and gas companies and two public bodies, to investigate the applicability of the AGA8 equation of state to rich natural gas mixtures. A major programme of work is now in progress at NEL to establish reference-quality measurements of density for ten natural gas mixtures typical of those recovered from North Sea condensate fields. The measurements are being made using the UK's primary standard densitometer for gases over a range of pressures and temperatures commensurate with typical metering conditions.

The principal objectives set by the JIP were to:-

- to determine the magnitude of the differences between the AGA8 equation of state and reference-quality density data produced for ten synthetic natural gas mixtures in the range $80 \geq p/\text{bar} \geq 180$ and $40 \geq t/^\circ\text{C} \geq 80$, which bracket current metering conditions; and
- to provide reference-quality density data for use in subsequent refinements to the AGA8 equation.

To prevent any loss of measurement accuracy in the near critical region and change of composition in the vicinity of the phase boundary it was agreed that the lower temperature of measurement for any specific system was a minimum of 10°C above the cricondenterm for the mixture.

2. DESIGN AND OPERATION OF THE FILLING CIRCUIT

The condensible nature of the rich natural gas mixtures required the use of an alternative filling circuit to that developed previously for the primary standard densitometer^[2]. Calculations showed that a significant source of measurement error could arise from small leaks of the test gas over prolonged periods of time from any part of the high-pressure circuit. Selective loss of the lighter components would lead to changes in the composition of the mixture and would, if not prevented, give rise to a significant systematic error of measurement. Circuit components with very low leakage rates were required to minimise this effect.

Though most of the existing pipework and valves might have proved suitable the leakage rate from one key component of the original pressure measurement circuit (a

hand-operated variable volume unit used to balance the pressure in the test and reference gas circuits) was known to be unsatisfactory. Despite modification, small but detectable leaks were still apparent from this component. A decision was taken to develop a new filling and pressure measurement circuit based on valves and fittings of the highest quality as used in the semiconductor industry. Although the valves have a working pressure limit of only 200 bar this was adequate for the planned series of measurements.

2.1 Minimisation of Loss of Component

As discussed any loss of component from the test mixtures during either the filling cycle or during the prolonged period of measurement would be selective and result in a change of composition of the test mixture. The problem of containment is exacerbated in this instance by the limited quantities of gas available. Great care was taken in the design of the loading facility to eliminate possible leakage sources and to prevent condensation from occurring in any part of the circuit.

A temperature-stabilised enclosure houses the new filling circuit, see Figure 1 for details. The enclosure is insulated and its temperature maintained at 55 °C by a heat exchange unit fed from a temperature-controlled circulation bath. The enclosure contains the sample gas cylinder, the compressor, all valves and most of the pipework.

Modifications were made to the compressor, a commercial, two-stage unit with a compression ratio of 40 to 1. The interstage cooler was removed to minimise the potential for phase changes resulting from rapid cooling, and of most of the original pipework replaced with low-leakage components. The compressor was also carefully adjusted to prevent stall at elevated pressures.

Diaphragm-sealed valves were utilised to eliminate the possibility of leakage past valve stems. Cajon VCR pipe fittings, suitable for both elevated pressure and high vacuum use, and welded joints, where possible, were used to minimise leakage from pipework and fittings.

The high-pressure line which leads from the filling circuit to the densitometer is trace heated and lagged. A resistance thermometer, placed in close thermal contact with the line, is used to monitor its temperature. The temperature of the line is maintained at 50.0 ± 0.1 °C by an electrical heater controlled by a three-term controller. Temperature fluctuations in the external components connected to the densitometer have an influence on the stability of the pressure and density of the test gas within the vessel. With moderately good temperature control the influence of these fluctuations can be reduced to acceptable levels by keeping the internal volume of the external circuit small compared to that of the densitometer. Here, the internal volume of the pipework, valves and transducer exposed to the test gas have been kept to some 4 ml, or about 1 % of the internal volume of the densitometer.

Prior to use the circuit was tested under vacuum and at pressure using both helium and nitrogen.

2.2 Pressure Measurement

Pressure measurements were made using a Parascientific transducer type 43K-101 which was supplied together with calibration certificate for use in the range 0-3000 psia at temperatures up to 125 °C. A 10 kg aluminium block was machined to house two such transducers together with two electric cartridge heaters and a platinum resistance thermometer. The block and the short length of pipework leading to the transducer were lagged with suitable insulation material. The temperature of this block is maintained at 50 ± 0.1 °C by a three-term proportional controller.

A digital display unit provides the necessary power supply to the transducer and undertakes the measurement of the time period for both the pressure and temperature elements. This display also gives a visual indication of the indicated pressure in bar. As the resolution of the display is limited to ± 0.01 bar it is not used for accurate measurement of pressure.

The pressure indicated by the transducer is a function of the period of oscillation of both the pressure and temperature components:-

$$p = p(\tau_p, \tau_T, a_1, \dots, a_{14}),$$

where τ_p and τ_T are the pressure and temperature periods, respectively, in μs , and a_1 to a_{14} are the calibration coefficients as determined by the supplier.

The calibration of the transducer was checked in situ against a Desgrange and Huot, metrology Class S2, gas-operated pressure balance together with a Druck digital pressure indicator for ambient pressure measurement. The uncertainty of the D&H balance is 0.005 % of indicated gauge pressure and that of the Druck is 0.015 % of ambient pressure. The circuit leading to the transducer was fitted with a small filter unit containing activated carbon to remove any traces of oil vapour which may be present in the nitrogen gas from the D&H balance. The checks on calibration were made at zero-pressure and at 10 bar intervals between 50 and 190 bar. The differences between the pressures calculated from the supplier's calibration equation and the known applied pressures are within a maximum of 14 mbar over the pressure range of the proposed measurements. Evidence from NIST (Boulder) and Imperial College suggested that the pressure component of calibration of this type of transducer remain constant over long periods of time, six months or more, but that the zero-pressure component, or offset, drifts more quickly with time. Software was developed to calculate the pressure at the transducer from its pressure and temperature periods. The software corrects the pressure calculated from the supplier's equation for the differences in pressure observed at calibration and for subsequent drifts in the zero-pressure offset. The results obtained to date suggest that the total uncertainty in the corrected pressure is within 7 mbar, or 0.01 % throughout the measurement range. This figure includes the uncertainty arising from the calculation of pressure heads in pipelines.

At the end of each set of isochoric measurements the pressure transducer is evacuated and the temperature and pressure period recorded. The zero-pressure offset is used to correct subsequent measurements of pressure. At the end of each series of

measurements on a mixture the calibration of the transducer is fully rechecked using the D&H and Druck pressure standards.

2.3 Density and Temperature Measurement

Density measurements were made using the primary standard densitometer, a dual-sinker magnetic-suspension densitometer, as described in reference 2. The only differences in equipment between the apparatus described and that used here relate to the use of the new filling circuit and the method of pressure measurement. The uncertainty in the measurement of pressure as assessed, from all observations made to date, is 0.01% of indicated pressure.

Temperature measurements were made using four standard 25 ohm platinum resistance thermometers as described in reference 2. The total uncertainty in measured temperature is 4 mK. The temperature in the main densitometer system can be set by computer controlled equipment to within a few milli-kelvin of any prescribed temperature in the interval -40 °C to 150 °C.

The total, or combined, uncertainty to be associated with each measurement of density at the specified temperature and pressure is given by the following expression:-

$$U_{\rho, \text{total}}^2 = U_{\rho}^2 + [(\partial\rho/\partial T)_p \cdot U_T]^2 + [(\partial\rho/\partial p)_T \cdot U_p]^2,$$

The measurement uncertainties in density, U_{ρ} , temperature, U_T , and pressure, U_p , were assessed for each individual measurement and take account of all factors excluding adsorption. The partial derivatives in the above expression were calculated at each point from the AGA8 equation of state. Using the above expression the combined uncertainty in density was calculated to be within 0.02% for each of the reported measurements.

2.4 Mixture Preparation and Handling

All of the gas mixtures were prepared for NEL by the National Institute for Standards and Technology (NIST) at Boulder, using their gravimetric standard. Each mixture was prepared by carefully weighing pre-determined quantities of the pure component gases into an evacuated and thoroughly degassed cylinder at 20 °C. The quantities of components added were such that the final filling pressure at this temperature was some 80 % of the dew-point pressure for the mixture. The filling pressures for the seven mixtures ranged from 22 to 35 bar at 20 °C. Since the quantity of gas contained in each 11 litre cylinder was limited, two cylinders of matching composition for each mixture were obtained.

Following shipment to NEL the gas cylinders were stored in a specially prepared room, fitted with gas sensors and an emergency evacuation system, and maintained at a temperature of around 55 °C (some 20 °C or more above the cricondentherms for the mixtures) for a minimum of three weeks prior to usage. The cylinders were turned on a regular basis during pre-treatment to ensure that any drop out of higher

hydrocarbons which might have taken place during shipment was completely reversed and that all components were in the gaseous phase.

2.5 Operating Procedure

Normally measurements of density would have been made on individual isotherms starting at the lowest pressure and steadily incrementing the pressure until the maximum test value had been reached. Because of the limited amount of gas contained in each sample cylinder and because of the possibility of selective loss of component from prolonged containment of the test gas in the compressor this procedure was rejected in favour of the following 'isochoric' method.

A planned measurement schedule for each mixture was prepared which conserved gas utilisation and minimised any loss of components through the gas compressor. A set of 48 state points for each mixture, uniformly distributed throughout the measurement range, were determined at eight prescribed temperatures using the AGA8 equation of state to model the mixture. The algorithm took no account of the small external volume of pipework linking the densitometer to the pressure transducer and the isolation valves or of the dilation of the densitometer and pipework with temperature and pressure. The first state point in each case corresponded to the highest pressure at the lowest temperature of measurement. Successive groups of state points corresponded to points on six 'isochores' spanning eight prescribed temperatures. Figure 2 shows the distribution, and the sequence, of measurement points for mixture 1. The filling and measurement sequence for each mixture was as follows:-

- (1) The densitometer and associated pipework were brought to working temperature, flushed several times with a small amount of test gas, then evacuated to a pressure of around 1 Pascal.
- (2) The densitometer was filled slowly with the test gas to the maximum working pressure at the lowest temperature of measurement.
- (3) The densitometer and pressure measurement system were isolated from the compressor and gas storage system.
- (4) Subsequent adjustments to the system pressure on the six 'isochores' were made by dropping the system temperature by 5 °C to the next predetermined measurement point.
- (5) On completion of measurements on an 'isochore the temperature was reset to the highest temperature for that isochore and the measurement of density repeated.
- (6) The system pressure was carefully reduced to the pressure corresponding to the first measurement point on the next isochore.

All pressure changes were made at the highest temperature of measurement for each isochore. A slow and controlled discharge was effected by returning the gas via a 3 m long capillary tube, maintained at around 54 °C, to the supply cylinder.

Density measurements at each of the 48 pre-determined state points for each mixture were made after full temperature and pressure stabilisation had been achieved. This normally took a period of 3 hours. The differences in density observed between the initial

and the repeat measurements on each isochore, made some days later, are consistent, when corrected to the same T and P, to within some 30 ppm. No observable changes in pressure were recorded between the first and repeat density measurement on each isochore.

3. RESULTS

3.1 Mixture Compositions

All gas mixtures have been prepared by the National Institute for Standards and Technology (NIST Boulder), using their gravimetric standard facility. The reported compositions of the mixtures used in this work are:-

Component	Composition/(% mole fraction)			
	Mixture 1A	Mixture 1B	Mixture 2B	Mixture 3A
methane	59.00282	59.00126	59.00555	58.98993
nitrogen	4.99504	5.00063	4.99786	5.01541
carbon dioxide	6.00502	5.99242	6.01770	5.97568
ethane	10.00080	9.99694	15.00506	18.01148
propane	14.01250	14.02653	9.99485	8.00367
n-butane	5.98382	5.98222	4.97898	3.29625
n-pentane	-	-	-	0.49186
n-hexane	-	-	-	0.21573
No. of components:	6	6	6	8
Molar mass / (kg/mol):	0.026171996	0.026171858	0.025327872	0.02490049
Cylinder Identity:	LL-10807	LL-10808	LL-10805	LL-10797

Each mixture was prepared by carefully weighing pre-determined quantities of the pure component gases into an evacuated and thoroughly degassed cylinder maintained at 20 °C. The purity of each of the component gases was verified by gas chromatography. The final filling pressure for each mixture was kept to 80% of the dew point pressure for the mixture at 20 °C. Filling pressures ranged from 22 to 35 bar.

3.2 The AGA8 Equation of State

The AGA8 equation was developed as a means of establishing accurate densities and compressibility factors for a range of natural gas mixtures and related hydrocarbon gases over a wide range of operational conditions. The coefficients of the equation were determined by regression to an extensive bank of experimental data for natural gas mixtures and for binary and higher order mixtures of hydrocarbons with nitrogen, carbon dioxide and other gases.

The uncertainties to be expected in density values calculated from AGA8 depend upon the composition of the natural gas and on both the temperature and pressure at the metering

conditions. The targeted uncertainties (at one standard deviation) for the AGA8 equation of state in terms of temperature and pressure are:-

Region	Temperature Range	Pressure Range	Uncertainty in Density
1	- 8 to 62°C	0 to 120 bar	0.1 %
2	- 60 to 120°C	0 to 170 bar	0.3 %
3	-130 to 200°C	0 to 700 bar	0.5 %
4	-130 to 200°C	0 to 1400 bar	1.0 %

The AGA8 equation is claimed to meet these expected or targeted uncertainties in density for gas mixtures having a normal range of compositions, see below, within Region 1 and in parts of Regions 2, 3, and 4. For the expanded range of compositions given in the following table the uncertainties in density are expected to be higher than those for the normal composition range, especially in Regions 2 to 4.

Component	Normal range		Expanded range	
	Lower Limit	Upper Limit	Lower Limit	Upper Limit
Methane	45	100	0	100
Nitrogen	0	50	0	100
Carbon dioxide	0	30	0	100
Ethane	0	10	0	100
Propane	0	4	0	12
Butanes	0	1	0	6
Pentanes	0	0.3	0	4
Hexanes plus	0	0.2	0	dew point

Details for seven inorganic compounds have been omitted from the above table. The temperatures and pressures at the metering conditions associated with the newer North Sea fields lie within Regions 1, 2 and 3 of the AGA8 equation. The composition of the natural gases extracted from these fields are, however, of much richer composition than those used in the development and testing of the AGA8 equation.

The measurements of density were compared with density values calculated from a software package based on the latest version of the AGA8 equation of state^[1]. The values of the constants and parameters of the equation used in the software implementation were adjusted in accordance with the errata issued in June 1993^[1]. The molar masses of the component gases were also replaced by the latest recommended values^[3].

All temperatures measured in the current programme of work are on the ITS-90 temperature scale^[4] whereas the AGA8 equation is based on the IPTS-68 scale^[5]. For the purpose of comparison, each of the measured values of temperature were converted to the IPTS-68 scale.

3.3. Comparison of Measurements with AGA8

Measurements on five gas mixtures have been completed. Outline details of the results for the first three mixtures are given here. Because of the commercial interest in the work only general trends can be given at this stage. Full details of the measurements and their comparison with the AGA8 equation may be published in the open literature at some future date.

For all of the reported measurements the total uncertainty in the measured value of density at the specified temperatures and pressures is within 0.02 %. The measured densities have been compared with values calculated from the AGA8 equation of state. The differences are defined in percentage terms as :

$$100 \cdot (\rho_{\text{meas}} - \rho_{\text{AGA8}}) / \rho_{\text{AGA8}}$$

Two forms of plot have been prepared; bubble plots , as described below; and a deviation plot showing the trend of the percentage differences for the various 'isochores' with density.

The bubble-plot diagram contains four main items:-

- a) a solid curve showing the calculated phase boundary for the mixture;
- (b) a dashed line showing the critical isochore for the mixture;
- (c) a series of circles centered at the pressure and temperature of each measurement of density. The diameters of the circles are proportional to the magnitude of the percentage differences at that point; and
- (d) a single circle in the top-left of the diagram showing the scale of the percentage differences. For commercial reasons this item is blanked out.

Plots showing the trend of the agreement between the measured and calculated densities are given in Figures 3 to 6. A similar comparison has been made for the BWRS equation of state. However, the agreement obtained between measured and calculated densities was almost an order of magnitude poorer than for the AGA8 equation. Comparisons with the NX19 and the Standing and Katz equations may be made at some future date.

3.4 Analysis of Results

From Figure 6 it can be seen that the AGA8 equation is in best overall agreement with the results for mixture 2A, followed fairly closely by those for mixture 3A. The differences for mixtures 1A and 1B, which have closely matched compositions, are considerably larger than for the other two mixtures. For all three mixtures the agreement improves both at low pressures and at high temperatures.

In the following table the compositions of the C₂ to C₆ components for the three mixtures are listed together with the limiting compositions of the same for both the normal and extended range of operation of the AGA8 equation, see section 3.2.

Component	Upper Limit of Normal Composition Range for AGA8 / %	Upper Limit of Extended Composition Range for AGA8 / %	Component Composition in Mixture/%		
			Mix. 1	Mix. 2A	Mix. 3A
Ethane	10	100	10	15	18
Propane	4	12	14 #	10	8
Butanes	1	6	6 #	5	3.3
Pentanes	0.3	4	-	-	0.5
Hexanes	0.2	dew point	-	-	0.22

From this table it should be noted that the composition of the C₂ to C₆ components of the mixtures, with one exception, all lie in the extended range of compositions. The propane content of mixture 1 lies beyond the limit of the extended range; the butane content of the same mixture is just within its limit for this range.

Of the differences observed those for mixture 1 are significantly larger than those for the other two mixtures. The best agreement between the results reported here and the AGA8 equation is for mixture 2A, followed by mixture 3A.

The higher hydrocarbon content of mixtures 2A and 3A are each within the extended composition limits of the AGA8 equation. Though good agreement is obtained with the data for both mixtures the predictive capability of the AGA8 equation is diminished by the presence of 0.5% pentane and 0.22% hexane in mixture 3A.

Mixture 1, however, exceeds the extended range composition limit for propane and is just within this limit for butane. It would therefore appear that the maximum differences between measured and calculated densities occur for those mixtures with component compositions above the extended range of compositions specified for the AGA8 equation.

4. CONCLUSIONS

The AGA8 equation of state^[1] gives a better representation of the data for these rich natural gas mixtures than had been expected at the outset of this work. Evidence to-date suggests that the maximum differences between measured and calculated densities occur for those mixtures with component compositions above, or possibly close to, the extended range of compositions specified for the AGA8 equation.

This result is not entirely unexpected and it is to the credit of the developers of the AGA8 equation that it performs as well as it does in the extended range of compositions.

The reference-quality density measured produced during the course of this JIP will allow refinements to be made to the parameters of the AGA8 equation which will:

- extend its normal compositional range; and
- improve its ability to determine accurately the density of a broad range of natural gas mixtures.

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Figure 1. Schematic Diagram of Modified Filling Circuit.

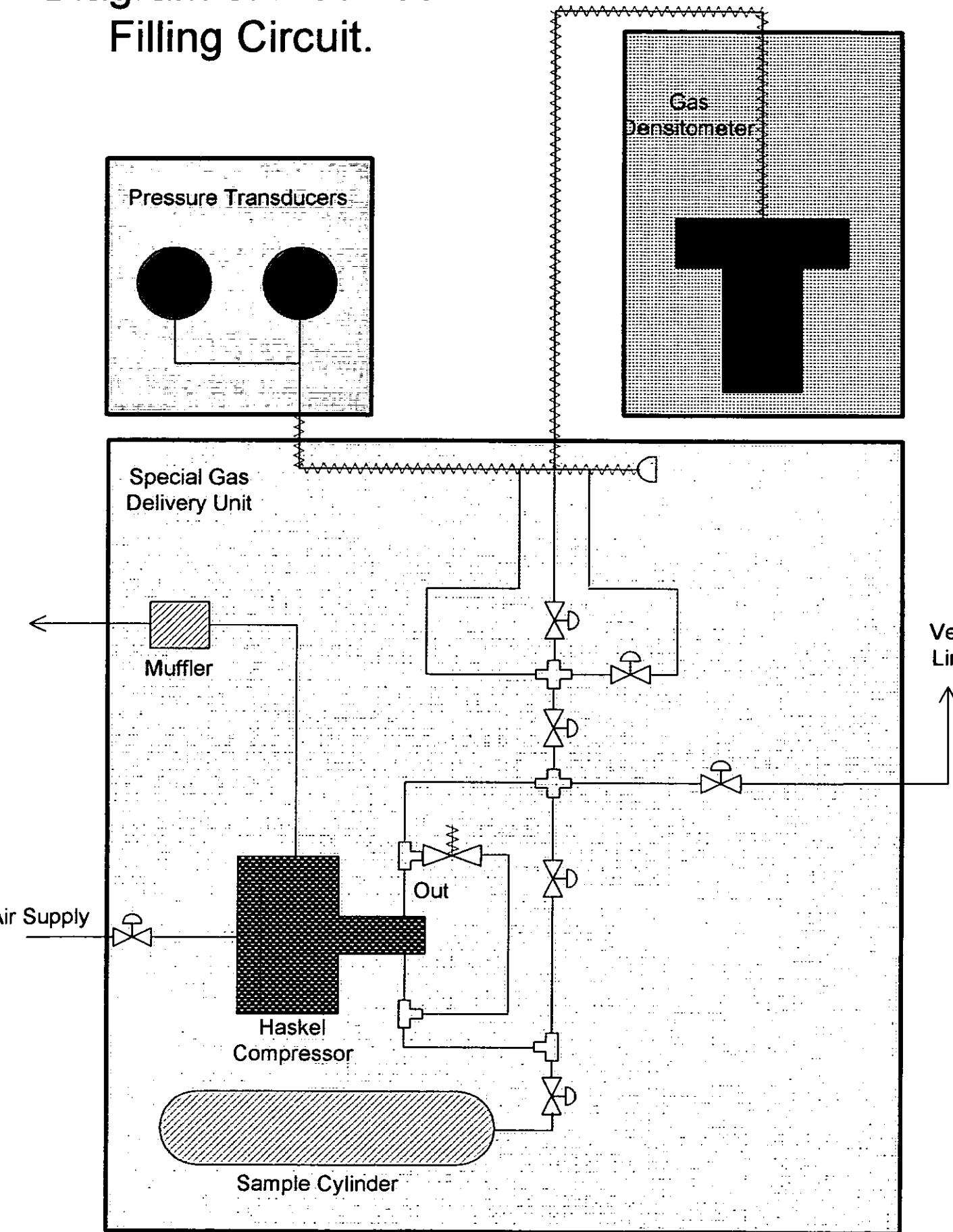
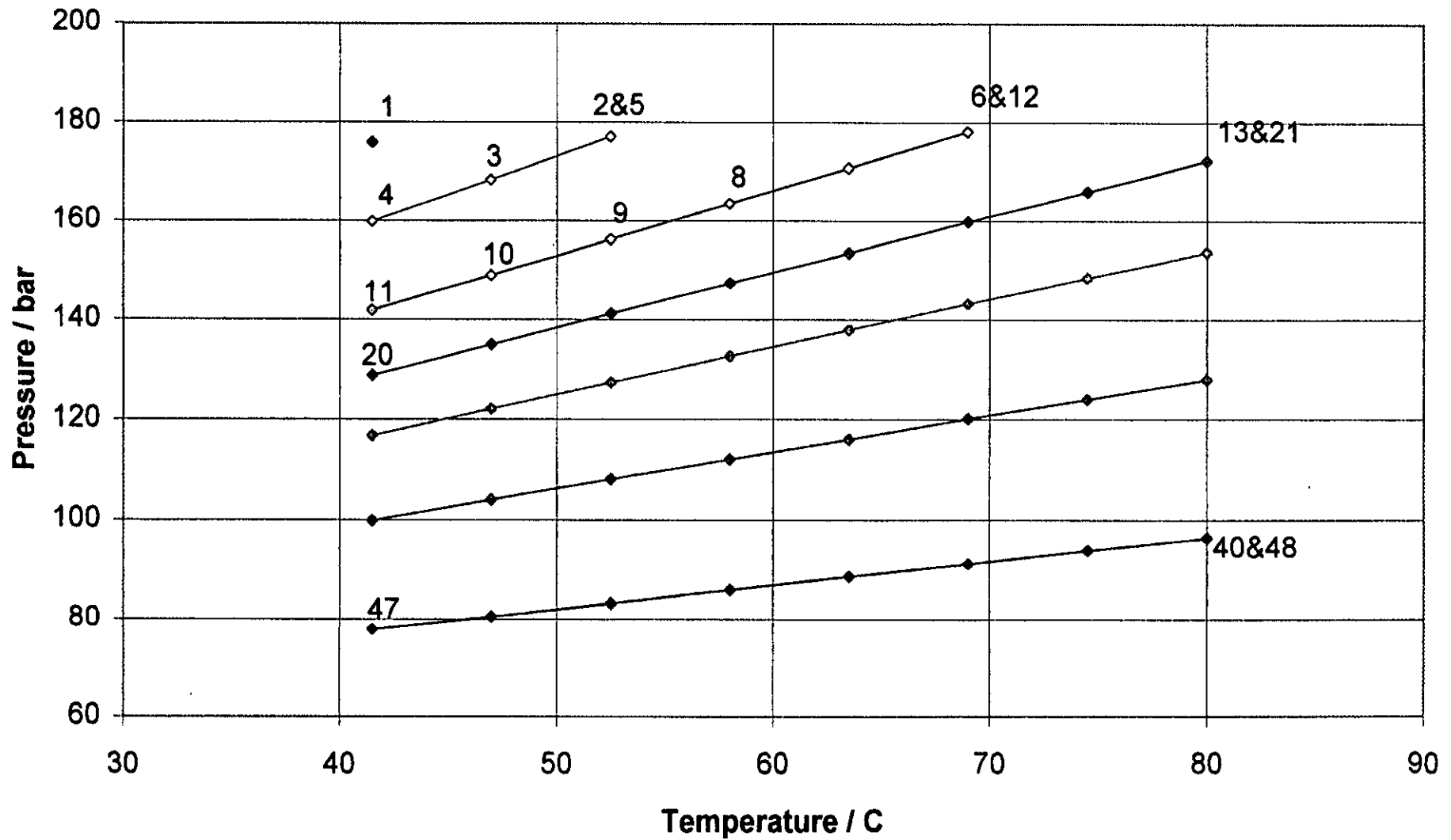


Figure 2. Sequence of Measurements for Mixture 1.



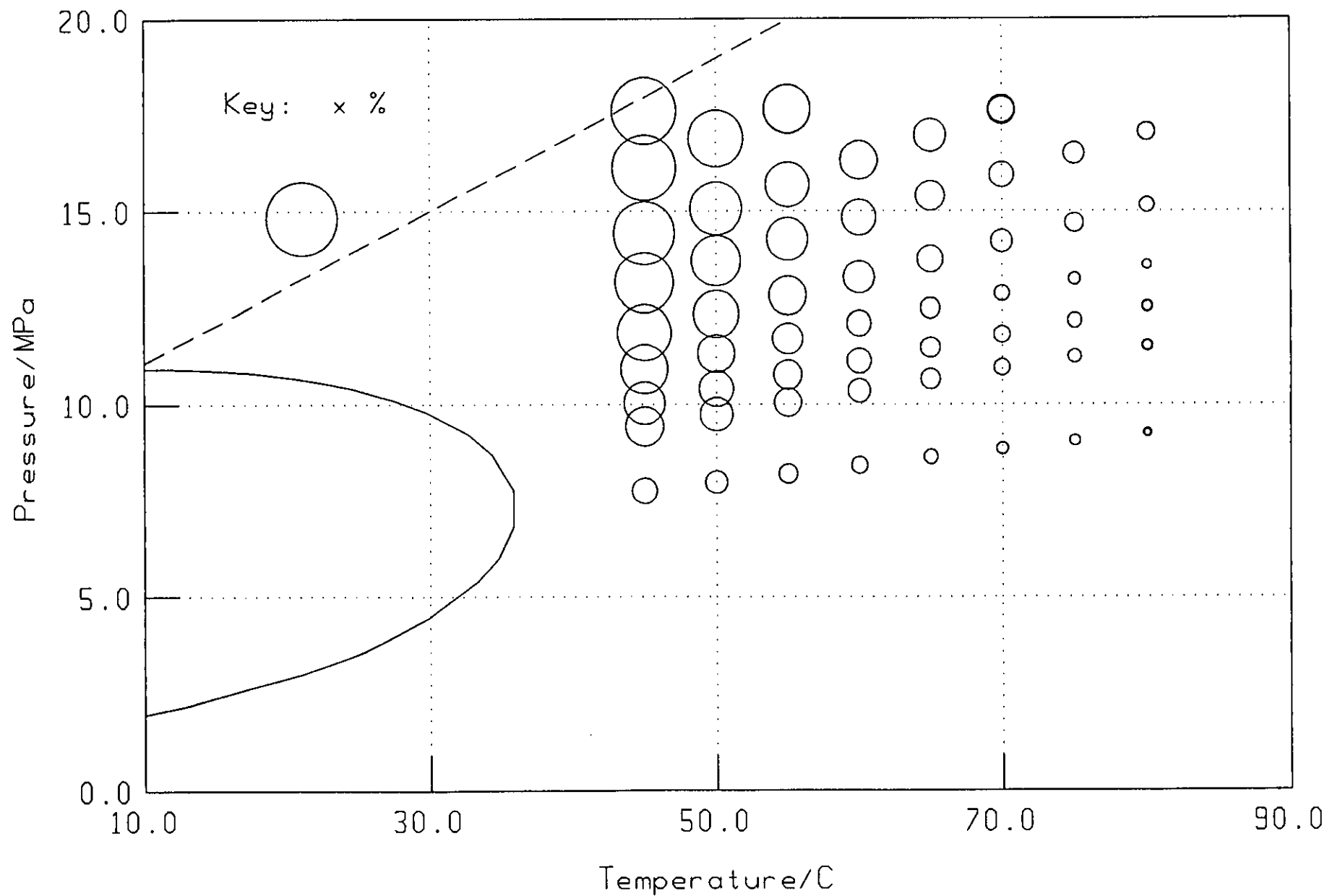


Fig.3 Comparison of density data for Mixture 1_ with the AGA8 eqn.

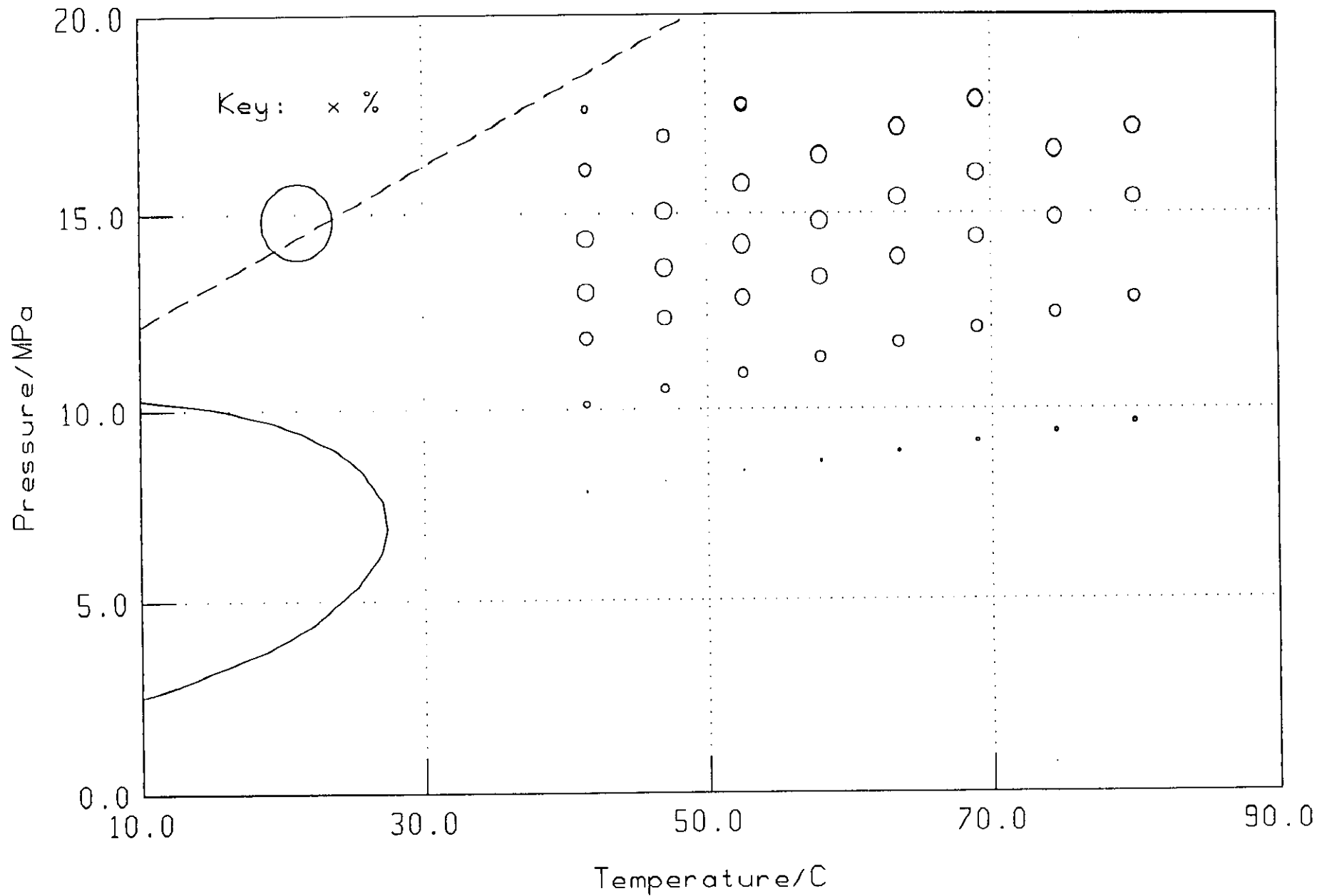


Fig.4 Comparison of density data for Mixture 2a with the AGA8 eqn.

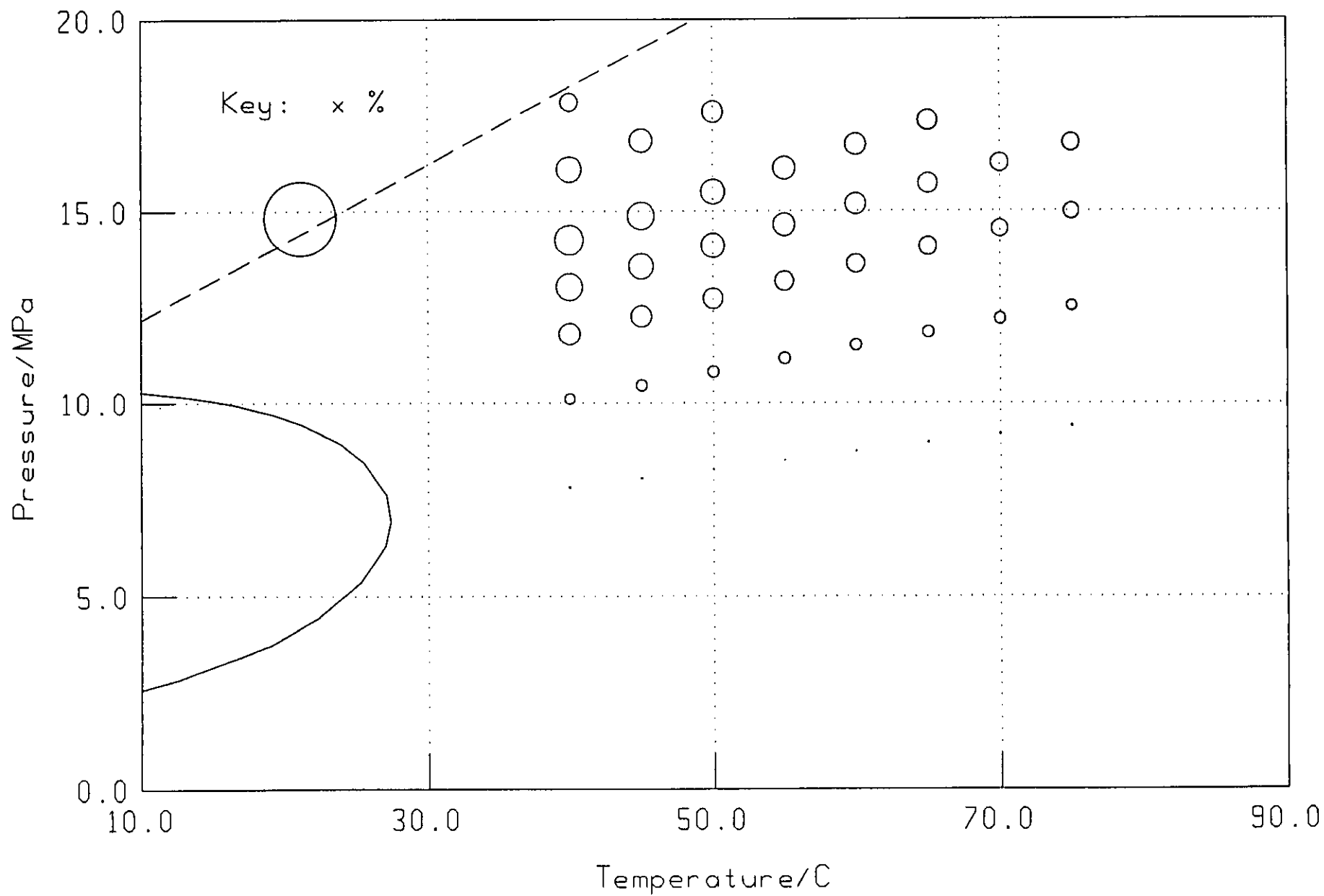


Fig.5 Comparison of density data for Mixture 3a with the AGA8 eqn.

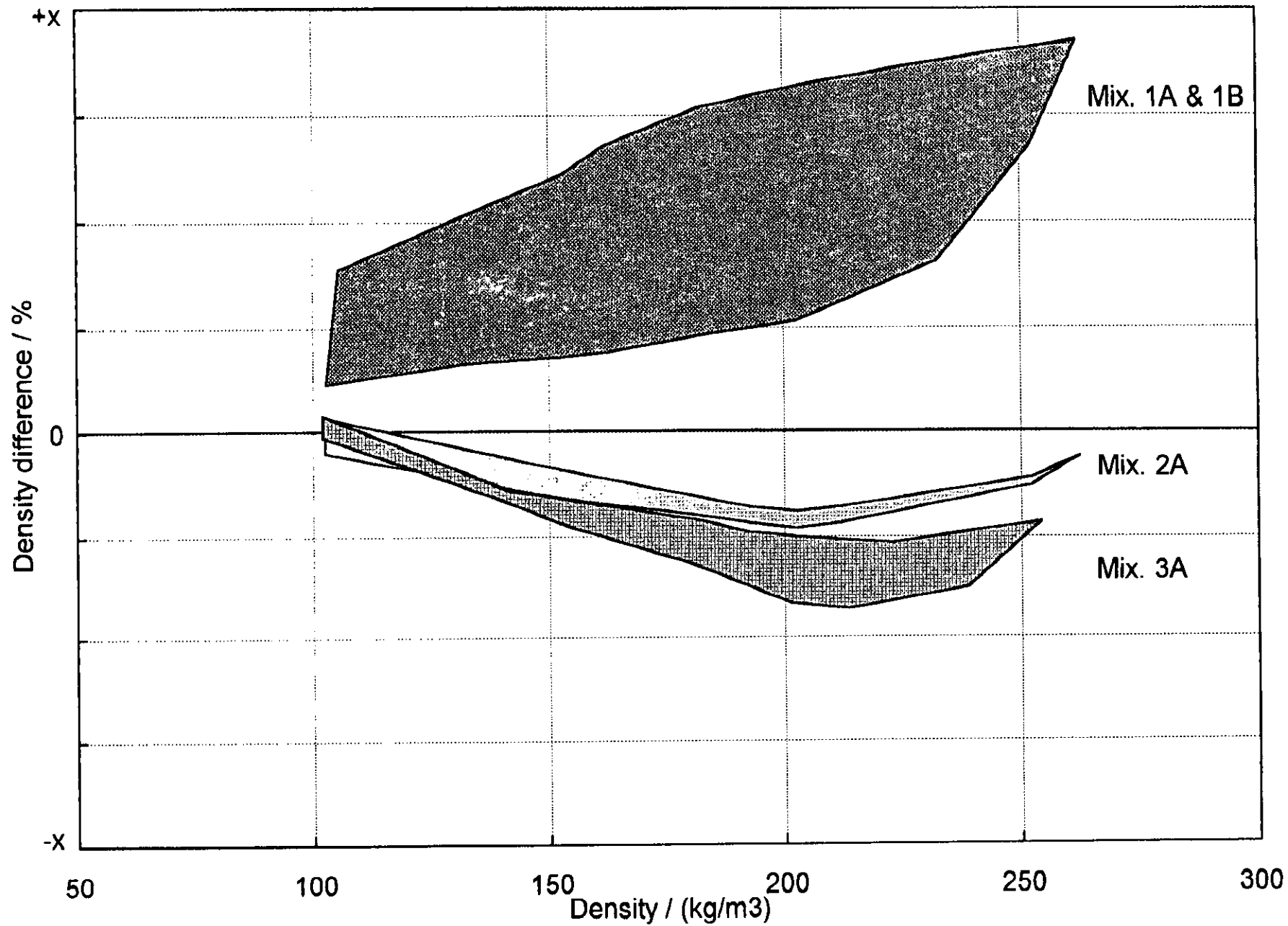


Fig. 6 Comparison of density data for Mixtures 1, 2A and 3A with the AGA8 eqn.