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The Development of a Novel Technique to Measure *In-Situ* Solubilities in
Supercritical Carbon Dioxide

by

Christopher Michael Stroich ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of Master of Science

in

Environmental Science

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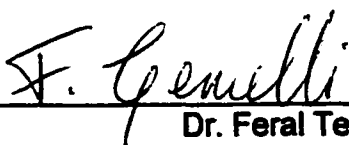
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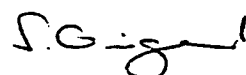
Environmental Science

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Thesis approved by committee on March 7, 2001

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Abstract

The research herein involves the development and verification of an *in-situ* solubility measurement technique in supercritical carbon dioxide (SC CO_2). The solubility measurement technique consists of a piezoelectric quartz crystal microbalance, which was used to measure the solubilities of β-carotene and copper thenoyltrifluoroacetone ($Cu(tta)_2$). The solubility of β-carotene in SC CO_2 was measured to be 9.57E-08 mol/mol at a CO_2 density of 0.7189 g/cm^3. The solubility of $Cu(tta)_2$ in SC CO_2 at densities of 0.6516 g/cm^3, 0.5948 g/cm3, 0.5407 g/cm^3, 0.4399 g/cm^3 were measured to be 1.81E-06 mol/mol, 8.36E-07 mol/mol, 3.75E-07 mol/mol, 3.36E-07 mol/mol, respectively. Finally, the solubilities for compounds of interest β-carotene and $Cu(tta)_2$ will be correlated using equations to calculate solubility, such as the density based Chrastil model and the Guigard-Stiver density-dependent solute solubility parameter model.

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I would like to thank my wife Nicole, whose continuous love, patience and advice helped me realize this project. I would also like to thank my parents for their unconditional love and support during my course of study at the University of Alberta.

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The assistance of all of the above-mentioned people and many others ensured that the entire undertaking ran smoothly. While many people contributed to this work and its interpretation, any errors and omissions are solely my own.

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1   Problem Statement

Throughout the world there has been a growing concern over soils polluted by industrial activity. These soils can be contaminated with a variety of substances, some readily remediable and others that are more difficult to remove. One of the most common and difficult types of soils to treat is a heavy metal contaminated soil. It has been estimated that metal contamination is present at more than two-thirds of the Superfund and DOD (Department of Defense) remediable sites within the U.S., with metals making up one half of the contaminants present at these sites (E.P.A., 1997a).

Some of the current technologies for treating these metal contaminated sites are electrokinetic separation, soil flushing and washing, solidification and stabilization, separation, excavation and off-site disposal (Roundtable, 1999). Although these methods are in use, there is a need for more effective technologies to treat this type of soil (E.P.A., 1997a). Supercritical fluid extraction (SFE) is a promising new technology that could remediate the heavy metal contaminated sites.

2   Introduction

2.1   What is a Supercritical Fluid (SCF)?

A supercritical fluid (SCF) is defined as a pure substance that exists above or at a specific critical temperature and critical pressure for that particular substance. The critical pressure and critical temperature critical point (Figure 2-1).
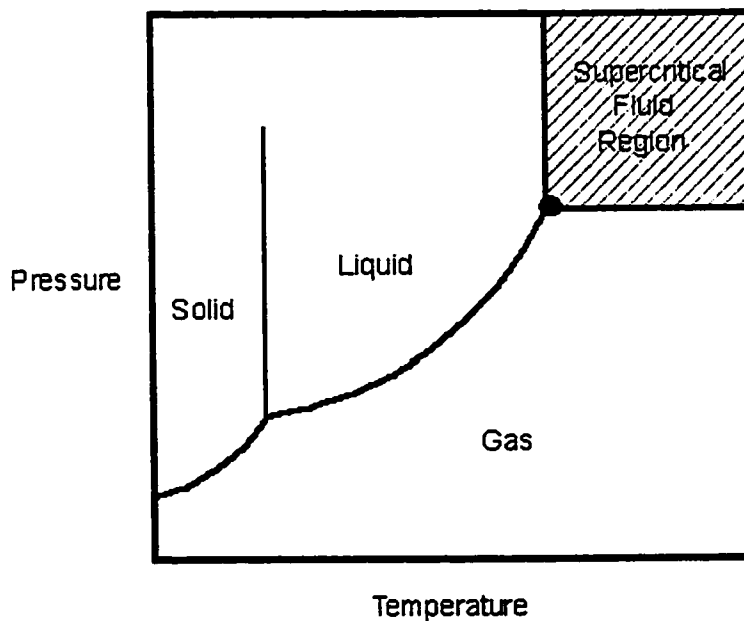
Figure 2-1. Schematic of a Phase diagram For a Pure Compound, Depicting the Supercritical Region

At the critical point, the gaseous and liquid phases of the substance become identical creating what is often termed a 'dense gas' (Brunner, 1994). Conversely, the more distant a substance is from the critical point the more distinct are the properties of gas and liquid. The properties embodied by the SCF are a mixture of the properties of the gas and liquid states. For instance, the SCF

exhibits gas-ike viscosity and diffusivity while retaining liquid-like densities (McHugh and Krukonis, 1994). These properties contribute to the usefulness of SCFs as extraction solvents; the fluid can easily disperse throughout a matrix and at the same time retain the density for ample contact and concentration gradients to operate. The low surface tension exhibited by the SCFs is a direct result of the previous properties, further enhancing its usefulness as an extractant. The resultant solvating power (the ability to dissolve a desired compound) of a SCF varies with each different compound at its critical state, however as a general rule of thumb the solvating power increases with increasing density of the specific component (Brunner, 1994).

2.2 Why use Supercritical Carbon Dioxide (SC CO₂) as a solvent?

The use of SCFs as solvents has shown its utility in many cases. The use of supercritical carbon dioxide (SC CO_2) as a solvent has many advantages over other substances such as organic and chlorinated solvents (Laitinen *et al.*, 1994). These advantages include properties such as: relative non-toxicity, low reactivity, non-flammability, lack of residue, the easily (technological) achievable critical point (304.15 Kelvin and 7.38 MPa) and its relative abundance and commercial availability.

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3 Objectives

The importance of understanding the solubility of solute is probably the most significant thermophysical property that must be determined and modelled in order to design efficient SFE processes (Bruno, 1991). Solubility measurements allow for effective design of SCF extraction processes by permitting the operating conditions to be optimized for maximum effectiveness (Bruno, 1991). Knowing the solubility of a solute in neat SC CO_2 and comparing it with the extraction data, an interpretation of different effects from the matrix, extraction technique and the effects of extraneous compounds can be ascertained.

The research herein involves the development and verification of an *in-situ* solubility measurement technique in SC CO_2. The solubility measurement technique consists of a piezoelectric quartz crystal microbalance (Guigard *et al.*, 1998) which, will be used to measure the solubilities of β-carotene and copper thenoyltrifluoroacetone (Cu(tta)$_2$) at different temperatures and pressures. The quartz crystal microbalance (QCM), with the desired compound adhered onto it's surface will be placed in a pressure vessel, which is in full contact with the SC CO_2. This technique provides the ability to take direct, real-time, rapid measurements of minute mass changes, which can be used to calculate solubility data.

β-Carotene is a well-studied compound for which thermophysical properties have been thoroughly investigated in SC CO_2 (Johannsen and Brunner, 1997; Mendes *et al.*, 1999; Sakaki, 1992; Skerget *et al.*, 1995). The

measurement of β-carotene solubility will be used to verify the (QCM) technique with other solubility measurement methods.

Copper thenoyltrifluoroacetone (Cu(tta)$_2$), a β-diketone metal chelate, whose solubility has not been measured extensively (Guigard, 1999) will be investigated at different pressure and temperature conditions to determine density dependent relationships on solubility.

Thenoyltrifluoroacetone (tta) was chosen as a compound to investigate for the following reasons:

➤ the limited solubility data of tta in SC CO$_2$,

➤ the relatively low toxicity of tta in the environment (Wai and Wang, 1997),

➤ the relatively high extraction efficiencies of tta in SC CO$_2$ (Wai *et al.*, 1996),

➤ the high stability of the β-diketones in SC CO$_2$ as compared to the low stability
   of dithiocarbamate metal complexes in water (Wai and Wang, 1997),

Copper will be used as a 'model' metal because of its relative non-hazardous properties. Copper is also a well-used metal in SFE processes and it is possible to compare this solubility data with other copper solubility and extraction data.

Finally, the solubilities for compounds of interest β-carotene and Cu(tta)$_2$ will be correlated using equations to calculate solubility, such as the density based Chrastil model (Chrastil, 1982) and the Guigard-Stiver density-dependent solute solubility parameter model (Guigard and Stiver, 1998). These models will be used because of the relative simplicity to obtain the correlations. These

models will also be used because of the absence of physico-chemical properties

for β-carotene and Cu(tta)$_2$.

4   Literature Review

This section will discuss the relevant literature pertaining to this research. An outline of this section is presented sequentially below.

➢ An overview of current soil remediation technologies for treating metal contaminated sites, including a description of SFE techniques to treat metal contaminated soil.

➢ The theory and practice behind the quartz crystal microbalance technique.

➢ A synopsis of other solubility measurement techniques in SC CO_2.

➢ A summary of solubility data for β-carotene in SC CO_2 from the current literature

➢ A description of the different chelating agents used with SC CO_2 and their respective solubility and extraction data from the current literature.

➢ An overview of the Chrastil and Guigard-Stiver Models used to correlate solubilities in SC CO_2.

4.1   Soil Remediation Technologies for Metal Contaminated Sites

The use of other methods to remediate metal contaminated soils by *in-situ* and *ex-situ* processes will be examined. An *in-situ* process is defined as treating soil without excavating or removal; possibly resulting in potentially significant cost savings. However, *in-situ* treatment usually requires greater time periods to complete. There is less certainty about the uniformity of treatment because of the variability in soil conditions and because the effectiveness of the process is more difficult to verify (Roundtable, 1999). The *ex-situ* process commonly requires shorter time periods than *in-situ* treatment, and there is more certainty about the

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consistency of treatment because of the ability to grade, blend and constantly mix the soil. *Ex-situ* treatment, however, requires excavation, leading to increased costs and engineering and possible hazardous exposure conditions to workers.

4.1.1 Separation

The separation process can be utilized in almost all of the remediation techniques that will be discussed throughout this literature review. The technique is based on the assumption that a large percentage of the contaminants are often associated or bound to fine soil particles (i.e. clay and silt). Under this assumption the contaminant is isolated (*ex-situ*) and concentrated into a smaller volume (by physical sorting), which needs subsequent treatment.

4.1.2 Solidification and Stabilization

In general, this process transforms potentially hazardous soils and sludges into less or non-hazardous solids. A transformation, by trapping or chemical immobilization through a physical or chemical means prevents migration and reduces mobility of the metal contaminant throughout the soil matrix. Solidification is the process whereby a solid block or a 'monolith' is produced from the contaminated soil, while stabilization (immobilization) is the process by which, through chemical and thermal interactions, the contaminants are transformed to less mobile forms (E.P.A., 1989). These two processes improve the handling and physical characteristics of the waste, decrease the

surface area of the mass through which loss of contaminant can occur and limit solubility of the contaminant within the soil (E.P.A., 1989).

The *ex-situ* process involves excavation and immobilization of the metal contaminant, which then requires disposal. The *ex-situ* processes include cement-based solidification, bitumization, solidification in emulsified asphalt, polyethylene extrusion and thermal vitrification. For the most part these processes are relatively effective at containing the contaminant following treatment, however there are some limitations. The limitations include combinations of wastes may be a problem to treat, the volume of the treated soil can almost double after processing, certain wastes may not be compatible for this process and environmental conditions can effect the long term stability of the waste.

The *in-situ* processes include *in-situ* vitrification and reagent based solidification and stabilization. Both of these processes are limited by the depth of contaminant, the further usage of the site and the possible costs for each process (E.P.A., 1997b).

4.1.3 Soil Washing and Flushing

In this process the soil is cleaned and the concentration of metal contaminant is reduced in concentration in the soil matrix. The contaminant is removed by dissolving or suspending it in a wash medium. Soil washing is an *ex-situ* process where a solvent is used to extract the desired contaminant from the soil. The effectiveness of this process depends on the nature of the contaminant, the solvent variety and the type of soil (the more porous the soil matrix the more

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effective the procedure). For the removal of metals two procedures can be used (E.P.A., 1997b). The first method uses hydrochloric acid or nitric acid to remove the metals. The main disadvantages of using this procedure are the resultant acidification of the soil, which may damage the soil matrix and the usually large quantities of secondary wastes requiring treatment (E.P.A., 1997b). The second method that is used is to add ligands or chelating agents to the soil or to the wash solution. The ligand or chelating agents form stable complexes with the metal, which can subsequently be recovered from the soil. The ligand or chelating agent (usually costly) may be recovered and reused in order for this method to be more cost effective. The overall costs of soil washing depends upon the volume of soil that needs to be treated, the type of metal and the soil particle size and distribution.

Soil flushing is an *in-situ* process. The metal contaminant is removed by solubilizing it in a solvent, which percolates downward through the soil matrix. The contaminant is subsequently leached into the ground water where it is extracted and treated. The limitations of this process range from the soil type (clay and silt soils have low permeability) to the type of contaminants targeted for removal (combinations of contaminants are difficult to remove).

4.1.4 Electrokinetic Remediation

Electrokinetic remediation is based on the principle that, passing a low intensity direct current through contaminated soil using two or more electrodes will mobilize certain charged types of contaminants through the soil to either the

anode or the cathode where they can be extracted. The contaminants are mobilized through the soil by (Rodsand and Acar., 1995) :

> Electromigration (movement of a charged chemical species under an electrical gradient) (dominant process)

> Electro-osmosis (transport of pore fluid under an electrical gradient)

> Electrophoresis (movement of charged particles under an electrical gradient) and

> Electrolysis (chemical reactions associated with an electric field).

The concentrated contaminated area around the anode and cathode can then be remediated by electroplating, precipitation or co-precipitation, pumping of water near the electrode or complexing the contaminants within an exchange resin (E.P.A., 1997b). This process has some limitations with regard to the soil chemistry; if the soil conductivity is high, large percentages of non-targeted contaminants can accumulate around the electrodes resulting in a larger amount of contaminated soil or contaminated water surrounding the electrode. During the process the current applied to the soil will cause generation of hydrogen ions at the anode and generation of hydroxide ions at the cathode, which builds a low pH zone and a high pH zone, respectively. The low pH solution will enhance the dissociation of positively charged contaminants from the soil surface by ion exchange and could also damage the soil. The high pH solution generated from the cathode will favour the sorption of the positively charged contaminants on soil surfaces, thus decreasing the contaminant removal efficiency.

4.1.5 Phytoremediation

Phytoremediation is the process whereby plants are used to remove or immobilize metal contaminants within the soil. This process includes all biological, chemical and physical processes that are influenced by plants and that aid in the cleanup of contaminated substances (Cunningham and Berti, 1993). In general two types of phytoremediation can be used to treat metal contaminated soils: phytoextraction and phytostabilization. Phytoextraction uses plants to accumulate or hyperaccumulate metal contaminants in their harvestable segments (shoots and roots). For a plant to remove a heavy metal from the soil the metal must be available for plant uptake. Metal bioavailability can be increased by using chelates, lowering the soil pH, growing plants that release root reductants, using microorganisms that facilitate metal uptake, causing competition for sorption sites and adding soil amendments that benefit plant establishment and growth (Cunningham and Ow, 1996). The plants are then harvested and composted or incinerated leaving a highly concentrated waste that can either be disposed of or recycled (E.P.A., 1997b).

Phytostabilization is the process by which contaminant tolerant plants are used to reduce contaminant mobility and limit the bioavailability of the specific metal contaminant. This process also has the potential to stabilize the soil, which reduces erosion and therefore the migration of the contaminated soil.

Phytoremediation is a potentially inexpensive process, but it has its limitations. The limitations of phytoremediation include remediation only within the plants root zone, the type of metal contaminant to be removed and seasonal

conditions that may affect the viability of this technique as a year-round process. Sites with highly concentrations of ions of metal contaminants may not be remediable by this method due to potential toxicity to the plants (Cunningham and Ow, 1996).

4.1.6 Excavation and off-site disposal

This remediation technology removes the contaminated soil from the site and disposes it into some type of treatment facility or land disposal facility. The relative effectiveness of this process depends upon the contaminant, the distance to be transported and the disposal site characteristics. Appropriately moving the waste to a more viable location may solve short-term needs, however the long-term treatment of that specific waste is debatable. To ensure proper decontamination, the waste may be treated by one of the above methods.

4.2 SC CO$_2$ Extraction of Metal Contamination of Soils

SC CO$_2$ is currently being used in lab and pilot scale environmental applications to decontaminate petroleum-contaminated soils. SC CO$_2$ can only dissolve non-polar substances in its pure form. The solvating properties of SC CO$_2$ can be varied by altering the temperature and pressure. The addition of 'modifiers' also can have a significant effect on the solvating powers of SC CO$_2$. Modifiers are substances that are added to the SCF in low concentrations (usually 5% or less on a volume/volume basis) (Phelps et al., 1996) that modify the polarizability of the SCF. Some modifiers that are currently used are water, ethanol and methanol (McHugh and Krukonis, 1994). Given the polar nature of

all metals in ionic form and the non-polar nature of SC CO_2, the direct dissolution of metals into the SC CO_2 is negligible. A ligand or chelate (a polydentate ligand) that is soluble in SC CO_2 must be added. This ligand binds to the metal and the resulting complex is soluble in the SCF. The resulting dissolved complex is 'washed' out of the soil matrix into a collection vessel where the pressure is released and the carbon dioxide is removed, leaving a concentrated metal-complex residual.

4.3 An Overview of Extraction and Solubility Measurement Techniques

Before an extraction is to be done, the solubility of the solute in the SCF must be determined at a specific temperature and pressure. Solubility measurements allow for effective design of SCF extraction processes by permitting the operating conditions to be optimized for maximum effectiveness (Bruno, 1991). It has been shown in the literature that different matrices exhibit different extraction efficiencies under similar conditions (Ashraf-Khorassani *et al.*, 1997b; Smart *et al.*, 1997; Wai and Wang, 1997). By knowing the solubility in neat SC CO_2 and comparing it with the extraction data, an interpretation of different effects from the matrix and modifiers can be ascertained. The following section will cover the basic principles of solubility measurements and extraction techniques used for assessing β-carotene and metal chelate solubility in SC CO_2.

4.3.1 Solubility Measurement Techniques

There are four commonly used techniques for solubility measurements with SCF systems. These are dynamic (flow) methods, static (equilibrium) methods, chromatographic methods and spectroscopic methods.

4.3.1.1 Dynamic (flow) Methods:

Dynamic methods involve the most simple and straightforward of designs (Bruno, 1991). The SCF is delivered to the system at a desired temperature and pressure and then flows through a pressure vessel holding the solute. Equilibrium is then assumed to be reached in the vessel with a specific flow rate (Bruno, 1991). The SCF, now saturated with the solute exits the vessel and is depressurized with a heated metering valve or restrictor. The solute precipitates from the solution and is analysed by an appropriate technique. The decompressed solvent is collected and measured. Knowing the SCF flow rates, the time of collection of the solvent sample and the concentration of the solute in the trapping solvent, the solubility can then be calculated (Cross *et al.*, 1996).

This method has advantages such as simple design and creation of rapid and reproducible data (McHugh and Krukonis, 1994). The disadvantages of this type of method are:

➤ undetected phase changes may occur,

➤ at high flow rates solutes may be pushed out of the vessel,

➤ the heated metering valve or restrictor can become plugged

➤ thermally unstable compounds may decompose through the heated metering valve (Bruno, 1991), (McHugh and Krukonis, 1994).

➤ measured solubilities may be a function of flow rate

➤ equilibrium may not be reached at the given flow rate

4.3.1.2 Static (Equilibrium) Methods

In the static method, the SCF and solute are placed in a pressure vessel. After the solute and SCF are isolated in the vessel, equilibrium is reached by recirlculating the SCF to ensure contact with the solute or allowing diffusion gradients to operate in the vessel. As the SC CO_2 solute mixture is recirculated, the absorbency is measured with either an infrared (IR) detector or an ultraviolet (UV) detector. When the absorbency is stabilized, it is assumed that equilibrium has been reached and the solubility can be calculated (Bruno, 1991). McHugh and Krukonis (1994) state that the advantages of this technique are that the phase transitions are determined visually and the solubilities are obtained without sampling. The limitations of this technique include measuring the solubility before equilibrium is reached and typically only one measurement can be obtained per vessel loading (McHugh and Krukonis, 1994).

4.3.1.3 Spectroscopic Methods

The spectroscopic methods differ from the dynamic and static methods that use spectroscopic devices. In this method spectroscopy is the main feature, and the SCF solution is present as a secondary feature of the analytical process (Bruno, 1991).

Three examples of spectroscopic methods are: using a high pressure thermostatted cell with UV-vis, using nuclear magnetic resonance (NMR) spectroscopy with a specially designed sample cell (Bruno, 1991) and using on-

line laser-induced fluorescence (Addleman *et al.*, 2000) to determine solubilities in SC CO_2. The advantage of spectroscopic methods is that they are *in-situ* methods that permit the diffusion rates to be observed, confirming when equilibrium has been reached. Some limitations in the UV-vis method include extensive calibration to determine the variation in molar absorption with SCF density and adsorption of the solute to the view cell windows from a saturated solution (Bartle *et al.*, 1992). With these problems addressed, this method can provide consistent results when measuring solubility (Bartle *et al.*, 1992).

4.3.1.4 The Quartz Crystal Microbalance Technique

Jacques and Pierre Curie first observed the piezoelectric effect in 1880. This effect was a result of mechanical stress applied to the surfaces of certain crystals, including quartz, which resulted in an electrical potential across the crystal. Thus the word piezoelectric was derived from the word *piezein*, meaning to press. The quartz crystal microbalance (QCM) technique acquires its title from its ability to measure the mass of thin films that have adhered to its surface. This is an extremely sensitive mass measurement with several nanogram sensitivity (Lu, 1984).

The QCM used in this set of experiments is a thin, AT-cut quartz crystal inserted between two silver electrodes. The AT-cut is the most commonly used type of crystal (Salt, 1987). An alternating electric field is used to make the crystal oscillate at its resonant frequency of 9 MHz.

Mass changes occurring at the crystal electrode surface result in frequency changes according to the well-established Sauerbrey equation

(Equation 4-1), named after the pioneer of this technique for measurement of film thickness.

$$\Delta F = \frac{-2 F_o{}^2 \Delta m}{A \sqrt{\mu_Q \rho_Q}}$$ (4-1)

With this equation, the mass change (Δm) can be calculated by obtaining the change in frequency (ΔF) and knowing the other constants such as the resonant frequency (F_o) of the quartz resonator, the active vibrating area (A), the shear modulus of quartz (μ_Q), and the density of quartz crystal (ρ_Q) (Table 5-1). There exists other methods to quantify the mass adsorbed onto the QCM surface described in Lu (1984), however the Sauerbrey method is one of the least complex methods and most widely used.

For accurate mass determination four conditions must be met (Lu, 1984):

1. The mass must be uniformly distributed over the entire electrode

2. The mass must completely adhere to the QCM

3. The active area of vibration must be completely covered

4. The area of the material must be known precisely

These conditions refer to the differential mass sensitivity initially discovered by Sauerbrey (1959). It was found that when a mass is placed on the electrode and was not uniformly distributed, the frequency shift was dependent on the position of the mass. It was found that the differential mass sensitivity reached a

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maximum near the centre of the electrode and reduced to zero slightly beyond the edge of the electrode (Lu, 1984).

Previous experiments by Otake *et al.* (1994) and Tsionsky *et al.* (1995) have used the QCM technique in both sub and supercritical CO_2. Both authors reaffirmed the frequency change (ΔF) of the QCM in SC CO_2 was described by Equation 4-2.

$$\Delta F = \Delta F_M + \Delta F_P + \Delta F_V + \Delta F_A \qquad\qquad (4\text{-}2)$$

where ΔF_m reflects the change in frequency due to additional mass, ΔF_P is the frequency change from the compression effect due to pressure of the fluid, ΔF_V is the frequency change due to the density and viscosity of the medium and ΔF_A is the frequency change due to the mass change of the adsorbed species. This equation accounts for the change in frequency caused by the interaction of the SC CO_2 on an ideally smooth electrode surface (Tsionsky *et al.*, 1995). A real surface is continually rough to varying degrees depending on the type of material the QCM is composed of. The roughness produces a residual effect, which further affects the frequency shift of the QCM. This residual effect can be accounted for by measuring the amount of SC CO_2 that is sorbed onto the QCM. Please see Section 6.6.3 for further discussion.

Other authors have used the QCM technique in SC CO_2 and subcritical CO_2 (ie: high pressure CO_2) systems. Wang *et al.* (1994) used the QCM technique to measure the solubility of high pressure CO_2 in poly(vinyl acetate) and poly(butyl methacyrlate). The frequency was measured then corrected for pressure, viscosity and density effects, and finally used to calculate the mass

fraction solubilities of CO_2 in the polymers. Aubert (1998) used the QCM technique to measure the solubility of CO_2 in several structurally different polymers. Using this technique Aubert (1998) was able to compare the solubility of CO_2 in the polymers to the different structural aspects of each polymer studied. Guigard (1999) used this technique to measure the solubilities two β-diketone metal chelates in SC CO_2 (see section 4.5.2); copper acetylacetone and copper thenoyltrifluoroacetone.

4.3.2 Extraction Methods

The methods that are used for extracting metal chelates from different matrices using SC CO_2 are relatively similar in design. The SC CO_2 is introduced into a vessel containing the sample that is to be extracted. The chelate and modifiers (if used) can be mixed with the SC CO_2 before entering the vessel or the chelate and modifiers are added to the vessel prior to adding the SC CO_2 to the extraction vessel. After the extraction vessel is pressurized with SC CO_2, the vessel and its contents are isolated and mixed (static condition). Following the static period, a flushing or dynamic period is initiated where the dissolved solute is washed out of the vessel with the solvent (SC CO_2).

In the next stage it is critical that the determination of the concentration of metal-chelate that has been extracted from a matrix is accurate. The method of analysis of the concentration is variable. Collecting the extractant in a solvent trap (i.e. methanol or chloroform) is a method to analyze the metal chelate. The compound is collected by means of a solvent trap where a capillary restrictor or backpressure regulator is used to depressurize the SC CO_2 metal chelate

mixture. The mixture is then analysed to determine the resultant concentration of metal chelate. This method does not allow for calculation of extraction kinetics as a result of bulk analysis of the metal chelate solvent mixture. This method does require depressurization and off gassing of the carbon dioxide which, could affect the results by affecting the solubility (solute falls out of solution and/or plugs restrictor) and stability (thermal degradation) of the metal chelate in the SC CO_2 solution (Guigard, 1999). To overcome this problem, Cross *et al.* (1996) injected a solvent at supercritical conditions that would dissolve the metal chelate immediately after the extraction vessel. The injected solvent dissolved all of the extracted metal chelate in the SC CO_2, and was collected in a solvent trap upon depressurization.

Another method to determine the concentration of extracted metal chelate is an on-line UV-visible flow through spectrophotometer with a high-pressure view cell and a solvent trap to collect the extracted metal chelate. An on-line detector is advantageous for this process because of the ability to take measurements without varying the temperature and pressure of the SC CO_2. (The solvating power of SC CO_2 can vary if the temperature or pressure is altered, thus affecting the solubility of the metal-chelate.) Another advantage of using the on-line UV spectrometer is that some compounds have been shown to thermally degrade when attempting to collect and quantify them via the solvent trap method, thus preventing analysis of the extraction and subsequent quantification.

The concentration of the metal-chelate can also be measured by the use of element selective detectors such as: microwave induced plasma, radio frequency plasma and inductively coupled plasma techniques (Lin *et al.*, 1995a). All of the element selective detector methods are much more costly than UV-vis analysis and offer (in terms of analysis) more than what a basic extraction of a single metal chelate requires.

A method that can be coupled to the above techniques would be to measure the amount of metal chelate in the soil before and after to determine extraction efficiency. This method could use neutron activation analysis (NAA), a non-destructive technique to determine the concentrations in the extracted sample. The NAA process, when used with another techniques to analyze the concentration in the extractant is a good verification of results. The difference in concentration in the soil sample can be compared to the concentration of metal chelate measured by one of the above techniques to analyze for mass closure. However, the matrix analysis technique should not be used as the sole method because of possible losses of metal chelate (i.e. adsorption to the vessel and experimental error).

4.4 Solubility Data For β-Carotene in SC CO_2

β-Carotene is a carotenoid, one of the major natural pigments that find widespread utilization in the food industry (Subra *et al.*, 1997). It is a hydrocarbon of 40 carbon atoms, lipid soluble, yellow to orange pigment and highly unsaturated. β-Carotene is known to degrade in the presence of heat, light and oxygen. The structure is shown in Figure 4-1.
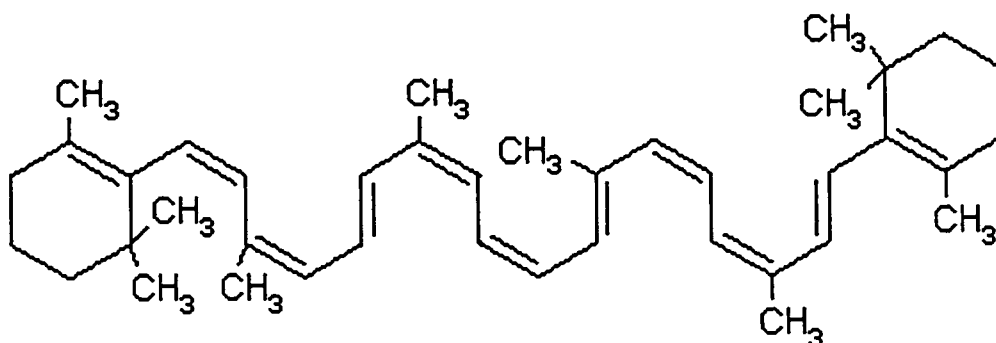
Figure 4-1 Structure of β-Carotene (NIST, 2000)

The solubility of β-Carotene has been investigated. Table 4-1 provides selected solubilities of β-carotene at SC CO_2 densities similar to those used in this study.

Table 4-1 Solubility of β-Carotene at Various Conditions in SC CO_2

Experimental Conditions			Solubility (mol/mol)	Reference
Pressure (MPa)	Temperature (K)	Density (g/cm^3)		
10.9	313	0.682	2.0E-07	Skerget et al. (1995)
12.8	313	0.741	1.81E-07	Skerget et al. (1995)
10.1	310	0.691	2.2E-08	Subra et al. (1997)
12.0	310	0.751	5.11E-08	Subra et al. (1997)
9.9	313	0.6206	1.1E-08	Sakaki (1992)
11.8	313	0.715	3.8E-08	Sakaki (1992)
12.0	313	0.721	3.0E-08	Mendes et al. (1999)

Subra et al. (1997) used a static recirculation technique that recirculated the SC CO_2 and solute for a period of 30 minutes. The process was monitored for β-carotene saturation in the SC CO_2 with an on-line UV-vis detector. Sampling was done by an on-line HPLC detector.

Sakaki (1992) measured the solubility of β-carotene using a dynamic one-pass flow method coupled to a supercritical fluid chromatography device. The single pass flow method may not guarantee the complete saturation of the SC CO_2 (Subra *et al.*, 1997). Skerget *et al.* (1995) used a static method where after equilibrium had been reached in the pressure cell (the method of determining equilibrium in the cell was not explicitly stated), the SC CO_2 and solute were collected in a solvent trap containing methanol. The resultant methanol β-carotene mixture was then analyzed by an UV-vis detector. Mendes *et al.* (1999) used a dynamic single pass flow method to measure the solubility of β-carotene. When equilibrium was reached (determined by measuring different flow rates through the equilibrium cell), the β-carotene was collected in a solvent trap containing n-hexane and further analyzed by UV-vis spectroscopy. The solubility conditions used for β-carotene solubility measurements are scattered in terms of specific temperatures and pressures.

4.5 Chelating Agents Used with SC CO_2

The importance of selecting the appropriate chelating agent is paramount for process viability (in terms of cost and effectiveness) and overall extraction efficiency. The following list identifies some important selection criteria for effective chelating agents (Beszedits and Netzer, 1997) to be used for extracting metals from soil:

> ➤ The chelate forms a highly soluble and stable complex with the metal over the required pH range.

> ➤ The metal chelate complexes formed are not adsorbed onto the soil.

➢ The biodegradative capacity of the chelate is low.

➢ The chelate and metal chelate has low toxicity and low environmental impact.

➢ The chelate is relatively cost effective.

➢ The metal chelate complex has fast complexation kinetics.

In addition to the above criteria, the chosen chelate should have selectivity for the desired metal(s) to be extracted and a known solubility to further refine the process of extraction. The conditions for extraction of metal chelates in SC CO_2 that are reported in the literature are diverse. Different pressures and temperatures are used. There is no standard procedure for conducting and measuring extraction efficiency. Diverse matrices such as filter paper, glass wool, sand, wood, clay-spiked soil and weathered heavy metal contaminated soil add to the varied data sets.

Throughout the literature, it has been shown that the metals that can be extracted from contaminated soils and other matrices using SCF extraction (SFE), consist of those metals that are not tightly bound to the matrix (i.e. leachable metals) (Smart et al., 1997). In general, the amount of metal extracted represents approximately 10-50% of the total metal in the soil (Smart et al., 1997). Acidifying the matrix increases the amount of leachable metal in the soil. In the presence of SC CO_2, it has been shown that the pH within a wet soil sample has been approximately determined to be 2.9 (due to the formation of carbonic acid when carbon dioxide is dissolved in water) (Toews et al., 1995). This formation of carbonic acid provides a temporary acidic environment in which

the extraction can take place (temporary until the pressure is released and the majority of carbon dioxide is dissipated as a gas). In the following sections, this increased extraction due to the presence of water is evident throughout the extraction data for various metal chelate complexes; the extractions in a wet versus dry environment are greater. Water also has a modifier effect. The SC CO_2 mixture becomes more polar due to the dissolution of the water, thus increasing the amount of metal chelate that is soluble in the SC CO_2 mixture. The use of methanol and water in extraction and solubility measurements clearly shows a positive effect on the solvating properties of the SC CO_2 for metal chelates.

The following section outlines the various chelating agents that have been investigated for use in SC CO_2.

4.5.1 Dithiocarbamates

The dithiocarbamates are derived from dithiocarbamic acid. The basic structure of the chelated ligand is R_2NCS_2X. The 'R' group is an alkyl group of varying length, and 'X' is a alkali metal cation such as cobalt, copper, mercury, nickel and zinc. The different dithiocarbamates used with SC CO_2 are shown in Table 4-2.

There are other dithiocarbamate chelating agents, with larger alkyl chain lengths, however these are difficult to synthesize. The difficult synthesis of the larger compounds as well as the relative ease at which the smaller chain length compounds diffuse and migrate out of the matrix in comparison to the larger

molecules makes the smaller dithiocarbamates the most applicable for the extraction process (Wai and Wang, 1997).

Table 4-2 The Most Commonly used Dithiocarbamate Chelating Agents used with SC CO_2.

Compound	Abrv.	"R" group
Bis-trifluoroethyldithiocarbamate	FDDC	$-CH_2CF_3$
Dibutyldithiocarbamate	BDC	$-C_4H_9$
Diethyldithiocarbamate	DDC	$-C_2H_5$
Dihexyldithiocarbamate	HDC	$-C_6H_{13}$
Dipentlydithiocarbamate	P5DC	$-C_5H_{11}$
Dipropyldithiocarbamate	P3DC	$-C_3H_7$
Pyrrolidinedithiocarbamate	PDC	$-CH_2(CH_2)_2CH_2-R+R)$

Investigations in the solubilities of different dithiocarbamate metal complexes have shown that higher pressures (higher densities) increase solubility (Laintz et al., 1991); (Wai and Wang, 1996). As well, alkyl chain lengths of greater magnitude show greater solubilities in SC CO_2 on a logarithmic scale (Wai and Wang, 1996). The positive effect of fluorination of the dithiocarbamate complex on solubility is also apparent; solubilities of the fluorinated ligand increase approximately two orders of magnitude (from 10^{-6} to 10^{-4}) from the non-fluorinated ligand (Laintz et al., 1991); (Wai and Wang, 1996); (Ashraf-Khorassani and Taylor, 1999). Table 4-3 and 4-4 illustrates some solubilities of the dithiocarbamates and metal dithiocarbamates in SC CO_2.

Table 4-3 Solubilities of Various Dithiocarbamate Complexes

Abrv.	Pressure (MPa)	Temp. (K)	Solubility (mol/L)	Reference
Bi(DDC)$_2$	10.1	323	1.3E-06	Laintz et al. (1991)
Bi(DDC)$_2$	15.2	323	9.0E-06	Laintz et al. (1991)
Bi(FDDC)$_2$	10.1	323	<1E-07	Laintz et al. (1991)
Bi(FDDC)$_2$	15.2	323	7.3E-04	Laintz et al. (1991)
Co(DDC)$_2$	10.1	323	2.4E-06	Laintz et al. (1991)
Co(FDDC)$_2$	10.1	323	8.0E-04	Laintz et al. (1991)
Cu(BDC)$_2$	10.1-23.3	333	(1.3-72)E-05	Wai and Wang (1996)
Cu(DDC)$_2$	10.1-23.3	333	(1.4-11)E-06	Wai and Wang (1996)
Cu(DDC)$_2$	11.7-24.3	308.15	(3.4-9)E-06	Cross et al. (1996)
Cu(DDC)$_2$	20.7-38.0	328.15	(7.4-28)E-06	Cross et al. (1996)
Cu(FDDC)$_2$	10.1-23.3	333	(9.1-40)E-04	Wai and Wang (1996)
Cu(HDC)$_2$	10.1-23.3	333	(2.1-28)E-04	Wai and Wang (1996)
Cu(P3DC)$_2$	10.1-23.3	333	(6.3-120)E-06	Wai and Wang (1996)
Cu(P5DC)$_2$	10.1-23.3	333	(9-180)E-05	Wai and Wang (1996)
Cu(PDC)$_2$	10.1-23.3	333	(4.1-40)E-07	Wai and Wang (1996)
Hg(BDC)$_2$	10.1-23.3	333	(5.6-56)E-05	Wai and Wang (1996)
Hg(DDC)$_2$	10.1-23.3	333	(6.8-53)E-06	Wai and Wang (1996)
Hg(DDC)$_2$	10.1	333	2.4E-03	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)$_2$	20.7	333	2.4E-03	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)$_2$	15.2	323	8.2E-06	Lin et al. (1995a)

(FDDC = Bis-trifluoroethyldithiocarbamate, BDC = Dibutyldithiocarbamate, DDC= Diethyldithiocarbamate, HDC = Dihexyldithiocarbamate, P5DC= Dipentlydithiocarbamate, P3DC = Dipropyldithiocarbamate, PDC = Pyrrolidinedithiocarbamate)

Table 4-4 Solubilities of Various Dithiocarbamate Complexes

Abrv.	Pressure (MPa)	Temp. (K)	Solubility (mol/L)	Reference
Hg(FDDC)$_2$	10.1-23.3	333	(3-14)E-03	Wai and Wang (1996)
Hg(FDDC)$_2$	10.1	333	4.6E-03	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$	20.7	333	1.4E-02	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$	15.2	323	5.0E-03	Lin *et al.* (1995a)
Hg(HDC)$_2$	10.1-23.3	333	(1.6-38)E-04	Wai and Wang (1996)
Hg(P3DC)$_2$	10.1-23.3	333	(1.2-23)E-05	Wai and Wang (1996)
Hg(P5DC)$_2$	10.1-23.3	333	(1-20)E-04	Wai and Wang (1996)
Hg(PDC)$_2$	10.1-23.3	333	(3.5-34)E-07	Wai and Wang (1996)
Na(DDC)$_2$	10.1	323	1.50E-04	Laintz *et al.* (1991)
Na(FDDC)$_2$	10.1	323	4.7E-03	Laintz *et al.* (1991)
Ni(DDC)$_2$	10.1	323	8.5E-07	Laintz *et al.* (1991)
Ni(FDDC)$_2$	10.1	323	7.2E-04	Laintz *et al.* (1991)
Zn(BDC)$_2$	10.1-23.3	333	(8.2-69)E-05	Wai and Wang (1996)
Zn(DDC)$_2$	10.1-23.3	333	(1.1-24)E-06	Wai and Wang (1996)
Zn(FDDC)$_2$	10.1-23.3	333	(9.5-90E-04)	Wai and Wang (1996)
Zn(HDC)$_2$	10.1-23.3	333	(3.2-58)E-04	Wai and Wang (1996)
Zn(P3DC)$_2$	10.1-23.3	333	(7.9-150)E-06	Wai and Wang (1996)
Zn(P5DC)$_2$	10.1-23.3	333	(1.6-32)E-04	Wai and Wang (1996)
Zn(PDC)$_2$	10.1-23.3	333	(3.2-90)E-07	Wai and Wang (1996)

(FDDC = Bis-trifluoroethyldithiocarbamate, BDC = Dibutyldithiocarbamate, DDC= Diethyldithiocarbamate, HDC = Dihexyldithiocarbamate, P5DC= Dipentlydithiocarbamate, P3DC = Dipropyldithiocarbamate, PDC = Pyrrolidinedithiocarbamate)

The solubilities of the different dithiocarbamates differ in magnitude from 10^{-2} to 10^{-7} mol/L at different pressures and temperatures. The solubility measurement technique used by each source was also different. Lin *et al.* (1995a) and Wai and Wang (1996) used the same technique of a static measurement for thirty minutes and the bubbling the contents of the vessel through chloroform and analysing with atomic absorption spectroscopy. Cross *et al.* (1996) used a dynamic method with an on-line UV-vis detector and atomic absorption spectroscopy to determine the concentration of the out flow from the vessel. Ashraf-Khorassani and Taylor (1999) used a static recirlculating technique, while Laintz *et al.* (1991) used a static technique in a high-pressure view cell to measure solubilities with UV-vis and IR detectors.

Wai *et al.* (1996) extracted cadmium, lead and mercury using four different dithiocarbamate reagents, DDC, FDDC, PDC and Et_2NH_2DDC from spiked sand and filter paper samples. At a temperature of 343 K and pressure of 20.3 MPa for the filter samples and 318 K and 25.3 MPa for the spiked sand sample, neat SC CO_2 and modified SC CO_2 were used. For DDC, FDDC, PDC and Et_2NH_2DDC the extraction efficiencies are summarized in Table 4-5, Table 4-6 and Table 4-7.

Wai *et al.* (1993) also examined the extraction efficiencies of mercury from wet or dry filter paper using the lithium salt of FDDC at 10.1 MPa and 313 K. The SC CO_2, which, was modified with 5% methanol, was used to extract from filter paper. The results are summarized in Table 4-6.

In a paper by Liu *et al.* (1993), copper, cobalt and zinc were extracted from sand and silica gel using the lithium salt of FDDC and both neat and

modified SC CO_2 at 20.3 MPa and 313 K. The results are shown in Table 4-5 and Table 4-7. Ashraf-Khorassani and Taylor (1999) used neat and 5% methanol modified SC CO_2 two conditions (20.3 MPa and 313 K and 40.5 MPa and 313 K) to extract mercury DDC and mercury FDDC from filter paper, sand and soil. The results are summarized in Table 4-5, Table 4-6 and Table 4-7.

As mentioned earlier, the positive effect that water has in the matrix can be observed in Table 4-6 and the positive effect from methanol on the solubilization of the metal chelate can be seen in all three previous tables.

The future applicability of utilizing dithiocarbamate reagents to remediate contaminated soils on a large scale may be limited. The dithiocarbamate reagents have been found to be unstable in water due to the acidic environment created in the SC CO_2 (from the formation of carbonic acid) (Toews et al., 1995). The necessity to remove the moisture from the soil and the absence of a pH drop may increase extraction costs and limit the amount of metals that are removed from the soil.

Table 4-5 Percent Recoveries of Dithiocarbamate Metal Complexes from Spiked Sand

Chelating Agent	Experimental Conditions		% Recovery of Metal						References
	Pressure (MPa)	Temp. (K)	Cu	Co	Zn	Cd	Pb	Hg	
(PDC)	10.1-25.3	318				13-19	19-43	23-26	Wai et al. (1996)
(PDC)*	10.1-25.3	318				33-53	53-64	45-57	Wai et al. (1996)
Et$_2$NH$_2$(DDC)	10.1-25.3	318				59-68	71-81	77-92	Wai et al. (1996)
Et$_2$NH$_2$(DDC)*	10.1-25.3	318				84	89-88	93	Wai et al. (1996)
Hg(DDC)$_2$	20.3	313						60	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)$_2$	40.5	313						90	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)$_2$*	40.5	313						93	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$	20.3	313						85	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$	40.5	313						90	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$*	40.5	313						96	Ashraf-Khorassani and Taylor (1999)
Li(FDDC)	10.1-25.3	318				91-92	83-91	93-94	Wai et al. (1996)
Li(FDDC)	20.3	313	69	55	63	65			Liu et al. (1993)
Li(FDDC)*	10.1-25.3	318				91-97	90-96	92-98	Wai et al. (1996)
Li(FDDC)*	20.3	313	68	77	84	72			Liu et al. (1993)
Na(DDC)	10.1-25.3	318				36-82	42-86	58-94	Wai et al. (1996)
Na(DDC)*	10.1-25.3	318				53-90	84-91	87-97	Wai et al. (1996)

*-SCCO$_2$ with 5% methanol

Table 4-6 Percent Recoveries of Dithiocarbamate Metal Complexes from Spiked Filter

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Chelating Agent	Experimental Conditions		% Recovery of Metal			References
	Pressure (MPa)	Temp. (K)	Cd	Pb	Hg	
A(PDC)	20.3	333	5	10	16	Wai et al. (1996)
A(PDC)*	20.3	333	17	50	40	Wai et al. (1996)
Et₂NH₂(DDC)	20.3	333	30	63	95	Wai et al. (1996)
Et₂NH₂(DDC)*	20.3	333	71	91	96	Wai et al. (1996)
Hg(DDC)₂	20.3	313			55	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)₂	40.5	313			88	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)₂*	40.5	313			91	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)₂	20.3	313			73	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)₂	40.5	313			81	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)₂*	40.5	313			101	Ashraf-Khorassani and Taylor (1999)
Li(FDDC)*+	10.1	323			99	Wai et al. (1996)
Li(FDDC)+	10.1	323			85	Wai et al. (1996)
Na(DDC)	20.3	333	37	70	93	Wai et al. (1996)
Na(DDC)*	20.3	333	74	91	92	Wai et al. (1996)

* - SCCO₂ with 5% methanol
+ - matrix wet

Table 4-7 Percent Recoveries of Dithiocarbamate Metal Complexes from a Spiked Sample

Chelating Agent	Experimental Conditions			% Recovery of Metal					References
	Pressure (MPa)	Temp. (K)	Matrix	Cu	Co	Zn	Cd	Hg	
Hg(DDC)$_2$	20.3	313	Soil					17	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)$_2$	40.5	313	Soil					28	Ashraf-Khorassani and Taylor (1999)
Hg(DDC)$_2$*	40.5	313	Soil					70	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$	20.3	313	Soil					92	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$	40.5	313	Soil					93	Ashraf-Khorassani and Taylor (1999)
Hg(FDDC)$_2$*	40.5	313	Soil					84	Ashraf-Khorassani and Taylor (1999)
Li(FDDC)*	10.1-25.3	318	Soil				87-98	87-82	Wai et al. (1996)
Li(FDDC)*	20.3	313	Silica gel	75	85	112	98		Liu et al. (1993)
Na(DDC)*	10.1-25.3	318	Soil				52-87	83-89	Wai et al. (1996)

* - SCCO$_2$ with 5% methanol

4.5.2 Beta-Diketones

The β-diketones form complexes with a metal ion through an enolate anion. The formation of the enolate ion is shown below in Figure 4-2.

$$R_1\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R_2 \rightleftharpoons R_1\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH=\overset{\overset{\displaystyle OH}{|}}{C}\text{-}R_2 \rightleftharpoons R_1\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH=\overset{\overset{\displaystyle O^-}{|}}{C}\text{-}R_2 + H^+$$
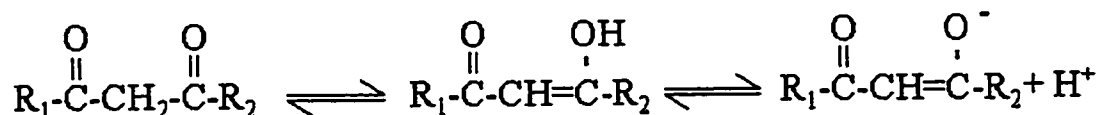
Figure 4-2 Formation of the Enolate Ion from a Generic β-Diketone

The most applicable β-diketones to SFE are those which exist for the most part in the enolate anion form in SC CO_2. The enol form can exchange its hydrogen ion with a metal ion and form a stable six-member ring, and thus chelate the metal (Yazdi, 1996). Examples of the fluorinated β-diketone compounds are given in the Table 4-8 below.

Table 4-8 The Most Commonly used β-Diketone Chelating Agents used with SC CO_2

Compound	Abrv.	"R_1" group	"R_2" group
Acetylacetone	acac	-CH₃	-CH₃
Trifluoroacetylacetone	tfa	-CH₃	-CF₃
Hexafluoroacetylacetone	hfa	-CF₃	-CF₃
Thenoyltrifluoroacetone	tta	-Thienyl group*	-CF₃
Heptafluorobutanoylpivaroylmethane	FOD	-C(CH₃)₃	-C₃H₇
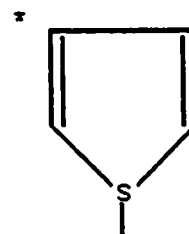
A positive effect of fluorination on the solubility of the β-diketones and metal chelated β-diketones can be seen in Table 4-9. In Table 4-9 the solubility data reported in the literature is summarized.

Table 4-9 Solubility of Free and Metal Complexed, β-Diketones

Abrv.	Pressure (MPa)	Temp. (K)	Solubility (mol/L)	References
Cu(tta)$_2$	10.3	313	5.04E-05	Guigard *et al.* (1998)
Cu(acac)$_2$	10.3	313	1.78E-04	Guigard *et al.* (1998)
Cu(acac)$_2$	12.0	423	2.54E-05	M'Hamdi *et al.* (1991)
Cu(acac)$_2$	17.0	443	2.93E-04	M'Hamdi *et al.* (1991)
Ba(hfa)$_2$	12.0	423	6.53E-04	M'Hamdi *et al.* (1991)
Ba(hfa)$_2$	17.0	443	1.36E-03	M'Hamdi *et al.* (1991)
Ba(hfa)$_2$	22.0	423	9.83E-04	M'Hamdi *et al.* (1991)
Cu(acac)$_2$	10.3	313	1.11E-04	Lagalante *et al.* (1995)
Cu(tfa)$_2$	10.3	313	4.39E-03	Lagalante *et al.* (1995)
Cu(hfa)$_2$	10.3	313	3.33E-02	Lagalante *et al.* (1995)
Cu(acac)$_2$	17.2	313	3.36E-04	Lagalante *et al.* (1995)
Cu(tfa)$_2$	17.2	313	7.34E-03	Lagalante *et al.* (1995)
Cu(hfa)$_2$	17.2	313	7.36E-02	Lagalante *et al.* (1995)
Ni(hfa)$_2$	19.6	333	8.0E-03	Ashraf-Khorassani *et al.* (1997a)
Cr(HFA)$_2$	19.6	333	>8.0E-02	Ashraf-Khorassani *et al.* (1997a)
Cr(acac)$_2$	24.6	318	3.17E-04	Cross *et al.* (1996)
Cr(acac)$_2$	11.8	318	1.03E-04	Cross *et al.* (1996)
Cr(acac)$_2$	30.1	328	5.00E-04	Cross *et al.* (1996)
Cr(acac)$_2$	15.0	328	1.66E-04	Cross *et al.* (1996)
Cu(acac)$_2$	22.0	423	5.99E-04	M'Hamdi *et al.* (1991)

(acac = Acetylacetone, tfa = Trifluoroacetylacetone, hfa= Hexafluoroacetylacetone, tta = Thenoyltrifluoroacetone)

The solubilities of the different β-diketones differ in magnitude from 10^{-2} to 10^{-5} mol/L at different pressures and temperatures. The solubility measurement technique used by each source was also different. Guigard *et al.* (1998) used a static method coupled with a quartz crystal microbalance technique to measure solubilities *in-situ*. Cross *et al.* (1996) used a dynamic method with an on line UV-vis detector and atomic absorption spectroscopy to determine the concentration of the chromium β-diketone in a solvent trap. Ashraf-Khorassani *et al.* (1997a) used a static recirlculating technique. M'Hamdi *et al.* (1991) used a dynamic technique where the solute was placed in an extraction column and SC CO_2 was passed through at the desired temperature and pressure. Measuring the weight

of the column before and after extraction and measuring the amount of SC CO2

that was passed through the column calculated solubilities. Lagalante *et al.*

(1995) used a static measurement technique where the solubilities of the β-

diketone chelates where measured *in-situ* with an UV-vis spectrophotometer.

In a paper by Wai and Wang (1996) the β-diketones (tfa, hfa and tta) were

examined for their extraction efficiencies of cadmium lead and mercury from

spiked sand and filter paper samples. At a temperature and pressure of 343 K

and 20.3 MPa, for the filter samples, and at conditions of 318 K and 250 MPa for

the spiked sand samples, respectively, the authors used neat and 5% methanol

modified SC CO_2. The results are summarized in Table 4-10 and Table 4-11. Lin

and Wai (1994) examined the extraction of trivalent lanthanide ions (lanthanum

[La], europium [Eu] and lutetium [Lu]) with hfa, tta and FOD from filter paper and

sand. The extractions were done at 15.2 MPa and 318 K and the authors used

neat and 5% methanol modified SC CO_2. For some of the extractions,

tributylphosphate (TBP) was added as a modifier in a 50/50 mix with the

specified β-diketone. The results are summarized in Table 4-10 and Table 4-11.

Table 4-10 Percent Recoveries of β-Diketone Metal Complexes from Spiked Filter Paper

| Chelating Agent | Experimental Conditions | | % Recovery of Metal | | | | | | Reference: |
	Pressure (MPa)	Temp (K)	La	Eu	Lu	Cd	Pb	Hg	
tfa	10.1-25.3	318				59-71	69-68	67-84	Wai et al. (1996)
tta	10.1-25.3	318				23-63	56-72	50-74	Wai et al. (1996)
hfa	10.1-25.3	318				70-65	70-66	65-70	Wai et al. (1996)
tfa*	10.1-25.3	318				89-93	84-70	87-94	Wai et al. (1996)
tta*	10.1-25.3	318				80-95	78-94	89-94	Wai et al. (1996)
hfa*	10.1-25.3	318				75-96	84-76	93-78	Wai et al. (1996)
FOD	15.2	333	10	13	19				Lin and Wai (1994)
tta	15.2	333	14	16	20				Lin and Wai (1994)
hfa	15.2	333	7	13	15				Lin and Wai (1994)
tfa	15.2	333	5	10	11				Lin and Wai (1994)
acac	15.2	333	5	4	6				Lin and Wai (1994)
FOD*	15.2	333	91	96	99				Lin and Wai (1994)
tta*	15.2	333	74	90	94				Lin and Wai (1994)
hfa*	15.2	333	70	93	95				Lin and Wai (1994)
tfa*	15.2	333	54	80	84				Lin and Wai (1994)
acac*	15.2	333	11	25	33				Lin and Wai (1994)
FODτ	15.2	333	92	94	95				Lin and Wai (1994)
tta τ	15.2	333	90	93	95				Lin and Wai (1994)
hfa τ	15.2	333	96	98	98				Lin and Wai (1994)
tfa τ	15.2	333	20	26	27				Lin and Wai (1994)
TBP only	15.2	333	2	3	4				Lin and Wai (1994)
acac τ	15.2	333	3	5	4				Lin and Wai (1994)

*-SCCO$_2$ with 5% methanol
τ-SCCO$_2$ with Tributylphosphate (TBP) (50/50 mix)

38

Table 4-11 Percent Recoveries of β-Diketone Metal Complexes from Spiked Sand

Experimental Conditions			% Recovery of Metal			Reference
Chelating Agent	Pressure (MPa)	Temp. (K)	La	Eu	Lu	
tta	15.2	333	29	40	60	Lin and Wai (1994)
tta τ	15.2	333	91	89	91	Lin and Wai (1994)

τ-SCCO$_2$ with Tributylphosphate (50/50 mix)

As can be seen in the above tables (Table 4-10 and Table 4-11) the positive effect that methanol has on the solubilization properties of SC CO$_2$ is evident. In Table 4-10 the percent recovery of cadmium, lead and mercury with the chelate tta in a spiked filter paper sample with 5% methanol increased by 20-50%. Although the trivalent lanthanides are not 'metals' in the true sense, the extractions shed light on the synergistic effect of TBP on removing the lanthanides from a given matrix. The increased recoveries observed could be an advantage in terms of scale up and process costs. TBP is a relatively inexpensive (compared to other ligands) and is readily available. By reducing the amount of chelate that must be used, and increasing the effectiveness of the chelate, TBP may aid in extractions significantly. The metal extraction data for the β-diketones is relatively sparse and further data are needed to examine the applicability of these ligands for a scaled up process (Lin and Wai, 1994).

4.5.3 Organophosphorous Reagents

Organophosphorous reagents have been traditionally used for metal extraction with conventional solvent systems. Recently, organophosphorous reagents have been used with SC CO$_2$ in an attempt to extract metals from soil. These compounds tend to be rather large molecules that show relatively high

solubility in SC CO_2. The most commonly used organophosphorous reagents are shown in Table 4-12.

Table 4-12 Organophosphorous Reagents

Compound	Abrv.
Tributylphosphate	TBP
Tributylphosphine oxide	TBPO
Triphenylphosphine oxide	TPPO
Trioctylphosphine oxide	TOPO
Cyanex 301	-
Cyanex 302	-
Di(2-ethylhexl)phosphoric acid	D2EHPA
Kelex 100	-

The solubilities of the organophosphorous chelates are relatively high and show increased values with increasing density. Table 4-13 illustrates the most commonly researched organophosphorous compound solubilities.

Table 4-13 Solubilities of Various Organophosphorous Compounds

Abbreviation	Pressure (MPa)	Temp. (K)	Solubility (mol/L)	Reference
TBP	20.3	333	1.2	Meguro et al. (1998)
TBP	20.3	333	0.85	Lin et al. (1995b)
TBPO	20.3	333	0.85	Lin et al. (1995b)
TOPO	20.3	318	6.50E-02	Lin et al. (1995b)
TPPO	20.3	333	7.63E-03	Lin et al. (1995b)
TOPO	15.2	313	5.18E-02	Lin et al. (1995b)
Cyanex 302	20.3	333	1.28E-01	Smart et al. (1997)
D2EHPA	20.3	333	0.16	Meguro et al. (1998)
Cu(Cyanex 301)	20.3	333	8.21E-03	Smart et al. (1997)
Cu(Cyanex 302)	20.3	333	2.90E-03	Smart et al. (1997)
Cu(Kelex 101)	20.3	333	4.80E-04	Smart et al. (1997)

The solubilities of the different organophosphorous reagents differ in magnitude from 10^0 to 10^{-4} mol/L at different pressures and temperatures. The solubility measurement technique used by each source was also different. Smart et al. (1997) used a static technique in a high-pressure view cell to measure solubilities with UV-vis and IR detectors. Lin et al. (1995b) used a technique of a

static measurement for thirty minutes followed by the bubbling of the SC CO_2/ chelate mixture through a solvent trap that contained chloroform and then analysing with atomic absorption spectroscopy. Meguro *et al.* (1998) used a dynamic technique to measure solubilities at various temperatures and pressures.

Metal extractions have been conducted by Smart *et al.* (1997), who examined four different types of matrices, including an inert cellulose matrix spiked with and without nitric acid with four different metals (copper, lead, zinc and cadmium). Others matrices were metal contaminated bentonite clay, copper contaminated soil and metal contaminated wood. For the majority of extractions, the conditions of the SC CO_2 were 20.3 MPa and 343 K. The inert matrix showed relatively good extraction efficiencies, although the different types of organophosphorous chelates exhibited different affinities to different metals. Four different reagents were used on the inert matrix, Cyanex 301 and 302, D2EHTPA and Kelex 100. The extraction efficiencies without the nitric acid had a very wide range from 1-100%. While the matrices that had 10 microliters of 0.1 mol/L of nitric acid solution added exhibited greater extraction efficiencies for all reagents, (which fell in the range of 90-100%). The greater extraction efficiencies are most likely due to the acidification of the matrix, making more metal available for chelation. The bentonite clay matrix was spiked with a similar metal complement as the inert matrix (copper, lead, zinc and cadmium), and Cyanex 302 was used as the chelating agent. The results of the extraction were that the lead and zinc were almost completely removed after 5 repeated extractions while the cadmium

and copper showed little or no removal from the clay. The soil sample contained arsenic as well as a number of different metals, such as copper, lead, chromium and zinc. The arsenic, copper, lead and zinc showed significant extraction efficiencies. The wood matrix was obtained from a wood treatment process in which the wood was shown to contain leachable quantities of copper, chromium and arsenic. After repeated extractions, the contaminant content was greatly reduced to minimal levels.

The effect of acidification of the soil matrix was further examined by Smart et al. (1997) by the addition of nitric acid to the sample. The observed effects indicate that an increase in the acidity of the matrix 'leaches' more metal contained within the sample, and thus makes more metal available for chelation and subsequent extraction in SC CO_2. Selectivity of certain metals is also observed. Although the apparent success of using the organophosphorous compounds for supercritical metal extraction is evident, the literature is lacking good data sets to be able to further evaluate these compounds for scaled up processes.

4.5.4 Macrocylic Ligands

This class of compounds includes the crown ether complexes, which are the only macrocylic ligands that have been investigated for the extraction of metals in SC CO_2. The crown ethers are a selective group of ligands, which are ionizable. The triazole group of crown ethers have been investigated by Wang (1995). Wang (1995) used a static technique in a high-pressure view cell to measure solubilities with UV-vis and IR detectors. The free ligand solubilities are

shown in Table 4-14. The metal chelate complex solubilities could not be found in the literature to date.

Table 4-14 Solubilities of Various Crown Ether Compounds

Abrv.	Pressure (MPa)	Temp. (K)	Solubility (mol/L)	References
Crown 1	20.3	333	1.3E-05	Wang (1995)
Crown 2	20.3	333	1.0E-05	Wang (1995)
Crown 3	20.3	333	4.3E-04	Wang (1995)
Crown 1*	20.3	333	2.1E-04	Wang (1995)
Crown 2*	20.3	333	2.0E-04	Wang (1995)
Crown 3*	20.3	333	1.3E-03	Wang (1995)

*-SCCO$_2$ with 5% methanol

Wang (1995) also examined the extraction of gold and mercury from filter paper and the extraction of mercury from sand. The results are tabulated below in Table 4-15.

Table 4-15 Percent Recoveries of Crown Ether Metal Complexes from Various Matrices

Chelating Agent	Experimental Conditions		Matrix	% Recovery of Metal		References
	Pressure (MPa)	Temp. (K)		Au	Hg	
Crown 1+	20.3	333	paper	17	64	Wang (1995)
Crown 1*+	20.3	333	paper	52	81	Wang (1995)
Crown 1*	20.3	333	paper	2	42	Wang (1995)
Crown 2+	20.3	333	paper	<1	26	Wang (1995)
Crown 2*+	20.3	333	paper	49	81	Wang (1995)
Crown 2*	20.3	333	paper	5	51	Wang (1995)
Crown 3+	20.3	333	paper	4	45	Wang (1995)
Crown 3+*	20.3	333	paper	79	98	Wang (1995)
Crown 3*	20.3	333	paper	6	60	Wang (1995)
Crown 3+	20.3	333	Sand		33	Wang (1995)
Crown 3*	20.3	333	Sand		78	Wang (1995)
Crown 3*+	20.3	333	Sand		95	Wang (1995)

* - SCCO$_2$ with 5% methanol
+ - matrix wet

Again the positive effect of methanol and water as modifiers can be observed. The selectivity of these compounds is also apparent. Further research is needed to understand the behaviour of the complexes in SC CO_2.

4.5.5 Hydroxamic acids

Hydroxamic acids are effective chelating agents for a broad range of transition metal ions. The basic structure for the hydroxamic acid ligands is illustrated in Figure 4-3. The corresponding "R" groups are defined in Table 4-16.

Some work has been done, investigating the use of various hydroxamic acids as chelating agents in SC CO_2 to extract metals from soil. In a paper by Glennon et al. (1997) applied the ligands in Table 4-16 to solubility and extraction experiments. The solubilities of the above hydroxamic acids were all determined at 333 K and 20.3 MPa with a static solubility measurement technique.

$$R_1\text{-}C\text{-}N\overset{\displaystyle O}{\underset{\displaystyle R_2}{\big\|}}\diagup^{\displaystyle OH}$$
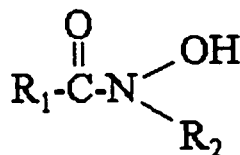
Figure 4-3 Basic Structure of a Hydroxamic Acid

Table 4-16 Various Hydroxamic Acids used in SC CO_2 Extractions

Compound	Abrv.	"R_1" group	"R_2" group
Perflourooctanohydroxamic acid	PFOHA	$-CF_3(CF_2)_6$	-H
Heptaflourobutyrichydroxamic acid	HFBHA	- $CF_3(CF_2)_2$	-H
N-Methylperflourooctanohydroxamic acid	MPFOHA	- $CF_3(CF_2)_6$	-CH_3
N-Methylheptaflourobutyrichydroxamic acid	MHFBHA	- $CF_3(CF_2)_2$	-CH_3

Table 4-17 Solubilities of Various Hydroxamic Acids at 333 k and 20.3 MPa

Abrv.	Solubility (mol/L)	References
PFOHA	>7.79E-02	Glennon et al. (1997)
HFBHA	4.40E-02	Glennon et al. (1997)
MPFOHA	3.65E-02	Glennon et al. (1997)
MHFBHA	2.99E-02	Glennon et al. (1997)

Extraction experiments were done using PFOHA to extract Fe(III) spiked onto filter paper (dry or wet) at 30.4 MPa and 343 Kelvin. The results showed that added water increased the percent extraction (from 90% to 97%). In a separate extraction, PFOHA displayed selective extraction of Fe(III) at 86% in the presence of a metal mixture of Fe(III), Cu(II), Pb(II), Mn(II) and Ni(II) (Glennon et al., 1997).

4.5.6 Other chelates

There has been some advancement towards the design of highly soluble chelating agents for use in SC CO_2. Conventional chelating agents (such as the dithiocarbamates) and non-conventional agents (such as the picolyl amines, bis(picolyl amines) and α-dithiols) have been functionalized with fluoroether, silicon or fluoroalkyl tails (Yazdi, 1996) and were shown to exhibit solubilities of 0.1 to 1 mol/L at room temperature and pressure. Extractions in SC CO_2 done from a lead spiked sand sample with the fluoroether analogues of the above mentioned ligands showed low percent extractions (20%-35%) (Yazdi, 1996). Although the initial extraction results may be reasonable, the cost of synthesis may outweigh the cost reduction by the potential low pressure and temperature in a scaled up process (Yazdi and Beckman, 1997).

4.6 Correlating Solubilities in SC CO_2

This section will give an overview of two different techniques to correlate the solubilities of β-carotene and $Cu(tta)_2$ in SC CO_2. The techniques used will be the Chrastil technique (Chrastil, 1982) and the Guigard-Stiver technique (Guigard and Stiver, 1998). These methods use previous solubility data and various physical parameters to correlate the solubilities of specific solutes in SC CO_2.

The Chrastil technique is the most widely used technique for correlating solubilities in SC CO_2 (Stiver and Rampley, 2000). The Chrastil technique describes solubility behaviour between the relationship of the logarithm of solubility and the logarithm of pure solvent density. It is widely used because it does not require any physical-chemical property data for the solute. The Chrastil technique assumes that the slopes derived from the isothermic plots of log-solubility vs. log-density for a specific solvent/solute system are linear and thus derive constant values to use in the correlating equation (Chrastil, 1982).

The Guigard-Stiver Solubility Correlation uses a density dependent solubility parameter approach to correlate the solubilities of solutes in SC CO_2. The solubility parameter approach is based on the regular solution theory and the activity coefficient of the solute in the supercritical phase. These are used by the Scatchard-Hildebrand equation to correlate the solubilities of solutes in SC CO_2. The regular solution theory describes a solution where there is no excess entropy or excess volume mixing upon the mixing of the components (Prausnitz et al., 1986).

4.7 Summary

This section included an overview of current soil remediation technologies for treating metal contaminated sites, the theory and practice behind the quartz crystal microbalance technique, a synopsis of other solubility measurement techniques in SC CO_2, a summary of the available solubility data for β-carotene in SC CO_2 from the current literature and a description of the different chelating agents used with SC CO_2 and their respective solubility and extraction data from the current literature. This section identifies the potential of using SC CO_2 to remove heavy metals from metal contaminated soils. This section also provides the necessary background for the reader to understand the further sections dealing with solubility measurements, and the use of the solubility correlating equations.

5 Materials and Methods

This section will discuss the SC CO_2 system, components and material design and sources. The methodology and procedures that were used in this work to conduct the solubility experiments will also be discussed.

5.1 Materials

This section will identify the source and type of materials used to implement this research. It will also describe in full detail the SC CO_2 system and components used for the solubility experiments.

5.1.1 SC CO_2 System

The SC CO_2 system that was used for the solubility experiments was similar to the design used in Guigard (1999), and was modified for the work herein. The author of this thesis solely completed the construction and assembly of the SC CO_2 system. A schematic of the SC CO_2 system is shown in Figure 5-1.
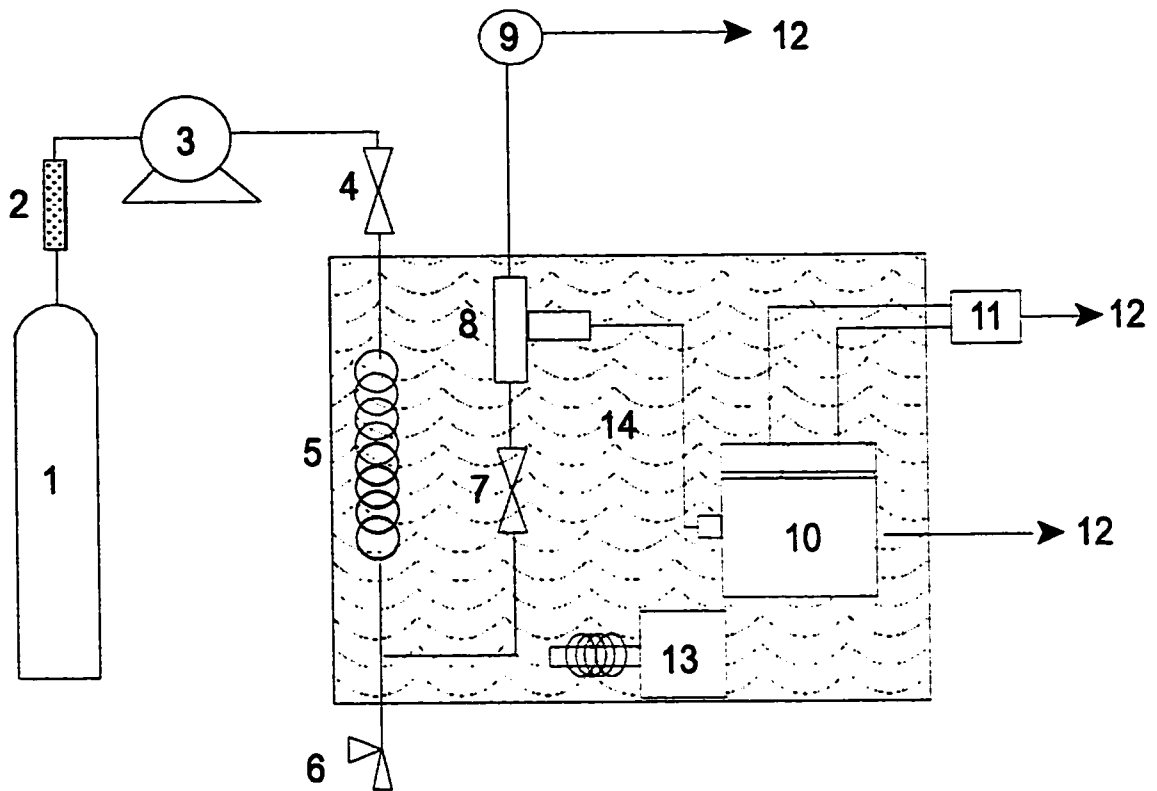
Legend

1. CO$_2$ Cylinder	6. Pressure Relief Valve	11. Oscillator
2. Filter	7. Ball Valve	12. To Data Acquisition System
3. Syringe Pump	8. Low Dead Volume Tee	13. Thermostatted Circulator
4. Check Valve	9. Pressure Transducer	14. Water bath
5. Preheating Coil	10. Pressure Vessel	

Figure 5-1 Schematic of SC CO$_2$ System

The CO_2 used for this work was Instrument grade 4.0, (>99% pure) obtained from Praxair Canada, Edmonton, Alberta. The CO_2 was filtered with a 0.5-micron and 10 micron filter before entering the pumps. Continuous pressure was maintained throughout the experiment with two ISCO model 500D syringe pumps equipped with a continuous flow check valve package. The temperature of the CO_2 in the syringe pumps was maintained by temperature control jackets, which circulated heated water from the circulating water bath around the two syringes. The pressure was also monitored through a pressure transducer obtained through Omega Engineering (model PX602).

All 1/16" stainless steel tubing (GC grade) that was used in the SC CO_2 system was obtained through Fisher Canada, while all Swagelok fittings and valves were obtained through Edmonton Valve and Fitting. All tubing, fittings and valves were pressure-rated to 31 MPa or greater. The stainless steel tubing used in the system was of varying inner diameter. From the pump through to the three-way valve an inner diameter of 1 mm was used. The tubing from the three-way valve to the low dead volume tee had an inner diameter of 0.5 mm. From the low dead volume tee to the pressure vessel tubing of an inner diameter of 0.013 mm was used. The small inner diameter tubing was used to minimize diffusion of SC CO_2 from the pressure vessel back upstream. Throughout this research, the SC CO_2 system was constantly checked and maintained for faulty fittings, leaks and damaged and/or worn out components. These checks helped to localize any leaks and problems to the pressure vessel and surrounding fittings.

During solubility experiments, the SC CO_2 system was pressurized to relatively high pressures (up to 12.0 MPa). These high pressures required a number of precautionary measures to be in place to ensure that the SC CO_2 system was operating safely. To ensure the pressure in the SC CO_2 system did not increase beyond the SC CO_2 system pressure limits, the syringe pumps were set to shut off when pressures exceeded 14.5 MPa. Also a pressure relief valve (set at 14.5 MPa) was installed within the SC CO_2 system. In case of failure of the pressure vessel and/or SC CO_2 system components, a containment vessel was used to encase the pressure vessel. Precautionary measures were also taken by placing the entire SC CO_2 system in the fume hood and closing the sash of the fume hood during an experiment.

The pressure vessel was similar to that used by Guigard (1999) and was modified by the author of this thesis. The pressure vessel was manufactured from 316 stainless steel to the specifications at Stamco Speciality Tool and Manufacturing Company (Edmonton, Alberta) and pressure rated to 31 MPa. Type 316 stainless steel was chosen because it exhibits the best corrosion resistance of the standard stainless steels. The volume of the pressure vessel was determined by measuring the amount of water that the vessel holds and then correlating that to the density of water at the temperature it was measured at. The calculated vessel volume was determined to be 1.49 cm^3 (please see section 6.2 for calculations). A schematic of the solubility vessel is illustrated in Figure 5-2.

Side View   Top View
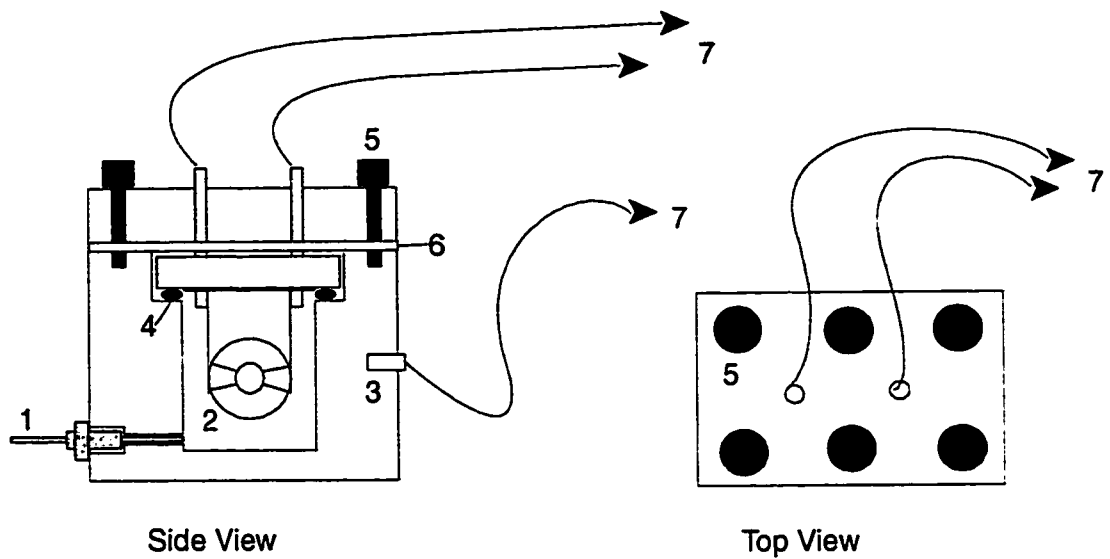
Legend

1. In From SC CO_2 System   5. Socket Head Cap Screw
2. QCM and Holder   6. Teflon™ Gasket
3. Thermistor   7. To Data Acquisition System
4. Teflon™ O-ring

Figure 5-2 Schematic of the Solubility Vessel

The quartz crystal and holder were sealed in the vessel with an upper and lower Teflon™ gasket that was carved out of sheet Teflon™. Teflon™ was chosen as the best gasket material because of its chemical inertness. A 9 MHz AT-cut quartz crystal with a silver electrode and glass holder was obtained through Lap-Tech Inc. (Bowmanville, Ontario). An illustration of the quartz crystal and holder used in this research is shown in Figure 5-3. The corresponding properties of this type of crystal are listed in Table 5-1
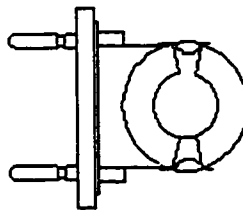
Figure 5-3 QCM in Holder

Table 5-1 Properties of 9 MHz AT-cut Quartz Crystal

Parameter	Symbol	Value	Units
Stiffness	μ_Q	2.901E10	N/m^2
Density	ρ_Q	2649	$Kg.m^2$
Thickness	t_Q	1.825E-4	m
Area	A	4.208E-05	m^2

The crystal was connected to an oscillator circuit that was similar to the circuit described in Guigard (1999). The different electrode type and design of the quartz crystal used in these experiments required some modifications to the oscillator circuit. The modified circuit was built with the help of the staff in the Department of Civil and Environmental Engineering at the University of Alberta. A

schematic of the oscillator circuit that was used in this research is illustrated in Figure 5-4.
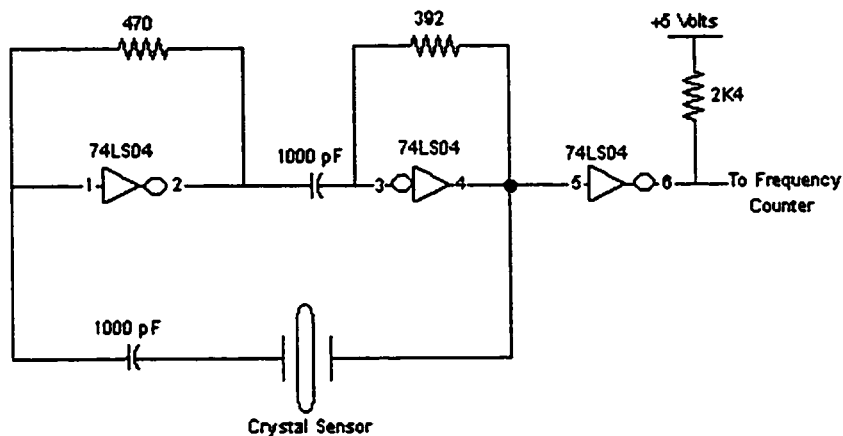
Figure 5-4 Schematic of the Oscillator Circuit

The temperature was maintained throughout the experiment with a Hacke D1 circulator in a water bath. The temperature was monitored in the water bath with a thermometer and within the pressure vessel with a YSI Precision thermistor (obtained through Newark Electronics). The thermistor was epoxied into the outer part of the pressure vessel wall with Circuit Works, Conductive Epoxy to enhance thermal conductivity.

An outer containment vessel (in which the pressure vessel was placed) was purchased to provide a waterproof environment, a safety capsule for the pressure vessel and a holder for the potassium hydroxide solution. The potassium hydroxide solution was used as a leak indicator; this is discussed further on in this section.

All signals from the pressure transducer, oscillator, thermistor and pumps were logged into a computer using a data acquisition card and National Instruments LabVIEW 5.1 software. The software allowed for real time display of the data. This real-time display provided a significant advantage in terms of monitoring the solubility measurement process. The data aquired by LabVIEW was written to a Microsoft Excel file where it was analyzed.

5.1.2 Chemicals Used

Table 5-2 provides a list of chemicals used in this work and their source and purity.

Table 5-2 Chemicals Used for this Research

Chemical	Source	Purity
Methanol	Fisher Scientific	>99%
Caffeine	Fisher Scientific	99%
Chloroform	Fisher Scientific	98%
β-Carotene	Sigma	99%
2-Thenoyltrifluoroacetone	Alfa Aesar	99%
Copper nitrate	Alfa Aesar	99%
Potassium Hydroxide	Fisher Scientific	98%
Methylene Chloride	Fisher Scientific	>99%

All flammable solvents, (methanol, methylene chloride and chloroform) were stored in proper storage facilities. β-Carotene was stored in a dark, cold environment (-10°C) to prevent degradation from heat and light.

5.2 Procedure

This section will outline the procedures and techniques that were required to prepare and execute a solubility experiment.

5.2.1 Synthesis of Copper thenoyltrifluoroacetone (Cu(tta)$_2$)

Cu(tta)$_2$ was not available commercially and therefore it was synthesized according to the procedures of Bertrand and Kaplan (1966) and Reid and Calvin (1950). The basic procedure was as follows:

➢ Add a known amount of copper nitrate pentahydrate (Cu(NO$_3$)$_2$•5H$_2$O) to a clean volumetric flask

➢ Add roughly 200 mL of deionized water to dissolve the copper nitrate

➢ Add a known amount of thenoyltrifluoroacetone (tta) to the volumetric flask

➢ Place the volumetric flask on a hot plate/stirrer

➢ Mix the solution at approximately 50^{0}C

➢ Continue until no more of the yellow chelating agent (tta) appeared and a green flocculent type solid was present

➢ Cool the solution and filter with deionized water

➢ Let dry

The Cu(tta)$_2$ was then analyzed with a melting point apparatus to ensure the prepared compound was indeed Cu(tta)$_2$. The melting point determinations can be found in Section 6.1. The Cu(tta)$_2$ was also analyzed by X-ray analysis, the results from this analysis can be found in Appendix A.

5.2.2 Solubility Experiments

For each solubility experiment a number of steps were required. First, the pumps were filled with CO$_2$ and the water bath turned on. This step enabled the CO$_2$ in the pumps to warm and stabilize in pressure. After warming, the pumps were then pressurized to the experimental pressure. The solute (β-carotene or

Cu(tta)$_2$) was then loaded onto the crystal electrode surface. This frequency data was recorded and logged via the LabVIEW software. Then the quartz crystal was placed in the pressure vessel and sealed. The sealed pressure vessel and the containment vessel were then gradually warmed on a hot plate to just below or above the experimental temperature. When these conditions were met the potassium hydroxide solution was placed in the containment vessel with the pressure vessel. The potassium hydroxide solution was used to detect leaks from the pressure vessel. The containment vessel was sealed and placed in the water bath and connected to the system. The vessel was allowed to sit for enough time in the water bath to stabilize the temperature to the experimental temperature. After temperature stabilization, the system was pressurized and the apparatus was monitored for leaks, constant response from the QCM and dissolution of solute from the crystal surface. The dissolution of solid from the QCM surface into the SC CO$_2$ caused an increase in frequency from the QCM. As this frequency stabilized, it was assumed that solubility was reached. Throughout the solubility experiment the frequency data were collected and logged to an Excel spreadsheet via the LabVIEW software. After the completion of a solubility experiment these frequency data were then analyzed for the different parameters (as outlined in Section 5.2.2.3) and the resultant solubility was calculated. The following section details some of the steps outlined above.

5.2.2.1 Mass loading on the QCM

The chemical Cu(tta)$_2$ or β-carotene was initially dissolved in a suitable solvent (methanol or chloroform, respectively) to create a solution of known

concentration. The solution was applied in small quantities to the QCM with a 5-microliter syringe. The volume of an individual application was usually 0.2 to 0.5 microliters. After each application the solvent evaporated off of the QCM leaving a crystalline solid. In order to have adequate mass deposited on the electrode surface for the solubility experiment, many applications with the microlitre syringe were required.

For initial experiments, to ensure that the solid completely adhered to the QCM, the loaded QCM was washed with deionized water and dried. The measured frequencies before and after washing showed no difference, thus concluding that the solid was completely adhered to the QCM.

The change in frequency during mass loading was monitored and collected with the data acquisition system. The overall frequency shift (final frequency minus the initial frequency) was then used in the Sauerbrey Equation (Equation 4-1) to calculate the total mass change on the surface of the electrode. This mass was then compared to the mass that was added onto the QCM with microlitre syringe based on the concentration of the solution and the volume applied.

5.2.2.2 The Frequency Response of the QCM in Neat SC CO_2

Before the solubility measurements could be conducted, the frequency change of the QCM due to the supercritical conditions needed to be calculated. A clean QCM was sealed in the pressure vessel and heated to the desired temperature. The pressure vessel was filled with SC CO_2 and pressurized to a specific pressure. The frequency shift due to SC CO_2 was observed. This

frequency shift is denoted as **FCO₂**, which is total frequency shift of the QCM in neat SC CO_2.

5.2.2.3 Solubility Measurements

After the mass was satisfactorily loaded onto the crystal, the loaded QCM was placed inside the pressure vessel. The sealed pressure vessel was then placed in the containment vessel. The containment vessel was then sealed using Apeizon Q sealing compound. This allowed for the wires and stainless steel tubing to pass, yet maintained an airtight seal.

For most of the experiments, a vile of potassium hydroxide solution was also placed inside the containment vessel. The potassium hydroxide (KOH) solution acted as a pH monitor. If there were a leak in the pressure vessel, the amount CO_2 inside the containment vessel would increase in concentration. This increase in concentration of CO_2 within the containment vessel would raise the concentration of carbonic acid in the KOH solution, thus decreasing the pH of the KOH solution. The KOH solution was prepared initially to a pH of 10.5. During each solubility experiment a similar volume beaker with the same volume of KOH was sealed and placed in the water bath. The beaker was sealed for the entire length of the solubility experiment. The KOH solution in the beaker acted as an experimental control. The pH was measured with pH strips obtained through Sigma-Aldrich. The strips had a sensitivity of 0.5 pH units and a range from 7-14 pH units.

The containment vessel containing the pressure vessel and KOH solution was then placed inside the water bath, connected to the SC CO_2 system and

allowed to warm to the desired temperature. After suitable warming, the three-way valve was opened and the solubility vessel was pressurized. After initial pressurization, the three-way valve was shut off to detect any leaks from the pressure vessel. If the pressure reading from the pressure transducer was kept constant for a period of roughly 3 minutes and no temperature drop was evident, this provided a strong indication that there were no leaks and the experiment was allowed to continue and the valve was re-opened.

Throughout the entire experiment, all frequency, temperature and pressure measurements were monitored and recorded every 2 seconds. The system was then left to equilibrate as the solute dissolved in the solvent. As expected, the frequency of the QCM increased over time, corresponding to the loss of mass from the crystal electrode. The experiment was allowed to continue until there was no frequency change of the QCM, which indicated that the solute had reached equilibrium in the SC CO_2 in the pressure vessel. At the end of the experiment, the three-way valve was turned off and the vessel was depressurized through the low-dead volume tee. The frequency of the QCM was allowed to stabilize and the data acquisition software was turned off. After depressurization, the containment vessel was opened and the pH of the KOH solution was measured. All data were then analyzed and solubilities calculated.

For each solubility experiment five different frequency measurements were taken during or before the solubility experiment.

- F_0 : the resonant frequency of the QCM before the mass was loaded onto the electrode surface.

- **FCO_2**: the total frequency shift of the QCM in neat SC CO_2.

- **F_1** : the frequency reading immediately preceding the pressurization of the pressure vessel (The mass was loaded onto the electrode surface, the QCM was placed inside the pressure vessel, the pressure vessel was at the experimental temperature and was connected to the SC CO_2 system.)

- **F_{dip}**: the lowest frequency reading after the pressurization had been initiated. F_{dip} is a combination of the FCO_2 value, the frequency change due to the SC CO_2 adsorbing on the loaded mass on the QCM surface and the changes of density and viscosity of the SC CO_2. This number was always significantly greater than the FCO_2 value due to the increased surface area from the solid that was adhered onto the electrode surface. (Thus allowing more SC CO_2 to adsorb onto the crystal surface.)

- **F_{final}** : the final frequency after the solute had reached equilibrium with the SC CO_2.

- **F-air** : the final frequency reading from the QCM after the pressure had been released from the pressure vessel.

With all of these measurements the solubility of the solute in SC CO_2 was calculated.

After each experiment, the pressure vessel and all of the tubing up to the low dead volume tee was cleaned with a suitable solvent, (chloroform or methanol) depending on the solute used (β-carotene and Cu(tta)$_2$, respectively). The tubing from the low dead volume tee to the three-way valve was cleaned on

a weekly basis. Any residual solvent from the cleaning process was blown out using filtered compressed air.

6 Results

The information in this section will summarize and describe any results pertaining to the solubility experiments in SC CO_2. The first sections will provide some of the preliminary results obtained prior to conducting the solubility experiments. The following sections will outline experiments that were conducted prior to the solubility experiments and the results from the solubility experiments themselves.

6.1 Analysis of Cu(tta)₂

To ensure that the preparation of Cu(tta)₂ was indeed Cu(tta)₂, a melting point determination was conducted. A total of four compounds with known melting points were used to calibrate the thermometer that was used in the melting point apparatus. Both the theoretical and measured melting points are given as ranges of temperatures. For the theoretical melting points, the suppliers give the range. The measured melting point range corresponds to the observance of the first liquid drop to the last liquid drop to appear. The compounds and their respective melting points (theoretical and measured) are listed in Table 6-1.

Table 6-1 Melting Point (m.p.) Information

Compound	Theoretical m.p. (^{0}C)	Measured m.p.(^{0}C)
Apidic Acid	151-152	141.5-144.5
p-Methylbenzoic acid	182-185	172-174
p-Hydroxybenzoic acid	213.5-217.5	208.5-209.5
Caffeine	233.5-236.5	227-231

For the four compounds listed in the above table, a calibration curve was plotted. The measured and theoretical melting points are represented in Figure 6-1 as averages of the ranges given. The theoretical melting point was plotted against the measured melting points.

y = 0.9517x + 17.599
R^2 = 0.9994
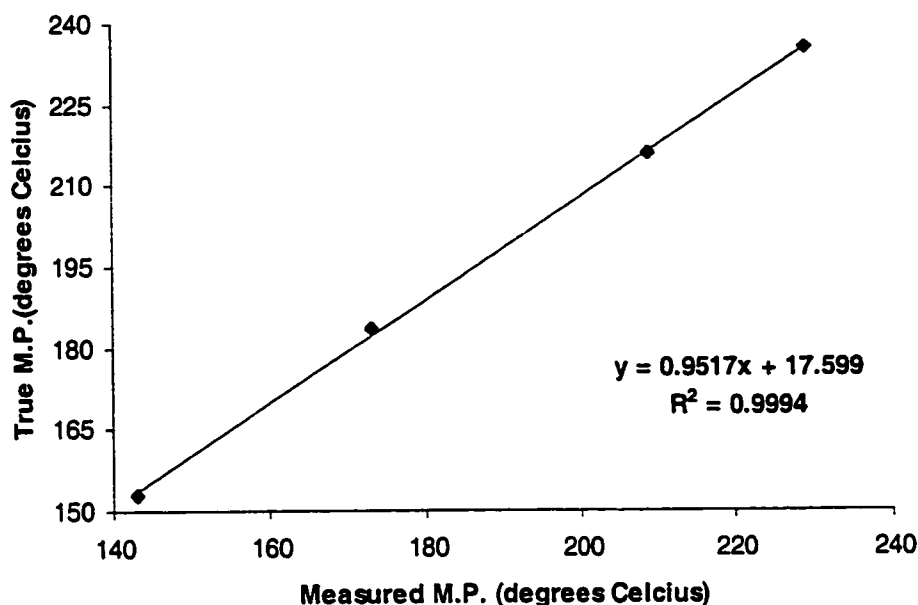
Figure 6-1 Calibration Curve for The Thermometer Used in the Melting Point Determination

The calibration curve was linearly fit and the corresponding equation can be seen in Figure 6-1. The equation has a R^2 value of 0.9994, which indicates a high level of linearity for the calibration curve.

The measured melting point range for Cu(tta)$_2$ was 233-237°C. When the measured averaged value (235°C) is put into the linear equation in the Figure 6-1, the melting point is calculated to be 242.2°C. The calculated value of 242.2°C compared to the theoretical average melting point for Cu(tta)$_2$ of 242.5°C (Berg

and Truemper, 1960) is very close. This indicates that the preparation of $Cu(tta)_2$ for this work was indeed $Cu(tta)_2$.

In addition to a melting point analysis, the prepared $Cu(tta)_2$ on a gold electrode was examined by X-ray analysis. From the chart in Appendix A, the peaks indicate the type of compounds present. All peaks that are shown (except the gold and silicon, which are from the electrode and quartz crystal, respectively) represent elements that make up $Cu(tta)_2$. The absence of other elements indicates that the preparation of $Cu(tta)_2$ produced pure $Cu(tta)_2$.

In Guigard (1999), the preparation technique for $Cu(tta)_2$ was verified to produce pure $Cu(tta)_2$ by melting point analysis and IR and x-ray techniques.

6.2 Measurement of Solubility Vessel Volume

Prior to starting any of the SC CO_2 experiments, the volume of the pressure vessel had to be determined.

The dry pressure vessel was weighed on an analytical balance and partially filled with water at $21^{\circ}C$. The vessel was filled to the top of the cavity where the o-rings were placed (Figure 6-2).

The partially filled vessel was then weighed. The difference between the dry vessel and partially filled vessel was adjusted to volume using the density of water at $21^{\circ}C$. Assuming that there would be no mixing with the SC CO_2 in the tube that connected the pressure vessel with the SC CO_2 system (because of the very small inner diameter of the stainless steel tubing), the vessel volume was considered only to be the cavity of the vessel. As a result, the volume for the fitting to that connected the vessel to the SC CO_2 needed to be subtracted from

the total measured volume (the tubing was not in place at the time of weighing, instead the fitting was plugged with a screw on plug obtained from Swagelok Inc.). From dimensions given from Swagelok Inc. and the dimensions of the space between the fitting and vessel wall, the extra volume was calculated to be 0.0193 cm^3. This volume was then subtracted from the calculated vessel volumes to obtain a final result. The final average for the vessel volume was calculated to be 1.490 cm^3 with a standard deviation of ±0.036. Relevant data and sample calculations are shown in Appendix B.
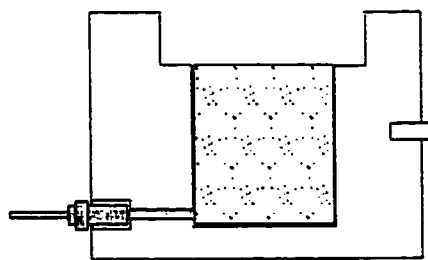
Water in Pressure Vessel

Figure 6-2 Side View of Water Filled Pressure Vessel

6.3 Temperature Data

Three devices monitored the temperature during a solubility experiment:

➤ a thermistor, which was placed inside the pressure vessel wall,

➤ a thermometer, which was placed in the water bath

➤ a temperature regulator within the circulator for the water bath.

For all experiments, the thermistor was assumed to be the most accurate of all the temperature monitoring devices. The thermistor was calibrated using the Steinhart and Hart equation (Equation 6-1).

$$\frac{1}{T} = a + b(LnR) + c(LnR)^3$$

where: T is temperature in Kelvin and R is resistance in ohms. The constants a, b and c were given by YSI (1997) to be 1.1303E-03, 2.339E-04 and 8.863E-08, respectively. These constants are derived from the calibration of the thermistor by the manufacturer (YSI, Ohio, U.S.A.).

This equation is the preferred mathematical expression for the resistance-temperature relationship for the type of thermistor used (YSI, 1997). The thermistor used is accurate within $\pm 0.2^0C$ between 0^0C and 70^0C (YSI, 1997).

For all successful solubility experiments (without leaks and/or a stable frequency reading from the QCM), the temperature varied no more than $\pm 0.4^0C$. The temperature data from a sample solubility experiment is graphically displayed Figure 6-3.

In this experiment, the CO_2 filled the vessel at time 0.15 indicated by a '1' on Figure 6-3. The initial drop in temperature of 0.38^0C is a result of the SC CO_2 entering the non-pressurized vessel. After the initial drop and throughout the solubility run, the temperature gradually increased to the set temperature (45.58^0C) of the surrounding system (water bath, containment vessel and the remaining SC CO_2 system). The difference in SC CO_2 density between the high and low temperatures is 0.005 g/cm^3. This difference in density is minimal, thus causing little effect on the final solubility measurement. The final drop in temperature (at 1.35 hours) (shown in Figure 6-3) was from the release of pressure from the pressure vessel after the solubility experiment was completed.
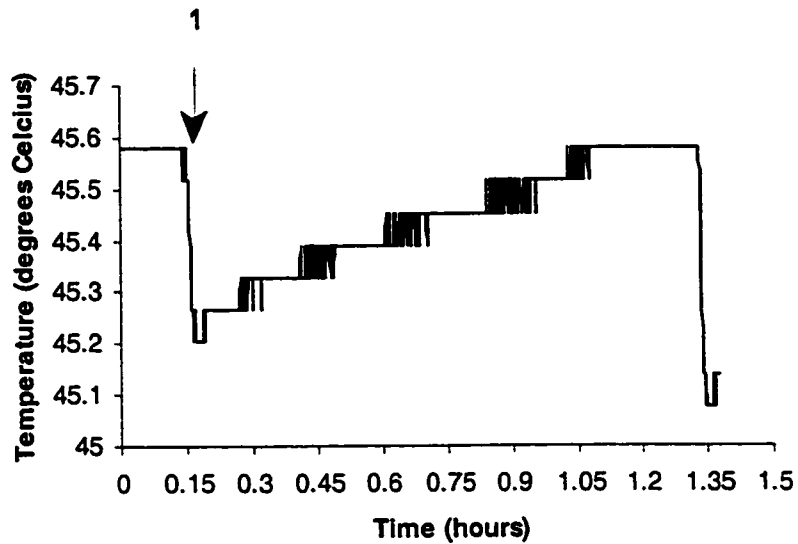
Figure 6-3 Temperature vs. Time For Solubility Run, July 25/00

The mean temperature for this experiment was $45.46°C$, the standard deviation was calculated to be $±0.12°C$. The data set for this sample run can be observed Appendix C.

For all solubility experiments, the thermistor was used to determine if there were any leaks in the pressure vessel during an experiment. Through careful and numerous observations of the real-time temperature measurement in SC CO_2 experiments, it was determined that if there were a leak from the pressure vessel, the temperature of the vessel would drop after the initial temperature drop caused by the SC CO_2 expanding into the pressure vessel. A temperature drop due to a leak would appear as a constant decrease over the entire length from when the leak developed. The majority of the leaks developed as soon as the SC CO_2 entered the pressure vessel. However, on two occasions, the pressure vessel developed a leak in the middle of a solubility experiment. These two

instances were easily detected using the real-time display provided by the LabVIEW software.

Figure 6-4 illustrates the temperature changes for a non-leak solubility run (July 20) versus a solubility run with a leak (July 12) somewhere in the pressure vessel.
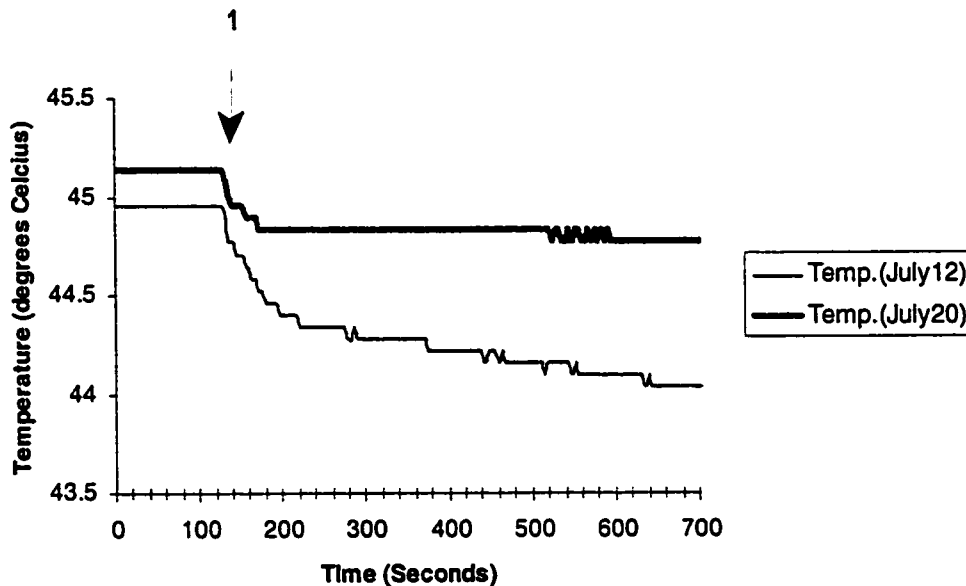
Figure 6-4 Illustration of Temperature Changes Due to a Leak versus no Leak

At 130 seconds (as indicated by a '1' on Figure 6-4) the pressure was turned on for both experiments. For the July 20th run the temperature dropped a total of 0.37°C over the observed time frame, while the July 12 run dropped 1.05°C over the same time frame. The temperature for the July 12th run continued to drop while the July 20th run stabilized and increased. The pH of the KOH solution inside the pressure vessel measured after the July 12th run was below 7.5 compared to the control on the same day of pH 9.5. The low pH in the

containment vessel also indicated that a leak had occurred. The KOH solution in the control and containment vessel on July 20th both measured a pH of 9.0.

6.4 Pressure Data

For each of the solubility experiments, the pressure was monitored in two locations: at the syringe pumps and at an external pressure transducer located below the low dead volume tee (see Figure 5-1). The pressure data from each location were recorded with each experiment. The syringe pumps were set to operate at a continuous pressure mode. This mode of operation allowed for continuous pressure to be maintained throughout the system while continuously allowing for pump refilling. The external pressure transducer was placed close to the pressure vessel to monitor the pressure downstream of the three-way valve.

The transducers in the syringe pumps were zeroed and calibrated to room atmospheric pressure frequently to ensure accuracy. The readings from the pump transducers were considered to be the most accurate, for they exhibited the least variation in pressure reading. The external transducer was calibrated using the pump transducers.

An example of pressure data from a typical solubility run is shown in Figure 6-5. The mean transducer pressure (while the SC CO_2 was pressurized) was 10.33 MPa with a standard deviation of ±0.08. The pump pressure was constant at 10.34 MPa. The data for Figure 6-5 can be found in Appendix D.

The external transducer also helped determine if there were any leaks in the pressure vessel. During the initial stages of a solubility experiment, after initial pressurization, the three-way valve (see Figure 5-1) was closed and the

pressure reading from the transducer was monitored for a drop in pressure. A drop in pressure indicated that leaks were present within the pressure vessel and/or the immediately surrounding fittings. An illustration of the pressure decrease due to a leak is shown in Figure 6-6.

Transducer Pressure   **Pump Pressure**
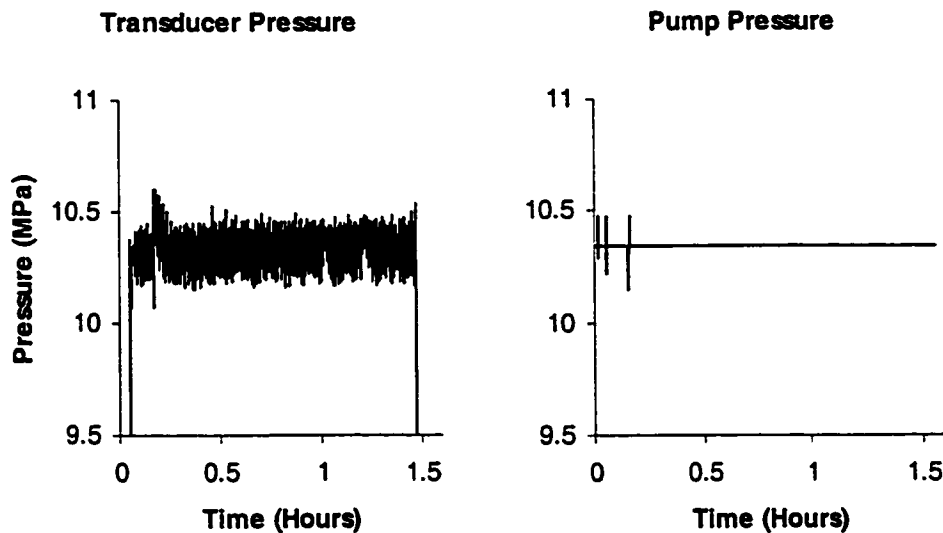
Figure 6-5 Comparing Pump Pressure to External Transducer Pressure, From Solubility Measurement on May 3/00

In Figure 6-6 the pressure was turned on at the three-way valve indicated by arrow '1'. The three-way valve was then closed as indicated by arrow '2'. Over the course of 16 seconds the pressure dropped rapidly indicating a leak in the pressure vessel. At arrow '3', the three-way valve was turned on again and the experiment was allowed to run for another twenty seconds before it was aborted. Temperature data from this experiment also indicated the existence of a leak.
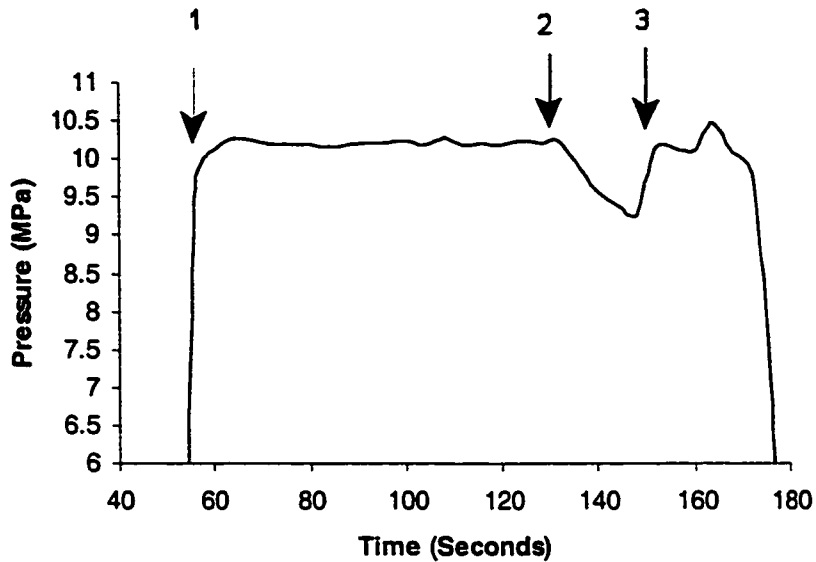
Figure 6-6 Example of Pressure Loss From Leak During A Solubility Experiment on July 18/00

6.5 Flow Data from the Syringe Pumps

For each of the solubility experiments, the flow data from the syringe pumps were recorded. Initially, the flow data from the pumps were intended to be used for leak detection. It was assumed that if there were no leaks in the SC CO_2 system after pressurization and temperature equilibration, the pump flow rates would reduce to a minimal amount (less than ±0.010 mL/minute). However, at pressures above 8.27 MPa, the flow rate of the pump was unstable. This variability was most likely due to the compressible nature of the SC CO_2 and the ball valves used in the check valves between the two syringe pumps (a further discussion on the pump flow rate can be found in Section 7.1.2). An illustration of the variability is displayed in Figure 6-7.

Flow Rate vs. Time, Feburary 22/00
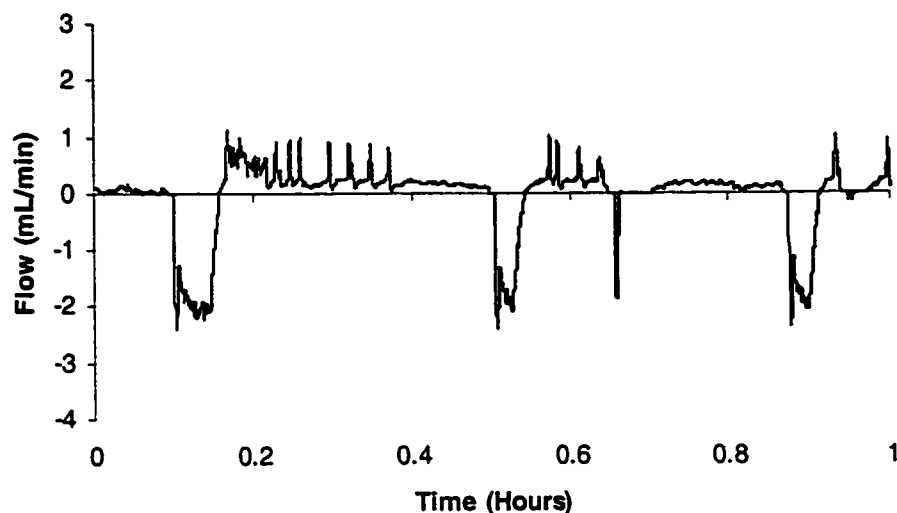
Figure 6-7 Flow Rate From Syringe Pump at 10.34 MPa and 318 K on February 22/00

During this experiment, the SC CO_2 system was not connected to the syringe pumps. The outlet from the syringe pumps was plugged, allowing only a small portion of the system to be checked for leaks. Both syringes were kept at a constant temperature during the entire experiment. All tubing and fittings were periodically checked for leaks, although none were found.

Based on the results presented in Figure 6-7, it was decided that the flow rate data from the pumps could not provide an adequate indication of leaks within the SC CO_2 system.

6.6 Quartz Crystal Microbalance Data

6.6.1 Resonant Frequency Measurements

Prior to the start of a mass loading and/or solubility experiment, the resonant frequency of the QCM at room temperature and room pressure was

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taken. The resonant frequency for each experiment was different. For each experiment the resonant frequency varied due to the relative position (mounting effects) and individual properties of each crystal. The quartz crystals that were used were rated to oscillate at 9 MHz. All resonant frequency measurements were slightly above or below this value. Thus, for each experiment, the resonant frequency was measured and used in related solubility and frequency mass calculations. An example of a resonant frequency measurement is shown below in Figure 6-8. The data for this experiment can be found in Appendix E.
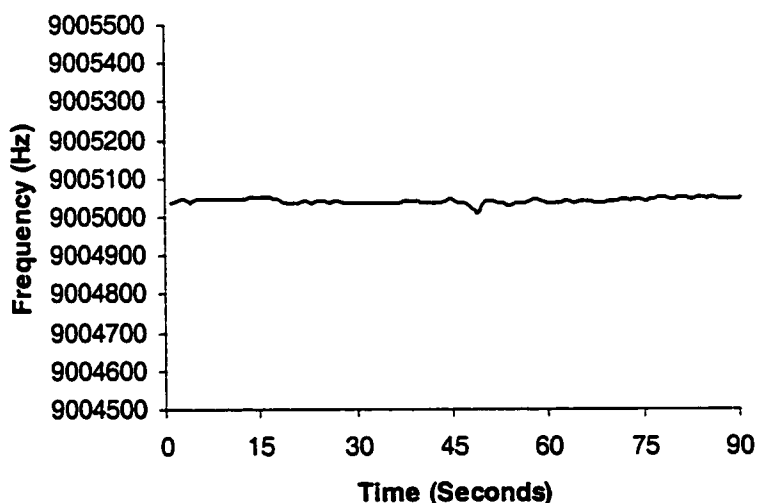
Figure 6-8 Resonant Frequency Measurement From April 26/00

In the experiment illustrated in Figure 6-8, the average resonant frequency measurement was 9005041 Hz, with a standard deviation of ±6.2Hz. Such a low standard deviation was common to all the resonant frequency measurements. Experiments with a relatively high standard deviation were aborted due to possible interference with the solubility measurements (further discussion about effects and sources of interference can be found in section 7.2).

6.6.2 QCM Mass Loading

A typical example of mass loading data obtained is shown in Figure 6-9. The data for this experiment can be seen in Appendix F.
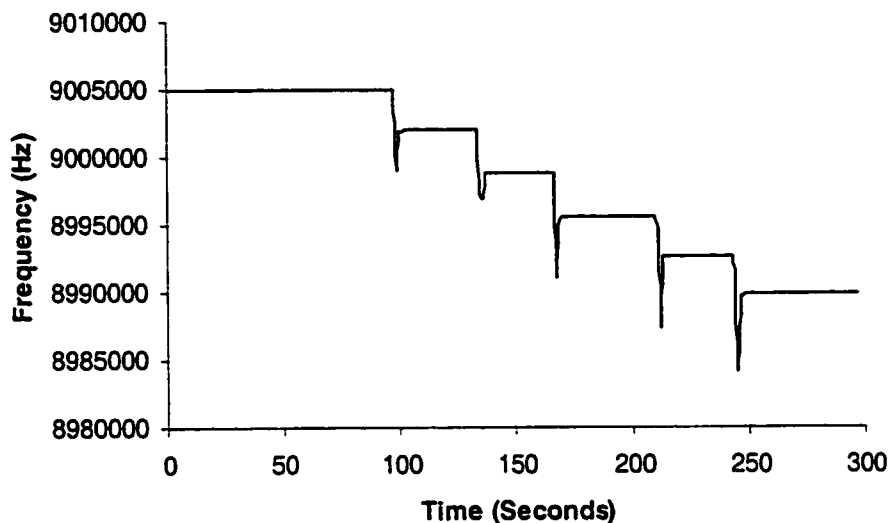
Figure 6-9 Mass loading of $Cu(TTA)_2$ (3.538E-05 g/mL), at 0.2 μL intervals

In Figure 6-9, each drop in frequency represents the addition of the $Cu(tta)_2$/methanol mixture added to the QCM surface in 0.2 μL increments. The sharp initial drop in frequency is due to the mass change on the QCM surface caused by the aliquot of $Cu(tta)_2$/methanol mixture. The initial drop is followed by a sharp increase in frequency, which is due to the solvent volatizing from the electrode surface. After all the solvent has volatilized, a stable frequency is attained. The QCM frequency at this point is lower than the initial frequency due to the crystallized solute on the electrode surface. More $Cu(tta)_2$ solution is added until there is sufficient solute on the crystal to satisfy the maximum

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solubility requirements, based on the volume of the vessel. The data for mass loading from β-carotene exhibited similar characteristics.

In the experimental run illustrated in Figure 6-9, a total volume of 1 μL was placed on the QCM. The mass added based on the volume and concentration of solution added was 3.54E-05 g, while the QCM frequency shift indicated (using the Sauerbrey Equation) an added mass of 3.46E-05 g. The mass reading that would be used in the solubility calculation was always the mass calculated using the QCM frequency reading. The QCM reading is considered more accurate than the mass added by the microlitre syringe due the potential sources of error associated with adding the mass with the syringe, such as: the loss of solute due to adherence of the solute to the tip of the microlitre syringe, the variability in the volume added to the QCM by the microlitre syringe and the uncertainty in the exact concentration of the solute/solvent mixture (Cu(tta)$_2$/methanol or β-carotene/chloroform). A listing of mass readings that were conducted for all successful solubility runs can be found in Appendix G.

6.6.3 Frequency Response of the QCM in Neat CO_2

Before the solubility measurements could be conducted, the frequency change due to the supercritical conditions was calculated. A clean QCM was sealed in the pressure vessel and heated to the desired temperature. The pressure vessel was filled with SC CO_2 and pressurized to a specific pressure. The frequency shift due to SC CO_2 was observed. An example of the total frequency shift (ΔFCO_2) induced by the SC CO_2 on the QCM is illustrated in Figure 6-10.
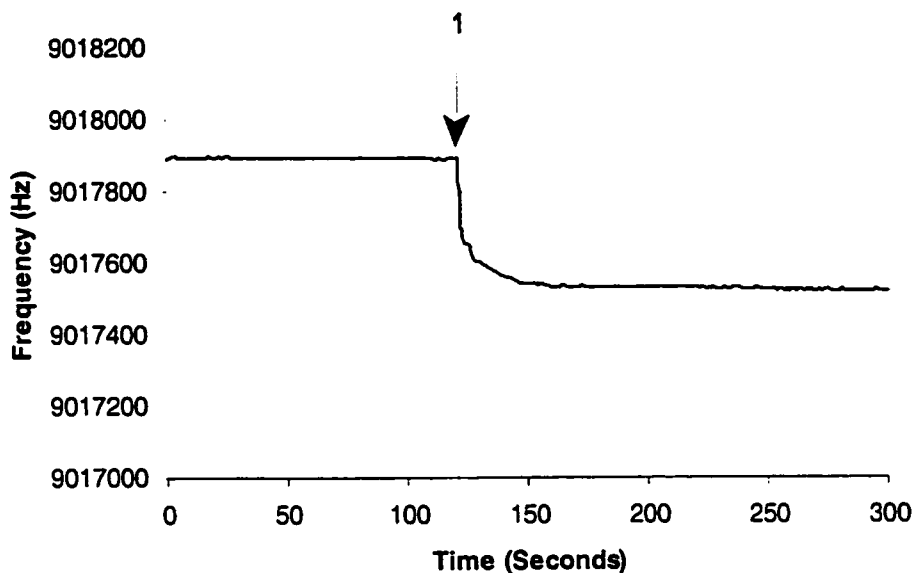
Figure 6-10 Frequency Change of the QCM Due to Neat SC CO_2 at 9.65 MPA and 313K on March 16/00

In this experimental run, the pressure was turned on at the three-way valve, as indicated by arrow '1'. The total frequency shift (ΔFCO_2) was 367 Hz. The data for this chart can be seen in Appendix H. Each different pressure and temperature condition had a minimum of two measurements. These data are summarized with the associated standard deviations in Table 6-2. At least two measurements were carried out for each different condition of pressure and temperature.

The observed ΔFCO_2 (total frequency shift), depends on the frequency change from the compression effect, due to pressure of the fluid (ΔF_P), the frequency due to the density and viscosity of the medium (ΔF_V) and the mass

change of the adsorbed species (ΔF_A) (Tsionsky *et al.*, 1995). ΔFCO_2 can be represented in Equation 6-2.

Table 6-2 Summary of Total Frequency Shifts at Different Temperatures and Pressures

Pressure (MPa)	Temperature (K)	Average ΔFCO_2 (Hz)	Standard Deviation (Hz)
8.27	313	-114	±44
9.65	313	-220	±10
10.3	313	-381	±13
12.0	313	-513	±9
15.0	313	-600	±24
9.65	318	-361	±31
10.3	318	-420	±21

$$\Delta FCO_2 = \Delta F_P + \Delta F_V + \Delta F_A \qquad\qquad (6\text{-}2)$$

6.6.3.1 ΔF_P

The frequency change due to the pressure of the fluid is expressed in Equation (6-3)

$$\Delta F_P = F_0 \alpha P \qquad\qquad (6\text{-}3)$$

where: F_0 represents the resonant frequency of the QCM, α is the proportionality constant, which is reported to be 1.05 E-05 MPa^{-1} (Otake *et al.*, 1994) and P is pressure in MPa.

6.6.3.2 ΔF_V

The frequency change from the density and viscosity of the medium can be calculated as follows.

$$\Delta F_v = -\left(\frac{C}{2}\right) * \left(\frac{\rho\mu}{\pi F_o}\right)$$

$$and : C = \frac{F_o}{t_Q \rho_Q}$$

The thickness and density (t_Q and ρ_Q respectively) for the 9 MHz quartz crystal used in this experiment can be found in Table 5-1. The symbols ρ and μ refer to the density and the viscosity of the medium, respectively, and C is the mass sensitivity of the quartz crystal.

6.6.3.2.1 Density Calculations

The SC CO_2 density used in the above calculation and all further calculations involving density was obtained using a density calculator. This calculator was created by the joint efforts of Greg Rampley and Warren Stiver at the University of Guelph, Canada (Stiver and Rampley, 2000). The calculator uses the modified Benedict-Webb-Rubin equation of state (MBWR-EOS) to calculate the pure fluid density of carbon dioxide based on a specified temperature and pressure. The original source for the MBWR-EOS is Jacobsen and Stewart (1973) with the carbon dioxide parameters originating from Ely *et al.* (1987).

6.6.3.2.2 Viscosity Calculations

The viscosity was calculated according to the Reichenberg method (Equation 6-5) found in Reid *et al.* (1984). This method estimates the viscosity ratio η/η^o. Where η is the calculated viscosity at high pressures and η^o is the low-pressure viscosity at the system temperature. Because the pure component

viscosity values are available for CO_2, the Reichenberg method is recommended by Reid *et al.* (1984).

$$\frac{\eta}{\eta^0} = 1 + Q \frac{A * P_r^{\frac{3}{2}}}{B * P_r + \left(1 + C * P_r^D\right)^{-1}}$$ (6-5)

where the constants A,B,C and D are functions of the reduced temperature (T_r)

$$A = \frac{a_1}{T_r} \exp\left(a_2 * T_r^a\right)$$

$$B = A\left(b_1 * T_r - b_2\right)$$

$$C = \frac{c_1}{T_r} \exp\left(c_2 * T_r^c\right)$$

$$D = \frac{d_1}{T_r} \exp\left(d_2 * T_r^d\right)$$

The values of the coefficients from Reid *et al.* (1984) for SC CO_2 are defined in Table 6-3. The actual viscosity was then calculated by determining η^0 and multiplying it by the ratio as calculated above. The η^0 value was determined by Equation (6-6).

Table 6-3 Reichenberg Coefficients

Symbol	Value
a1	1.98E-03
a2	5.2683
A	-0.5767
b1	1.6552
b2	1.276
c1	0.1319
c2	3.7035
C	-79.8678
d1	2.9496
d2	2.919
D	-16.6169

$$\eta^0 = \frac{(26.69)(M*T)^{0.5}}{\sigma^2 \Omega_v}$$

(6-6)

where η^0 is the low pressure viscosity (μP), M is the molecular weight of CO_2 (g/mol), T is the temperature (K), σ is the hard sphere diameter (Angstroms) and Ω_v is the collision integral (defined below).

The σ value is 3.941 Å and can be found in Appendix B from Reid *et al.* (1984). This Appendix lists the Lennard-Jones Potentials as determined from experimental viscosity data. The Ω_v value is calculated below (Equation 6-7).

$$\Omega_v = \left[A(T^*)^{-B} \right] + C\left[\exp(-D*T^*) \right] + E\left[\exp(-F*T^*) \right]$$

(6-7)

where:

$T^* = \kappa T/\varepsilon$ (where κ/ε can be found with the σ values in Reid *et al.* (1984))

Table 6-4   Coefficients

Symbol	Value
A=	1.16145
B=	0.14874
C=	0.52487
D=	0.7732
E=	2.16178
F=	2.43787

6.6.3.3 ΔF_A

As stated in Section 4.3.1.4 the Sauerbrey Equation (Equation 4-1) can be used to calculate the mass adsorbed onto the QCM surface. In this case, the amount of SC CO_2 adsorbed onto the surface of the QCM is not exactly known. An estimation of the ΔF_A is obtained by accounting for the frequency change due

to pressure of the fluid (ΔF_P) and the frequency change due to the density and viscosity of the medium (ΔF_V) and then subtracting the total frequency shift (ΔFCO_2, Equation 6-2). This results in a frequency shift that can be converted into a mass change with the Sauerbrey Equation (Equation 4-1).

6.6.3.4 Summary of Effects From ΔF_P, ΔF_V and ΔF_A

Table 6-5 shows the change of the QCM frequency from the pressure effect, the viscosity effect and the frequency change due to the SC CO_2 adsorbing onto the QCM surface (ΔF_P, ΔF_V and ΔF_A, respectively).

Table 6-5 Change of QCM Frequency Due to Pressure, Viscosity and SC CO_2 Sorption

Pressure (MPa)	Temperature (Kelvin)	ΔF_P (Hz)	ΔF_V (Hz)	ΔF_A (Hz)
9.65	313	905	-300.6	-824.7
10.3	313	970	-336.1	-1014.8
12	313	1130	-371.7	-1266.4
15	313	1410	-405.0	-1602.1
9.65	318	905	-211.7	-1054.6
10.3	318	970	-260.8	-1129.2

6.7 Solubility Experiments

Figure 6-11 illustrates the frequency reading throughout a solubility experiment.
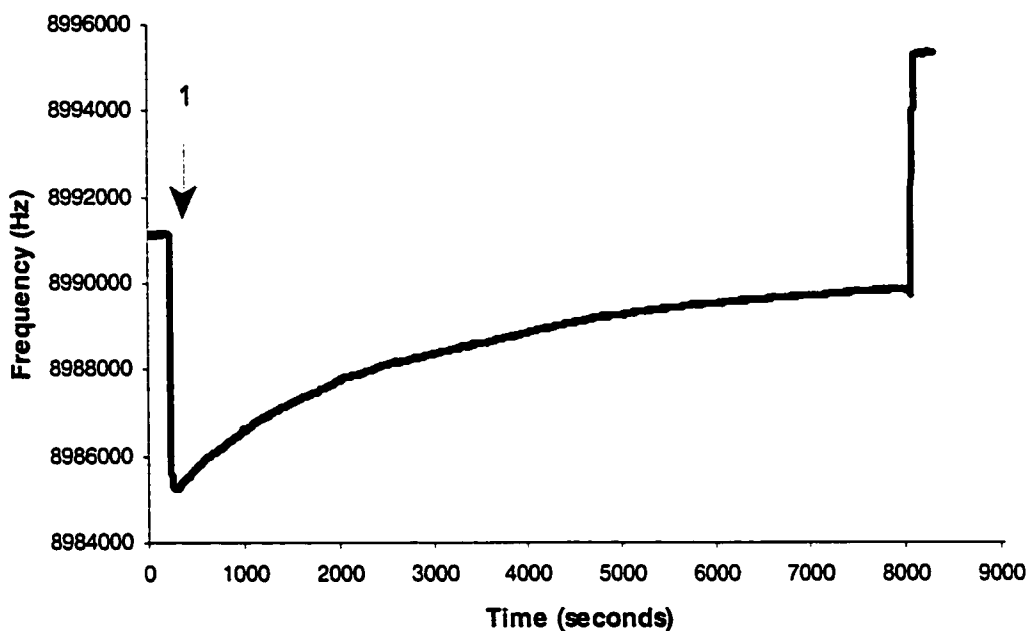
Figure 6-11 Frequency Reading of a Typical Solubility Experiment on July 5/00, Cu(tta)₂ at 313 K and 9.65 MPa

Opening the three-way valve, as indicated by arrow '1', pressurized the vessel. Over the course of two hours, the solute was left to dissolve into the SC CO_2. When the frequency had stabilized, it was assumed that the solute (Cu(tta)₂ or β-carotene) had reached equilibrium with the solvent (SC CO_2), and maximum solubility had been achieved. In Figure 6-11, at 2.17 hours (7812 seconds) the three-way valve was closed and the pressure in the solubility vessel was released. The sharp increase in frequency is due to the SC CO_2 desorbing off the electrode and Cu(tta)₂ from the QCM and the change in the viscosity and

density of the CO_2. When the QCM stabilized at a new frequency after the pressure had been released the experiment was terminated.

Table 6-6 gives a review of the six different frequency measurements (as discussed in Section 5.2.2) that were taken during or before the solubility experiments is shown below.

Table 6-6 Definition of Frequency Measurement Symbols

Abbreviation	Definition
F_0	the resonant frequency of the QCM (at ambient T and P)
FCO_2	total frequency shift (in neat SC CO_2)
F_1	frequency reading immediately preceding pressurization
F_{dip}	the lowest frequency reading after the pressurization
F_{final}	frequency after the solute had reached equilibrium with the SC CO_2
F-air	frequency reading after the pressure had been released

6.7.1 Solubility Calculations

For each experiment, the solubility was calculated in three ways. The first solubility calculation method was based on the frequency change from F_{dip} to F_{final}. This difference accounted for the total frequency change from the QCM in the SC CO_2. The second method of calculating solubilities used the difference from F_{dip} to F_{final} as in method one, but also took into account the amount of SC CO_2 sorbed onto the mass that was adhered to the electrode surface. The third way of calculating solubility was based on taking the difference from F_1 and F-air. This frequency difference accounted for the total frequency change of the QCM at atmospheric pressure. Each method used to calculate solubilities is described in detail below.

6.7.1.1 Solubility Calculation Based on the Difference Between F-dip and F-Final

This calculation method uses the frequency difference between F_{dip} and F_{final} being converted into a change in mass at the electrode surface. This mass is calculated using the Sauerbrey equation (Equation 4-1). From this change in mass in solute on the electrode surface the mole fraction solubility (Sol) is calculated by converting the solute mass change to moles and then dividing by moles of CO_2 used in the experiment (calculated by the vessel volume and the density of the SC CO_2). The calculation is done according to Equation 6-8.

$$Sol\left(mol/mol\right) = \left(\frac{\Delta m}{M.W._{solute}}\right) * \left(\frac{M.W._{CO_2}}{\rho_{CO_2} * Vol[PressureVessel]}\right) \qquad (6\text{-}8)$$

$$where:$$

$$\Delta m = \frac{\left(F_{dip} - F_{final}\right) * A * \sqrt{\rho_Q \mu_Q}}{-2 * F_0^2}$$

6.7.1.2 Solubility Calculation Taking into Account SC CO_2 Sorption

This calculation method is similar to the previous method, however the molecular weight (M.W.) of the solute is adjusted to correct for SC CO_2 sorption to the solute on the QCM. The difference between F-dip and F-final is now assumed to be due to the mass of solute dissolved off of the electrode and the SC CO_2 that is sorbed to the mass on the electrode. The change in mass using the Sauerbrey equation (Equation 4-1) is still calculated, however this Δm must be adjusted.

To adjust the change in mass of the solute due to SC CO_2 sorption, the frequency change due to the SC CO_2 sorption onto the solute must be found. This is done using the Sauerbrey Equation to account for the amount of SC CO_2 sorbed onto the solute at the beginning of a solubility experiment Equation 6-9.

$$\Delta mCO_2 = \frac{(Fdip - F_1 - FCO_2)* A*\sqrt{\rho_Q \mu_Q}}{-2 * F_0{}^2} \text{ (Sauerbrey equation)} \qquad (6\text{-}9)$$

To account for the sorption of the SC CO_2 on the solute, the M.W. of the solute must be adjusted. This calculation uses the ratio of the change in mass on the QCM due to the SC CO_2 sorbed and the total mass added to the QCM before the solubility experiment (ΔmCO_2 and Δm_{Solute}, respectively) to adjust the M.W. of the solute. The calculation for the adjusted M.W. of the solute is shown in Equation 6-10 .

$$M.W._{Adjusted} = \left[\left(\frac{\Delta mCO_2}{\Delta m_{Solute}} \right) * M.W._{Solute} \right] + M.W._{Solute} \qquad (6\text{-}10)$$

In Equation 6-10, ΔmCO_2 is calculated using the Sauerbrey Equation (above) and Δm_{Solute} is the mass of solute initially added to the QCM before placing it in the pressure vessel.

To calculate the solubility, the difference between F-final and F-dip is calculated as using Equation 6-8. However the overall change in mass (Δm) off

of the QCM must be adjusted for the newly adjusted M.W. of the solute. This adjusted mass uses the symbol $\Delta m'$. The calculation is shown below.

$$\Delta m' = \Delta m * \left(M.W._{Solute} \middle/ M.W._{Adjusted} \right)$$
(6-11)

In Equation 6-11, Δm is calculated by Sauerbrey Equation (Equation 6-8) and M.W.$_{Adjusted}$ is calculated using Equation 6-10. Now using the $\Delta m'$ value in Equation 6-8 the solubility is calculated.

6.7.1.3 Calculating Solubility Values From Frequency Readings in Air

This method is the same as the first method using Equation 6-8. However, instead of using the frequency difference between F-dip and F-final, the frequency difference between F_1 and F-air is used.

6.7.2 Solubility Results For β-Carotene

The solubility of β-carotene was measured at 313 K and 12.0 MPa. The QCM technique, has been used to measure solubilities of $Cu(tta)_2$ and $Cu(acac)_2$ in SC CO_2 (Guigard,1999). By choosing a compound, whose solubilities have been thoroughly investigated in SC CO_2 (β-carotene), the QCM technique can be confirmed as a viable solubility measurement technique. β-Carotene was chosen because of its applicability for the QCM technique and the relative abundance of solubility values obtained by other workers. In Table 6-7 a summary of the solubility data measured in this work, at a density of 0.7189 g/cm^3 (313.15 K and

12.0 MPa) is shown. The units for the solubility of β-carotene are in mole fraction.

Table 6-7 Mole Fraction Solubility of β-Carotene at 12.0 MPa and 313 K

Date	Method 1	Method 2	Method 3
Jun-15	2.30E-07	1.40E-07	6.70E-07
Jun-19	1.38E-07	8.64E-08	1.66E-07
Jun-20	9.53E-08	6.46E-08	6.71E-07
Jun-21	1.44E-07	7.86E-08	3.17E-07
Jun-22	1.23E-07	1.09E-07	3.19E-07

Mean	1.46E-07	9.57E-08	4.29E-07
Standard Deviation	5.08E-08	2.94E-08	2.29E-07
Percent Std. Dev.	34.8%	30.7%	53.4%

6.7.3 Solubility Results For Cu(tta)$_2$

The solubility of Cu(tta)$_2$ was measured at four different conditions. Each condition was chosen based on available data to compare with and to determine experimentally a density relationship with solubility (this is elaborated in Section 7.8). The pressure conditions that Cu(tta)$_2$ was measured at were 9.65 MPa and 10.34 MPa. These pressures were alternated with two temperatures, 313 K and 318 K. A summary of the mole fraction solubility data for each condition is shown in Tables 6-8, 6-9, 6-10, and 6-11.

Table 6-8 Solubility Data for Cu(tta)₂ at 10.34 MPa and 313 K

Date	Density (g/cm³)	Solubility (mol/mol)		
		Method 1	Method 2	Method 3
May 03	0.6516	1.89E-06	1.57E-06	3.46E-05
May 2(b)	0.6516	1.09E-06	9.89E-07	3.94E-05
May 02	0.6516	1.91E-06	1.61E-06	2.82E-05
April 28	0.6516	3.74E-06	3.08E-06	2.77E-06

Mean (mol fraction)	2.16E-06	1.81E-06	2.63E-05
Standard Deviation	1.12E-06	8.93E-07	1.63E-05
Percent Std. Dev.	51.9%	49.3%	62%

Table 6-9 Solubility Data for Cu(tta)₂ at 9.65 MPa and 313 K

Date	Density (g/cm³)	Solubility (mol/mol)		
		Method 1	Method 2	Method 3
June 30	0.5948	9.66E-07	7.67E-07	4.72E-06
July 4	0.5948	1.17E-06	9.08E-07	2.89E-06
July 5	0.5948	1.03E-06	8.32E-07	4.12E-06

Mean (mol fraction)	1.05E-06	8.36E-07	3.91E-06
Standard Deviation	1.02E-07	7.06E-08	9.33E-07
Percent Std. Dev.	9.7%	8.4%	23.9%

Table 6-10 Solubility Data for Cu(tta)₂ at 10.34 MPa and 318 K

Date	Density (g/cm³)	Solubility (mol/mol)		
		Method 1	Method 2	Method 3
July 20	0.5407	3.87E-07	3.22E-07	6.24E-06
July 25	0.5407	6.37E-07	5.5E-07	4.86E-06
July 25(2)	0.5407	3.02E-07	2.52E-07	6.04E-06

Mean	4.42E-07	3.75E-07	5.71E-06
Standard Deviation	1.74E-07	1.56E-07	7.48E-07
Percent Std. Dev.	39.4%	41.6%	13.1%

Table 6-11 Solubility Data for Cu(tta)₂ at 9.65 MPa and 318 K

Date	Density (g/cm³)	Solubility (mol/mol)		
		Method 1	Method 2	Method 3
April 3	0.4399	5.44E-07	4.82E-07	3.31E-06
March 28	0.4399	1.81E-07	1.69E-07	3.3E-06
March 27	0.4399	2.13E-07	1.83E-07	1.5E-06
March 23	0.4399	4.62E-07	4.15E-07	n/a
March 22	0.4399	5.69E-07	4.35E-07	2.62E-06

Mean (mol fraction)	3.94E-07	3.37E-07	2.68E-06
Standard Deviation	1.84E-07	1.49E-07	8.55E-07
Percent Std. Dev.	46.7%	44.2%	31.9%

n/a-not available

In the preceding tables Method 2, gave the lowest solubility value for all data points. The variability for the all methods of solubility measurements ranges from 8% - 52%.

7 Discussion

The first part of this section will discuss the design and operation of the solubility measurement apparatus. The discussion will include possible complications with this solubility measurement technique that were overcome during the course of this research project. Secondly, the solubility data (for β-carotene and $Cu(tta)_2$) will be compared to literature data and the relationship of $Cu(tta)_2$ solubility to density will be examined. The final section will examine two different mathematical models to correlate solubility, and compare the correlations of the models to the solubility data obtained in this research.

7.1 SC CO_2 Solubility Apparatus

The SC CO_2 system for this project was designed and built during the first months of research. As a result of a first time implementation, a number of problems had to be circumvented before the SC CO_2 system was operating reliably and correctly.

7.1.1 Leaks Within the SC CO_2 System

Upon initial assembly of the SC CO_2 system, the leaks within the fittings were minimal and easy to detect and fix. However, leaks developed in other parts of the system over time and required enhanced problem solving.

The first leaks to develop were in the pressure relief valve. After the SC CO_2 system had been pressurized and heated a few times the valve would crack at a lower pressure than it had originally been set for. The valve was disassembled and checked for malfunctions and seal damage. Initially the seals

were replaced with the same material assuming that the seals were not the cause of the malfunction (it was not apparent that the seals were damaged). The malfunction continued until the o-rings within the pressure relief valve were replaced with o-rings made of a different compound.

Upon careful examination of the o-rings, it was observed that the o-rings that were in contact with the SC CO_2 were blistered and disintegrating. The type of material used for the o-rings was a type of fluoroelastomer rubber called Viton™. This elastomer is resistant to a wide range of oils and solvents and should be chemically resistant to SC CO_2. The most probable cause of the o-ring breakdown was due to the porous nature of the Viton™ elastomer. Under supercritical conditions the CO_2 filled the pores of the Viton™ elastomer o-rings. As the system was rapidly depressurized the trapped CO_2 caused the elastomer to expand. Over a series of system pressurizations and depressurizations the elastomer degraded until it was no longer functional and caused a malfunction in the pressure relief valve.

To address this problem, new seals and o-rings were ordered for the pressure relief valve and the check valve (elastomer degradation was also found in the o-rings and seals of the check valve). The compound used to replace the Viton™ was Nitrile. Nitrile is an elastomer with high resiliency, abrasion resistance, low porosity and a good resistance to solvents, oil and water. The Nitrile seals successfully resisted degradation upon repeated usage in the SC CO_2 system.

7.1.2 Leaks within The Syringe Pumps

Initially, one of the measures that was thought to determine if there were any leaks in the system, was observing the flow rate from the syringe pumps. Once the SC CO_2 system was pressurized and temperature equilibrated, the pump flow rate was assumed to reduce to minimal values (below 0.010 mL/min). During the experiments in which leaks were being assessed, the flow rate of the pumps did not drop to minimal levels. Through the course of trail and error, the entire SC CO_2 system was dismantled up to the syringe pumps. After much consultation with the technical support staff from the syringe pump supplier, ISCO, two possible problems were identified as being sources of the abnormal flow rates. The first possible source was a malfunction with the main seal within one or both of the syringe pumps. This situation, although a possibility, was an unlikely cause of the malfunction due to the fact that the pumps were in operation for less than six months. The second probable cause was a malfunction of the check valves between the two syringe pumps.

The malfunction in the check valves was checked by plugging the outlet port (to the SC CO_2 system) from the check valve package and disconnecting the tube that connected the CO_2 cylinder and immersing it in a cup of water. According to the technical experts at ISCO, the syringe pumps, full of pressurized CO_2 should exhibit a small back-flow towards the cylinder. Observing a bubble every half-minute in the cup of water would indicate this small back-flow. When the tube was placed in the water there was a significant back-flow (approximately 120 bubbles a minute) from the syringe pumps. This indicated that one or more

check valves were malfunctioning and that they would need to be cleaned or replaced. Each valve was checked individually by isolating one pump and substituting the bottom check valve with all existing check valves. It was determined that all valves were malfunctioning. The most probable cause of the malfunctions was micro-particulate that had adhered to the stainless steel ball inside the check valves. The most likely particulate source was from the CO_2 cylinders. Although there was a 10-micron filter already in place after the CO_2 cylinder it was not sufficient to block particulate matter that was smaller in size. Thus, a 0.5 micron filter was installed downstream of the 10 micron filter to remedy this problem.

As recommended by the Technicians at ISCO, the valves were sonicated in methanol in an attempt to clean the stainless steel balls. The check valves were then placed back into the valve package and tested. This proved to be unsuccessful and new check valves were ordered and installed.

The attempt to reduce the flow rate from the syringe pumps was partially successful. The flow rate did reduce to zero or near zero during the course of pressurized operation. However this low flow rate was evident for only a part of the operation. The rest of the time the flow rate increased and decreased from +2 mL/min to –2 mL/min. An illustration of this can be seen in Figure 6-7.

In a final attempt to stabilize the flow rate the pressure transducers on the syringe pumps were reset. Unfortunately this did not resolve the problem. The technical staff at ISCO was again contacted and the following reasons were given to possibly explain the uneven flow rates.

1. The uneven flow rates were due to the highly compressible nature of the SC CO_2 at the experimental pressures and highly sensitive pressure transducers. The pumps were having to constantly adjust to maintain constant pressure

2. The check valves in the check valve package operated on a ball valve design. This design, although functional, was not as effective as the air actuated valve package in reducing the back-flow from the CO_2 pumps to zero.

Forthese reasons and the lack of success in maintaining a near zero flow rate, the method of determining leaks in the SC CO_2 system by assessing the flow rate from the syringe pumps was abandoned.

7.1.3 Vessel Design and Seals

The pressure vessel was designed and manufactured during the first months of research. The pressure vessel was designed to withstand 31 MPa of pressure, but was not tested at this pressure. Seals had to be designed and fit independently. The first seals that were used were a Nitrile elastomer o-ring fit to the inside of the pressure vessel, on which the crystal holder would be compressed. The Nitrile elastomer had lower porosity than the Viton™, however after an extended pressure test the removed Nitrile o-ring was noticeably larger than when it was placed inside the vessel. The increased expansion was due to trapped CO_2 in the o-ring, causing it to expand. The trapped CO_2, added an uncertainty to the vessel volume, and it was concluded that the Nitrile o-ring could not be used in the pressure vessel for a solubility application. More research was done to find a compressible seal that had low porosity.

The last manufactured o-ring used was a Teflon™ encapsulated Viton™ o-ring. The Teflon™ provided chemical inertness and a seal around the Viton™ o-ring, while at the same time the encapsulated Viton™ provided the supple properties needed to compress the crystal holder to maintain a high-pressure seal. During pressurization experiments, the encapsulated o-rings proved to be successful in maintaining a seal in the pressure vessel. However, it was found that during extended periods of time, at solubility experimental conditions, the Teflon™ sheath encapsulating the o-ring would crack and SC CO_2 would come in contact with the Viton™ o-ring. This failure of the Teflon™ sheath was most likely due to the compression of the Teflon™ sheath between the holder and the vessel. The non-flexible Teflon™ would puncture, allowing the SC CO_2 to come into contact with the Viton™. During depressurization of the pressure vessel, the Viton™ would expand and burst the Teflon™ sheath, and on one occasion this bursting caused the quartz crystal to fracture. This type of o-ring was immediately discarded thereafter.

The final type of seal was gaskets that were fitted to the oblong shape of the crystal holder. The seals were carved out of sheet Teflon™ that was 1/16" inch thick. Because of the high compression forces exhibited on the seal by the crystal holder one Teflon™ gasket was not sufficient to maintain a high-pressure seal. The Teflon™ would stretch and become thin around the edges where it was in contact with the crystal holder. Therefore two gaskets were used. For each experiment the top gasket (the gasket in direct contact with the crystal holder) was newly carved and the bottom gasket was the top gasket used from a

previous experiment. With this configuration, a high-pressure seal was maintained for most of the solubility experiments.

7.1.4 Quartz Crystal Holder

The pressure vessel was designed to fit the HC 27/U glass holder with quartz crystal blank manufactured by Lap-tech Inc. The glass holder was chosen instead of a metal holder, with the prospect of placing a stir bar inside the vessel during a solubility experiment. The stir bar was to be driven by a magnetic stirrer, which was submersed in the water bath. (It was assumed that the small magnetic stir bar would sit on the bottom of the vessel and not attach itself to the crystal holder.) Unfortunately in further experiments the stir bar was observed to attach itself to the metal clips from the holder that attached to the crystal (Figure 7-1), thus stirring was not possible.

As stated above, compression of the holder onto a gasket or o-ring inside the pressure vessel maintained an effective seal in the pressure vessel. During the experiments using the Nitrile and Teflon™ encapsulated Viton™ o-rings, the crystal holder did not show any signs of deterioration. This was due to the compressible nature of the o-ring material. When the carved Teflon™ gaskets were used, the holders began to crack after regular usage. The sheet Teflon's™ consistency resembles that of a stiff plastic and is not very compressible. The glass holders could not withstand the variable and intense pressure put on by forcing a leak-proof seal and as a result cracked in various locations.

As the number of operable (uncracked) quartz crystal holders became limited, there was a necessity to find a solution to this problem. One solution was

to order more of the same crystal holders with quartz crystals (blanks) attached. As stated above the holders showed cracking after a number of uses, when a solution was needed there was only a few successful solubility experiments to be completed to finish this research. This solution, to order more crystals and holders, although the most obvious was not chosen. The decision was made because the time it would take for new blanks and holders to be manufactured from Lap-Tech Inc. (about 8-9 weeks) and that the quartz crystals were still operable despite the cracked holders (the cracked holders did not permit an effective seal to be maintained but did not affect the crystal oscillation).

A solution that was attempted was to use an epoxy resin to glue the cracks in the holder. The epoxy was prevented from coming in contact with the SC CO_2 by placing Teflon™ tape on the underside of the crystal holder. Unfortunately, this was only a temporary fix as the holders continued to crack and disintegrate.

Another possible solution was to find a metal holder of the same dimensions of the glass holder. Unfortunately, even though Lap-Tech Inc. did manufacture metal holders but not to the same dimensions as the glass holders. The metal holders could not be retrofit into the current vessel, thus the pressure vessel would need to be redesigned. As a last resort this would have been done, however the next solution was attempted first and proved to be successful.

The solution taken to remedy this problem was to attempt to reattach the quartz crystals to new holders obtained from Lap-Tech Inc.. The difficulty in implementing this course of action was that the quartz crystals were very fragile,

and that the quartz crystals could not be physically removed from the electrode attachments. (The quartz crystals were attached to the electrodes from the holder by a conductive resin. This meant that the crystals would have to be cut off the holder and attached to a new holder.) In Figure 7-1, the arrows indicate where the metal electrodes on the crystal holder were cut.
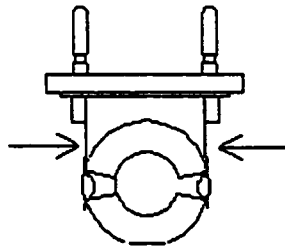
Figure 7-1 QCM in Holder

In order to maintain a stable frequency, the crystal would also have to be reattached in a way to allow an electrical current through the metal. The reattachment would also have to withstand the SC CO_2 conditions inside the pressure vessel.

Firstly, solder was used in an attempt to reattach the crystal to the new holders. The solder did not work because of the high temperatures generated during the soldering process. (The high temperatures cracked the quartz crystal) The last resort was to use the Circuit Works conductive epoxy that was used to cement the thermistor into the wall of the pressure vessel. As it turned out, this epoxy was similar to the type of resin that Lap-Tech used to attach the quartz crystal to the holder.

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The crystals were carefully cut off of the cracked holders using thin jeweller's files, reattached to the new holders with the conductive epoxy and then baked at 150-200°C to set the epoxy. This temporary solution (the holders still cracked) allowed for the rest of the solubility experiments to be completed.

During the final months of this research the crystal holders seemed to crack more frequently and quicker than at the initial stages of the solubility experiments. This problem was identified to be a result of uneven pressure distribution caused by the socket head cap screws on the vessel lid. The screws were not replaced during the entire research and began to wear, along with the threads in the pressure vessel for the socket head cap screws. This was evident when one of the screws stripped when attempting to tighten the vessel lid. The wearing of the screw and the hole in which the screw was placed in caused this uneven pressure distribution. This was fixed by re-tapping all the screw holes and replacing the screws.

7.2 Procedure

During the course of the research, the procedure and protocol was refined to ensure the consistency of the solubility results and minimize sources of error. The quartz crystal microbalance frequency was affected by different interferences, that caused loss or disturbance of oscillation of the QCM. An example of the loss of a stable frequency during a solubility experiment on March 9/00 is shown in Figure 7-2.
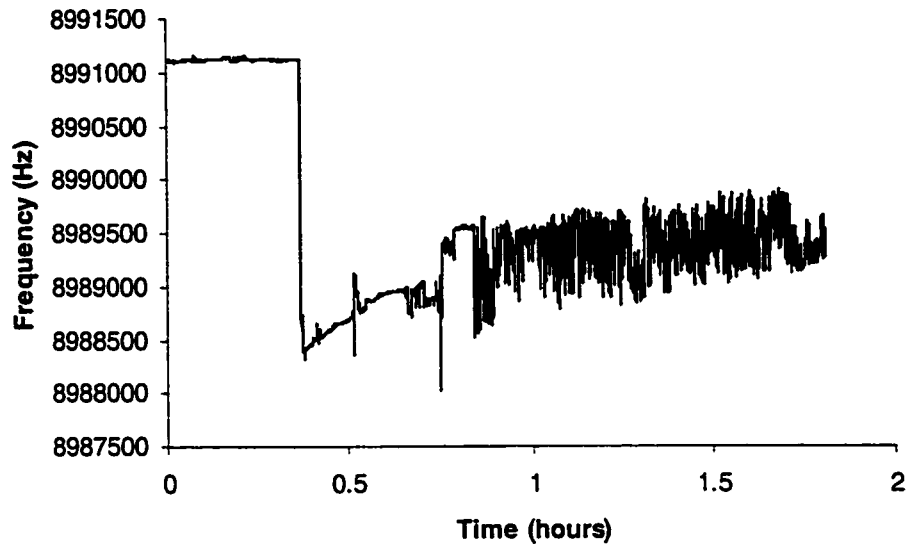
Figure 7-2 Example of QCM Frequency Interference

At the 0.5 hour mark there was a jump and drop in the crystal frequency. From experience, this turned out to be a clear indication that there was some source of interference with the QCM frequency. This interference in frequency often progressed to larger disturbances, which led to unsuccessful experiments. For this reason when frequency jumps and drops were observed during an experiment, the solubility experiment was aborted and begun anew.

When the crystal was initially tested if the oscillator was working there was a source of interference as a result of the distance that the oscillator was from the quartz crystal. The initial distance from the oscillator was approximately two meters. With this configuration a stable signal from the QCM could not be taken. Lu (1984.) states (in section V, D, Associated Electronics) that "the allowable distance between the crystal and the oscillator may be up to 1 m depending on the operating frequency and the circuit design". This is as a result of the QCM

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being an integral part of the electronic circuit. Thus, the farther the distance between the oscillator and the QCM, the greater the outside sources of interference that can influence the active circuit. This was remedied by shortening the length of the wires from the QCM to the oscillator to 0.5 m.

Another problem that arose was interference due to the wiring from the oscillator, pressure transducer and thermistor to the data acquisition card in the computer. The wiring was not shielded, and as a result, the current flowing through the wire emitted an electromagnetic signal that interfered with the QCM resonant frequency. Shielding all wires that were near the oscillator surmounted this problem.

Another source of interference was due to the circulator for the water bath. As the heater in the circulator would turn on and off the frequency of the QCM would noticeably shift. This occurred when the oscillator and the circulator were drawing power from the same outlet. This problem was overcome by isolating the oscillator power source.

The last main source of electrical interference was due to the wires from the vessel and the tubing of the SC CO_2 system coming in contact with the metal edge of the water bath. If the tubing and wires were in contact with the metal edge of the water bath the QCM frequently displayed characteristics as in Figure 7-2 above. Isolating contact of all tubing and wires from the water bath minimized this source of interference.

Eliminating the sources of electrical interference assisted in maintaining a stable frequency reading from the QCM.

7.3 Materials

To determine if the preparation of $Cu(tta)_2$ produced pure $Cu(tta)_2$, a melting point analysis was conducted. The temperature range of available compounds used to calibrate the thermometer used in the melting point analysis, necessitated an extrapolation of the melting point calibration curve (Figure 6-1). The nearest temperature on the curve to the $Cu(tta)_2$ temperature measurement was less than $10^{\circ}C$. Given the high degree of linearity of the melting point curve (0.9994) and the relative closeness of the nearest calibrated temperature, the extrapolation for the $Cu(tta)_2$ theoretical melting point (based on the calibration equation) has a high degree of accuracy. The other potential source of error within the melting point analysis is the exactness of the measurement. As stated previously, the temperature range corresponds to the observance of the first liquid drop to the last liquid drop to appear. Although this observation is subjective, it has shown to be effective in determining the melting point of compounds.

Another concern with the materials used in the solubility experiments was the potential degradation of β-carotene. As stated previously, β-carotene is sensitive to heat and light. For all experiments the β-carotene was stored in a freezer at $-18^{\circ}C$, the solutions (β-carotene in chloroform) were stored in a refrigerator and re-mixed every two days to prevent degradation of the β-carotene. When preparing for a solubility experiment the β-carotene was exposed as little as possible to light (mass loading was done with minimal light

conditions in the laboratory), and loaded into the pressure vessel quickly thereafter.

In other solubility experiments carried out by Subra *et al.* (1997) β-carotene was quantified for any degradation. In Subra *et al.* (1997) no degradation was observed during sample analysis. The solubility measurement technique that was used was a static recirculation technique. From these results, the degradation of the β-carotene in SC CO_2 can be considered insignificant. However, the sample preparation technique for β-carotene was not revealed, and this could have lead to degradation of the β-carotene before the experimental quantification. For further discussion please see section 7.6.

7.4 Mass Loading Effect

Before the solubility experiments were initiated, each type of potential solubility compound was tested on the QCM. This testing was done to determine if the specific compound could accurately be quantified by the QCM. The spreading and adherence of the solute to the electrode surface also ultimately affected the behaviour and response of the QCM in the SC CO_2. If the solutes were improperly loaded, a number of situations would arise, such as a loss of the frequency reading, inaccurate mass measurements and frequency instability. In addition to the spreading and adherence of the solute to the QCM, the amount of mass placed on the QCM was a critical factor in determining the compounds that were chosen to verify this solubility technique. At high mass loads above 1.0E-04 grams, the QCM would no longer resonate or would provide inaccurate mass readings. This factor limited the possible candidates for measuring solubility with

the QCM technique to a few low solubility compounds. Each solute/solvent combination exhibits different responses and therefore must be examined independently.

The $Cu(tta)_2$-methanol mixture (at all concentrations) evenly distributed over the entire surface of the electrode. The comparison of most of the applications with the syringe to the QCM showed approximately 6%($\pm$1%) (Table G-1). The even spreading was as a result of the volatility of the solvent and the structure of the crystallized $Cu(tta)_2$ (a powder-like deposition). Methanol has a lower volatility than the chlorinated solvents used with the other compounds. The lower volatility allowed the crystallized $Cu(tta)_2$ to evenly distribute on the electrode surface. A scanning electron micrograph (SEM) image at 800X magnification (Figure 7-3) shows the edge of the $Cu(tta)_2$ on the electrode surface and the relatively even distribution of the $Cu(tta)_2$.

In this SEM, the crystalline structure of $Cu(tta)_2$ is shown. The small crystal formation, as well as the even spreading of the $Cu(tta)_2$ on the electrode surface contributed to the precise mass readings from the QCM.

As a result of limited solubility data for $Cu(tta)_2$ there was a need to attempt to verify this *in-situ* solubility technique. Initially, caffeine was chosen because of the relative abundance of solubility data in SC CO_2 (Johannsen and Brunner, 1994). The caffeine was mixed with methylene chloride in varying concentrations, and attempted to load onto the crystal. For all of the various attempts, the frequency mass reading when compared to the mass added based on the concentration and volume of the solution was above the expected result,

on average between 80-100%. It was determined that the reason for the high frequency mass readings was that the caffeine was not evenly distributing over the entire electrode surface due to the highly volatile nature of the chlorinated solvent and the crystalline structure of the caffeine. The caffeine crystallized in long structures (as observed visually on the electrode surface) that did not entirely cover the electrode surface. This uneven, horizontal and vertical distribution on the electrode surface caused inaccurate mass readings. As mentioned previously in section 4.3.1.4, for accurate mass determination it is stated that the mass must be evenly distributed over the entire electrode.
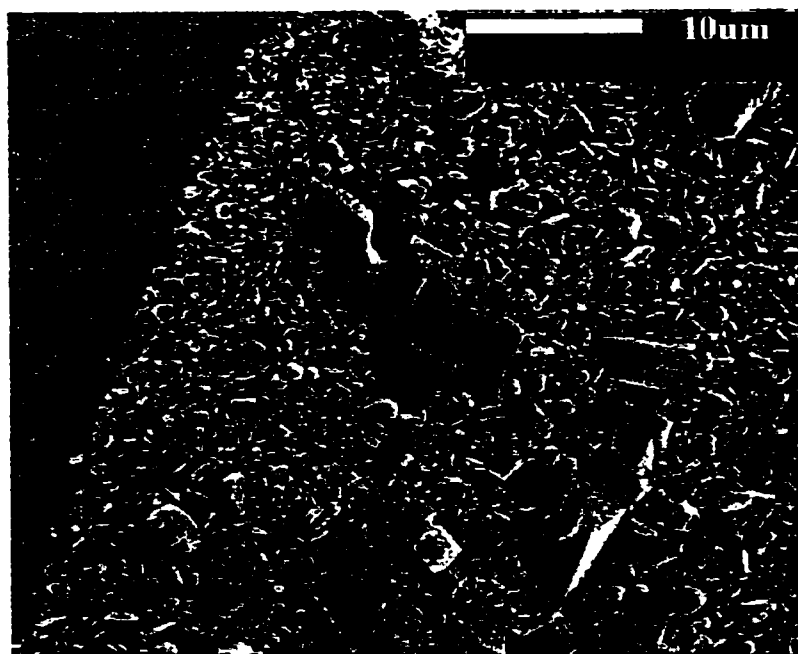
Figure 7-3 SEM of Cu(tta)$_2$ on the Electrode of the QCM at 800X Magnification

The second choice to verify the in-situ solubility technique was a β-carotene-chloroform mixture. This compound was chosen because of the relative

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abundance of solubility data in SC CO_2 (Subra *et al.*, 1997) and the low solubility exhibited in SC CO_2 (this prevented mass overloading of the QCM).

At high concentrations above 1.0E-03 g of β-carotene per mL of chloroform the crystallized β-carotene exhibited a non-uniform distribution on the electrode surface. The most probable explanation for this was due to the volatile nature of the solvent used. The chlorinated solvent volatilized too quickly to allow for smooth horizontal distribution on the electrode surface. This non-uniform distribution contributed to an inaccurate mass reading that usually was more than the expected amount, typically around 80-100% of the volume placed on the electrode. Dilute solutions (approximately 3.0E-04 to 5.0E-04 g/mL) and numerous small volume applications with the microlitre syringe circumvented this problem. The average mass reading for the β-carotene was 23.7% with a standard deviation of ±8% (Table F-2).

The mass loading effects of the QCM are due to the mass sensitivity of the QCM. According to Lu (1984), if the mass is limited to a small area of the crystal surface the resultant position of that mass (on the crystal surface) will induce a frequency shift. Lu (1984) found that the mass sensitivity was at a maximum at the centre of the crystal and reduced to zero slightly beyond d the boundary of the electrode. The term "differential mass sensitivity" is used to describe this phenomenon. The differential mass sensitivity is defined as the frequency shift due to an infinitesimal point of mass at a particular point on the crystal electrode surface (Lu, 1984).

Despite this phenomenon, experimental results show that as long as the whole area of the electrode is covered the theoretical equations (ie. the Sauerbrey Equation) are still valid (Lu, 1984). This indicates that the entire differential mass sensitivity is integrated over the whole electrode surface, generating a predictable effect (Lu, 1984).

7.5 FCO₂ Values with a Silver and Gold Electrode

As stated previously the experimental procedures and conditions used in this research were slightly different from the methods used by Guigard (1999). Guigard (1999) used a QCM with a gold electrode, while this work used a silver electrode. The primary difference in the different electrodes was the surface characteristics on the electrode surface. Figure 7-4 shows two scanning electron micrographs (SEM) at 3000X magnification (the silver electrode (left) and the gold electrode (right)).
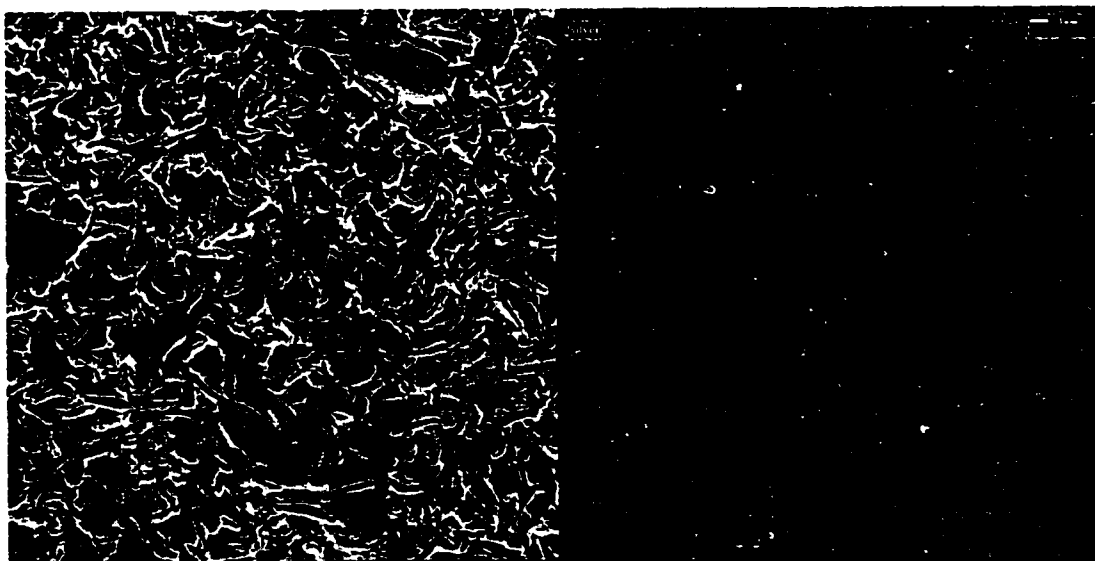
Figure 7-4 SEMs for the Silver (Left) and Gold (Right) Electrodes at 3000x Magnification

7.6 Summary of Methods Used to Calculate Solubility Values

The different methods used to calculate solubilities in this work are described in the previous sections. Of these three methods, the least accurate method for determining the solubilities is method 3. This method relies on the frequency readings at atmospheric pressure, after the pressure vessel was depressurized. During depressurization the solute falls out of the SC CO_2, depositing on the vessel walls and on the QCM. This re-deposition of solute on the QCM electrode and on the quartz crystal affects the final frequency reading. Re-deposition will cause the frequency reading to be lower than expected, while interferences caused by the decrease in depressurization may cause the frequency to be higher or lower.

Method 1 and method 2 are similar, by taking the difference in frequency in the SC CO_2, however method 2 takes into account the SC CO_2 adsorbed onto the solute that is adhered to the electrode. Because of this, method 2 (solubility calculation taking into account the SC CO_2 sorption) is considered the most accurate. Any solubility values from this work that are reported herein will be using Method 2.

7.7 Comparison of β-Carotene Solubilities

A summary table for solubilities of β-carotene in SC CO_2 is shown in Table 7-1. This table includes mole fraction solubilities from the literature in the density range of 0.616-0.750 g/cm^3 and the mole fraction solubilities obtained from this work at 0.718 g/cm^3. The percent variability was also calculated for all the data points as the standard deviation divided by the reported mean. These values

were either taken as reported in the original reference were calculated from reported results given in the specific reference. Figure 7-4, graphically illustrates the solubility values reported in Table 7-1.

The high range of discrepancy within the data can be attributed to the type of experimental techniques used to measure the solubility of β-carotene, the purity of the β-carotene used for experimentation and the fact that β-carotene exhibits a very low solubility in SC CO_2 (Johannsen and Brunner, 1997; Mendes *et al.*, 1999; Subra *et al.*, 1997).

The type of experimental techniques used to measure the solubilities of β-carotene illustrated in Figure 7-4 from the different authors were all different and subject to different sources of error.

Table 7-1 Summary of β-Carotene Solubilities in SC CO_2

Experimental Conditions			Solubility (mol/mol)	Percent Variability	References
Pressure (MPa)	Temp. (K)	Density (g/cm³)			
10.9	313	0.682	2.0E-07	±13%	Skerget et al. (1995)
12.8	313	0.741	1.81E-07	±13%	Skerget et al. (1995)
10.1	310	0.691	2.2E-08	±5%	Subra et al. (1997)
12.0	310	0.751	5.11E-08	±5%	Subra et al. (1997)
9.87	313	0.6206	1.1E-08	±10%	Sakaki (1992)
11.8	313	0.715	3.8E-08	±10%	Sakaki (1992)
12.0	313	0.721	3.0E-08	±10%	Mendes et al. (1999)
12.0	313	0.721	9.57E-08	±31%	This Work
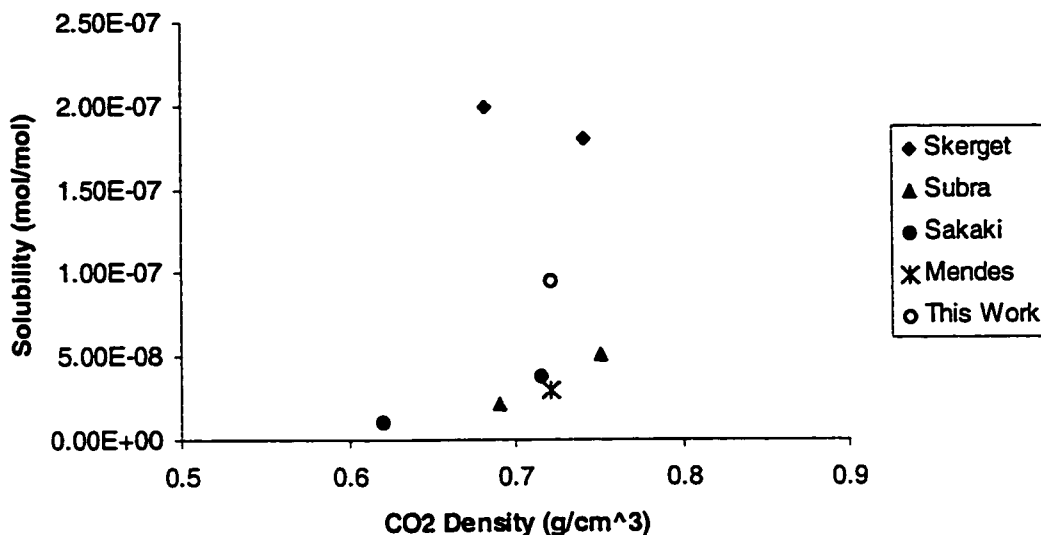
Figure 7-5 Summary of β-Carotene Solubilities in SC CO₂

Mendes *et al.* (1999) used a dynamic single pass flow method and UV-vis spectroscopy to determine the solubility of β-carotene. Several sources have indicated that using a dynamic single pass flow method may not guarantee the saturation of the SC CO₂ with the desired solute (Bruno, 1991; Subra *et al.*, 1997; McHugh and Krukonis, 1994). The possibility of the SC CO₂ not being saturated with β-carotene is evident when the solubility for β-carotene at lower densities from Mendes *et al.* (1999) ais compared to other workers (Sakaki, 1992); (Subra *et al.*, 1997) at similar conditions. The solubilities reported from Mendes *et al.* (1999) indicate at lower densities the results are lower than compared to of other workers.

Sakaki (1992) also measured the solubility of β-carotene using a dynamic one-pass flow method coupled to a supercritical fluid chromatography device. Again the single pass flow method may not guarantee the complete saturation of the SC CO₂ and may give lower results than expected.

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Subra *et al.* (1997) used a static recirculation technique that recirculated the SC CO_2 and solute for a period of 30 minutes. The saturation of the SC CO_2 was assured in this experimental technique, however the relative error for the experimental technique could have influenced the solubility results. The relative error for this experimental method was reported to be as high as 40% for samples done with SC CO_2 (Subra *et al.*, 1997). The high relative error was attributed to the extremely small amount of solute that was sampled (6.0E-08 g). The high relative error indicates that at low concentrations this particular method of solubility analysis may not be as effective as other methods to measure solubilities in SC CO_2.

Skerget *et al.* (1995) used a static method to measure the solubility of β-carotene. The solute was collected in a solvent-trap containing methanol and analyzed by an UV-vis detector. Of the data investigated here, the data of Skerget *et al.* (1995) and Subra *et al.* (1997) were obtained by a static method to measure the solubility of β-carotene. The static method of analysis assures the solute-solvent equilibrium is reached. However, if the solvent trap is not covered when the CO_2 is bubbled through, the volatilization of the methanol from the solvent trap could result in higher concentrations of solute in the solvent trap, Stone and Taylor (2000). Thus, the reported solubilities could be higher than the actual value. The purity of the β-carotene used by Skerget *et al.* (1995) was 95%. Other workers (including this work) used β-carotene with purities of >98%. The impurities in the β-carotene used by Skerget *et al.* (1995) could have resulted in higher reported solubilities. In a paper by Guclu-Ustundag and Temelli (2000) the

effect of the purity of lipids was examined with respect to lipid solubilities in SC CO_2. Higher solubilities in SC CO_2 were observed when the purity of the lipids was low. The solubility measurements from Skerget *et al.* (1995) were higher than all other workers.

The solubility measurement from this work follows the trend of the data set presented in Figure 7-4. The method used in this research was an *in-situ* static technique, which produced higher results than the dynamic single pass method used by Mendes *et al.* (1999) and Sakaki (1992) and the static recirculation technique by Subra *et al.* (1997). The difficulty in quantifying low concentrations and achieving solute-solvent equilibrium from the methods used by Subra *et al.* (1997), Mendes *et al.* (1999) and Sakaki (1992), respectively, may be the limiting factor in the accuracy of the solubility measurements. The high results from Skerget *et al.* (1995) indicate that the purity of the β-carotene that was used (95%) might affect the solubility result (for this work a purity of >99% was used).

The differences observed with all the data investigated, in terms of the experimental technique and solubility measurement method, leads to difficulty comparing the reported results on an equal scale. These differences are a probable cause of the high range of data observed in Figure 7-4. However, the solubility result from this work is similar to other solubility values within the observed density range.

In comparing the percent error associated with the replicates, all workers used at least two measurements to determine the data points. For this work, 5 data points were obtained over a four-day period. The slightly higher percent

error from this work (23.7%) can be related to the mass loading effects. As stated previously the β-carotene was placed onto the crystal electrode over several applications (sometimes as many as 40 applications). This provided a relative continuous layer of β-carotene that gave a relatively accurate mass reading. However, due to the fact that the β-carotene characteristically exhibited higher mass readings than the volume placed on the electrode (23.7%±8%), it can be assumed that this layer was not completely uniform, which may have resulted in discrepancies in the replicated data.

The results from Guigard (1999) with Cu(tta)$_2$ also exhibit a similar phenomenon that was observed with the β-carotene results from this work (the β-carotene characteristically exhibited higher mass readings than the volume placed on the electrode). As stated in Guigard (1999), the mass frequency shift over-predicted the expected mass that was placed on the electrode in 86% of the experiments done with Cu(tta)$_2$. This over prediction was in the range of 27-28%(±2%) (Guigard, 1999).

In 14% of results where the mass added to the electrode did not illicit a higher frequency response, the solubility results from Guigard (1999) did not show any correlation between mass reading and a lower solubility value (when compared to the mean value from Guigard (1999) and the solubility values from this work). This would suggest that the frequency measurements for the solubility results are independent from the initial mass discrepancies from the QCM.

In Section 8, design considerations of the QCM are discussed in terms of loading volatile solvent mixtures onto the surface of the electrode to enhance even layering.

7.8 Comparison of Cu(tta)₂ Solubilities

Table 7-2 shows the solubility results obtained in this work and by Guigard (1999) for the solubility of $Cu(tta)_2$. Both methods employed the *in-situ* QCM measurement technique, however there were differences in materials and equipment, which have been discussed previously.

Table 7-2 Summary of Cu(tta)₂ Solubilities in SC CO₂

Experimental Conditions			Solubility (mol/mol)	Percent Variability	References
Pressure (MPa)	Temp. (K)	Density (g/cm³)			
10.34	313.15	0.6516	1.81E-06	49%	This Work
10.34	313.15	0.6516	3.20E-06	56%	(Guigard, 1999)
9.65	313.15	0.5948	8.36E-07	8%	This Work
10.34	318.15	0.5407	3.75E-07	42%	This Work
9.65	318.15	0.4399	3.37E-07	44%	This Work
9.65	318.15	0.4399	8.58E-07	79%	(Guigard, 1999)

A graphical illustration for the above table depicting the relationship of solubility to density can be seen in Figure 7-6.

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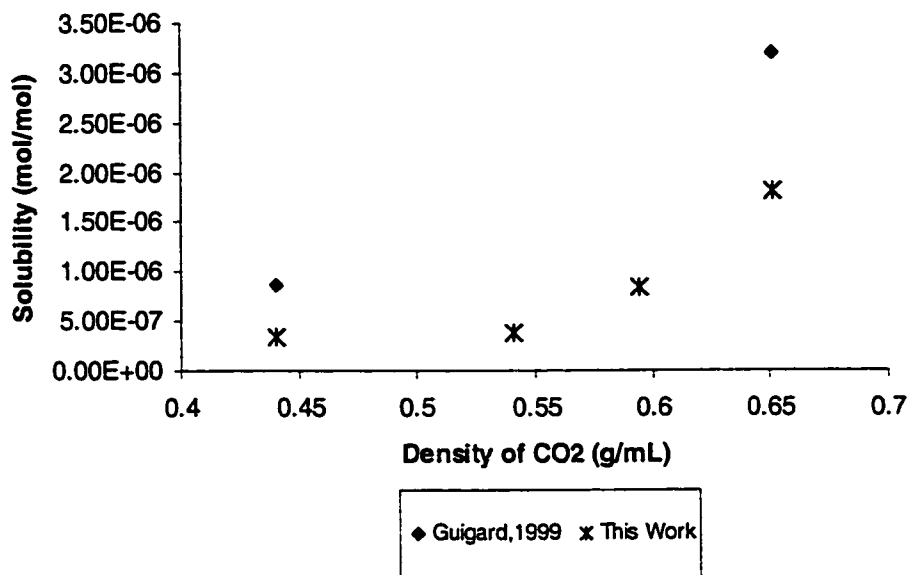
Figure 7-6 Summary of Cu(tta)$_2$ Solubilities in SC CO$_2$

It is evident that with increasing density of the SC CO$_2$ the solubility of the Cu(tta)$_2$ increases. For this work, between the densities of 0.4399 g/cm^3 and 0.5407 g/cm^3 there is little increase in solubility. However, between 0.5407 g/cm^3 and 0.6516 g/cm^3, the solubility dramatically increases by almost an order of magnitude. This behaviour is influenced by one main effect. As the density increases, there is an increase in the solvent power of the SC CO$_2$, thus an observed increase in solubility. These results indicate that the optimal conditions for extracting and/or observing the solubility of the Cu(tta)$_2$ lies above the condition of 0.5407 g/cm^3. The results of Guigard (1999) support this phenomenon as well, although the solubility results are higher than those of this work.

In comparing the previous data by Guigard (1999), the data from this work is lower. This may be due to the high percent variability (79% and 56%) that

occurred in the replicate samples done at 0.4399 g/cm^3 and 0.6516 g/cm^3, respectively. To determine if the results obtained from this work and the results obtained from Guigard (1999) were statistically different, two statistical tests were performed on the two similar sets at each density (densities of. 0.4399 and 0.6516 g/cm^3). Firstly a two sample F-test was performed to determine if the variances of each data set (at the specific density) were equal. An equal variance assumption is needed to conduct a two-sample t-test. The t-test determines if the means of the each data set are equal (means have no statistical difference) (Box *et al.*, 1978). The results for each density are as follows:

> for the density of 0.4399 g/cm^3 the F-test result was that the variances from each data set (this work and Guigard (1999)) were equal and the t-test showed that the means (from this work and Guigard (1999)) showed no statistical difference at a 5% level of significance.

> for the density of 0.6516 g/cm^3 the F-test result was that the variances from each data set (this work and Guigard (1999)) were found to be statistically equivalent and the t-test showed that the means (from this work and Guigard (1999)) showed no statistical difference at a 10% level of significance.

The results from the statistical analysis can be seen in Appendix I.

For this work, the solubility of $Cu(tta)_2$ was measured at 4 densities in SC CO_2. These results were compared to the solubility data (at two densities) reported by Guigard (1999). The solubility results from this work and Guigard (1999) show no statistical difference. Although the high amount of SC CO_2

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sorbed to the gold electrode used by Guigard (1999) as compared to the silver electrode used in this work could have contributed in decreased sensitivity and increased variability in the QCM frequency. Thus, possibly accounting for the increased standard deviation associated with the $Cu(tta)_2$ solubilities from Guigard (1999), when compared to the standard deviations from this work.

7.9 Assessing the Sources of Variability in the QCM Technique

The possible sources of random variability for the solubility experiments conducted with the in-situ QCM method is:

> the variation of the temperature

> the variation from the frequency measurement (resonant frequency and FCO_2 values)

> the variation in the vessel volume

The thermistor used to measure the temperature during the solubility experiments had an error associated with it of $\pm 0.2^0C$, within the experimental conditions. The variation of temperature throughout any solubility experiment was reported in Section 6.3 to be no more than $\pm 0.4^0C$ during any solubility experiment.

The maximum variation of the resonant frequency measurement exhibited a variability of $\pm$ 6Hz. This low variation was a constant phenomenon in all the solubility experiments. Through trial and error it was found that if the variability was noticeably higher there was some type of interference with the QCM. This resultant interference ultimately affected the solubility experiment, thus the experiment was aborted and begun anew.

The standard deviations for the FCO_2 values are reported in Table 6-5. The vessel volume was calculated in section 6.2. The standard deviation associated with the vessel volume measurements of is ± 0.04 cm^3.

To calculate the propagation of errors associated with all the sources Equation 7-1 is used (Box et al., 1978), (Price, 2000).

$$ S_u = \sqrt{\left(\frac{\partial u}{\partial x}\right)^2_{y,z} s^2_x + \left(\frac{\partial u}{\partial y}\right)^2_{x,z} s^2_y + \left(\frac{\partial u}{\partial z}\right)^2_{y,x} s^2_z} \quad (7\text{-}1) $$

Where: s_u is the standard deviation as it relates to each individual solubility measurement at a specific density, $\partial u/\partial x$ is the partial derivative assigned to "x" of the equation used to calculate a final result (in this case it is the solubility equations (Equation 6-8), s_x is the standard deviation of the that assigned value (resonant frequency, vessel volume, temperature fluctuation)

From Equation 6-8 the combined equation for a solubility measurement for a solute in SC CO_2 is illustrated in Equation 7-2.

$$ Sol\left(mol/mol\right) = \left(\frac{\left(F_{dip} - F_{final}\right)*A*\sqrt{\rho_Q \mu_Q}}{-2\left(F_0 + FCO_2\right)*M.W._{solute}}\right) * \left(\frac{M.W._{\cdot CO_2}}{\rho_{CO_2}*Vol[PressureVessel]}\right) \quad (7\text{-}2) $$

To simplify the calculation F_{dip}, F_{final} and F_0 will be treated as the same variable. The F_0 value has a standard deviation associated with it, however F_{dip} and F_{final} do not have an associated standard deviation. The F_{dip} value is independent on each measurement but still could have the error in frequency

associated with it. Furthermore the F_{final} frequency reading is similar to the F_0 values, in stability and relative standard deviation. The other assumption to be made is for the ρ_{CO2} measurement. The density of the CO_2 is calculated by the modified Benedict-Webb-Rubin Equation-of-State, which relates temperature and pressure to calculate the density of the CO_2 (Stiver and Rampley, 2000). Assuming the standard deviation from the temperature measurements introduces the greatest source of error, the relative percent standard deviation used for the ρCO_2 value is the same as the relative percent standard deviation for the temperature. The other measurements FCO_2 and the volume of the pressure vessel will be treated as independent. Therefore a total of four error sources will be accounted for in Equation 7-2. The rest of the values are constants in the equation and will not be differentiated.

The four differentiated equations can be found in Appendix J. The resultant error associated with the QCM solubility measurement technique at different densities and for the different compounds is shown below in Table 7-3.

Table 7-3 Propagated Error

Density	Compound	Calculated Std. Dev.	Percent of Reported Result
0.595	$Cu(tta)_2$	3.28E-09	1%
0.6516	$Cu(tta)_2$	4.26E-09	1%
0.4399	$Cu(tta)_2$	9.59E-09	3%
0.5407	$Cu(tta)_2$	6.88E-09	2%
0.7189	β-Carotene	2.78E-09	3%

In Table 7-3 the maximum amount of error associated with a solubility measurement was 3%. In the calculations the most predominant factor governing

the propagated error was the value from the FCO_2. The higher standard deviation from the FCO_2 values was from the extreme sensitivity of the QCM measurement system. The frequency (as stated previously) was subject to a wide variety of interference sources. The total propagated error, when compared to the standard deviation associated with the solubility measurement replicates for each density is comparatively low (±31% for the β-carotene and from ±8% to ±49% for $Cu(tta)_2$). The higher error associated with the replicates indicates that the propagated error is not accounting for all the sources of potential error within the QMC measurement technique. The majority of the remaining error is most likely due to the uneven distribution of mass on the electrode, experimenter error and other electrical interference sources. However, these sources of error are not quantifiable using this method to propagate the error.

7.10 Correlating Solubilities in SC CO_2

This section will implement two different techniques to correlate the solubilities of β-carotene and $Cu(tta)_2$ in SC CO_2. The techniques used will be the Chrastil technique (Chrastil, 1982) and the Guigard-Stiver technique (Guigard and Stiver, 1998). These methods use previous solubility data and various physical parameters to correlate the solubilities of specific solutes in SC CO_2.

7.10.1 The Chrastil Technique

The Chrastil technique is the most widely used technique for correlating SC CO_2 solubilities (Stiver and Rampley, 2000). The Chrastil technique describes solubility behaviour between the solubility of a solute and pure solvent density.

The Chrastil technique is widely used because it does not require any physical-chemical property data for the solute. The form of the Chrastil correlating equation is:

$$y_2 = \rho_1^k \exp\left(\frac{a}{T} + b\right)$$ (7-3)

where: y_2 is the solute's solubility (g/L), ρ_1 is the density of the SC CO_2 (g/L), T is the temperature (Kelvin), k is the association constant and a and b are constants taking into account the total heat of reaction (ΔH) and the molecular weight of the solute. From Chrastil (1982), the constants a and b can also be estimated by plotting the logarithm of solubility vs. the logarithm of density and using the following Equations (7-4).

$$a = \frac{\kappa T_2 T_1 \ln\left(\frac{I_1}{I_2}\right)}{T_2 - T_1}$$

$$b = -\kappa \ln I_1 - \frac{a}{T_1} = -\kappa \ln I_2 - \frac{a}{T_2}$$ (7-4)

and :

$$\kappa = 1 / slope$$

where T is the temperature (Kelvin) and I is the intercept of the specific isothermic plot. The association constant, k, is the slope derived from an isothermic plot of log solubility vs. log density for a particular solute in SC CO_2. The Chrastil technique assumes that the slopes derived from the isothermic plots of log-solubility vs. log-density for a specific solvent/solute system are linear and have very similar association constant values (Chrastil, 1982). It has been shown with other authors that the Chrastil equation can be simplified. From

Addleman *et al.* (2000) the following equation can be used to correlate solubilities, by predicting a linear relationship between ln D and ln y.

$$\ln y = k \ln D + C \qquad (7\text{-}5)$$

where y is the solubility in (g/L) and D is the density of the SC CO_2 (g/L), k is the slope and C is the intercept of the ln y vs. ln D graph at a specific temperature.

7.10.2 The Guigard-Stiver Solubility Correlation

This method uses a density dependent solubility parameter approach to correlate the solubilities of solutes in SC CO_2. The solubility parameter approach is based on the regular solution theory and the activity coefficient of the solute in the supercritical phase. The regular solution theory and the activity coefficient of the solute in the supercritical phase are used in the Scatchard-Hildebrand equation to correlate the solubilities of solutes in SC CO_2. The regular solution theory states that upon the mixing of the components of a solution there is no excess entropy or excess volume mixing (Prausnitz *et al.*, 1986). The Guigard-Stiver approach is a modification of the Scatchard-Hildebrand equation in an attempt to correlate solubilities in SC CO_2, which can be seen in Equation (7-6).

$$y_2 = \exp\left(\frac{-\Delta H^m_{fus}}{RT_m}\left(\frac{T_m}{T}-1\right)-\frac{v_2^L \phi_1^2}{RT}(\delta_2 - \delta_1)^2\right)$$

and :

$$\phi_1 = \frac{y_1 v_1^L}{y_1 v_1^L + y_2 v_{21}^L} \qquad (7\text{-}6)$$

$$\delta_2 = a + b\rho_1^c$$

$$\delta_1 = 3.02\left(\frac{p_{c1}^{1/2}}{\rho_{c1}}\right)\rho_1$$

where y_2 is the solute's solubility (mol/mol), ΔH_{fus}^m is the solute's enthalpy of fusion (J/mol), T_m is the melting point of the solute (Kelvin), v_2^L is the solute's molar volume (cm³/mol), R is the gas constant (J/mol*K), ϕ_1 is the supercritical fluid's volume fraction, δ_2 is the solute's solubility parameter (MPa$^{1/2}$), δ_1 is the supercritical fluid's solubility parameter (MPa$^{1/2}$), ρ_1 is the supercritical fluid's density (g/cm³), P_c is the critical pressure of the SC CO_2 (MPa), ρ_c is the critical density of the SC CO_2 (g/cm³) and a, b and c are adjustable fitting parameters, which are independent of temperature.

7.10.2.1   Correlated β-Carotene Solubilities

Table 7-4 shows the Chrastil association constants used for β-carotene by different authors.

Table 7-4 Chrastil Modelled Constants for β-Carotene (from Equation 7-5)

k	a	b	Reference:
8.01	-11950.9	24	Stiver and Rampley (2000)
9.79	-12611.2	26	Subra *et al.* (1997)
5.47	6287.9	-15.43	Skerget *et al.* (1995)

The reference by Stiver and Rampley (2000) combines all available data sources from temperatures ranging from 303-343 Kelvin and reports solubility in mole fraction. The values of Subra *et al.* (1997) and Skerget *et al.* (1995) are taken directly from their respective sources. The solubility results from Subra *et al.* (1997) and Skerget *et al.* (1995) are reported in mole fraction and g/L, respectively.

The value derived for the association constant depends on the data set that is used to plot the log-log graph. Thus different authors present different *k*

values for different solute solubilities in SC CO_2. The original Chrastil article correlated the solubilities in units of g/L as opposed to mol/mol used here. This difference affects the values of the constants a, b and k but does not alter the performance of the model (Stiver and Rampley, 2000). The properties for β-carotene and SC CO_2 that are used for the Guigard-Stiver correlation are shown in Table 7-5. Table 7-6 summarizes the reported experimental solubilities and the correlated solubilities (from the Chrastil and Guigard-Stiver techniques) for β-carotene at 313 K and 12.0 MPa

Table 7-5 Guigard-Stiver Parameters for β-Carotene

Symbol	Value	Units
ΔH_{fus}^{m}	56000	J/mol
T_m	456	Kelvin
V_2^L	536.88	cm^3/mol
R	8.314	J/mol*K
ϕ_1	1	n/a
ρ_1	0.721	g/cm^3
P_c^1	7.3843	MPa
ρ_c^1	0.4665	g/cm^3
a	12.2	n/a
b	11.5525	n/a
c	1.35144	n/a

For the value of ϕ_1, the solubility of the solute in SC CO_2 is small enough that it is safe to assume that ϕ_1 has a value of 1. The values of a, b and c were obtained from Stiver and Rampley (2000). These values included all known references that measured the solubility of β-carotene within the temperature and pressure range of 310-340K and 9.7-31 MPa, respectively. The solubility value that can be calculated from the above parameters at 313 K and 12.0 MPa is 5.74E-08 mol/mol.

Table 7-6 Summary of Experimental and Correlated β-Carotene Solubilities in SC CO$_2$ at

313 K and 12.0 MPa

Solubility (mol/mol)		Reference
5.04E-08	Chrastil Technique	Stiver and Rampley (2000)
3.18E-08	Chrastil Technique	Subra et al. (1997)
5.74E-08	Guigard-Stiver Technique	Stiver and Rampley (2000)
1.83E-07	Chrastil Technique	Skerget et al. (1995)
3.00E-08	Experimental Result	Mendes et al. (1999)
9.57E-08	Experimental Result	This Work

The relative percent standard deviation for the data set presented in Table 7-6 is high (78%). This is as a result of the data set that each reference used to obtain the parameters to correlate the solubilities. As stated previously Stiver and Rampley (2000) used all available data sets to correlate the β-carotene solubilities, (the majority of which, were examined in section 4.4 and 7.6 above). The combined data sets used by Stiver and Rampley (2000) to correlate the solubility of β-carotene using the Guigard-Stiver and the Chrastil techniques produced very similar results (5.04E-08 and 5.74E-08 mol/mol, respectively).

The greater part of the references used by Stiver and Rampley (2000) were lower solubility values than this work and Skerget et al. (1995) (9.57E-08 mol/mol and 1.83E-07 mol/mol, respectively). Thus the correlated values from Stiver and Rampley (2000) reflect the trend of the entire data set.

7.10.2.2   Correlated Cu(tta)$_2$ Solubilities

For Cu(tta)$_2$, the individual Chrastil association constants *a* and *k* must be estimated. The available physical-chemical data do not provide the heat of reaction (ΔH) for Cu(tta)$_2$. The *a* and *k* values for a similar β-diketone copper

chelate $(Cu(acac)_2)$, will be used as a first approximation. These values are derived from a combination of all literature data sets compiled by Stiver and Rampley (2000). Table 7-7 provides the corresponding constants and Chrastil correlated solubility values for $Cu(tta)_2$.

Table 7-7 Chrastil Parameters Used for $Cu(tta)_2$

Chrastil k	Chrastil a	Chrastil b	Reference
2.17	-2221.37	-3.48	Stiver and Rampley (2000)

As a second approximation, Equation 7-5 will be used with all four of the experimental data points form this work. This will be done to give a better estimation of the predicted solubilities using the Chrastil model.

The properties for $Cu(tta)_2$ and SC CO_2 that are used for the Guigard-Stiver correlation are shown in Table 7-8.

Table 7-8 $Cu(tta)_2$ Guigard-Stiver Parameters

Symbol	Value	Units
ΔH_{fus}^m	n/a	J/mol
T_m	513	Kelvin
V_2^L	269.2	cm^3/mol
R	8.314	J/mol*K
ϕ_1	1	n/a
P_c^1	7.3843	MPa
ρ_c^1	0.4665	g/cm^3

n/a-not available

For the value of ϕ_1, the solubility of the solute in SC CO_2 is small enough that it is safe to assume that ϕ_1 has a value of 1. Since the ΔH_{fus} value for $Cu(tta)_2$ is not known, the ΔH_{fus} for $Cu(acac)_2$ is used (37121 J/mol). The molar density and melting point for $Cu(tta)_2$ values were obtained from Guigard (1999). The

correlated solubility values must be calculated at each condition. For the δ_2 value

the fitting parameters *a, b* and *c* were simultaneously fit to the experimental data

for this work using the technique of least squares analysis. By altering the fitting

parameters, the sum of the squared differences between the experimental data

and the correlated solubility values can be minimized, thus providing a best-fit

mathematical description of the experimental results. To quantify the accuracy

of the fitting parameters and consequently the accuracy of the correlated

solubility results, the 'average absolute relative deviation' (AARD) can be

calculated according to Equation 7.7. The AARD is expressed as a percent, a

lower value indicates a good fit to the experimental data.

$$AARD(\%) = \frac{1}{n} \left| \sum \frac{y_{2(exp)} - y_{2(reg)}}{y_{2(exp)}} \right| * 100 \qquad (7.7)$$

The respective Guigard-Stiver fitting parameters that were calculated using

the data from this work are shown below.

Table 7-9 Guigard-Stiver Fitting Parameters for Cu(tta)₂

Fitting Parameters	
a	-4.52566
b	23.13909
c	2.669415

Table 7-10 summarizes the experimental values for Cu(tta)₂ (from this work)

as well the Chrastil correlated values using the first approximation method

(based on the data from Cu(acac)₂).

Table 7-10 Cu(tta)$_2$ Experimental and Chrastil Correlated Values From the First Approximation Method

Experimental Conditions			Solubility (mol/mol)	Solubility from Aprox. 1 (mol/mol)
Pressure (MPa)	Temp. (K)	Density (g/cm^3)		
10.34	313.15	0.6516	1.81E-06	1.01E-05
9.65	313.15	0.5948	8.36E-07	9.23E-06
10.34	318.15	0.5407	3.75E-07	6.71E-06
9.65	318.15	0.4399	3.37E-07	4.79E-06

The Cu(tta)$_2$ solubility values using the first approximation method are approximately one order of magnitude higher than the experimental results from this work in Table 7-10. The inability to estimate the Chrastil constants (for the first approximation method) from the experimental data from this work, necessitated using the Chrastil constants for Cu(acac)$_2$. Cu(acac)$_2$ has a higher reported solubility, thus influencing the Chrastil association constants.

Table 7-11 summarizes the experimental values for Cu(tta)$_2$ (from this work) as well the Chrastil correlated values using the second approximation method (based on the data from this work).

Table 7-11 Cu(tta)$_2$ Experimental and Chrastil Correlated Values From the Second Approximation Method

Experimental Conditions			Solubility (mol/mol)	Chrastil Parameters (from Equation 7-7)		Correlated Solubility Value (mol/mol)
Pressure (MPa)	Temp. (K)	Density (g/cm^3)		k	c	
10.34	313.15	0.6516	1.81E-06	5.1074	-37.712	1.32E-06
9.65	313.15	0.5948	8.36E-07	5.1074	-37.712	9.05E-07
10.34	318.15	0.5407	3.75E-07	5.1074	-37.712	6.12E-07
9.65	318.15	0.4399	3.37E-07	5.1074	-37.712	2.62E-07

The second approximation method used all four experimental solubility data points of $Cu(tta)_2$ to correlate the $Cu(tta)_2$ solubilities in SC CO_2. Although the k and C value for the Chrastil model has been shown to be temperature dependant ((Addleman *et al.*, 2000), (Subra *et al.*, 1997)), this approach was taken because of the small difference in temperature (5^0C) and the low number of experimental $Cu(tta)_2$ data points. The AARD value from the second approximation method is 30.9%.

Table 7-12 summarizes the experimental values for $Cu(tta)_2$ (from this work) as well as the Guigard-Stiver and Chrastil (approximation 2) correlated values.

Table 7-12 Summary of Experimental And Correlated $Cu(tta)_2$ Solubilities in SC CO_2

Temperature (K)	Density (g/cm³)	Experimental Solubility (mol/mol)	Chrastil Correlated Solubility (mol/mol)	Guigard-Stiver Correlated Solubility (mol/mol)
313.15	0.6516	1.81E-06	1.32E-06	1.80E-06
318.15	0.5948	8.36E-07	9.05E-07	8.66E-07
313.15	0.5407	3.75E-07	6.12E-07	3.07E-07
318.15	0.4399	3.37E-07	2.62E-07	3.49E-07

The experimental solubility column represents the results obtained in this work. The experimental values from this work and the Guigard-Stiver correlation show a good fit (AARD is 6.4%), while the AARD from the second approximation of the Chrastil correlation is 30.9%. A graphical illustration is shown in Figure 7-7.
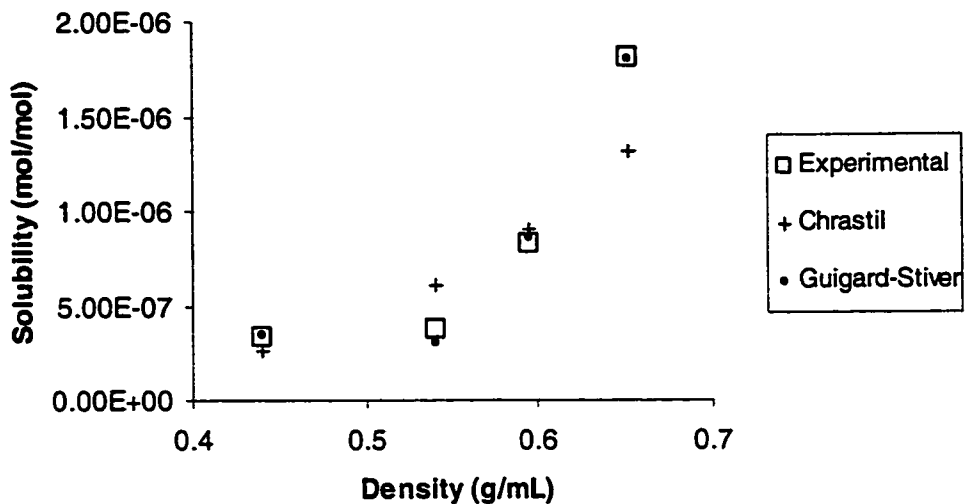
Figure 7-7 Solubility vs. Density, Experimental, Chrastil and Guigard-Stiver Correlated Values for Cu(tta)₂

The Chrastil technique for correlating the solubilities of Cu(tta)$_2$ shows a relatively good fit in establishing a close fitting correlation . The higher AARD (30.9%), (than the AARD for the Guigard-Stiver correlation) is due to the low number of experimental isothermic data points for Cu(tta)$_2$ and the approximation used to derive the Chrastil correlated solubilities.

The percent AARD for the Guigard-Stiver correlated data is calculated to be 6.4%. This highly accurate fit is primarily due to the small number of data points. The estimated ΔH_{fus} intricately affects the obtained parameters, but does not affect the performance of the model. Therefore the fitting parameters serve only as a estimate until such time when the ΔH_{fus} for Cu(tta)$_2$ is reported.

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8 Conclusions and Recommendations

This section will present an overview of the material presented in this thesis. The conclusion section will summarize the research that was conducted and obtained through the course of this project. The recommendations section will offer comments towards the enhancement and improvement of further research dealing with the quartz crystal microbalance as an *in-situ* solubility measurement technique.

8.1 Conclusions

During the course of this research a novel technique was developed to measure solubilities in SC CO_2. The technique involved using a piezoelectric quartz crystal microbalance to measure solubilities *in-situ* for two compounds (β-carotene and $Cu(tta)_2$) in SC CO_2.

The SC CO_2 system used for this research was designed and built by the author of this thesis. In developing this new technique, many unforeseen technical difficulties presented themselves. Each problem was individually identified and solved. The technical difficulties were part of the development process; and in the end served to further the quartz crystal microbalance technique towards a reliable and accurate solubility measurement technique in SC CO_2.

The solubility of β-carotene was measured at 0.7189 g/cm^3 (313 K and 10.34 MPa). The experimental solubility result from this work for β-carotene was 9.57E-08 mol/mol ($\pm$30.7%). As a result of the diverse solubility conditions and solubility measurement techniques for β-carotene, it is difficult to compare the

results from this work to the results of other workers. However, the solubility result from this work is similar to other solubility values within the observed density range.

The solubility of $Cu(tta)_2$ in SC CO_2 was measured at four conditions. The conditions were chosen to allow comparison of measured values with other available data and to determine experimentally a density relationship with solubility. The pressure conditions for the solubility measurements were 9.65 MPa and 10.34 MPa. These pressures were alternated with two temperatures, 313 K and 318 K. The measured $Cu(tta)_2$ solubilities in SC CO_2 at densities of 0.6516 g/cm^3, 0.5948 g/cm3, 0.5407 g/cm^3, 0.4399 g/cm^3 are 1.81E-06 mol/mol, 8.36E-07 mol/mol, 3.75E-07 mol/mol, 3.36E-07 mol/mol, respectively.

When comparing the solubility results obtained in this work to previous work done by Guigard (1999), the experimental results for this work and Guigard (1999) show no statistical difference. The methods used to determine solubility for both Guigard (1999) and this work utilized the QCM technique.

The Chrastil and Guigard-Stiver solubility correlation techniques were used to correlate the solubilities of β-carotene and $Cu(tta)_2$ in SC CO_2. The Chrastil and Guigard-Stiver correlations for β-carotene were slightly lower than the result reported in this work. The fact that the majority of the data used in the correlations by both models for β-carotene were lower than the result reported in this work, largely influenced the outcome of the models.

Due to the lack of ΔH value and the low number of experimental data points for $Cu(tta)_2$, two approximation methods were used to correlate solubilities

using the Chrastil technique. The first approximation used the Chrastil association constants from $Cu(acac)_2$, a similar β-diketone metal chelate. However, due to the fact that the $Cu(acac)_2$ solubilities are higher than the $Cu(tta)_2$ values, the corresponding Chrastil association constants for $Cu(acac)_2$, influenced the correlation of $Cu(tta)_2$, predicting much higher solubility results than expected (one order of magnitude). The second approximation used all four experimental solubility data points of $Cu(tta)_2$ to correlate the $Cu(tta)_2$ solubilities in SC CO_2. Although the k and C value for the Chrastil model has been shown to be temperature dependant, this approach was taken because of the small difference in temperature (5^0C) and the low number of experimental $Cu(tta)_2$ data points. The AARD value from the second approximation method is 30.9%.

The solubilities of $Cu(tta)_2$ was also correlated by the Guigard–Stiver technique. This method used the ΔH_{fusion} from $Cu(acac)_2$ in substitution for the absence of the particular physical-chemical data for $Cu(tta)_2$. The model was fit using the least squares analysis technique. This technique helped establish close fitting parameters that produced correlated data that had an AARD of 6.4%.

Overall the solubilities of β-carotene measured in this work helped verify the QCM technique as an accurate and reliable method to measure solubilities in SC CO_2.

The measured $Cu(tta)_2$ solubilities established a solubility-density relationship, which identified optimal extraction conditions (within the observed densities) for $Cu(tta)_2$ in neat SC CO_2. By knowing the solubility of $Cu(tta)_2$ in neat SC CO_2, extractions of $Cu(tta)_2$ from different matrices such as filter paper,

glass wool, sand and soil can be examined. By identifying the optimal extraction conditions, a feasible and efficient supercritical carbon dioxide extraction system can be designed for future work to remediate heavy metals from contaminated soils.

8.2 Recommendations

The recommendations for future work beyond the work presented in this thesis are:

> To design a new pressure vessel to fit a QCM with a metal holder. This would eliminate the problems of the disintegrating glass holders and possibly provide a more reliable high-pressure seal in the pressure vessel.

> To design a type of a 'well', which would fit onto the quartz crystal exposing only the electrode surface. This well could be partially covered after a solute/solvent mixture is placed on the electrode surface. Covering the well would possibly provide a slower volatilization of the solvent, thus enhancing even layering of a solute on the electrode surface. This would further extend the range of compounds available to be measured by the QCM technique.

> The QCM technique is also limited to the amount of mass that can be added to the QCM surface. The mass limit is an inherent characteristic of the oscillator used to sustain oscillation in the QCM. The QCM impedance increases proportionally with the mass load, when the impedance reaches some critical value the oscillator circuit is unable to sustain oscillating the crystal. The addition of a network or spectrum analyzer would extend the

measurement range because of the ability of network or spectrum analyzer to actively sustain oscillation in the crystal for short periods of time. This means that the network or spectrum analyzer circumvents the problem with sustaining oscillation in a feedback loop and can measure quartz crystals with high impedance values. Thus, further extending the range of compounds that can be measure with the QCM technique.

> To obtain more solubility measurements at higher densities in neat SC CO_2 for β-carotene. At higher densities a very large number of solubility data points exist for β-carotene. The increased measurements would help further validate the QCM technique and establish more accurate solubility correlation models.

> To obtain more solubility measurements at higher densities in neat SC CO_2 for $Cu(tta)_2$. The increased measurements would establish more accurate solubility correlation models, and better determine the optimal extraction range for $Cu(tta)_2$.

> To obtain solubilities of $Cu(tta)_2$ in SC CO_2 in the presence of modifiers (such as methanol and water) and other compounds that have shown to enhance extraction of metals with tta (such as TBP).

> To begin extractions of copper and other metals form different matrices in SC CO_2. The extractions will provide lab scale results, which will further advance SFE technology to pilot scale and possible commercial applications.

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Appendix A: X-ray Analysis of Cu(tta)$_2$

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X-ray Display 1
Acquisition completed.                                      K

                                                              854 FS
                    ■   CuTTA-xray  overview

                         S



                   Si



         F   Cu                                    Cu
                                                              Au
   0.0          2.0          4.0          6.0          8.0          10.0
                              keV
```
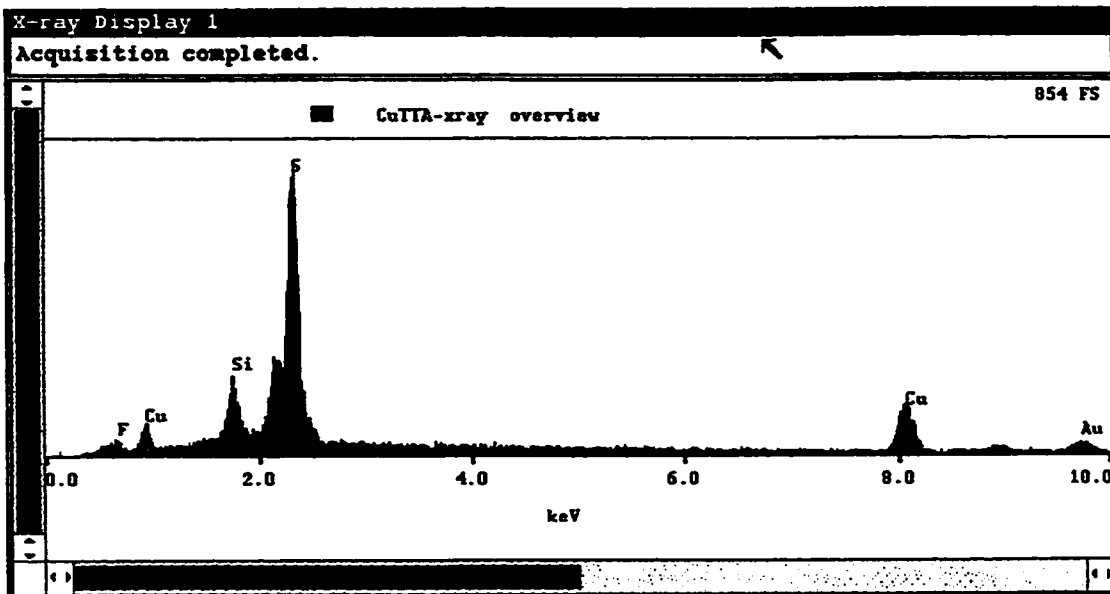
PGT Rough surface/particle analysis   Mon Feb 28 14:35:57 2000

Phi-Rho-Z Method, variable-width filter

Sample /xd1/window1/#1,CuTTA-xray.spt
Accelerating Voltage: 20.00 keV
Takeoff Angle: 65.30 degrees
Library for system standards: /imix/spectra/system_standards.dir

Elm	Rel. K	Norm wt%	Atomic %
F	0.0000	63.85	80.98
S	0.1245	14.28	10.73
Cu	0.1931	21.87	8.29

| Total | | 100.00 | 100.00 |

Goodness of fit   1.82

WARNING:Residual peak at approximately 8062 ev

WARNING:Residual peak at approximately 9718 ev

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Appendix B: Tabulated Vessel Volume Measurements

Table B-1 Tabulated Vessel Volume Measurements

Trial	Weight of Vessel (gm)	(+Water) (gm)	Difference (gm)	Corr for water at 21°C (mL)	Minus Extra Voumel (mL)
1	195.348	196.814	1.466	1.469	1.450
2	195.348	196.861	1.512	1.515	1.496
3	195.350	196.911	1.560	1.563	1.544
4	195.351	196.836	1.485	1.488	1.469
5	195.352	196.861	1.510	1.512	1.493

Mean	1.490 (mL)
Standard Deviation	0.035

Appendix C: Temperature Data From July 25/00 Solubility Experiment

Time (hours)	Temperature (Celsius)				
0	45.58	0.056	45.58	0.113	45.58
0.001	45.58	0.057	45.58	0.114	45.58
0.002	45.58	0.058	45.58	0.116	45.58
0.003	45.58	0.059	45.58	0.117	45.58
0.004	45.58	0.060	45.58	0.118	45.58
0.006	45.58	0.061	45.58	0.119	45.58
0.007	45.58	0.062	45.58	0.120	45.58
0.008	45.58	0.063	45.58	0.121	45.58
0.009	45.58	0.064	45.58	0.122	45.58
0.010	45.58	0.066	45.58	0.123	45.58
0.011	45.58	0.067	45.58	0.124	45.58
0.012	45.58	0.068	45.58	0.126	45.58
0.013	45.58	0.069	45.58	0.127	45.58
0.014	45.58	0.070	45.58	0.128	45.58
0.016	45.58	0.071	45.58	0.129	45.58
0.017	45.58	0.072	45.58	0.130	45.58
0.018	45.58	0.073	45.58	0.131	45.58
0.019	45.58	0.074	45.58	0.132	45.58
0.020	45.58	0.076	45.58	0.133	45.58
0.021	45.58	0.077	45.58	0.134	45.58
0.022	45.58	0.078	45.58	0.136	45.58
0.023	45.58	0.079	45.58	0.137	45.58
0.024	45.58	0.080	45.58	0.138	45.58
0.026	45.58	0.081	45.58	0.139	45.58
0.027	45.58	0.082	45.58	0.140	45.58
0.028	45.58	0.083	45.58	0.141	45.58
0.029	45.58	0.084	45.58	0.142	45.58
0.030	45.58	0.086	45.58	0.143	45.52
0.031	45.58	0.087	45.58	0.144	45.58
0.032	45.58	0.088	45.58	0.146	45.52
0.033	45.58	0.089	45.58	0.147	45.52
0.034	45.58	0.090	45.58	0.148	45.52
0.036	45.58	0.091	45.58	0.149	45.58
0.037	45.58	0.092	45.58	0.150	45.58
0.038	45.58	0.093	45.58	0.151	45.52
0.039	45.58	0.094	45.58	0.152	45.52
0.040	45.58	0.096	45.58	0.153	45.52
0.041	45.58	0.097	45.58	0.154	45.52
0.042	45.58	0.098	45.58	0.156	45.52
0.043	45.58	0.099	45.58	0.157	45.45
0.044	45.58	0.100	45.58	0.158	45.39
0.046	45.58	0.101	45.58	0.159	45.33
0.047	45.58	0.102	45.58	0.160	45.33
0.048	45.58	0.103	45.58	0.161	45.33
0.049	45.58	0.104	45.58	0.162	45.27
0.050	45.58	0.106	45.58	0.163	45.27
0.051	45.58	0.107	45.58	0.164	45.27
0.052	45.58	0.108	45.58	0.166	45.27
0.053	45.58	0.109	45.58	0.167	45.20
0.054	45.58	0.110	45.58	0.168	45.27
		0.111	45.58	0.169	45.27
		0.112	45.58	0.170	45.27

0.171	45.20	0.229	45.27	0.287	45.33
0.172	45.20	0.230	45.27	0.288	45.33
0.173	45.20	0.231	45.27	0.289	45.33
0.174	45.20	0.232	45.27	0.290	45.27
0.176	45.20	0.233	45.27	0.291	45.33
0.177	45.20	0.234	45.27	0.292	45.33
0.178	45.20	0.236	45.27	0.293	45.33
0.179	45.20	0.237	45.27	0.294	45.33
0.180	45.20	0.238	45.27	0.296	45.33
0.181	45.20	0.239	45.27	0.297	45.33
0.182	45.20	0.240	45.27	0.298	45.33
0.183	45.20	0.241	45.27	0.299	45.33
0.184	45.20	0.242	45.27	0.300	45.33
0.186	45.20	0.243	45.27	0.301	45.27
0.187	45.20	0.244	45.27	0.302	45.27
0.188	45.20	0.246	45.27	0.303	45.33
0.189	45.27	0.247	45.27	0.304	45.33
0.190	45.20	0.248	45.27	0.306	45.33
0.191	45.27	0.249	45.27	0.307	45.33
0.192	45.27	0.250	45.27	0.308	45.33
0.193	45.27	0.251	45.27	0.309	45.33
0.194	45.27	0.252	45.27	0.310	45.33
0.196	45.27	0.253	45.27	0.311	45.33
0.197	45.27	0.254	45.27	0.312	45.33
0.198	45.27	0.256	45.27	0.313	45.33
0.199	45.27	0.257	45.27	0.314	45.33
0.200	45.27	0.258	45.27	0.316	45.33
0.201	45.27	0.259	45.27	0.317	45.33
0.202	45.27	0.260	45.27	0.318	45.33
0.203	45.27	0.261	45.27	0.319	45.33
0.204	45.27	0.262	45.27	0.320	45.33
0.206	45.27	0.263	45.27	0.321	45.27
0.207	45.27	0.264	45.27	0.322	45.33
0.208	45.27	0.266	45.27	0.323	45.33
0.209	45.27	0.267	45.27	0.324	45.33
0.210	45.27	0.268	45.27	0.326	45.33
0.211	45.27	0.269	45.27	0.327	45.33
0.212	45.27	0.270	45.27	0.328	45.33
0.213	45.27	0.271	45.27	0.329	45.33
0.214	45.27	0.272	45.33	0.330	45.33
0.216	45.27	0.273	45.27	0.331	45.33
0.217	45.27	0.274	45.27	0.332	45.33
0.218	45.27	0.276	45.33	0.333	45.33
0.219	45.27	0.277	45.27	0.334	45.33
0.220	45.27	0.278	45.33	0.336	45.33
0.221	45.27	0.279	45.33	0.337	45.33
0.222	45.27	0.280	45.33	0.338	45.33
0.223	45.27	0.281	45.27	0.339	45.33
0.224	45.27	0.282	45.27	0.340	45.33
0.226	45.27	0.283	45.33	0.341	45.33
0.227	45.27	0.284	45.33	0.342	45.33
0.228	45.27	0.286	45.27	0.343	45.33

0.344	45.33	0.402	45.33	0.460	45.33
0.346	45.33	0.403	45.33	0.461	45.39
0.347	45.33	0.404	45.33	0.462	45.39
0.348	45.33	0.406	45.33	0.463	45.39
0.349	45.33	0.407	45.33	0.464	45.33
0.350	45.33	0.408	45.33	0.466	45.39
0.351	45.33	0.409	45.33	0.467	45.39
0.352	45.33	0.410	45.39	0.468	45.33
0.353	45.33	0.411	45.33	0.469	45.39
0.354	45.33	0.412	45.33	0.470	45.39
0.356	45.33	0.413	45.33	0.471	45.39
0.357	45.33	0.414	45.33	0.472	45.39
0.358	45.33	0.416	45.33	0.473	45.39
0.359	45.33	0.417	45.33	0.474	45.39
0.360	45.33	0.418	45.33	0.476	45.39
0.361	45.33	0.419	45.33	0.477	45.39
0.362	45.33	0.420	45.33	0.478	45.39
0.363	45.33	0.421	45.39	0.479	45.33
0.364	45.33	0.422	45.33	0.480	45.39
0.366	45.33	0.423	45.39	0.481	45.39
0.367	45.33	0.424	45.39	0.482	45.39
0.368	45.33	0.426	45.33	0.483	45.39
0.369	45.33	0.427	45.33	0.484	45.39
0.370	45.33	0.428	45.33	0.486	45.39
0.371	45.33	0.429	45.39	0.487	45.33
0.372	45.33	0.430	45.33	0.488	45.39
0.373	45.33	0.431	45.33	0.489	45.39
0.374	45.33	0.432	45.33	0.490	45.39
0.376	45.33	0.433	45.33	0.491	45.39
0.377	45.33	0.434	45.33	0.492	45.39
0.378	45.33	0.436	45.39	0.493	45.39
0.379	45.33	0.437	45.39	0.494	45.39
0.380	45.33	0.438	45.33	0.496	45.39
0.381	45.33	0.439	45.39	0.497	45.39
0.382	45.33	0.440	45.33	0.498	45.39
0.383	45.33	0.441	45.39	0.499	45.39
0.384	45.33	0.442	45.33	0.500	45.39
0.386	45.33	0.443	45.33	0.501	45.39
0.387	45.33	0.444	45.33	0.502	45.39
0.388	45.33	0.446	45.39	0.503	45.39
0.389	45.33	0.447	45.33	0.504	45.39
0.390	45.33	0.448	45.39	0.506	45.39
0.391	45.33	0.449	45.39	0.507	45.39
0.392	45.33	0.450	45.39	0.508	45.39
0.393	45.33	0.451	45.33	0.509	45.39
0.394	45.33	0.452	45.39	0.510	45.39
0.396	45.33	0.453	45.39	0.511	45.39
0.397	45.33	0.454	45.39	0.512	45.39
0.398	45.33	0.456	45.33	0.513	45.39
0.399	45.33	0.457	45.33	0.514	45.39
0.400	45.33	0.458	45.39	0.516	45.39
0.401	45.33	0.459	45.33	0.517	45.39

0.518	45.39	0.576	45.39	0.633	45.39
0.519	45.39	0.577	45.39	0.634	45.39
0.520	45.39	0.578	45.39	0.636	45.39
0.521	45.39	0.579	45.39	0.637	45.39
0.522	45.39	0.580	45.39	0.638	45.39
0.523	45.39	0.581	45.39	0.639	45.45
0.524	45.39	0.582	45.39	0.640	45.45
0.526	45.39	0.583	45.39	0.641	45.39
0.527	45.39	0.584	45.39	0.642	45.39
0.528	45.39	0.586	45.39	0.643	45.45
0.529	45.39	0.587	45.39	0.644	45.45
0.530	45.39	0.588	45.39	0.646	45.45
0.531	45.39	0.589	45.39	0.647	45.39
0.532	45.39	0.590	45.39	0.648	45.45
0.533	45.39	0.591	45.39	0.649	45.39
0.534	45.39	0.592	45.39	0.650	45.39
0.536	45.39	0.593	45.39	0.651	45.45
0.537	45.39	0.594	45.39	0.652	45.45
0.538	45.39	0.596	45.39	0.653	45.45
0.539	45.39	0.597	45.39	0.654	45.45
0.540	45.39	0.598	45.39	0.656	45.45
0.541	45.39	0.599	45.39	0.657	45.39
0.542	45.39	0.600	45.39	0.658	45.39
0.543	45.39	0.601	45.39	0.659	45.45
0.544	45.39	0.602	45.39	0.660	45.39
0.546	45.39	0.603	45.39	0.661	45.45
0.547	45.39	0.604	45.39	0.662	45.39
0.548	45.39	0.606	45.39	0.663	45.39
0.549	45.39	0.607	45.45	0.664	45.45
0.550	45.39	0.608	45.39	0.666	45.39
0.551	45.39	0.609	45.45	0.667	45.39
0.552	45.39	0.610	45.45	0.668	45.45
0.553	45.39	0.611	45.39	0.669	45.39
0.554	45.39	0.612	45.39	0.670	45.45
0.556	45.39	0.613	45.45	0.671	45.45
0.557	45.39	0.614	45.39	0.672	45.45
0.558	45.39	0.616	45.39	0.673	45.45
0.559	45.39	0.617	45.39	0.674	45.45
0.560	45.39	0.618	45.45	0.676	45.45
0.561	45.39	0.619	45.39	0.677	45.45
0.562	45.39	0.620	45.39	0.678	45.45
0.563	45.39	0.621	45.39	0.679	45.39
0.564	45.39	0.622	45.39	0.680	45.39
0.566	45.39	0.623	45.39	0.681	45.39
0.567	45.39	0.624	45.39	0.682	45.45
0.568	45.39	0.626	45.39	0.683	45.39
0.569	45.39	0.627	45.45	0.684	45.45
0.570	45.39	0.628	45.39	0.686	45.45
0.571	45.39	0.629	45.39	0.687	45.39
0.572	45.39	0.630	45.39	0.688	45.45
0.573	45.39	0.631	45.39	0.689	45.45
0.574	45.39	0.632	45.45	0.690	45.45

0.691	45.45	0.749	45.45	0.807	45.45
0.692	45.45	0.750	45.45	0.808	45.45
0.693	45.45	0.751	45.45	0.809	45.45
0.694	45.45	0.752	45.45	0.810	45.45
0.696	45.45	0.753	45.45	0.811	45.45
0.697	45.45	0.754	45.45	0.812	45.45
0.698	45.45	0.756	45.45	0.813	45.45
0.699	45.45	0.757	45.45	0.814	45.45
0.700	45.45	0.758	45.45	0.816	45.45
0.701	45.45	0.759	45.45	0.817	45.45
0.702	45.39	0.760	45.45	0.818	45.45
0.703	45.45	0.761	45.45	0.819	45.45
0.704	45.45	0.762	45.45	0.820	45.45
0.706	45.45	0.763	45.45	0.821	45.45
0.707	45.45	0.764	45.45	0.822	45.45
0.708	45.45	0.766	45.45	0.823	45.45
0.709	45.45	0.767	45.45	0.824	45.45
0.710	45.45	0.768	45.45	0.826	45.45
0.711	45.45	0.769	45.45	0.827	45.45
0.712	45.45	0.770	45.45	0.828	45.45
0.713	45.45	0.771	45.45	0.829	45.45
0.714	45.45	0.772	45.45	0.830	45.45
0.716	45.45	0.773	45.45	0.831	45.45
0.717	45.45	0.774	45.45	0.832	45.45
0.718	45.45	0.776	45.45	0.833	45.45
0.719	45.45	0.777	45.45	0.834	45.45
0.720	45.45	0.778	45.45	0.836	45.45
0.721	45.45	0.779	45.45	0.837	45.45
0.722	45.45	0.780	45.45	0.838	45.45
0.723	45.45	0.781	45.45	0.839	45.45
0.724	45.45	0.782	45.45	0.840	45.45
0.726	45.45	0.783	45.45	0.841	45.52
0.727	45.45	0.784	45.45	0.842	45.45
0.728	45.45	0.786	45.45	0.843	45.45
0.729	45.45	0.787	45.45	0.844	45.45
0.730	45.45	0.788	45.45	0.846	45.45
0.731	45.45	0.789	45.45	0.847	45.45
0.732	45.45	0.790	45.45	0.848	45.45
0.733	45.45	0.791	45.45	0.849	45.45
0.734	45.45	0.792	45.45	0.850	45.52
0.736	45.45	0.793	45.45	0.851	45.45
0.737	45.45	0.794	45.45	0.852	45.45
0.738	45.45	0.796	45.45	0.853	45.52
0.739	45.45	0.797	45.45	0.854	45.52
0.740	45.45	0.798	45.45	0.856	45.45
0.741	45.45	0.799	45.45	0.857	45.52
0.742	45.45	0.800	45.45	0.858	45.45
0.743	45.45	0.801	45.45	0.859	45.52
0.744	45.45	0.802	45.45	0.860	45.52
0.746	45.45	0.803	45.45	0.861	45.45
0.747	45.45	0.804	45.45	0.862	45.52
0.748	45.45	0.806	45.45	0.863	45.45

0.864	45.45	0.922	45.45	0.980	45.52
0.866	45.45	0.923	45.45	0.981	45.52
0.867	45.45	0.924	45.45	0.982	45.52
0.868	45.45	0.926	45.45	0.983	45.52
0.869	45.45	0.927	45.52	0.984	45.52
0.870	45.52	0.928	45.52	0.986	45.52
0.871	45.45	0.929	45.52	0.987	45.52
0.872	45.45	0.930	45.52	0.988	45.52
0.873	45.45	0.931	45.45	0.989	45.52
0.874	45.45	0.932	45.52	0.990	45.52
0.876	45.52	0.933	45.52	0.991	45.52
0.877	45.52	0.934	45.52	0.992	45.52
0.878	45.45	0.936	45.52	0.993	45.52
0.879	45.52	0.937	45.45	0.994	45.52
0.880	45.45	0.938	45.52	0.996	45.52
0.881	45.52	0.939	45.52	0.997	45.52
0.882	45.52	0.940	45.45	0.998	45.52
0.883	45.45	0.941	45.52	0.999	45.52
0.884	45.45	0.942	45.52	1.000	45.52
0.886	45.52	0.943	45.52	1.001	45.52
0.887	45.52	0.944	45.52	1.002	45.52
0.888	45.52	0.946	45.52	1.003	45.52
0.889	45.52	0.947	45.52	1.004	45.52
0.890	45.45	0.948	45.52	1.006	45.52
0.891	45.52	0.949	45.52	1.007	45.52
0.892	45.52	0.950	45.52	1.008	45.52
0.893	45.52	0.951	45.52	1.009	45.52
0.894	45.52	0.952	45.52	1.010	45.52
0.896	45.45	0.953	45.52	1.011	45.52
0.897	45.52	0.954	45.52	1.012	45.52
0.898	45.45	0.956	45.45	1.013	45.52
0.899	45.45	0.957	45.52	1.014	45.52
0.900	45.52	0.958	45.52	1.016	45.52
0.901	45.45	0.959	45.52	1.017	45.52
0.902	45.52	0.960	45.52	1.018	45.52
0.903	45.45	0.961	45.52	1.019	45.52
0.904	45.52	0.962	45.52	1.020	45.52
0.906	45.52	0.963	45.52	1.021	45.52
0.907	45.45	0.964	45.52	1.022	45.52
0.908	45.52	0.966	45.52	1.023	45.52
0.909	45.45	0.967	45.52	1.024	45.52
0.910	45.52	0.968	45.52	1.026	45.52
0.911	45.52	0.969	45.52	1.027	45.52
0.912	45.52	0.970	45.52	1.028	45.52
0.913	45.45	0.971	45.52	1.029	45.58
0.914	45.52	0.972	45.52	1.030	45.58
0.916	45.45	0.973	45.52	1.031	45.52
0.917	45.52	0.974	45.52	1.032	45.52
0.918	45.52	0.976	45.52	1.033	45.52
0.919	45.52	0.977	45.52	1.034	45.52
0.920	45.52	0.978	45.52	1.036	45.52
0.921	45.52	0.979	45.52	1.037	45.58

1.038	45.58	1.096	45.58	1.153	45.58
1.039	45.52	1.097	45.58	1.154	45.58
1.040	45.58	1.098	45.58	1.156	45.58
1.041	45.52	1.099	45.58	1.157	45.58
1.042	45.58	1.100	45.58	1.158	45.58
1.043	45.58	1.101	45.58	1.159	45.58
1.044	45.52	1.102	45.58	1.160	45.58
1.046	45.52	1.103	45.58	1.161	45.58
1.047	45.58	1.104	45.58	1.162	45.58
1.048	45.58	1.106	45.58	1.163	45.58
1.049	45.52	1.107	45.58	1.164	45.58
1.050	45.58	1.108	45.58	1.166	45.58
1.051	45.52	1.109	45.58	1.167	45.58
1.052	45.58	1.110	45.58	1.168	45.58
1.053	45.52	1.111	45.58	1.169	45.58
1.054	45.58	1.112	45.58	1.170	45.58
1.056	45.58	1.113	45.58	1.171	45.58
1.057	45.58	1.114	45.58	1.172	45.58
1.058	45.52	1.116	45.58	1.173	45.58
1.059	45.52	1.117	45.58	1.174	45.58
1.060	45.58	1.118	45.58	1.176	45.58
1.061	45.58	1.119	45.58	1.177	45.58
1.062	45.58	1.120	45.58	1.178	45.58
1.063	45.58	1.121	45.58	1.179	45.58
1.064	45.58	1.122	45.58	1.180	45.58
1.066	45.52	1.123	45.58	1.181	45.58
1.067	45.58	1.124	45.58	1.182	45.58
1.068	45.58	1.126	45.58	1.183	45.58
1.069	45.58	1.127	45.58	1.184	45.58
1.070	45.58	1.128	45.58	1.186	45.58
1.071	45.58	1.129	45.58	1.187	45.58
1.072	45.58	1.130	45.58	1.188	45.58
1.073	45.58	1.131	45.58	1.189	45.58
1.074	45.58	1.132	45.58	1.190	45.58
1.076	45.58	1.133	45.58	1.191	45.58
1.077	45.58	1.134	45.58	1.192	45.58
1.078	45.52	1.136	45.58	1.193	45.58
1.079	45.58	1.137	45.58	1.194	45.58
1.080	45.58	1.138	45.58	1.196	45.58
1.081	45.58	1.139	45.58	1.197	45.58
1.082	45.58	1.140	45.58	1.198	45.58
1.083	45.58	1.141	45.58	1.199	45.58
1.084	45.58	1.142	45.58	1.200	45.58
1.086	45.58	1.143	45.58	1.201	45.58
1.087	45.58	1.144	45.58	1.202	45.58
1.088	45.58	1.146	45.58	1.203	45.58
1.089	45.58	1.147	45.58	1.204	45.58
1.090	45.58	1.148	45.58	1.206	45.58
1.091	45.58	1.149	45.58	1.207	45.58
1.092	45.58	1.150	45.58	1.208	45.58
1.093	45.58	1.151	45.58	1.209	45.58
1.094	45.58	1.152	45.58	1.210	45.58

1.211	45.58	1.269	45.58	1.327	45.58
1.212	45.58	1.270	45.58	1.328	45.58
1.213	45.58	1.271	45.58	1.329	45.58
1.214	45.58	1.272	45.58	1.330	45.58
1.216	45.58	1.273	45.58	1.331	45.58
1.217	45.58	1.274	45.58	1.332	45.58
1.218	45.58	1.276	45.58	1.333	45.52
1.219	45.58	1.277	45.58	1.334	45.45
1.220	45.58	1.278	45.58	1.336	45.39
1.221	45.58	1.279	45.58	1.337	45.33
1.222	45.58	1.280	45.58	1.338	45.20
1.223	45.58	1.281	45.58	1.339	45.20
1.224	45.58	1.282	45.58	1.340	45.14
1.226	45.58	1.283	45.58	1.341	45.14
1.227	45.58	1.284	45.58	1.342	45.14
1.228	45.58	1.286	45.58	1.343	45.14
1.229	45.58	1.287	45.58	1.344	45.14
1.230	45.58	1.288	45.58	1.346	45.08
1.231	45.58	1.289	45.58	1.347	45.14
1.232	45.58	1.290	45.58	1.348	45.08
1.233	45.58	1.291	45.58	1.349	45.08
1.234	45.58	1.292	45.58	1.350	45.08
1.236	45.58	1.293	45.58	1.351	45.08
1.237	45.58	1.294	45.58	1.352	45.08
1.238	45.58	1.296	45.58	1.353	45.08
1.239	45.58	1.297	45.58	1.354	45.08
1.240	45.58	1.298	45.58	1.356	45.08
1.241	45.58	1.299	45.58	1.357	45.08
1.242	45.58	1.300	45.58	1.358	45.08
1.243	45.58	1.301	45.58	1.359	45.08
1.244	45.58	1.302	45.58	1.360	45.08
1.246	45.58	1.303	45.58	1.361	45.08
1.247	45.58	1.304	45.58	1.362	45.14
1.248	45.58	1.306	45.58	1.363	45.08
1.249	45.58	1.307	45.58	1.364	45.08
1.250	45.58	1.308	45.58	1.366	45.08
1.251	45.58	1.309	45.58	1.367	45.08
1.252	45.58	1.310	45.58	1.368	45.08
1.253	45.58	1.311	45.58	1.369	45.14
1.254	45.58	1.312	45.58	1.370	45.14
1.256	45.58	1.313	45.58	1.371	45.14
1.257	45.58	1.314	45.58	1.372	45.14
1.258	45.58	1.316	45.58	1.373	45.14
1.259	45.58	1.317	45.58	1.374	45.14
1.260	45.58	1.318	45.58	1.376	45.14
1.261	45.58	1.319	45.58	1.377	45.14
1.262	45.58	1.320	45.58		
1.263	45.58	1.321	45.58		
1.264	45.58	1.322	45.58		
1.266	45.58	1.323	45.58		
1.267	45.58	1.324	45.58		
1.268	45.58	1.326	45.58		

Appendix D: Pump Pressure Data and External Transducer Data During Solubility Run of May 3/00

Time (Hours)	Transducer Pressure (MPa)	Pump Pressure (MPa)
0.00	-0.06	10.34
0.00	-0.06	10.34
0.00	0.10	10.34
0.00	0.00	10.34
0.00	-0.06	10.34
0.00	0.11	10.34
0.00	-0.09	10.34
0.00	0.10	10.34
0.00	0.06	10.34
0.01	0.03	10.34
0.01	0.01	10.34
0.01	0.13	10.34
0.01	0.07	10.34
0.01	0.12	10.34
0.01	0.09	10.34
0.01	-0.02	10.34
0.01	-0.06	10.34
0.01	0.09	10.34
0.01	0.11	10.34
0.01	-0.06	10.34
0.01	-0.01	10.34
0.01	0.02	10.34
0.01	0.10	10.34
0.01	-0.04	10.34
0.01	-0.03	10.34
0.01	-0.01	10.34
0.01	0.08	10.34
0.02	0.02	10.29
0.02	0.08	10.39
0.02	0.07	10.47
0.02	0.06	10.39
0.02	0.01	10.34
0.02	0.10	10.34
0.02	-0.11	10.34
0.02	0.05	10.34
0.02	0.04	10.34
0.02	-0.02	10.34
0.02	-0.02	10.34
0.02	-0.04	10.34
0.02	0.05	10.34
0.02	0.07	10.34
0.02	0.08	10.34
0.02	0.15	10.34
0.02	0.04	10.34
0.02	0.08	10.34
0.03	-0.04	10.34
0.03	0.13	10.34
0.03	-0.01	10.34
0.03	0.11	10.34
0.03	0.10	10.34
0.03	0.09	10.34
0.03	-0.06	10.34
0.03	-0.05	10.34
0.03	0.04	10.34
0.03	-0.06	10.34
0.03	0.11	10.34
0.03	0.08	10.34
0.03	0.10	10.34
0.03	0.06	10.34
0.03	0.00	10.34
0.03	0.03	10.34
0.03	-0.02	10.34
0.03	-0.02	10.34
0.04	-0.03	10.34
0.04	0.05	10.34
0.04	0.08	10.34
0.04	0.14	10.34
0.04	-0.02	10.34
0.04	0.04	10.34
0.04	-0.06	10.34
0.04	-0.06	10.34
0.04	-0.09	10.34
0.04	-0.04	10.34
0.04	-0.03	10.34
0.04	0.06	10.34
0.04	0.09	10.34
0.04	-0.09	10.34
0.04	0.09	10.34
0.04	-0.02	10.34
0.04	-0.09	10.34
0.04	0.12	10.34
0.05	-0.04	10.34
0.05	-0.07	10.34
0.05	0.13	10.34
0.05	-0.02	10.34
0.05	0.08	10.34
0.05	0.11	10.34
0.05	-0.06	10.34
0.05	0.05	10.34
0.05	0.09	10.34
0.05	-0.04	10.34
0.05	8.40	10.22
0.05	8.49	10.30
0.05	8.83	10.40
0.05	9.02	10.48
0.05	10.06	10.41
0.05	10.37	10.34
0.05	10.30	10.34
0.05	10.07	10.34
0.06	10.22	10.34
0.06	10.22	10.34

0.06	10.23	10.34	0.09	10.27	10.34
0.06	10.28	10.34	0.09	10.26	10.34
0.06	10.34	10.34	0.09	10.39	10.34
0.06	10.31	10.34	0.09	10.36	10.34
0.06	10.28	10.34	0.09	10.39	10.34
0.06	10.30	10.34	0.09	10.18	10.34
0.06	10.34	10.34	0.09	10.38	10.34
0.06	10.31	10.34	0.09	10.35	10.34
0.06	10.29	10.34	0.09	10.37	10.34
0.06	10.26	10.34	0.09	10.25	10.34
0.06	10.27	10.34	0.09	10.27	10.34
0.06	10.26	10.34	0.09	10.32	10.34
0.06	10.34	10.34	0.09	10.31	10.34
0.06	10.34	10.34	0.09	10.24	10.34
0.06	10.32	10.34	0.09	10.36	10.34
0.06	10.27	10.34	0.09	10.42	10.34
0.07	10.27	10.34	0.09	10.39	10.34
0.07	10.28	10.34	0.09	10.28	10.34
0.07	10.29	10.34	0.10	10.24	10.34
0.07	10.30	10.34	0.10	10.38	10.34
0.07	10.32	10.34	0.10	10.37	10.34
0.07	10.28	10.34	0.10	10.22	10.34
0.07	10.31	10.34	0.10	10.36	10.34
0.07	10.28	10.34	0.10	10.27	10.34
0.07	10.35	10.34	0.10	10.35	10.34
0.07	10.31	10.34	0.10	10.28	10.34
0.07	10.30	10.34	0.10	10.36	10.34
0.07	10.31	10.34	0.10	10.26	10.34
0.07	10.29	10.34	0.10	10.26	10.34
0.07	10.31	10.34	0.10	10.26	10.34
0.07	10.34	10.34	0.10	10.35	10.34
0.07	10.32	10.34	0.10	10.27	10.34
0.07	10.36	10.34	0.10	10.26	10.34
0.07	10.36	10.34	0.10	10.24	10.34
0.08	10.29	10.34	0.10	10.44	10.34
0.08	10.28	10.34	0.10	10.37	10.34
0.08	10.35	10.34	0.11	10.33	10.34
0.08	10.39	10.34	0.11	10.43	10.34
0.08	10.32	10.34	0.11	10.36	10.34
0.08	10.29	10.34	0.11	10.41	10.34
0.08	10.41	10.34	0.11	10.42	10.34
0.08	10.27	10.34	0.11	10.35	10.34
0.08	10.27	10.34	0.11	10.21	10.34
0.08	10.39	10.34	0.11	10.35	10.34
0.08	10.24	10.34	0.11	10.17	10.34
0.08	10.26	10.34	0.11	10.36	10.34
0.08	10.36	10.34	0.11	10.42	10.34
0.08	10.39	10.34	0.11	10.29	10.34
0.08	10.22	10.34	0.11	10.35	10.34
0.08	10.32	10.34	0.11	10.17	10.34
0.08	10.30	10.34	0.11	10.42	10.34
0.08	10.37	10.34	0.11	10.36	10.34

0.11	10.38	10.34	0.14	10.32	10.34
0.11	10.23	10.34	0.14	10.25	10.34
0.12	10.28	10.34	0.14	10.35	10.34
0.12	10.33	10.34	0.14	10.19	10.34
0.12	10.26	10.34	0.15	10.19	10.34
0.12	10.41	10.34	0.15	10.37	10.34
0.12	10.18	10.34	0.15	10.27	10.34
0.12	10.35	10.34	0.15	10.39	10.34
0.12	10.40	10.34	0.15	10.21	10.34
0.12	10.37	10.34	0.15	10.25	10.34
0.12	10.39	10.34	0.15	10.24	10.34
0.12	10.23	10.34	0.15	10.20	10.34
0.12	10.24	10.34	0.15	10.27	10.34
0.12	10.41	10.34	0.15	10.36	10.34
0.12	10.25	10.34	0.15	10.33	10.34
0.12	10.23	10.34	0.15	10.31	10.34
0.12	10.40	10.34	0.15	10.38	10.34
0.12	10.20	10.34	0.15	10.34	10.34
0.12	10.36	10.34	0.15	10.25	10.34
0.12	10.23	10.34	0.15	10.22	10.34
0.13	10.22	10.34	0.15	10.40	10.34
0.13	10.38	10.34	0.15	10.26	10.34
0.13	10.29	10.34	0.16	10.22	10.34
0.13	10.21	10.34	0.16	10.28	10.34
0.13	10.37	10.34	0.16	10.31	10.34
0.13	10.23	10.34	0.16	10.37	10.15
0.13	10.40	10.34	0.16	10.32	10.21
0.13	10.36	10.34	0.16	10.34	10.38
0.13	10.27	10.34	0.16	10.28	10.48
0.13	10.27	10.34	0.16	10.28	10.40
0.13	10.27	10.34	0.16	10.32	10.34
0.13	10.42	10.34	0.16	10.30	10.34
0.13	10.24	10.34	0.16	10.27	10.34
0.13	10.32	10.34	0.16	10.21	10.34
0.13	10.28	10.34	0.16	10.31	10.34
0.13	10.42	10.34	0.16	10.33	10.34
0.13	10.31	10.34	0.16	10.07	10.34
0.13	10.20	10.34	0.16	10.32	10.34
0.14	10.38	10.34	0.16	10.31	10.34
0.14	10.20	10.34	0.16	10.16	10.34
0.14	10.22	10.34	0.17	10.37	10.34
0.14	10.22	10.34	0.17	10.36	10.34
0.14	10.23	10.34	0.17	10.35	10.34
0.14	10.22	10.34	0.17	10.51	10.34
0.14	10.44	10.34	0.17	10.56	10.34
0.14	10.39	10.34	0.17	10.36	10.34
0.14	10.36	10.34	0.17	10.50	10.34
0.14	10.42	10.34	0.17	10.60	10.34
0.14	10.22	10.34	0.17	10.53	10.34
0.14	10.34	10.34	0.17	10.43	10.34
0.14	10.38	10.34	0.17	10.40	10.34
0.14	10.27	10.34	0.17	10.51	10.34

0.17	10.47	10.34	0.20	10.45	10.34
0.17	10.58	10.34	0.20	10.32	10.34
0.17	10.55	10.34	0.20	10.40	10.34
0.17	10.42	10.34	0.20	10.32	10.34
0.17	10.36	10.34	0.20	10.31	10.34
0.17	10.42	10.34	0.20	10.52	10.34
0.18	10.36	10.34	0.20	10.45	10.34
0.18	10.50	10.34	0.20	10.37	10.34
0.18	10.49	10.34	0.21	10.47	10.34
0.18	10.48	10.34	0.21	10.47	10.34
0.18	10.54	10.34	0.21	10.43	10.34
0.18	10.43	10.34	0.21	10.34	10.34
0.18	10.59	10.34	0.21	10.33	10.34
0.18	10.60	10.34	0.21	10.46	10.34
0.18	10.37	10.34	0.21	10.43	10.34
0.18	10.41	10.34	0.21	10.34	10.34
0.18	10.51	10.34	0.21	10.42	10.34
0.18	10.35	10.34	0.21	10.28	10.34
0.18	10.50	10.34	0.21	10.30	10.34
0.18	10.37	10.34	0.21	10.45	10.34
0.18	10.30	10.34	0.21	10.54	10.34
0.18	10.35	10.34	0.21	10.51	10.34
0.18	10.41	10.34	0.21	10.44	10.34
0.18	10.52	10.34	0.21	10.35	10.34
0.19	10.57	10.34	0.21	10.28	10.34
0.19	10.44	10.34	0.21	10.25	10.34
0.19	10.37	10.34	0.22	10.32	10.34
0.19	10.53	10.34	0.22	10.26	10.34
0.19	10.45	10.34	0.22	10.43	10.34
0.19	10.47	10.34	0.22	10.30	10.34
0.19	10.50	10.34	0.22	10.45	10.34
0.19	10.41	10.34	0.22	10.21	10.34
0.19	10.36	10.34	0.22	10.29	10.34
0.19	10.40	10.34	0.22	10.25	10.34
0.19	10.54	10.34	0.22	10.41	10.34
0.19	10.48	10.34	0.22	10.45	10.34
0.19	10.33	10.34	0.22	10.23	10.34
0.19	10.42	10.34	0.22	10.45	10.34
0.19	10.37	10.34	0.22	10.20	10.34
0.19	10.54	10.34	0.22	10.25	10.34
0.19	10.53	10.34	0.22	10.22	10.34
0.19	10.54	10.34	0.22	10.34	10.34
0.20	10.53	10.34	0.22	10.39	10.34
0.20	10.37	10.34	0.22	10.25	10.34
0.20	10.53	10.34	0.23	10.43	10.34
0.20	10.58	10.34	0.23	10.31	10.34
0.20	10.46	10.34	0.23	10.28	10.34
0.20	10.39	10.34	0.23	10.28	10.34
0.20	10.25	10.34	0.23	10.23	10.34
0.20	10.39	10.34	0.23	10.30	10.34
0.20	10.32	10.34	0.23	10.35	10.34
0.20	10.44	10.34	0.23	10.39	10.34

0.23	10.44	10.34	0.26	10.36	10.34
0.23	10.32	10.34	0.26	10.45	10.34
0.23	10.23	10.34	0.26	10.34	10.34
0.23	10.36	10.34	0.26	10.36	10.34
0.23	10.28	10.34	0.26	10.41	10.34
0.23	10.29	10.34	0.26	10.26	10.34
0.23	10.48	10.34	0.26	10.38	10.34
0.23	10.22	10.34	0.26	10.39	10.34
0.23	10.40	10.34	0.26	10.38	10.34
0.23	10.50	10.34	0.26	10.21	10.34
0.24	10.38	10.34	0.26	10.25	10.34
0.24	10.27	10.34	0.26	10.34	10.34
0.24	10.45	10.34	0.27	10.41	10.34
0.24	10.38	10.34	0.27	10.37	10.34
0.24	10.28	10.34	0.27	10.18	10.34
0.24	10.26	10.34	0.27	10.20	10.34
0.24	10.39	10.34	0.27	10.33	10.34
0.24	10.29	10.34	0.27	10.27	10.34
0.24	10.25	10.34	0.27	10.36	10.34
0.24	10.39	10.34	0.27	10.22	10.34
0.24	10.31	10.34	0.27	10.21	10.34
0.24	10.23	10.34	0.27	10.18	10.34
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0.24	10.38	10.34	0.27	10.36	10.34
0.24	10.40	10.34	0.27	10.41	10.34
0.25	10.31	10.34	0.27	10.28	10.34
0.25	10.38	10.34	0.27	10.35	10.34
0.25	10.36	10.34	0.28	10.19	10.34
0.25	10.33	10.34	0.28	10.23	10.34
0.25	10.19	10.34	0.28	10.43	10.34
0.25	10.21	10.34	0.28	10.39	10.34
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0.25	10.39	10.34	0.28	10.37	10.34
0.25	10.40	10.34	0.28	10.37	10.34
0.25	10.41	10.34	0.28	10.41	10.34
0.25	10.38	10.34	0.28	10.23	10.34
0.25	10.32	10.34	0.28	10.25	10.34
0.25	10.22	10.34	0.28	10.39	10.34
0.25	10.34	10.34	0.28	10.30	10.34
0.25	10.36	10.34	0.28	10.35	10.34
0.26	10.26	10.34	0.28	10.20	10.34
0.26	10.27	10.34	0.28	10.42	10.34
0.26	10.25	10.34	0.29	10.35	10.34
0.26	10.21	10.34	0.29	10.29	10.34
0.26	10.20	10.34	0.29	10.22	10.34
0.26	10.30	10.34	0.29	10.25	10.34

0.29	10.21	10.34	0.32	10.40	10.34
0.29	10.18	10.34	0.32	10.28	10.34
0.29	10.37	10.34	0.32	10.39	10.34
0.29	10.23	10.34	0.32	10.23	10.34
0.29	10.18	10.34	0.32	10.33	10.34
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0.29	10.36	10.34	0.32	10.43	10.34
0.29	10.28	10.34	0.32	10.31	10.34
0.29	10.23	10.34	0.32	10.44	10.34
0.29	10.41	10.34	0.32	10.17	10.34
0.29	10.27	10.34	0.32	10.42	10.34
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0.30	10.38	10.34	0.33	10.21	10.34
0.30	10.36	10.34	0.33	10.21	10.34
0.30	10.21	10.34	0.33	10.39	10.34
0.30	10.23	10.34	0.33	10.23	10.34
0.30	10.20	10.34	0.33	10.16	10.34
0.30	10.19	10.34	0.33	10.23	10.34
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0.30	10.25	10.34	0.33	10.25	10.34
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0.30	10.18	10.34	0.33	10.38	10.34
0.30	10.26	10.34	0.33	10.25	10.34
0.30	10.24	10.34	0.33	10.34	10.34
0.30	10.20	10.34	0.33	10.28	10.34
0.30	10.24	10.34	0.33	10.45	10.34
0.30	10.43	10.34	0.33	10.27	10.34
0.31	10.34	10.34	0.33	10.31	10.34
0.31	10.39	10.34	0.33	10.37	10.34
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0.31	10.25	10.34	0.34	10.36	10.34
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0.31	10.32	10.34	0.34	10.38	10.34
0.31	10.42	10.34	0.34	10.36	10.34
0.31	10.41	10.34	0.34	10.33	10.34
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0.31	10.24	10.34	0.34	10.33	10.34
0.31	10.26	10.34	0.34	10.39	10.34
0.31	10.32	10.34	0.34	10.31	10.34
0.31	10.37	10.34	0.34	10.30	10.34
0.31	10.28	10.34	0.34	10.25	10.34
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0.31	10.35	10.34	0.34	10.40	10.34
0.32	10.34	10.34	0.34	10.36	10.34
0.32	10.28	10.34	0.34	10.33	10.34

0.35	10.37	10.34	0.37	10.27	10.34
0.35	10.18	10.34	0.37	10.35	10.34
0.35	10.25	10.34	0.38	10.18	10.34
0.35	10.40	10.34	0.38	10.15	10.34
0.35	10.34	10.34	0.38	10.21	10.34
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0.36	10.41	10.34	0.39	10.39	10.34
0.36	10.39	10.34	0.39	10.25	10.34
0.37	10.41	10.34	0.39	10.33	10.34
0.37	10.42	10.34	0.39	10.23	10.34
0.37	10.15	10.34	0.40	10.44	10.34
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0.37	10.23	10.34	0.40	10.36	10.34
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0.37	10.23	10.34	0.40	10.36	10.34
0.37	10.39	10.34	0.40	10.43	10.34
0.37	10.40	10.34	0.40	10.17	10.34
0.37	10.32	10.34	0.40	10.22	10.34
0.37	10.27	10.34	0.40	10.37	10.34
0.37	10.37	10.34	0.40	10.24	10.34
0.37	10.41	10.34	0.40	10.26	10.34
0.37	10.26	10.34	0.40	10.35	10.34
0.37	10.33	10.34	0.40	10.32	10.34

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0.40	10.26	10.34	0.43	10.21	10.34
0.40	10.41	10.34	0.43	10.22	10.34
0.40	10.26	10.34	0.43	10.23	10.34
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0.41	10.21	10.34	0.44	10.23	10.34
0.41	10.40	10.34	0.44	10.30	10.34
0.41	10.44	10.34	0.44	10.38	10.34
0.41	10.39	10.34	0.44	10.38	10.34
0.41	10.37	10.34	0.44	10.26	10.34
0.41	10.29	10.34	0.44	10.23	10.34
0.41	10.21	10.34	0.44	10.33	10.34
0.41	10.43	10.34	0.44	10.25	10.34
0.41	10.42	10.34	0.44	10.40	10.34
0.41	10.40	10.34	0.44	10.26	10.34
0.41	10.20	10.34	0.44	10.38	10.34
0.41	10.23	10.34	0.44	10.30	10.34
0.41	10.26	10.34	0.44	10.23	10.34
0.41	10.39	10.34	0.44	10.38	10.34
0.41	10.36	10.34	0.44	10.33	10.34
0.41	10.42	10.34	0.44	10.19	10.34
0.42	10.39	10.34	0.44	10.29	10.34
0.42	10.42	10.34	0.44	10.21	10.34
0.42	10.30	10.34	0.45	10.28	10.34
0.42	10.25	10.34	0.45	10.29	10.34
0.42	10.43	10.34	0.45	10.42	10.34
0.42	10.34	10.34	0.45	10.26	10.34
0.42	10.34	10.34	0.45	10.39	10.34
0.42	10.35	10.34	0.45	10.28	10.34
0.42	10.29	10.34	0.45	10.29	10.34
0.42	10.23	10.34	0.45	10.26	10.34
0.42	10.37	10.34	0.45	10.22	10.34
0.42	10.31	10.34	0.45	10.23	10.34
0.42	10.28	10.34	0.45	10.40	10.34
0.42	10.44	10.34	0.45	10.43	10.34
0.42	10.35	10.34	0.45	10.22	10.34
0.42	10.44	10.34	0.45	10.25	10.34
0.42	10.36	10.34	0.45	10.23	10.34
0.42	10.25	10.34	0.45	10.41	10.34
0.43	10.33	10.34	0.45	10.22	10.34
0.43	10.43	10.34	0.45	10.22	10.34
0.43	10.24	10.34	0.46	10.21	10.34
0.43	10.29	10.34	0.46	10.26	10.34
0.43	10.21	10.34	0.46	10.19	10.34
0.43	10.27	10.34	0.46	10.51	10.34
0.43	10.42	10.34	0.46	10.41	10.34
0.43	10.38	10.34	0.46	10.25	10.34
0.43	10.30	10.34	0.46	10.43	10.34
0.43	10.43	10.34	0.46	10.38	10.34
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0.43	10.39	10.34	0.46	10.42	10.34

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0.46	10.41	10.34	0.49	10.34	10.34
0.46	10.34	10.34	0.49	10.34	10.34
0.46	10.43	10.34	0.49	10.23	10.34
0.46	10.41	10.34	0.49	10.25	10.34
0.46	10.39	10.34	0.49	10.26	10.34
0.46	10.34	10.34	0.49	10.34	10.34
0.47	10.32	10.34	0.49	10.27	10.34
0.47	10.20	10.34	0.49	10.23	10.34
0.47	10.36	10.34	0.50	10.41	10.34
0.47	10.43	10.34	0.50	10.21	10.34
0.47	10.28	10.34	0.50	10.32	10.34
0.47	10.35	10.34	0.50	10.33	10.34
0.47	10.24	10.34	0.50	10.39	10.34
0.47	10.30	10.34	0.50	10.21	10.34
0.47	10.23	10.34	0.50	10.26	10.34
0.47	10.19	10.34	0.50	10.40	10.34
0.47	10.38	10.34	0.50	10.28	10.34
0.47	10.41	10.34	0.50	10.26	10.34
0.47	10.41	10.34	0.50	10.29	10.34
0.47	10.28	10.34	0.50	10.41	10.34
0.47	10.33	10.34	0.50	10.32	10.34
0.47	10.30	10.34	0.50	10.41	10.34
0.47	10.31	10.34	0.50	10.40	10.34
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0.48	10.45	10.34	0.50	10.25	10.34
0.48	10.35	10.34	0.50	10.45	10.34
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0.48	10.38	10.34	0.51	10.25	10.34
0.48	10.44	10.34	0.51	10.25	10.34
0.48	10.27	10.34	0.51	10.28	10.34
0.48	10.39	10.34	0.51	10.40	10.34
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0.48	10.44	10.34	0.51	10.21	10.34
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0.48	10.26	10.34	0.51	10.28	10.34
0.48	10.24	10.34	0.51	10.21	10.34
0.48	10.25	10.34	0.51	10.22	10.34
0.48	10.28	10.34	0.51	10.27	10.34
0.48	10.38	10.34	0.51	10.23	10.34
0.48	10.29	10.34	0.51	10.41	10.34
0.48	10.45	10.34	0.51	10.40	10.34
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0.49	10.30	10.34	0.52	10.44	10.34

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0.52	10.41	10.34	0.55	10.37	10.34
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0.55	10.22	10.34	0.57	10.22	10.34
0.55	10.33	10.34	0.57	10.32	10.34
0.55	10.40	10.34	0.58	10.32	10.34
0.55	10.38	10.34	0.58	10.39	10.34

0.58	10.23	10.34	0.61	10.34	10.34
0.58	10.23	10.34	0.61	10.37	10.34
0.58	10.37	10.34	0.61	10.24	10.34
0.58	10.48	10.34	0.61	10.40	10.34
0.58	10.25	10.34	0.61	10.34	10.34
0.58	10.26	10.34	0.61	10.35	10.34
0.58	10.43	10.34	0.61	10.44	10.34
0.58	10.44	10.34	0.61	10.46	10.34
0.58	10.28	10.34	0.61	10.21	10.34
0.58	10.39	10.34	0.61	10.29	10.34
0.58	10.38	10.34	0.61	10.36	10.34
0.58	10.34	10.34	0.61	10.27	10.34
0.58	10.24	10.34	0.61	10.25	10.34
0.58	10.42	10.34	0.61	10.42	10.34
0.58	10.36	10.34	0.61	10.30	10.34
0.58	10.29	10.34	0.61	10.29	10.34
0.59	10.42	10.34	0.61	10.24	10.34
0.59	10.24	10.34	0.61	10.21	10.34
0.59	10.25	10.34	0.62	10.35	10.34
0.59	10.25	10.34	0.62	10.28	10.34
0.59	10.38	10.34	0.62	10.30	10.34
0.59	10.38	10.34	0.62	10.44	10.34
0.59	10.31	10.34	0.62	10.37	10.34
0.59	10.33	10.34	0.62	10.34	10.34
0.59	10.24	10.34	0.62	10.45	10.34
0.59	10.35	10.34	0.62	10.40	10.34
0.59	10.35	10.34	0.62	10.45	10.34
0.59	10.37	10.34	0.62	10.40	10.34
0.59	10.35	10.34	0.62	10.37	10.34
0.59	10.39	10.34	0.62	10.45	10.34
0.59	10.41	10.34	0.62	10.31	10.34
0.59	10.38	10.34	0.62	10.21	10.34
0.59	10.33	10.34	0.62	10.22	10.34
0.59	10.24	10.34	0.62	10.25	10.34
0.60	10.26	10.34	0.62	10.46	10.34
0.60	10.27	10.34	0.62	10.21	10.34
0.60	10.41	10.34	0.63	10.24	10.34
0.60	10.29	10.34	0.63	10.21	10.34
0.60	10.29	10.34	0.63	10.42	10.34
0.60	10.27	10.34	0.63	10.22	10.34
0.60	10.29	10.34	0.63	10.41	10.34
0.60	10.32	10.34	0.63	10.38	10.34
0.60	10.37	10.34	0.63	10.38	10.34
0.60	10.41	10.34	0.63	10.26	10.34
0.60	10.39	10.34	0.63	10.35	10.34
0.60	10.25	10.34	0.63	10.38	10.34
0.60	10.27	10.34	0.63	10.24	10.34
0.60	10.29	10.34	0.63	10.42	10.34
0.60	10.38	10.34	0.63	10.37	10.34
0.60	10.42	10.34	0.63	10.33	10.34
0.60	10.34	10.34	0.63	10.26	10.34
0.60	10.24	10.34	0.63	10.24	10.34

0.63	10.40	10.34	0.66	10.34	10.34
0.63	10.42	10.34	0.66	10.16	10.34
0.64	10.19	10.34	0.66	10.19	10.34
0.64	10.43	10.34	0.66	10.23	10.34
0.64	10.28	10.34	0.67	10.23	10.34
0.64	10.47	10.34	0.67	10.29	10.34
0.64	10.21	10.34	0.67	10.38	10.34
0.64	10.40	10.34	0.67	10.34	10.34
0.64	10.44	10.34	0.67	10.39	10.34
0.64	10.41	10.34	0.67	10.28	10.34
0.64	10.27	10.34	0.67	10.41	10.34
0.64	10.25	10.34	0.67	10.35	10.34
0.64	10.23	10.34	0.67	10.38	10.34
0.64	10.43	10.34	0.67	10.23	10.34
0.64	10.26	10.34	0.67	10.25	10.34
0.64	10.24	10.34	0.67	10.41	10.34
0.64	10.34	10.34	0.67	10.30	10.34
0.64	10.22	10.34	0.67	10.32	10.34
0.64	10.34	10.34	0.67	10.27	10.34
0.64	10.37	10.34	0.67	10.25	10.34
0.65	10.21	10.34	0.67	10.37	10.34
0.65	10.37	10.34	0.67	10.38	10.34
0.65	10.42	10.34	0.68	10.34	10.34
0.65	10.24	10.34	0.68	10.24	10.34
0.65	10.21	10.34	0.68	10.37	10.34
0.65	10.29	10.34	0.68	10.46	10.34
0.65	10.34	10.34	0.68	10.19	10.34
0.65	10.40	10.34	0.68	10.25	10.34
0.65	10.25	10.34	0.68	10.27	10.34
0.65	10.36	10.34	0.68	10.27	10.34
0.65	10.25	10.34	0.68	10.37	10.34
0.65	10.28	10.34	0.68	10.26	10.34
0.65	10.32	10.34	0.68	10.46	10.34
0.65	10.42	10.34	0.68	10.44	10.34
0.65	10.33	10.34	0.68	10.23	10.34
0.65	10.32	10.34	0.68	10.19	10.34
0.65	10.34	10.34	0.68	10.21	10.34
0.65	10.30	10.34	0.68	10.30	10.34
0.66	10.39	10.34	0.68	10.24	10.34
0.66	10.27	10.34	0.68	10.21	10.34
0.66	10.31	10.34	0.69	10.21	10.34
0.66	10.35	10.34	0.69	10.43	10.34
0.66	10.33	10.34	0.69	10.40	10.34
0.66	10.28	10.34	0.69	10.43	10.34
0.66	10.30	10.34	0.69	10.24	10.34
0.66	10.25	10.34	0.69	10.23	10.34
0.66	10.42	10.34	0.69	10.42	10.34
0.66	10.18	10.34	0.69	10.41	10.34
0.66	10.27	10.34	0.69	10.25	10.34
0.66	10.20	10.34	0.69	10.43	10.34
0.66	10.36	10.34	0.69	10.33	10.34
0.66	10.26	10.34	0.69	10.32	10.34

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0.69	10.46	10.34	0.72	10.44	10.34
0.69	10.40	10.34	0.72	10.42	10.34
0.69	10.33	10.34	0.72	10.26	10.34
0.69	10.23	10.34	0.72	10.37	10.34
0.69	10.44	10.34	0.72	10.20	10.34
0.69	10.38	10.34	0.72	10.29	10.34
0.69	10.22	10.34	0.72	10.28	10.34
0.70	10.42	10.34	0.72	10.22	10.34
0.70	10.35	10.34	0.73	10.40	10.34
0.70	10.37	10.34	0.73	10.38	10.34
0.70	10.43	10.34	0.73	10.36	10.34
0.70	10.28	10.34	0.73	10.36	10.34
0.70	10.41	10.34	0.73	10.31	10.34
0.70	10.24	10.34	0.73	10.39	10.34
0.70	10.44	10.34	0.73	10.42	10.34
0.70	10.24	10.34	0.73	10.42	10.34
0.70	10.40	10.34	0.73	10.30	10.34
0.70	10.19	10.34	0.73	10.26	10.34
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0.70	10.45	10.34	0.73	10.34	10.34
0.70	10.40	10.34	0.73	10.35	10.34
0.70	10.32	10.34	0.73	10.41	10.34
0.70	10.44	10.34	0.73	10.24	10.34
0.71	10.40	10.34	0.73	10.28	10.34
0.71	10.28	10.34	0.73	10.38	10.34
0.71	10.25	10.34	0.73	10.35	10.34
0.71	10.48	10.34	0.74	10.35	10.34
0.71	10.42	10.34	0.74	10.35	10.34
0.71	10.28	10.34	0.74	10.36	10.34
0.71	10.38	10.34	0.74	10.31	10.34
0.71	10.29	10.34	0.74	10.31	10.34
0.71	10.39	10.34	0.74	10.31	10.34
0.71	10.44	10.34	0.74	10.41	10.34
0.71	10.28	10.34	0.74	10.44	10.34
0.71	10.41	10.34	0.74	10.38	10.34
0.71	10.37	10.34	0.74	10.45	10.34
0.71	10.33	10.34	0.74	10.25	10.34
0.71	10.39	10.34	0.74	10.29	10.34
0.71	10.40	10.34	0.74	10.24	10.34
0.71	10.29	10.34	0.74	10.24	10.34
0.71	10.36	10.34	0.74	10.24	10.34
0.71	10.45	10.34	0.74	10.41	10.34
0.72	10.41	10.34	0.74	10.31	10.34
0.72	10.32	10.34	0.75	10.23	10.34
0.72	10.21	10.34	0.75	10.26	10.34
0.72	10.33	10.34	0.75	10.41	10.34
0.72	10.29	10.34	0.75	10.38	10.34
0.72	10.23	10.34	0.75	10.23	10.34
0.72	10.39	10.34	0.75	10.33	10.34
0.72	10.30	10.34	0.75	10.39	10.34
0.72	10.20	10.34	0.75	10.47	10.34

0.75	10.33	10.34	0.78	10.34	10.34
0.75	10.24	10.34	0.78	10.46	10.34
0.75	10.39	10.34	0.78	10.38	10.34
0.75	10.25	10.34	0.78	10.32	10.34
0.75	10.27	10.34	0.78	10.26	10.34
0.75	10.38	10.34	0.78	10.36	10.34
0.75	10.29	10.34	0.78	10.42	10.34
0.75	10.21	10.34	0.78	10.42	10.34
0.75	10.25	10.34	0.78	10.38	10.34
0.75	10.40	10.34	0.78	10.26	10.34
0.76	10.36	10.34	0.79	10.19	10.34
0.76	10.37	10.34	0.79	10.23	10.34
0.76	10.27	10.34	0.79	10.25	10.34
0.76	10.25	10.34	0.79	10.26	10.34
0.76	10.38	10.34	0.79	10.41	10.34
0.76	10.33	10.34	0.79	10.28	10.34
0.76	10.31	10.34	0.79	10.24	10.34
0.76	10.22	10.34	0.79	10.21	10.34
0.76	10.38	10.34	0.79	10.44	10.34
0.76	10.20	10.34	0.79	10.36	10.34
0.76	10.33	10.34	0.79	10.35	10.34
0.76	10.23	10.34	0.79	10.38	10.34
0.76	10.36	10.34	0.79	10.42	10.34
0.76	10.36	10.34	0.79	10.44	10.34
0.76	10.21	10.34	0.79	10.36	10.34
0.76	10.22	10.34	0.79	10.33	10.34
0.76	10.22	10.34	0.79	10.40	10.34
0.76	10.25	10.34	0.79	10.44	10.34
0.76	10.33	10.34	0.80	10.40	10.34
0.77	10.25	10.34	0.80	10.26	10.34
0.77	10.23	10.34	0.80	10.34	10.34
0.77	10.45	10.34	0.80	10.39	10.34
0.77	10.37	10.34	0.80	10.27	10.34
0.77	10.31	10.34	0.80	10.41	10.34
0.77	10.25	10.34	0.80	10.29	10.34
0.77	10.41	10.34	0.80	10.36	10.34
0.77	10.34	10.34	0.80	10.45	10.34
0.77	10.42	10.34	0.80	10.33	10.34
0.77	10.28	10.34	0.80	10.23	10.34
0.77	10.19	10.34	0.80	10.44	10.34
0.77	10.41	10.34	0.80	10.33	10.34
0.77	10.24	10.34	0.80	10.41	10.34
0.77	10.39	10.34	0.80	10.20	10.34
0.77	10.40	10.34	0.80	10.29	10.34
0.78	10.36	10.34	0.80	10.32	10.34
0.78	10.29	10.34	0.80	10.26	10.34
0.78	10.24	10.34	0.81	10.45	10.34
0.78	10.45	10.34	0.81	10.21	10.34
0.78	10.22	10.34	0.81	10.19	10.34
0.78	10.36	10.34	0.81	10.36	10.34
0.78	10.39	10.34	0.81	10.25	10.34
0.78	10.45	10.34	0.81	10.30	10.34

0.81	10.34	10.34	0.84	10.33	10.34
0.81	10.41	10.34	0.84	10.42	10.34
0.81	10.43	10.34	0.84	10.40	10.34
0.81	10.28	10.34	0.84	10.25	10.34
0.81	10.33	10.34	0.84	10.35	10.34
0.81	10.26	10.34	0.84	10.28	10.34
0.81	10.28	10.34	0.84	10.44	10.34
0.81	10.39	10.34	0.84	10.41	10.34
0.81	10.40	10.34	0.84	10.26	10.34
0.81	10.28	10.34	0.84	10.39	10.34
0.81	10.25	10.34	0.84	10.17	10.34
0.81	10.31	10.34	0.84	10.45	10.34
0.82	10.41	10.34	0.84	10.29	10.34
0.82	10.30	10.34	0.84	10.25	10.34
0.82	10.34	10.34	0.85	10.27	10.34
0.82	10.23	10.34	0.85	10.24	10.34
0.82	10.25	10.34	0.85	10.42	10.34
0.82	10.23	10.34	0.85	10.44	10.34
0.82	10.26	10.34	0.85	10.18	10.34
0.82	10.37	10.34	0.85	10.22	10.34
0.82	10.28	10.34	0.85	10.45	10.34
0.82	10.44	10.34	0.85	10.43	10.34
0.82	10.18	10.34	0.85	10.42	10.34
0.82	10.36	10.34	0.85	10.43	10.34
0.82	10.40	10.34	0.85	10.40	10.34
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0.83	10.45	10.34	0.85	10.42	10.34
0.83	10.38	10.34	0.85	10.22	10.34
0.83	10.34	10.34	0.86	10.30	10.34
0.83	10.18	10.34	0.86	10.42	10.34
0.83	10.40	10.34	0.86	10.38	10.34
0.83	10.42	10.34	0.86	10.38	10.34
0.83	10.36	10.34	0.86	10.44	10.34
0.83	10.35	10.34	0.86	10.37	10.34
0.83	10.42	10.34	0.86	10.29	10.34
0.83	10.24	10.34	0.86	10.35	10.34
0.83	10.22	10.34	0.86	10.29	10.34
0.83	10.42	10.34	0.86	10.24	10.34
0.83	10.23	10.34	0.86	10.21	10.34
0.83	10.40	10.34	0.86	10.42	10.34
0.83	10.32	10.34	0.86	10.39	10.34
0.83	10.39	10.34	0.86	10.23	10.34
0.83	10.40	10.34	0.86	10.24	10.34
0.83	10.28	10.34	0.86	10.38	10.34
0.84	10.40	10.34	0.86	10.28	10.34
0.84	10.28	10.34	0.86	10.31	10.34
0.84	10.25	10.34	0.87	10.46	10.34
0.84	10.34	10.34	0.87	10.37	10.34

0.87	10.23	10.34	0.90	10.31	10.34
0.87	10.24	10.34	0.90	10.39	10.34
0.87	10.30	10.34	0.90	10.42	10.34
0.87	10.28	10.34	0.90	10.32	10.34
0.87	10.28	10.34	0.90	10.27	10.34
0.87	10.33	10.34	0.90	10.39	10.34
0.87	10.47	10.34	0.90	10.25	10.34
0.87	10.33	10.34	0.90	10.18	10.34
0.87	10.36	10.34	0.90	10.27	10.34
0.87	10.45	10.34	0.90	10.29	10.34
0.87	10.40	10.34	0.90	10.39	10.34
0.87	10.25	10.34	0.90	10.40	10.34
0.87	10.30	10.34	0.90	10.20	10.34
0.87	10.42	10.34	0.90	10.25	10.34
0.87	10.38	10.34	0.90	10.26	10.34
0.87	10.21	10.34	0.90	10.40	10.34
0.88	10.36	10.34	0.90	10.46	10.34
0.88	10.38	10.34	0.90	10.21	10.34
0.88	10.25	10.34	0.91	10.43	10.34
0.88	10.24	10.34	0.91	10.26	10.34
0.88	10.30	10.34	0.91	10.39	10.34
0.88	10.49	10.34	0.91	10.21	10.34
0.88	10.25	10.34	0.91	10.39	10.34
0.88	10.42	10.34	0.91	10.44	10.34
0.88	10.30	10.34	0.91	10.32	10.34
0.88	10.24	10.34	0.91	10.25	10.34
0.88	10.29	10.34	0.91	10.23	10.34
0.88	10.40	10.34	0.91	10.31	10.34
0.88	10.21	10.34	0.91	10.33	10.34
0.88	10.26	10.34	0.91	10.41	10.34
0.88	10.30	10.34	0.91	10.27	10.34
0.88	10.24	10.34	0.91	10.24	10.34
0.88	10.41	10.34	0.91	10.42	10.34
0.88	10.23	10.34	0.91	10.31	10.34
0.89	10.25	10.34	0.91	10.17	10.34
0.89	10.22	10.34	0.91	10.34	10.34
0.89	10.41	10.34	0.92	10.28	10.34
0.89	10.21	10.34	0.92	10.38	10.34
0.89	10.32	10.34	0.92	10.26	10.34
0.89	10.26	10.34	0.92	10.25	10.34
0.89	10.32	10.34	0.92	10.41	10.34
0.89	10.35	10.34	0.92	10.22	10.34
0.89	10.45	10.34	0.92	10.23	10.34
0.89	10.25	10.34	0.92	10.27	10.34
0.89	10.22	10.34	0.92	10.24	10.34
0.89	10.40	10.34	0.92	10.38	10.34
0.89	10.34	10.34	0.92	10.21	10.34
0.89	10.46	10.34	0.92	10.27	10.34
0.89	10.34	10.34	0.92	10.26	10.34
0.89	10.41	10.34	0.92	10.44	10.34
0.89	10.34	10.34	0.92	10.32	10.34
0.89	10.26	10.34	0.92	10.40	10.34

0.92	10.34	10.34	0.95	10.34	10.34
0.92	10.43	10.34	0.95	10.26	10.34
0.93	10.40	10.34	0.95	10.23	10.34
0.93	10.41	10.34	0.95	10.23	10.34
0.93	10.32	10.34	0.96	10.44	10.34
0.93	10.22	10.34	0.96	10.35	10.34
0.93	10.23	10.34	0.96	10.39	10.34
0.93	10.25	10.34	0.96	10.29	10.34
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0.93	10.32	10.34	0.96	10.46	10.34
0.93	10.40	10.34	0.96	10.33	10.34
0.93	10.27	10.34	0.96	10.28	10.34
0.93	10.35	10.34	0.96	10.34	10.34
0.93	10.29	10.34	0.96	10.33	10.34
0.93	10.40	10.34	0.96	10.41	10.34
0.93	10.27	10.34	0.96	10.21	10.34
0.93	10.24	10.34	0.96	10.27	10.34
0.93	10.46	10.34	0.96	10.42	10.34
0.93	10.40	10.34	0.96	10.33	10.34
0.93	10.46	10.34	0.96	10.28	10.34
0.94	10.30	10.34	0.96	10.22	10.34
0.94	10.39	10.34	0.96	10.42	10.34
0.94	10.38	10.34	0.97	10.31	10.34
0.94	10.26	10.34	0.97	10.22	10.34
0.94	10.44	10.34	0.97	10.32	10.34
0.94	10.25	10.34	0.97	10.21	10.34
0.94	10.27	10.34	0.97	10.25	10.34
0.94	10.26	10.34	0.97	10.39	10.34
0.94	10.42	10.34	0.97	10.29	10.34
0.94	10.29	10.34	0.97	10.22	10.34
0.94	10.31	10.34	0.97	10.44	10.34
0.94	10.23	10.34	0.97	10.27	10.34
0.94	10.24	10.34	0.97	10.27	10.34
0.94	10.28	10.34	0.97	10.45	10.34
0.94	10.39	10.34	0.97	10.26	10.34
0.94	10.25	10.34	0.97	10.35	10.34
0.94	10.45	10.34	0.97	10.40	10.34
0.94	10.23	10.34	0.97	10.30	10.34
0.95	10.23	10.34	0.97	10.45	10.34
0.95	10.40	10.34	0.97	10.25	10.34
0.95	10.41	10.34	0.98	10.40	10.34
0.95	10.27	10.34	0.98	10.40	10.34
0.95	10.41	10.34	0.98	10.32	10.34
0.95	10.34	10.34	0.98	10.26	10.34
0.95	10.43	10.34	0.98	10.25	10.34
0.95	10.40	10.34	0.98	10.41	10.34
0.95	10.30	10.34	0.98	10.37	10.34
0.95	10.41	10.34	0.98	10.25	10.34
0.95	10.25	10.34	0.98	10.42	10.34
0.95	10.30	10.34	0.98	10.42	10.34
0.95	10.26	10.34	0.98	10.39	10.34
0.95	10.32	10.34	0.98	10.40	10.34

0.98	10.40	10.34	1.01	10.46	10.34
0.98	10.38	10.34	1.01	10.40	10.34
0.98	10.21	10.34	1.01	10.28	10.34
0.98	10.24	10.34	1.01	10.34	10.34
0.98	10.22	10.34	1.01	10.34	10.34
0.98	10.40	10.34	1.01	10.30	10.34
0.99	10.40	10.34	1.01	10.32	10.34
0.99	10.43	10.34	1.01	10.26	10.34
0.99	10.43	10.34	1.02	10.37	10.34
0.99	10.35	10.34	1.02	10.38	10.34
0.99	10.27	10.34	1.02	10.41	10.34
0.99	10.41	10.34	1.02	10.43	10.34
0.99	10.24	10.34	1.02	10.38	10.34
0.99	10.38	10.34	1.02	10.42	10.34
0.99	10.24	10.34	1.02	10.38	10.34
0.99	10.18	10.34	1.02	10.34	10.34
0.99	10.24	10.34	1.02	10.37	10.34
0.99	10.43	10.34	1.02	10.35	10.34
0.99	10.40	10.34	1.02	10.38	10.34
0.99	10.23	10.34	1.02	10.36	10.34
0.99	10.34	10.34	1.02	10.34	10.34
0.99	10.27	10.34	1.02	10.34	10.34
0.99	10.30	10.34	1.02	10.36	10.34
0.99	10.18	10.34	1.02	10.40	10.34
1.00	10.32	10.34	1.02	10.36	10.34
1.00	10.43	10.34	1.02	10.34	10.34
1.00	10.20	10.34	1.03	10.36	10.34
1.00	10.25	10.34	1.03	10.34	10.34
1.00	10.31	10.34	1.03	10.33	10.34
1.00	10.31	10.34	1.03	10.37	10.34
1.00	10.34	10.34	1.03	10.41	10.34
1.00	10.39	10.34	1.03	10.34	10.34
1.00	10.27	10.34	1.03	10.31	10.34
1.00	10.38	10.34	1.03	10.40	10.34
1.00	10.30	10.34	1.03	10.41	10.34
1.00	10.32	10.34	1.03	10.35	10.34
1.00	10.24	10.34	1.03	10.31	10.34
1.00	10.38	10.34	1.03	10.40	10.34
1.00	10.29	10.34	1.03	10.32	10.34
1.00	10.23	10.34	1.03	10.41	10.34
1.00	10.19	10.34	1.03	10.38	10.34
1.00	10.29	10.34	1.03	10.40	10.34
1.01	10.37	10.34	1.03	10.42	10.34
1.01	10.32	10.34	1.03	10.37	10.34
1.01	10.44	10.34	1.04	10.28	10.34
1.01	10.46	10.34	1.04	10.30	10.34
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1.01	10.40	10.34	1.04	10.41	10.34
1.01	10.41	10.34	1.04	10.36	10.34
1.01	10.43	10.34	1.04	10.30	10.34
1.01	10.30	10.34	1.04	10.25	10.34
1.01	10.43	10.34	1.04	10.40	10.34

1.04	10.29	10.34	1.07	10.32	10.34
1.04	10.43	10.34	1.07	10.38	10.34
1.04	10.35	10.34	1.07	10.25	10.34
1.04	10.39	10.34	1.07	10.18	10.34
1.04	10.44	10.34	1.07	10.38	10.34
1.04	10.41	10.34	1.07	10.34	10.34
1.04	10.35	10.34	1.07	10.47	10.34
1.04	10.37	10.34	1.07	10.33	10.34
1.04	10.22	10.34	1.07	10.34	10.34
1.04	10.24	10.34	1.07	10.24	10.34
1.05	10.37	10.34	1.07	10.39	10.34
1.05	10.23	10.34	1.07	10.32	10.34
1.05	10.40	10.34	1.08	10.39	10.34
1.05	10.27	10.34	1.08	10.38	10.34
1.05	10.20	10.34	1.08	10.22	10.34
1.05	10.26	10.34	1.08	10.23	10.34
1.05	10.21	10.34	1.08	10.25	10.34
1.05	10.21	10.34	1.08	10.40	10.34
1.05	10.41	10.34	1.08	10.42	10.34
1.05	10.39	10.34	1.08	10.31	10.34
1.05	10.22	10.34	1.08	10.32	10.34
1.05	10.43	10.34	1.08	10.22	10.34
1.05	10.39	10.34	1.08	10.37	10.34
1.05	10.34	10.34	1.08	10.32	10.34
1.05	10.26	10.34	1.08	10.22	10.34
1.05	10.30	10.34	1.08	10.36	10.34
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1.06	10.30	10.34	1.08	10.31	10.34
1.06	10.27	10.34	1.08	10.26	10.34
1.06	10.20	10.34	1.09	10.30	10.34
1.06	10.17	10.34	1.09	10.32	10.34
1.06	10.34	10.34	1.09	10.34	10.34
1.06	10.39	10.34	1.09	10.23	10.34
1.06	10.25	10.34	1.09	10.38	10.34
1.06	10.35	10.34	1.09	10.23	10.34
1.06	10.27	10.34	1.09	10.21	10.34
1.06	10.32	10.34	1.09	10.37	10.34
1.06	10.35	10.34	1.09	10.21	10.34
1.06	10.36	10.34	1.09	10.39	10.34
1.06	10.34	10.34	1.09	10.43	10.34
1.06	10.37	10.34	1.09	10.31	10.34
1.06	10.28	10.34	1.09	10.18	10.34
1.06	10.30	10.34	1.09	10.26	10.34
1.06	10.35	10.34	1.09	10.23	10.34
1.06	10.23	10.34	1.09	10.21	10.34
1.07	10.42	10.34	1.09	10.24	10.34
1.07	10.32	10.34	1.09	10.40	10.34
1.07	10.27	10.34	1.10	10.23	10.34
1.07	10.45	10.34	1.10	10.30	10.34
1.07	10.31	10.34	1.10	10.44	10.34
1.07	10.26	10.34	1.10	10.28	10.34

1.10	10.33	10.34	1.13	10.22	10.34
1.10	10.25	10.34	1.13	10.40	10.34
1.10	10.36	10.34	1.13	10.27	10.34
1.10	10.43	10.34	1.13	10.24	10.34
1.10	10.27	10.34	1.13	10.32	10.34
1.10	10.26	10.34	1.13	10.28	10.34
1.10	10.43	10.34	1.13	10.28	10.34
1.10	10.27	10.34	1.13	10.34	10.34
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1.10	10.21	10.34	1.13	10.28	10.34
1.10	10.19	10.34	1.13	10.25	10.34
1.10	10.33	10.34	1.13	10.39	10.34
1.11	10.23	10.34	1.13	10.40	10.34
1.11	10.28	10.34	1.13	10.27	10.34
1.11	10.36	10.34	1.14	10.38	10.34
1.11	10.37	10.34	1.14	10.37	10.34
1.11	10.28	10.34	1.14	10.37	10.34
1.11	10.38	10.34	1.14	10.40	10.34
1.11	10.20	10.34	1.14	10.47	10.34
1.11	10.33	10.34	1.14	10.45	10.34
1.11	10.35	10.34	1.14	10.34	10.34
1.11	10.26	10.34	1.14	10.25	10.34
1.11	10.25	10.34	1.14	10.23	10.34
1.11	10.34	10.34	1.14	10.48	10.34
1.11	10.40	10.34	1.14	10.24	10.34
1.11	10.27	10.34	1.14	10.31	10.34
1.11	10.37	10.34	1.14	10.37	10.34
1.11	10.43	10.34	1.14	10.41	10.34
1.11	10.35	10.34	1.14	10.26	10.34
1.11	10.25	10.34	1.14	10.28	10.34
1.12	10.44	10.34	1.14	10.39	10.34
1.12	10.23	10.34	1.14	10.26	10.34
1.12	10.40	10.34	1.15	10.42	10.34
1.12	10.41	10.34	1.15	10.32	10.34
1.12	10.39	10.34	1.15	10.35	10.34
1.12	10.30	10.34	1.15	10.46	10.34
1.12	10.36	10.34	1.15	10.22	10.34
1.12	10.39	10.34	1.15	10.30	10.34
1.12	10.26	10.34	1.15	10.35	10.34
1.12	10.45	10.34	1.15	10.39	10.34
1.12	10.43	10.34	1.15	10.43	10.34
1.12	10.25	10.34	1.15	10.25	10.34
1.12	10.29	10.34	1.15	10.31	10.34
1.12	10.25	10.34	1.15	10.30	10.34
1.12	10.45	10.34	1.15	10.26	10.34
1.12	10.40	10.34	1.15	10.21	10.34
1.12	10.45	10.34	1.15	10.36	10.34
1.12	10.43	10.34	1.15	10.32	10.34
1.13	10.34	10.34	1.15	10.22	10.34
1.13	10.24	10.34	1.15	10.31	10.34

1.16	10.31	10.34	1.18	10.38	10.34
1.16	10.40	10.34	1.18	10.40	10.34
1.16	10.42	10.34	1.19	10.27	10.34
1.16	10.21	10.34	1.19	10.36	10.34
1.16	10.20	10.34	1.19	10.39	10.34
1.16	10.31	10.34	1.19	10.36	10.34
1.16	10.38	10.34	1.19	10.27	10.34
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1.16	10.26	10.34	1.19	10.38	10.34
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1.16	10.41	10.34	1.19	10.36	10.34
1.16	10.42	10.34	1.19	10.29	10.34
1.16	10.31	10.34	1.19	10.26	10.34
1.16	10.39	10.34	1.19	10.43	10.34
1.16	10.39	10.34	1.19	10.25	10.34
1.16	10.26	10.34	1.19	10.40	10.34
1.16	10.36	10.34	1.19	10.25	10.34
1.17	10.29	10.34	1.19	10.19	10.34
1.17	10.29	10.34	1.19	10.26	10.34
1.17	10.32	10.34	1.20	10.23	10.34
1.17	10.45	10.34	1.20	10.30	10.34
1.17	10.25	10.34	1.20	10.42	10.34
1.17	10.36	10.34	1.20	10.32	10.34
1.17	10.36	10.34	1.20	10.37	10.34
1.17	10.35	10.34	1.20	10.40	10.34
1.17	10.31	10.34	1.20	10.35	10.34
1.17	10.28	10.34	1.20	10.46	10.34
1.17	10.32	10.34	1.20	10.39	10.34
1.17	10.25	10.34	1.20	10.39	10.34
1.17	10.42	10.34	1.20	10.42	10.34
1.17	10.35	10.34	1.20	10.32	10.34
1.17	10.22	10.34	1.20	10.39	10.34
1.17	10.26	10.34	1.20	10.35	10.34
1.17	10.36	10.34	1.20	10.31	10.34
1.17	10.19	10.34	1.20	10.45	10.34
1.18	10.32	10.34	1.20	10.40	10.34
1.18	10.37	10.34	1.20	10.45	10.34
1.18	10.39	10.34	1.21	10.38	10.34
1.18	10.43	10.34	1.21	10.32	10.34
1.18	10.27	10.34	1.21	10.35	10.34
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1.18	10.44	10.34	1.21	10.40	10.34
1.18	10.42	10.34	1.21	10.42	10.34
1.18	10.23	10.34	1.21	10.37	10.34
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1.18	10.33	10.34	1.21	10.42	10.34

1.21	10.41	10.34	1.24	10.33	10.34
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1.23	10.31	10.34	1.26	10.27	10.34
1.23	10.35	10.34	1.26	10.45	10.34
1.23	10.46	10.34	1.26	10.20	10.34
1.23	10.34	10.34	1.26	10.26	10.34
1.23	10.36	10.34	1.26	10.33	10.34
1.23	10.30	10.34	1.26	10.25	10.34
1.23	10.41	10.34	1.26	10.34	10.34
1.23	10.36	10.34	1.26	10.42	10.34
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1.24	10.36	10.34	1.26	10.30	10.34
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1.24	10.45	10.34	1.27	10.25	10.34
1.24	10.30	10.34	1.27	10.44	10.34
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1.24	10.42	10.34	1.27	10.26	10.34
1.24	10.25	10.34	1.27	10.24	10.34
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1.24	10.29	10.34	1.27	10.28	10.34

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1.27	10.35	10.34	1.30	10.38	10.34
1.27	10.21	10.34	1.30	10.24	10.34
1.27	10.24	10.34	1.30	10.30	10.34
1.27	10.22	10.34	1.30	10.44	10.34
1.27	10.22	10.34	1.30	10.41	10.34
1.27	10.32	10.34	1.30	10.37	10.34
1.28	10.40	10.34	1.30	10.44	10.34
1.28	10.17	10.34	1.30	10.28	10.34
1.28	10.38	10.34	1.31	10.31	10.34
1.28	10.38	10.34	1.31	10.44	10.34
1.28	10.46	10.34	1.31	10.27	10.34
1.28	10.32	10.34	1.31	10.47	10.34
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1.28	10.23	10.34	1.31	10.36	10.34
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1.28	10.22	10.34	1.31	10.24	10.34
1.28	10.19	10.34	1.31	10.24	10.34
1.28	10.25	10.34	1.31	10.22	10.34
1.28	10.42	10.34	1.31	10.45	10.34
1.28	10.34	10.34	1.31	10.44	10.34
1.28	10.33	10.34	1.31	10.40	10.34
1.29	10.40	10.34	1.31	10.37	10.34
1.29	10.28	10.34	1.31	10.38	10.34
1.29	10.24	10.34	1.32	10.27	10.34
1.29	10.41	10.34	1.32	10.26	10.34
1.29	10.24	10.34	1.32	10.42	10.34
1.29	10.32	10.34	1.32	10.44	10.34
1.29	10.23	10.34	1.32	10.32	10.34
1.29	10.26	10.34	1.32	10.44	10.34
1.29	10.22	10.34	1.32	10.37	10.34
1.29	10.37	10.34	1.32	10.24	10.34
1.29	10.33	10.34	1.32	10.28	10.34
1.29	10.33	10.34	1.32	10.29	10.34
1.29	10.19	10.34	1.32	10.21	10.34
1.29	10.38	10.34	1.32	10.44	10.34
1.29	10.30	10.34	1.32	10.22	10.34
1.29	10.30	10.34	1.32	10.23	10.34
1.29	10.40	10.34	1.32	10.33	10.34
1.29	10.32	10.34	1.32	10.36	10.34
1.30	10.41	10.34	1.32	10.34	10.34
1.30	10.30	10.34	1.32	10.37	10.34
1.30	10.22	10.34	1.33	10.43	10.34
1.30	10.36	10.34	1.33	10.29	10.34
1.30	10.25	10.34	1.33	10.39	10.34
1.30	10.26	10.34	1.33	10.36	10.34
1.30	10.45	10.34	1.33	10.35	10.34
1.30	10.24	10.34	1.33	10.43	10.34

1.33	10.42	10.34	1.36	10.18	10.34
1.33	10.42	10.34	1.36	10.43	10.34
1.33	10.27	10.34	1.36	10.30	10.34
1.33	10.25	10.34	1.36	10.26	10.34
1.33	10.33	10.34	1.36	10.36	10.34
1.33	10.40	10.34	1.36	10.20	10.34
1.33	10.31	10.34	1.36	10.26	10.34
1.33	10.28	10.34	1.36	10.43	10.34
1.33	10.26	10.34	1.36	10.29	10.34
1.33	10.43	10.34	1.36	10.34	10.34
1.33	10.33	10.34	1.36	10.30	10.34
1.33	10.33	10.34	1.36	10.24	10.34
1.34	10.40	10.34	1.36	10.35	10.34
1.34	10.40	10.34	1.36	10.27	10.34
1.34	10.29	10.34	1.37	10.39	10.34
1.34	10.28	10.34	1.37	10.25	10.34
1.34	10.27	10.34	1.37	10.27	10.34
1.34	10.34	10.34	1.37	10.42	10.34
1.34	10.25	10.34	1.37	10.36	10.34
1.34	10.30	10.34	1.37	10.33	10.34
1.34	10.43	10.34	1.37	10.29	10.34
1.34	10.33	10.34	1.37	10.33	10.34
1.34	10.19	10.34	1.37	10.25	10.34
1.34	10.29	10.34	1.37	10.36	10.34
1.34	10.35	10.34	1.37	10.37	10.34
1.34	10.32	10.34	1.37	10.44	10.34
1.34	10.34	10.34	1.37	10.42	10.34
1.34	10.22	10.34	1.37	10.39	10.34
1.34	10.35	10.34	1.37	10.32	10.34
1.34	10.37	10.34	1.37	10.24	10.34
1.35	10.31	10.34	1.37	10.43	10.34
1.35	10.43	10.34	1.37	10.27	10.34
1.35	10.23	10.34	1.38	10.34	10.34
1.35	10.31	10.34	1.38	10.33	10.34
1.35	10.27	10.34	1.38	10.41	10.34
1.35	10.25	10.34	1.38	10.24	10.34
1.35	10.33	10.34	1.38	10.40	10.34
1.35	10.45	10.34	1.38	10.29	10.34
1.35	10.42	10.34	1.38	10.41	10.34
1.35	10.32	10.34	1.38	10.29	10.34
1.35	10.24	10.34	1.38	10.38	10.34
1.35	10.34	10.34	1.38	10.27	10.34
1.35	10.44	10.34	1.38	10.35	10.34
1.35	10.36	10.34	1.38	10.34	10.34
1.35	10.27	10.34	1.38	10.26	10.34
1.35	10.24	10.34	1.38	10.39	10.34
1.35	10.26	10.34	1.38	10.24	10.34
1.35	10.34	10.34	1.38	10.35	10.34
1.36	10.20	10.34	1.38	10.33	10.34
1.36	10.47	10.34	1.38	10.28	10.34
1.36	10.40	10.34	1.39	10.31	10.34
1.36	10.31	10.34	1.39	10.38	10.34

1.39	10.37	10.34	1.42	10.37	10.34
1.39	10.25	10.34	1.42	10.24	10.34
1.39	10.28	10.34	1.42	10.28	10.34
1.39	10.30	10.34	1.42	10.33	10.34
1.39	10.32	10.34	1.42	10.38	10.34
1.39	10.25	10.34	1.42	10.28	10.34
1.39	10.40	10.34	1.42	10.23	10.34
1.39	10.37	10.34	1.42	10.27	10.34
1.39	10.46	10.34	1.42	10.33	10.34
1.39	10.38	10.34	1.42	10.26	10.34
1.39	10.42	10.34	1.42	10.40	10.34
1.39	10.33	10.34	1.42	10.25	10.34
1.39	10.43	10.34	1.42	10.20	10.34
1.39	10.20	10.34	1.42	10.31	10.34
1.39	10.21	10.34	1.42	10.27	10.34
1.39	10.26	10.34	1.42	10.38	10.34
1.40	10.42	10.34	1.42	10.27	10.34
1.40	10.36	10.34	1.42	10.32	10.34
1.40	10.40	10.34	1.43	10.20	10.34
1.40	10.29	10.34	1.43	10.27	10.34
1.40	10.37	10.34	1.43	10.44	10.34
1.40	10.19	10.34	1.43	10.27	10.34
1.40	10.41	10.34	1.43	10.42	10.34
1.40	10.39	10.34	1.43	10.35	10.34
1.40	10.33	10.34	1.43	10.41	10.34
1.40	10.21	10.34	1.43	10.37	10.34
1.40	10.28	10.34	1.43	10.32	10.34
1.40	10.29	10.34	1.43	10.40	10.34
1.40	10.23	10.34	1.43	10.40	10.34
1.40	10.36	10.34	1.43	10.29	10.34
1.40	10.26	10.34	1.43	10.24	10.34
1.40	10.36	10.34	1.43	10.39	10.34
1.40	10.42	10.34	1.43	10.22	10.34
1.40	10.41	10.34	1.43	10.21	10.34
1.41	10.24	10.34	1.43	10.42	10.34
1.41	10.29	10.34	1.43	10.35	10.34
1.41	10.26	10.34	1.44	10.29	10.34
1.41	10.41	10.34	1.44	10.24	10.34
1.41	10.28	10.34	1.44	10.21	10.34
1.41	10.26	10.34	1.44	10.38	10.34
1.41	10.38	10.34	1.44	10.26	10.34
1.41	10.40	10.34	1.44	10.26	10.34
1.41	10.42	10.34	1.44	10.26	10.34
1.41	10.39	10.34	1.44	10.30	10.34
1.41	10.35	10.34	1.44	10.36	10.34
1.41	10.22	10.34	1.44	10.23	10.34
1.41	10.34	10.34	1.44	10.44	10.34
1.41	10.17	10.34	1.44	10.28	10.34
1.41	10.31	10.34	1.44	10.33	10.34
1.41	10.26	10.34	1.44	10.41	10.34
1.41	10.23	10.34	1.44	10.36	10.34
1.41	10.47	10.34	1.44	10.29	10.34

1.44	10.36	10.34	1.47	5.51	10.34
1.44	10.45	10.34	1.47	0.20	10.34
1.45	10.28	10.34	1.47	0.51	10.34
1.45	10.37	10.34	1.47	0.49	10.34
1.45	10.31	10.34	1.48	0.34	10.34
1.45	10.42	10.34	1.48	0.02	10.34
1.45	10.25	10.34	1.48	0.00	10.34
1.45	10.29	10.34	1.48	0.14	10.34
1.45	10.21	10.34	1.48	0.11	10.34
1.45	10.39	10.34	1.48	0.04	10.34
1.45	10.50	10.34	1.48	0.16	10.34
1.45	10.29	10.34	1.48	0.09	10.34
1.45	10.41	10.34	1.48	0.12	10.34
1.45	10.37	10.34	1.48	0.05	10.34
1.45	10.39	10.34	1.48	0.07	10.34
1.45	10.39	10.34	1.48	0.15	10.34
1.45	10.32	10.34	1.48	0.09	10.34
1.45	10.22	10.34	1.48	-0.04	10.34
1.45	10.33	10.34	1.48	0.11	10.34
1.45	10.44	10.34	1.48	0.08	10.34
1.46	10.24	10.34	1.48	0.01	10.34
1.46	10.43	10.34	1.48	0.06	10.34
1.46	10.38	10.34	1.49	-0.01	10.34
1.46	10.39	10.34	1.49	0.02	10.34
1.46	10.39	10.34	1.49	-0.03	10.34
1.46	10.44	10.34	1.49	0.10	10.34
1.46	10.34	10.34	1.49	-0.06	10.34
1.46	10.35	10.34	1.49	-0.09	10.34
1.46	10.18	10.34	1.49	-0.04	10.34
1.46	10.37	10.34	1.49	0.06	10.34
1.46	10.17	10.34	1.49	0.14	10.34
1.46	10.36	10.34	1.49	0.14	10.34
1.46	10.37	10.34	1.49	0.10	10.34
1.46	10.37	10.34	1.49	-0.11	10.34
1.46	10.20	10.34	1.49	-0.07	10.34
1.46	10.27	10.34	1.49	0.03	10.34
1.46	10.27	10.34	1.49	-0.02	10.34
1.46	10.42	10.34	1.49	-0.05	10.34
1.47	10.42	10.34	1.49	0.05	10.34
1.47	10.40	10.34	1.49	-0.06	10.34
1.47	10.18	10.34	1.50	0.11	10.34
1.47	10.44	10.34	1.50	-0.05	10.34
1.47	10.39	10.34	1.50	-0.06	10.34
1.47	10.28	10.34	1.50	0.12	10.34
1.47	10.35	10.34	1.50	-0.08	10.34
1.47	10.36	10.34	1.50	0.08	10.34
1.47	10.49	10.34	1.50	-0.01	10.34
1.47	9.69	10.34	1.50	0.05	10.34
1.47	10.11	10.34	1.50	0.01	10.34
1.47	10.27	10.34	1.50	0.09	10.34
1.47	10.51	10.34	1.50	-0.08	10.34
1.47	5.99	10.34	1.50	-0.03	10.34

1.50	-0.08	10.34	1.53	-0.02	10.34
1.50	-0.01	10.34	1.53	0.10	10.34
1.50	-0.06	10.34	1.53	0.09	10.34
1.50	-0.06	10.34	1.53	0.08	10.34
1.50	0.11	10.34	1.53	-0.07	10.34
1.50	-0.06	10.34	1.53	-0.06	10.34
1.51	-0.06	10.34	1.53	0.03	10.34
1.51	0.10	10.34	1.53	-0.07	10.34
1.51	0.00	10.34	1.54	0.10	10.34
1.51	-0.06	10.34	1.54	0.06	10.34
1.51	0.11	10.34	1.54	0.09	10.34
1.51	-0.09	10.34	1.54	0.05	10.34
1.51	0.10	10.34	1.54	-0.01	10.34
1.51	0.06	10.34	1.54	0.01	10.34
1.51	0.03	10.34	1.54	-0.03	10.34
1.51	0.01	10.34	1.54	-0.04	10.34
1.51	0.12	10.34	1.54	-0.04	10.34
1.51	0.06	10.34	1.54	0.04	10.34
1.51	0.12	10.34	1.54	0.07	10.34
1.51	0.09	10.34	1.54	0.12	10.34
1.51	-0.03	10.34	1.54	-0.03	10.34
1.51	-0.06	10.34	1.54	0.02	10.34
1.51	0.09	10.34	1.54	-0.07	10.34
1.51	0.10	10.34	1.54	-0.07	10.34
1.52	-0.07	10.34	1.54	-0.11	10.34
1.52	-0.01	10.34	1.54	-0.05	10.34
1.52	0.02	10.34	1.55	-0.04	10.34
1.52	0.10	10.34	1.55	0.05	10.34
1.52	-0.04	10.34	1.55	0.08	10.34
1.52	-0.04	10.34	1.55	-0.11	10.34
1.52	-0.02	10.34	1.55	0.07	10.34
1.52	0.07	10.34	1.55	-0.04	10.34
1.52	0.02	10.34	1.55	-0.11	10.34
1.52	0.07	10.34	1.55	0.10	10.34
1.52	0.07	10.34	1.55	-0.06	10.34
1.52	0.05	10.34	1.55	-0.09	10.34
1.52	0.00	10.34	1.55	0.11	10.34
1.52	0.10	10.34	1.55	-0.04	10.34
1.52	-0.12	10.34	1.55	0.06	10.34
1.52	0.04	10.34	1.55	0.09	10.34
1.52	0.03	10.34	1.55	-0.08	10.34
1.52	-0.03	10.34	1.55	0.03	10.34
1.53	-0.03	10.34	1.55	0.08	10.34
1.53	-0.05	10.34	1.55	-0.04	10.34
1.53	0.04	10.34	1.56	0.02	10.34
1.53	0.06	10.34	1.56	0.12	10.34
1.53	0.07	10.34			
1.53	0.14	10.34			
1.53	0.03	10.34			
1.53	0.07	10.34			
1.53	-0.05	10.34			
1.53	0.12	10.34			

Appendix E: Resonant Frequency Measurements From April26/00

Time (seconds)	Frequency (Hz)
1	9005038
2	9005042
3	9005046
4	9005034
5	9005046
6	9005046
7	9005046
8	9005046
9	9005046
10	9005046
11	9005046
12	9005046
13	9005046
14	9005050
15	9005050
16	9005050
17	9005046
18	9005046
19	9005034
20	9005034
21	9005038
22	9005042
23	9005038
24	9005042
25	9005042
26	9005038
27	9005042
28	9005038
29	9005038
30	9005038
31	9005038
32	9005034
33	9005038
34	9005038
35	9005038
36	9005034
37	9005038
38	9005042
39	9005042
40	9005038
41	9005038
42	9005038
43	9005038
44	9005042
45	9005046
46	9005038
47	9005038
48	9005022
49	9005009
50	9005038
51	9005042
52	9005038
53	9005034
54	9005030
55	9005034
56	9005038
57	9005042
58	9005046
59	9005042
60	9005038
61	9005038
62	9005038
63	9005042
64	9005038
65	9005042
66	9005042
67	9005038
68	9005038
69	9005038
70	9005042
71	9005042
72	9005046
73	9005042
74	9005046
75	9005042
76	9005046
77	9005046
78	9005050
79	9005046
80	9005046
81	9005050
82	9005050
83	9005046
84	9005050
85	9005046
86	9005050
87	9005046
88	9005046
89	9005046
90	9005046

Appendix F: Example of Mass Loading Data

Time (seconds)	Frequency (Hz)				
1	9005038	51	9005042	103	9002006
2	9005042	52	9005038	104	9002022
3	9005046	53	9005034	105	9002022
4	9005034	54	9005030	106	9002022
5	9005046	55	9005034	107	9002018
6	9005046	56	9005038	108	9002018
7	9005046	57	9005042	109	9002026
8	9005046	58	9005046	110	9002026
9	9005046	59	9005042	111	9002026
10	9005046	60	9005038	112	9002030
11	9005046	61	9005038	113	9002034
12	9005046	62	9005038	114	9002039
13	9005046	63	9005042	115	9002043
14	9005050	64	9005038	116	9002043
15	9005050	65	9005042	117	9002047
16	9005050	66	9005042	118	9002047
17	9005046	67	9005038	119	9002047
18	9005046	68	9005038	120	9002047
19	9005034	69	9005038	121	9002051
20	9005034	70	9005042	122	9002051
21	9005038	71	9005042	123	9002047
22	9005042	72	9005046	124	9002051
23	9005038	73	9005042	125	9002055
24	9005042	74	9005046	126	9002051
25	9005042	75	9005042	127	9002051
26	9005038	76	9005046	128	9002055
27	9005042	77	9005046	129	9002051
28	9005038	78	9005050	130	9002039
29	9005038	79	9005046	131	9002039
30	9005038	80	9005046	132	9002034
31	9005038	81	9005050	133	9002034
32	9005034	82	9005050	134	9002030
33	9005038	83	9005046	135	8997147
34	9005038	84	9005050	136	8996944
35	9005038	85	9005046	137	8998729
36	9005034	86	9005050	138	8998794
37	9005038	87	9005046	139	8998818
38	9005042	88	9005046	140	8998827
39	9005042	89	9005046	141	8998831
40	9005038	90	9005046	142	8998827
41	9005038	91	9005054	143	8998823
42	9005038	92	9005042	144	8998827
43	9005038	93	9005042	145	8998831
44	9005042	94	9005038	146	8998835
45	9005046	95	9005038	147	8998839
46	9005038	96	9005034	148	8998835
47	9005038	97	9005030	149	8998839
48	9005022	98	9001747	150	8998843
49	9005009	99	8998997	151	8998847
50	9005038	100	9001860	152	8998847
		101	9001974	153	8998851
		102	9001998	154	8998851

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155	8998851	207	8995580	259	8989843
156	8998851	208	8995576	260	8989847
157	8998855	209	8995576	261	8989847
158	8998855	210	8995576	262	8989847
159	8998859	211	8994072	263	8989843
160	8998859	212	8987314	264	8989847
161	8998851	213	8992482	265	8989851
162	8998863	214	8992612	266	8989855
163	8998863	215	8992652	267	8989847
164	8998847	216	8992664	268	8989847
165	8998847	217	8992676	269	8989855
166	8998843	218	8992676	270	8989843
167	8998831	219	8992680	271	8989843
168	8991197	220	8992680	272	8989847
169	8994452	221	8992680	273	8989851
170	8995463	222	8992693	274	8989847
171	8995540	223	8992688	275	8989851
172	8995560	224	8992688	276	8989847
173	8995568	225	8992688	277	8989859
174	8995572	226	8992693	278	8989847
175	8995564	227	8992693	279	8989847
176	8995576	228	8992693	280	8989847
177	8995580	229	8992697	281	8989847
178	8995580	230	8992697	282	8989847
179	8995580	231	8992701	283	8989847
180	8995568	232	8992697	284	8989847
181	8995576	233	8992701	285	8989847
182	8995585	234	8992701	286	8989847
183	8995568	235	8992701	287	8989847
184	8995589	236	8992705	288	8989847
185	8995580	237	8992697	289	8989847
186	8995585	238	8992709	290	8989847
187	8995589	239	8992697	291	8989847
188	8995585	240	8992688	292	8989847
189	8995585	241	8992693	293	8989847
190	8995589	242	8992688	294	8989847
191	8995589	243	8992688	295	8989847
192	8995593	244	8991027	296	8989847
193	8995589	245	8984185	297	8989847
194	8995593	246	8989621		
195	8995589	247	8989758		
196	8995589	248	8989802		
197	8995593	249	8989810		
198	8995593	250	8989815		
199	8995593	251	8989815		
200	8995593	252	8989823		
201	8995593	253	8989819		
202	8995597	254	8989827		
203	8995597	255	8989827		
204	8995593	256	8989827		
205	8995593	257	8989827		
206	8995601	258	8989843		

Appendix G: Table of All Mass Loading Data

Table G-1 Mass Loading Data Table for Cu(tta)$_2$

Date	Mass Added (gm)	Calculated Mass (gm)	% Difference	Calculated Solubility (mol/mol)
May-03	5.57E-05	6.38E-05	14.5%	1.57E-06
May-2 (b)	4.87E-05	5.29E-05	8.6%	9.88E-07
May-02	4.87E-05	5.20E-05	6.8%	1.60E-06
Apr-28	3.48E-05	3.77E-05	8.3%	3.08E-06
Apr-03	3.54E-05	3.39E-05	-4.2%	4.82E-07
Mar-28	2.83E-05	2.91E-05	2.8%	1.69E-07
Mar-27	2.83E-05	2.66E-05	-6.0%	1.83E-07
Mar-23	3.18E-05	3.25E-05	2.2%	4.15E-07
Mar-22	2.55E-05	2.65E-05	3.9%	4.36E-07
Jun-30	5.92E-05	5.68E-05	-4.1%	7.67E-07
Jul-04	3.83E-05	4.06E-05	6.0%	9.08E-07
Jul-05	4.52E-05	5.52E-05	22.1%	8.32E-07
Jul-13	4.18E-05	4.14E-05	-1.0%	1.47E-06
Jul-20	4.87E-05	6.23E-05	27.9%	3.23E-07
Jul-25	4.87E-05	5.01E-05	2.9%	5.52E-07
Jul 25(b)	4.87E-05	5.84E-05	19.9%	2.52E-07

Mean:	6.9%
% Std. Dev.	1%

Table G-2 Mass Loading Data Table for β-carotene

Date	Mass Added (gm)	Calculated Mass (gm)	% Difference	Calculated Solubility (mol/mol)
Jun-15	1.04E-05	1.29E-05	19.4%	1.40E-07
Jun-19	4.30E-06	4.91E-06	12.4%	8.64E-08
Jun-20	9.46E-06	1.43E-05	33.8%	6.46E-08
Jun-21	4.52E-06	6.03E-06	25.0%	7.86E-08
Jun-22	4.52E-06	6.25E-06	27.7%	1.09E-07

Mean:	23.7%
% Std. Dev.	8%

% Difference = (Calculated Mass − Mass Added)/Calculated Mass

Appendix H: Frequency Response of QCM From Neat SC CO₂ on March 16/00

Time (seconds)	Frequency (Hz)	Time	Frequency	Time	Frequency
0	9017889	50	9017897	102	9017897
1	9017897	51	9017897	103	9017897
2	9017897	52	9017897	104	9017897
3	9017901	53	9017893	105	9017897
4	9017897	54	9017897	106	9017897
5	9017897	55	9017893	107	9017893
6	9017897	56	9017897	108	9017897
7	9017897	57	9017897	109	9017897
8	9017897	58	9017897	110	9017893
9	9017897	59	9017897	111	9017893
10	9017897	60	9017897	112	9017889
11	9017897	61	9017897	113	9017893
12	9017897	62	9017897	114	9017893
13	9017897	63	9017893	115	9017889
14	9017897	64	9017897	116	9017889
15	9017897	65	9017897	117	9017893
16	9017897	66	9017897	118	9017897
17	9017897	67	9017897	119	9017893
18	9017901	68	9017897	120	9017897
19	9017897	69	9017897	121	9017897
20	9017897	70	9017897	122	9017706
21	9017897	71	9017893	123	9017694
22	9017901	72	9017897	124	9017657
23	9017897	73	9017897	125	9017657
24	9017897	74	9017897	126	9017641
25	9017901	75	9017897	127	9017624
26	9017897	76	9017897	128	9017612
27	9017897	77	9017893	129	9017608
28	9017897	78	9017897	130	9017604
29	9017897	79	9017897	131	9017600
30	9017897	80	9017893	132	9017596
31	9017897	81	9017893	133	9017592
32	9017897	82	9017897	134	9017588
33	9017897	83	9017897	135	9017584
34	9017897	84	9017897	136	9017580
35	9017897	85	9017897	137	9017576
36	9017897	86	9017897	138	9017572
37	9017893	87	9017897	139	9017568
38	9017897	88	9017893	140	9017564
39	9017897	89	9017893	141	9017559
40	9017897	90	9017893	142	9017559
41	9017897	91	9017897	143	9017559
42	9017897	92	9017897	144	9017555
43	9017897	93	9017893	145	9017551
44	9017897	94	9017893	146	9017551
45	9017897	95	9017893	147	9017547
46	9017897	96	9017893	148	9017547
47	9017897	97	9017893	149	9017547
48	9017897	98	9017897	150	9017547
49	9017893	99	9017897	151	9017543
		100	9017897	152	9017547
		101	9017893	153	9017543

154	9017543	206	9017535	258	9017527
155	9017539	207	9017535	259	9017527
156	9017543	208	9017531	260	9017523
157	9017539	209	9017531	261	9017527
158	9017539	210	9017531	262	9017523
159	9017539	211	9017531	263	9017527
160	9017535	212	9017531	264	9017527
161	9017535	213	9017531	265	9017527
162	9017535	214	9017531	266	9017523
163	9017535	215	9017531	267	9017527
164	9017535	216	9017531	268	9017523
165	9017539	217	9017531	269	9017527
166	9017535	218	9017531	270	9017523
167	9017535	219	9017531	271	9017523
168	9017535	220	9017531	272	9017527
169	9017535	221	9017531	273	9017523
170	9017535	222	9017527	274	9017523
171	9017535	223	9017531	275	9017527
172	9017535	224	9017531	276	9017527
173	9017539	225	9017527	277	9017523
174	9017535	226	9017531	278	9017523
175	9017535	227	9017527	279	9017523
176	9017535	228	9017531	280	9017523
177	9017535	229	9017527	281	9017523
178	9017535	230	9017527	282	9017527
179	9017535	231	9017527	283	9017523
180	9017535	232	9017527	284	9017523
181	9017531	233	9017531	285	9017523
182	9017531	234	9017527	286	9017523
183	9017531	235	9017527	287	9017523
184	9017535	236	9017531	288	9017523
185	9017535	237	9017531	289	9017523
186	9017535	238	9017531	290	9017523
187	9017535	239	9017527	291	9017523
188	9017535	240	9017527	292	9017523
189	9017531	241	9017527	293	9017523
190	9017531	242	9017527	294	9017523
191	9017531	243	9017527	295	9017523
192	9017535	244	9017527	296	9017527
193	9017535	245	9017527	297	9017523
194	9017531	246	9017531	298	9017523
195	9017535	247	9017527	299	9017523
196	9017531	248	9017527	300	9017523
197	9017531	249	9017527	301	9017523
198	9017531	250	9017527	302	9017523
199	9017535	251	9017527	303	9017523
200	9017535	252	9017527	304	9017523
201	9017531	253	9017527	305	9017523
202	9017531	254	9017527	306	9017523
203	9017531	255	9017523	307	9017523
204	9017531	256	9017527	308	9017523
205	9017531	257	9017523	309	9017519

310	9017523	362	9017551	414	9017860
311	9017523	363	9017551	415	9017877
312	9017523	364	9017551	416	9017893
313	9017523	365	9017551	417	9017897
314	9017523	366	9017564	418	9017897
315	9017519	367	9017555	419	9017905
316	9017523	368	9017551	420	9017913
317	9017523	369	9017551	421	9017901
318	9017523	370	9017551	422	9017864
319	9017523	371	9017641	423	9017868
320	9017519	372	9017653	424	9017873
321	9017523	373	9017629	425	9017877
322	9017519	374	9017629	426	9017897
323	9017523	375	9017649	427	9017921
324	9017523	376	9017592	428	9017925
325	9017519	377	9017592	429	9017925
326	9017519	378	9017588	430	9017856
327	9017523	379	9017592	431	9017864
328	9017519	380	9017608	432	9017868
329	9017519	381	9017320	433	9017873
330	9017523	382	9017072	434	9017873
331	9017519	383	9016799	435	9017864
332	9017523	384	9017169	436	9017864
333	9017523	385	9017881	437	9017864
334	9017519	386	9018003	438	9017868
335	9017523	387	9017958	439	9017873
336	9017519	388	9017885	440	9017877
337	9017519	389	9017848	441	9017881
338	9017523	390	9017791	442	9017913
339	9017523	391	9017763	443	9017921
340	9017523	392	9017820	444	9017905
341	9017523	393	9017799	445	9017913
342	9017523	394	9017868	446	9017913
343	9017523	395	9017913	447	9017929
344	9017519	396	9017864	448	9017913
345	9017523	397	9017897	449	9017893
346	9017519	398	9017868	450	9017901
347	9017519	399	9017848	451	9017868
348	9017527	400	9017864	452	9017860
349	9017641	401	9017836	453	9017864
350	9017572	402	9017816	454	9017877
351	9017559	403	9017828	455	9017881
352	9017555	404	9017836	456	9017877
353	9017551	405	9017816	457	9017877
354	9017555	406	9017844	458	9017873
355	9017551	407	9017828	459	9017873
356	9017551	408	9017836	460	9017873
357	9017555	409	9017844	461	9017881
358	9017551	410	9017877	462	9017885
359	9017551	411	9017897	463	9017885
360	9017551	412	9017897	464	9017881
361	9017551	413	9017852	465	9017877

466	9017877	518	9017901	570	9017909
467	9017877	519	9017901	571	9017909
468	9017873	520	9017901	572	9017909
469	9017873	521	9017901	573	9017909
470	9017877	522	9017897	574	9017909
471	9017877	523	9017897	575	9017909
472	9017868	524	9017897	576	9017909
473	9017868	525	9017905	577	9017909
474	9017881	526	9017901	578	9017909
475	9017885	527	9017901	579	9017913
476	9017885	528	9017897	580	9017909
477	9017885	529	9017893	581	9017909
478	9017885	530	9017889	582	9017909
479	9017885	531	9017889	583	9017909
480	9017881	532	9017885	584	9017909
481	9017885	533	9017885	585	9017909
482	9017873	534	9017885	586	9017913
483	9017860	535	9017885	587	9017913
484	9017864	536	9017885	588	9017909
485	9017864	537	9017885	589	9017913
486	9017860	538	9017885	590	9017909
487	9017860	539	9017885	591	9017917
488	9017856	540	9017885	592	9017917
489	9017860	541	9017885	593	9017917
490	9017860	542	9017885	594	9017917
491	9017864	543	9017885	595	9017917
492	9017864	544	9017885	596	9017921
493	9017864	545	9017885	597	9017917
494	9017860	546	9017885	598	9017917
495	9017860	547	9017885	599	9017917
496	9017860	548	9017885	600	9017917
497	9017864	549	9017885	601	9017917
498	9017864	550	9017885	602	9017917
499	9017864	551	9017889	603	9017917
500	9017860	552	9017889	604	9017917
501	9017860	553	9017885	605	9017917
502	9017864	554	9017885	606	9017917
503	9017860	555	9017909	607	9017917
504	9017864	556	9017905	608	9017917
505	9017864	557	9017905	609	9017917
506	9017860	558	9017909	610	9017917
507	9017860	559	9017909	611	9017917
508	9017860	560	9017909	612	9017917
509	9017864	561	9017909	613	9017917
510	9017860	562	9017905	614	9017917
511	9017909	563	9017909	615	9017917
512	9017909	564	9017909	616	9017917
513	9017917	565	9017909	617	9017913
514	9017905	566	9017909	618	9017913
515	9017901	567	9017909	619	9017913
516	9017905	568	9017909	620	9017913
517	9017901	569	9017909	621	9017917

622	9017917	674	9017909	726	9017889
623	9017913	675	9017905	727	9017889
624	9017917	676	9017905	728	9017889
625	9017917	677	9017905	729	9017889
626	9017917	678	9017901	730	9017893
627	9017913	679	9017901	731	9017893
628	9017913	680	9017901	732	9017893
629	9017917	681	9017901	733	9017893
630	9017917	682	9017901	734	9017893
631	9017913	683	9017901	735	9017893
632	9017913	684	9017901	736	9017893
633	9017913	685	9017905	737	9017889
634	9017913	686	9017901	738	9017889
635	9017913	687	9017897	739	9017889
636	9017913	688	9017905	740	9017889
637	9017913	689	9017897	741	9017893
638	9017913	690	9017897	742	9017889
639	9017917	691	9017897	743	9017889
640	9017913	692	9017897	744	9017889
641	9017913	693	9017893	745	9017889
642	9017913	694	9017893	746	9017889
643	9017917	695	9017893	747	9017893
644	9017913	696	9017893	748	9017893
645	9017913	697	9017893	749	9017889
646	9017917	698	9017893	750	9017893
647	9017913	699	9017889	751	9017889
648	9017917	700	9017893	752	9017889
649	9017917	701	9017893	753	9017889
650	9017913	702	9017893	754	9017893
651	9017913	703	9017893	755	9017893
652	9017917	704	9017893	756	9017893
653	9017917	705	9017893	757	9017889
654	9017913	706	9017893	758	9017893
655	9017913	707	9017893	759	9017893
656	9017917	708	9017889	760	9017893
657	9017917	709	9017893	761	9017893
658	9017913	710	9017893	762	9017889
659	9017913	711	9017889	763	9017889
660	9017909	712	9017893	764	9017889
661	9017913	713	9017893	765	9017889
662	9017913	714	9017889	766	9017889
663	9017913	715	9017893	767	9017893
664	9017913	716	9017889	768	9017889
665	9017913	717	9017893	769	9017889
666	9017913	718	9017889	770	9017893
667	9017913	719	9017889	771	9017889
668	9017913	720	9017889	772	9017889
669	9017909	721	9017889	773	9017889
670	9017909	722	9017893		
671	9017909	723	9017889		
672	9017913	724	9017889		
673	9017909	725	9017893		

Appendix I: Statistical Analysis of Cu(tta)$_2$ Data From this work and

Guigard (1999)

Table I-1 Solubility Data at 9.65 MPa and 318 K from This Work and Guigard (1999)

Solubility From This Work (mol/mol)	Solubility From Guigard (1999) (mol/mol)
4.82E-07	2.25E-06
1.69E-07	2.56E-07
1.83E-07	9.41E-07
4.15E-07	2.33E-07
4.35E-07	9.60E-07
3.37E-07	1.50E-06
	4.80E-07
	2.38E-07

Table I-2 Tabulated F-test Results for the Data in Table I-1

	This Work	Guigard (1999)
Mean	3.37E-07	8.5725E-07
Variance	1.77E-14	5.21061E-13
Observations	6	8
df	5	7
F cal	0.0339699	
P(F<=f) one-tail	0.0008993	
F Critical one-tail	0.2050911	

F calculated < F critical, fail to reject the hypothesis that the variances are equal. Now assuming equal variances, do an two sample T-test to determine if the means from Table I-1 are equal

Table I-3 Tabulated T-test Results for the Data in Table I-1

	This Work	Guigard (1999)
Mean	3.37E-07	8.5725E-07
Variance	1.77E-14	5.21061E-13
Observations	6	8
Pooled Variance	3.113E-13	
Hypothesized Mean Difference	0	
df	12	
t Stat	-1.7266006	
P(T<=t) one-tail	0.0549335	
t Critical one-tail	1.7822867	
P(T<=t) two-tail	0.109867	
t Critical two-tail	2.1788128	

T calculated < T critical, fail to reject the hypothesis that the means from

Table I-1 are equal.

Table I-4 Solubility Data at 10.34 MPa and 313 K from This Work and Guigard (1999)

Solubility From This Work (mol/mol)	Solubility From Guigard (1999) (mol/mol)
1.57E-06	2.40E-06
9.89E-07	3.66E-06
1.61E-06	1.77E-06
3.08E-06	1.70E-06
	6.46E-06

Table I-5 Tabulated F-test Results for the Data in Table I-4

	This Work	Guigard (1999)
Mean	1.813E-06	3.20E-06
Variance	7.973E-13	3.20E-06
Observations	4	5
df	3	4
F	0.2021737	
P(F<=f) one-tail	0.1100042	
F Critical one-tail	0.2171179	

F calculated < F critical, fail to reject the hypothesis that the variances are

equal. Now assuming equal variances, do an two sample T-test to determine if

the means from Table I-4 are equal.

Table I-6 Tabulated T-test Results for the Data in Table I-4

	This Work	Guigard (1999)
Mean	1.81E-06	3.20E-06
Variance	7.97E-13	3.94E-12
Observations	4	5
Pooled Variance	2.595E-12	
Hypothesized Mean Difference	0	
df	7	
t Stat	-1.281541	
P(T<=t) one-tail	0.1204092	
t Critical one-tail	1.8945775	
P(T<=t) two-tail	0.2408184	
t Critical two-tail	2.3646226	

T calculated < T critical, fail to reject the hypothesis that the means from Table I-4 are equal.

Appendix J: Partially Differentiated Equations With Respect to Four Variables

$$\frac{\partial u}{\partial Vol} = \left(\frac{\left(F_{dip} - F_{final}\right) * A * \sqrt{\rho_Q \mu_Q} * M.W._{\cdot CO_2}}{-2\left(F_0^2 + 2F_0 FCO_2 + FCO_2^2\right) * M.W._{\cdot solute} * \rho_{CO_2}} \right)_{F_0, FCO_2, \rho CO_2}$$

$$\frac{\partial u}{\partial F_0} = \left(\frac{A * \sqrt{\rho_Q \mu_Q} * \rho_{CO_2} * M.W._{\cdot CO_2}}{-2\left(-2\left(F_0^3\right) + 2FCO_2 + FCO_2^2\right) * M.W._{\cdot solute} * Vol[Pressure Vessel]} \right)_{Vol, FCO_2, \rho CO_2}$$

$$\frac{\partial u}{\partial FCO_2} = \left(\frac{\left(F_{dip} - F_{final}\right) * A * \sqrt{\rho_Q \mu_Q} * \rho_{CO_2} * M.W._{\cdot CO_2}}{-2\left(F_0^2 + 2F_0 - 2\left(FCO_2^3\right)\right) * M.W._{\cdot solute} * Vol[Press Vessel]} \right)_{F_0, Vol, \rho CO_2}$$

$$\frac{\partial u}{\partial \rho CO_2} = \left(\frac{\left(F_{dip} - F_{final}\right) * A * \sqrt{\rho_Q \mu_Q} * M.W._{\cdot CO_2}}{-2\left(F_0^2 + 2F_0 FCO_2 + FCO_2^2\right) * M.W._{\cdot solute} * Vol[Press Vessel]} \right)_{Vol, FCO_2, F_0}$$