A High-Pressure Multi-Component Phase Equilibria Setup Utilising Online Gas Chromatography

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The design and optimisation of supercritical extraction processes rely on thermodynamic models capable of accurately predicting phase behaviour. Developing such models requires accurate and comprehensive experimental phase equilibria data and, in particular, multi-component data. Synthetic methods, albeit well-established, are not ideal for studying ternary - and higher mixtures. A static-analytic phase equilibria setup was designed, constructed and commissioned. The high-pressure, visual, variable volume phase equilibrium cell is suited for multi-component mixtures and operable at temperatures and pressures up to 150 °C and 30 MPa. The setup is fitted with two ROLSI™ samplers connected to an online gas chromatograph. The sampling height of both ROLSI™ is adjustable. This enables simultaneous withdrawal of two samples from any vertical position within the cell. The gas chromatograph, equipped with two FIDs, one TCD, four columns and two switching valves, enables simultaneous analyses of two samples with constituents ranging from permanent gases to mid-length hydrocarbons.

INTRODUCTION

Supercritical fluid applications have developed to fulfil a vital role in the food and beverage, petroleum, natural gas, biochemical, pharmaceutical, polymer and coatings industries [1-6]. Developing, operating and optimising the equipment and processes serving these industries require robust thermodynamic models [7-9]. Improving the quality and output of phase equilibria data on which these models are based will, in turn, enable improved design and operation of supercritical extraction equipment [10-12]. Large amounts of high pressure / supercritical phase behaviour data are available for binary mixtures. The collection of binary data is by no means complete, but techniques are well understood and - developed. However, multi-component phase behaviour data is required, and lacking. Since phase equilibria of three or more components is not easily measured with synthetic methods, the need for an analytical technique developed [13].

Within the analytical grouping, methods are classified according to if and how species move in and through the experimental system. In static-analytic systems, species do not move through the experimental setup. For dynamic-analytic systems, comprising single-phase circulation, multi-phase circulation, continuous-flow and semi-flow, the converse is true. In both circulation systems mentioned above, circulation is either co-current or counter-current. Some of the overriding factors influencing the choice between static-analytic or dynamic-analytic are [14-18]:

a) Hardware associated with flow - and circulation systems often require greater capital investment.
b) Thermally labile compounds are more easily investigated with continuous- and semi-flow equipment.
c) Counter-current circulation improves phase contact, but co-current circulation minimises contamination across the phase interface.
d) Circulation - and static systems (closed circuit) require fewer feed products, and are better suited to investigate costly chemicals.
e) In dynamic systems, but circulation systems especially, pulsation disturbances due to pumping is a known problem.
f) Sample extractors suited for static systems do exist, but are limited in variety.
g) Multi-port sampling valves, well-suited for circulation systems, seldom enable operation at both high temperatures and high pressures.

For the equipment discussed here, the main requirements are the extraction of small equilibrium samples from high-pressure, high-temperature, two-phase ternary mixtures, determining the composition of said samples, and the ability to investigate costly solutes available in small quantities only. Given these prerequisites, whilst being mindful of the factors listed above, the authors decided on a static-analytic setup utilising dual ROLSI™ samplers and online gas chromatographic (GC) analyses.

The remainder of this paper discusses additional detailed design considerations and the manner in which these were incorporated. An overview of the experimental system is presented. The authors provide concluding remarks on difficulties experienced during the commissioning and validation processes.

DESIGN CONSIDERATIONS

Observation of the internal volume

It is valuable to observe the entire equilibrium cell internal volume. The phase interface height varies between runs, and identification thereof is important to ensure sampling from the correct phase. This is even more important when sampling from a three phase region. Also, operating the system in synthetic (stoichiometric) mode requires identification of bubble-point and dew-point phase transitions. The customised sight glass housing is conical toward the open end in order to increase the attainable viewing angle. Upon procurement, the sight glass and housing was precision-measured using Mitutoyo Coordinate Measuring Machine inspection. The internal geometry was designed to align with this taper, allowing observation of the complete internal volume.

Internal geometry constraints

Sufficient vertical separation between top and bottom sampling points minimises the potential of sample contamination due to clouding across the phase interface. However, piston diameter should be sufficiently small to enable incremental adjustments to system volume and pressure. In addition, equilibrium cell construction from one piece of material reduces the potential for leakages and material failure. Also, 28 mm was the largest-diameter sight glass

obtainable, which satisfies the necessary guarantees. The cylinder, for piston movement, should align with the bottom of the equilibrium cell so as to enable the magnet to move up and down the entire length thereof. The internal geometry design, shown in Figure 1~~Figure 1~~, satisfies all these constraints.

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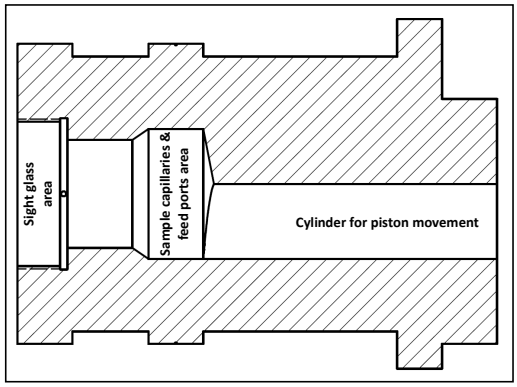

Figure 1: Equilibrium cell internal geometry design

A 3D linear finite element method analysis was used to determine the Von Mises stress distribution in the equilibrium cell structure. The final model, with 35 753 elements and 22 843 nodes, was validated with a mesh refinement study on a former model of 174 972 elements and 247 523 nodes. Results were satisfactory. Prior to experimental work, the equilibrium cell was hydrostatically tested for pressure integrity.

Experimental system adaptability

The system was designed to allow flexibility in approach. It can be operated in either analytical or synthetic mode, at a maximum pressure and temperature of 30 MPa and 150 °C respectively. During operation, equilibrium cell volume can be varied between 75 and 125 ml. The system is equipped with two ROLSI^{TM} enabling simultaneous sampling; two parallel GC pathways enable simultaneous injection and analyses. Great efficiency of the extraction-and-analyses process is achieved. Whilst maintaining equilibrium cell pressure, the height of both ROLSI^{TM} can be adjusted. This allows the adaptation of sampling points according to phase interface height. The arrangement of feed lines, feed valves and vacuum lines support the introduction of additional pressurised solvent during operation. This enables one to efficiently move across the entire pseudo-binary composition range for a given loaded solute mixture.

Dead volume minimisation

Minimisation of equilibrium cell dead volume is essential, and this was considered throughout the design. Pressure measurements are performed with a melt pressure transmitter, of which the diaphragm is flush with the equilibrium cell interior. The transmitter opening seals 6 mm from the cell interior, and possesses a diametrical annular space of 0.15 mm. The feed ports of diameter 1 mm, 1 mm, and 2 mm respectively, seal 2 mm from the equilibrium cell interior. The two ROLSI^{TM} capillary openings seal 3.7 mm from the equilibrium cell interior, and possess a diametrical annular space of 0.1 mm. The Sitec Sieber sight glass seals 19 mm

from the interior glass face, and possesses a diametrical annular space of 0.4 mm. The piston seals 10 mm behind the piston surface, and possesses a diametrical annular space of 0.15 mm. This corresponds to a total maximum potential dead volume of 0.61 ml.

EXPERIMENTAL SETUP

The major components of the setup are shown and listed in Figure 2~~Figure 2~~, Figure 3~~Figure 3~~ and Table 1~~Table 1~~.

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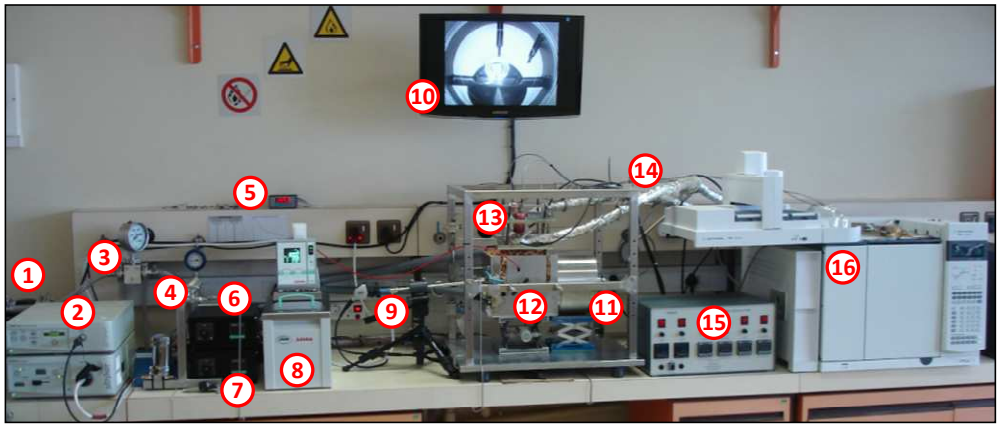

Figure 2: An overview of the experimental setup

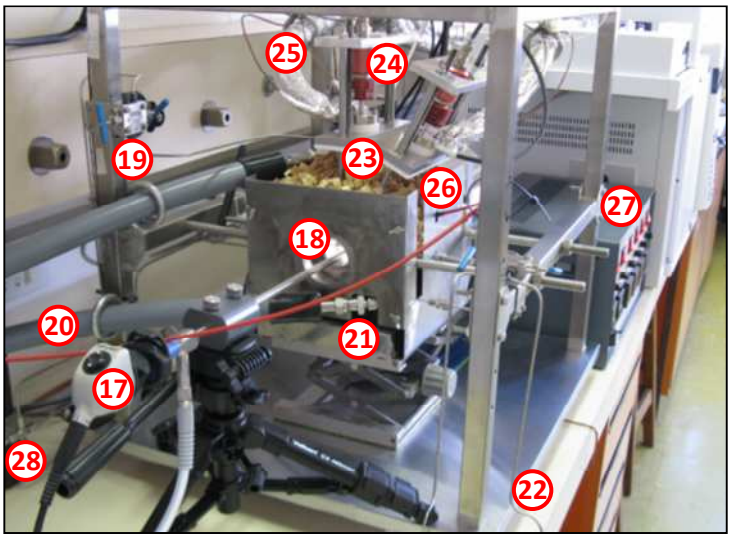

Figure 3: Equipment central to the experimental setup

Major components of high-pressure multi-component phase equilibria setup			
1	Vacuum pump	15	ROLSI™ control box
2	Camera and light source	16	Gas chromatograph
3	Vacuum gauge	17	Camera head
4	Pressurised solvent	18	Sight glass
5	Pressure display	19	Feed line manifold
6	Transfer tubing temperature control	20	Heatig circulator tubing
7	Pressurised solvent temperature control	21	Magnetic stirrer
8	Heating circulator	22	Pressurised solvent feed line
9	Camer head and endoscope	23	ROLSI™ displacement device
10	Monitor	24	ROLSI™
11	Pressure intensifier and piston	25	Transfer tubing
12	Equilibrium cell	26	Pt100
13	ROLSI™	27	ROLSI™ control box
14	Transfer tubing	28	Vacuum connection

Table 1: Major components of the experimental system

Equilibrium cell, feed lines and sampling points

A cross section through the area dedicated to feed ports and sampling capillaries (refer to Figure 1~~Figure 1~~) is shown in Figure 4~~Figure 4~~.

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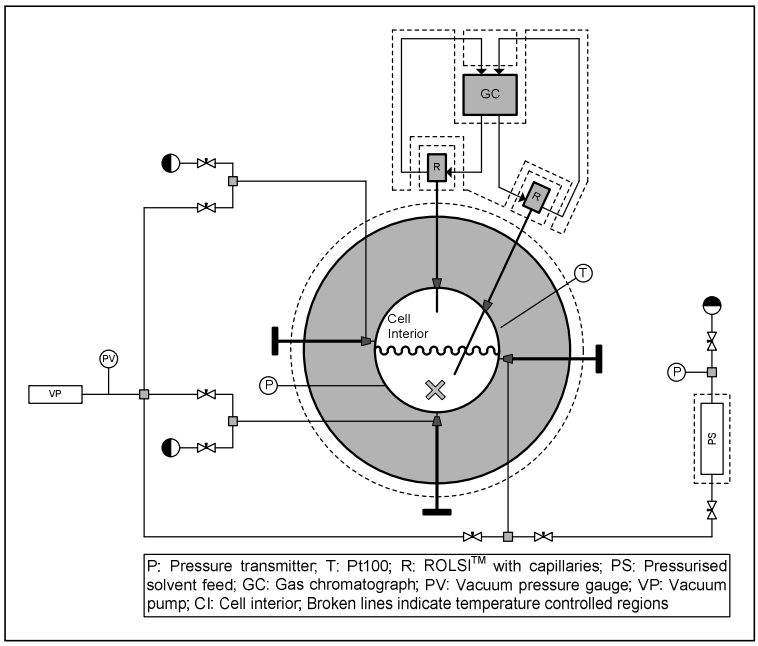

Figure 4: Cross section through area for feed lines and sampling capillaries

The equilibrium cell is fitted with three feed ports, two of which are normally used for loading and vacuuming. The third port is mostly used for draining and cleaning the cell. Starting a run, a mixture of solutes is loaded via syringe. The solutes are degassed by vacuum

exposure, followed by repeated flushes with the solvent of choice. Pressurised solvent is fed from a heated high-pressure cylinder. At this point, the quantity of solvent is chosen to produce a solvent-poor bulk composition. In progressing through the experimental run, additional solvent is introduced until the desired pseudo-binary composition range is covered.

A Julabo ME-6 heating circulator is used to circulate heating fluid through a jacket surrounding the equilibrium cell. Temperature is measured with an external Class B 1/3 DIN Julabo Pt100. Pressure is measured with an ONEhalf20 melt pressure transmitter (nonlinearity and repeatability of 0.25 % and 0.10 % of full scale output respectively). A pressure intensifier, in conjunction with high-pressure N_2, is used for piston movements. Stirring is accomplished with an external magnetic stirrer. Prior to sampling, the stirrer is stopped allowing phase settling to take place. Extracted samples pass through the capillaries, enter the heated transfer tubing, undergo vaporization and are swept onward to the GC inlets.

Approach to GC analyses

Figure 5~~Figure 5~~ indicates the configuration of ROLSI^{TM} samplers, transfer tubing, split-splitless inlets, columns, switch valves and detectors.

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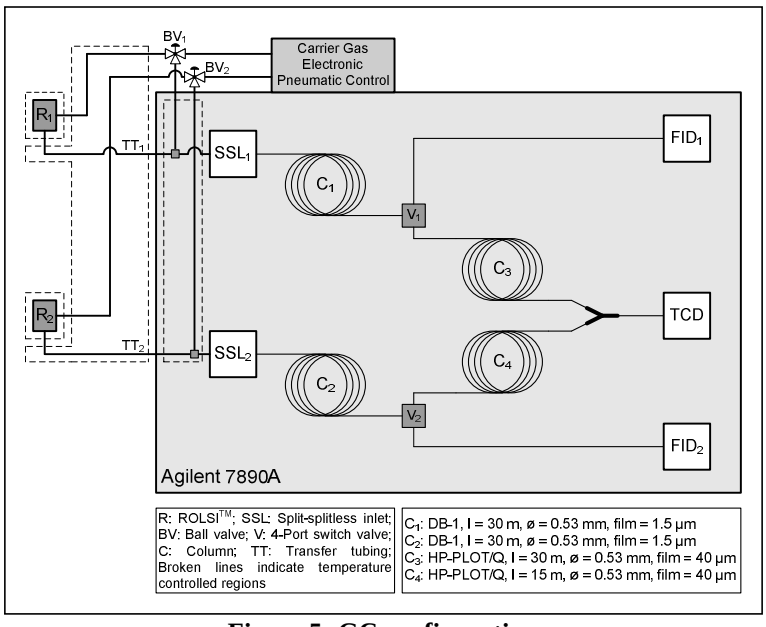

Figure 5: GC configuration

Helium carrier gas is continuously routed, via heated transfer tubing, to and from the ROLSI^{TM}. The ball valves, BV_1 and BV_2, enable elimination of one or both ROLSI^{TM} for maintenance purposes. Extracted samples are vaporized, enter the split-splitless inlets and pass through columns C_1 and C_2 respectively. The DB-1 columns retain higher-boiling solutes, whilst allowing the lower-boiling solvent to pass quickly. If the solvent is not suited for FID detection (for example, CO_2), the switch valves V_1 and V_2 direct the lighter fractions toward columns C_3 and C_4. These columns differ in length and cause staggering of the two

solvent peaks on one TCD. After all solvent has passed V_1 and V_2, these are switched and the separated higher-boiling solutes are routed toward the FIDs. If the solvent is suited for FID detection (for example, ethane or propane), all flow is directed toward the FIDs. This robust configuration enables analyses of mixtures with constituents ranging from permanent gases to mid-length hydrocarbons. Figure 6~~Figure 6~~ shows two FID chromatograms for dual simultaneous ROLSI™ injections from a ternary system containing the solutes dodecanol and hexadecane.

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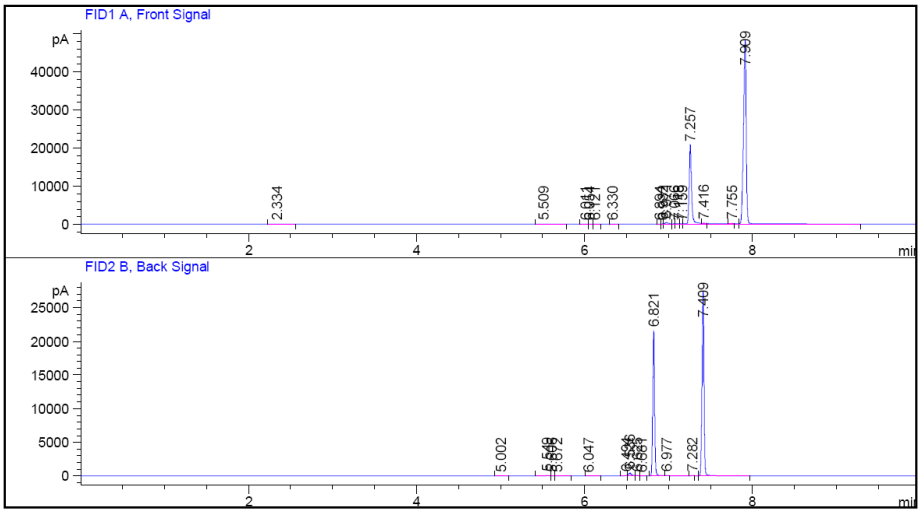

Figure 6: Simultaneous separation of dodecanol and hexadecane

COMMISSIONING AND VALIDATION – PROBLEMS EXPERIENCED

A number of difficulties were experienced during the commissioning and validations stages. These are discussed below.

Capillary droplet formation

In an attempt to characterize equipment behaviour, both ROLSI™ were operated in the lighter gaseous phase. Droplets, with densities similar to the bottom liquid-like phase, formed on the capillary tips (refer to Figure 7~~Figure 7~~). Viscosities of hydrocarbons in the C_{10} – C_{16} range aggravate the problem. After falling from the capillaries, the capillary openings were covered in a thin film with composition similar to the bottom phase. Removal of this film is possible through multiple ROLSI™ purges, but comparative sampling requires synchronisation of droplet formation rates. Leaving the system overnight, both in the absence of stirring and utilising slow tranquil stirring, still resulted in capillary droplet formation. Aggressive stirring is not a remedy since phase settling is required prior to sampling. Tests had shown the droplet formation rate to be largely independent of ROLSI™ temperature.

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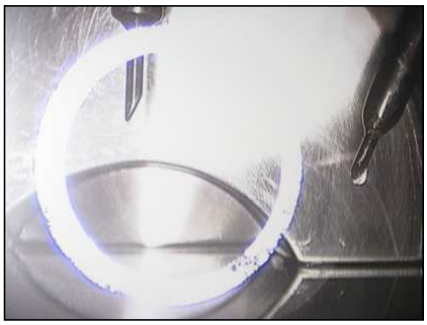

Figure 7: Droplet formation on diagonal capillary with no droplet on vertical capillary

Capillary blockages

Given the ROLSI^{TM} capillary internal diameter of approximately 0.15 mm, capillary blockages are known to occur. Great care was taken to ensure a clean and particulate-free internal environment. Yet, capillary blockages did occur, resulting in severe downtime. This problem can to a large extent be avoided by sampling only during the absence of stirring, and after a degree of phase settling has taken place; this allows all potential micro-particulates to settle below the sampling points.

Sample vaporization, transfer, splitting and injection

After sample extraction from the equilibrium cell this 'parcel of compounds' undergoes vaporization, transfer, division due to split ratio, and injection. For multi-component mixtures containing species with greatly varying boiling points, the complexities associated with this pathway increase substantially. Online injected samples and manually injected samples enter the GC inlet in two different areas. These are areas A and B respectively in Figure 8~~Figure 8~~.

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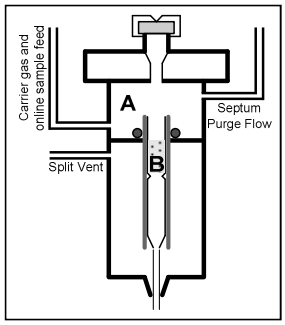

Figure 8: Difference in online – and manual sample introduction points

At present, a quantitative calibration procedure producing calibrated correction factors (not to be confused with response factors) is utilised. Important factors influencing this procedure are syringe type (plunger-in-barrel versus plunger-in-needle), syringe handling technique, injection technique, needle termination height, sample volume dependency of true split ratio, inlet temperature, and liner geometry and - design [19]. These factors require careful consideration to ensure sufficient similarity between the methods of online – and manual

sample introduction. Shown in Figure 9~~Figure 9~~ is a series of 25 ethane injections at varying ROLSI^{TM} opening times.

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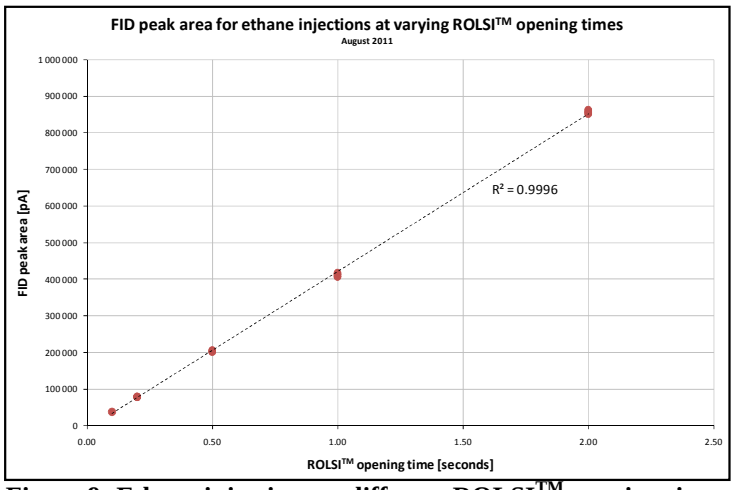

Figure 9: Ethane injections at different ROLSI^{TM} opening times

CONCLUSIONS AND FURTHER WORK

A static phase equilibria setup utilising online GC analyses to generate experimental high-pressure multi-component phase equilibria data was designed, constructed and commissioned. The equipment satisfies the original aims, whilst simultaneously allowing flexibility in operation.

Current experimental work on ternary supercritical solvent-alkane-alcohol systems continues. The systems CO_2 – *n*-dodecane – 1-tetradecanol, CO_2 – *n*-tetradecane – 1-dodecanol, CO_2 – *n*-dodecane – 1-dodecanol and CO_2 – *n*-tetradecane – 1-tetradecanol are the immediate focus. These data, together with binary data for the corresponding CO_2 – hydrocarbon mixtures and pilot plant experiments for CO_2 – *n*-tetradecane – 1-dodecanol [20-21], present a powerful platform enabling thermodynamic modelling and process optimisation. Solute expansion in the C_{10} to C_{16} range, and inclusion of ethane and propane as potential solvents are envisaged.

ACKNOWLEDGEMENTS

The financial assistance of Sasol (Pty) Ltd, the Department of Trade and Industry (DTI) of South Africa through the Technology and Human Resources for Industry Programme (THRIP) and the Department of Labour (DoL) of South Africa towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the sponsors.

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