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**DETECTION OF METALLOPORPHYRINS IN
CRUDE PETROLEUM USING
MAGNETIC CIRCULAR DICHROISM**

by

JEFFREY A. WARNER, B.Sc.

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

Department of Chemistry

Carleton University
Ottawa, Ontario
July, 1992

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**Detection of Metalloporphyrins in
Crude Petroleum using
Magnetic Circular Dichroism**

submitted by **JEFFREY A. WARNER, B.Sc.**

in partial fulfillment of the requirements for

the degree of Master of Science

Thesis Supervisor

Chair, Department of Chemistry

Carleton University
September, 1992

ABSTRACT

Nitrogen compounds in crude petroleum have deleterious effects on refinery operations and can cause acid rain upon combustion. Metalloporphyrins, which are a part of this nitrogen content, may act as markers for all the nitrogen compounds in crude oils. Due to their large magnetic rotation, metalloporphyrins are the ideal targets for fast monitoring by magnetic circular dichroism (MCD) spectroscopy.

A MCD instrument was calibrated over its entire wavelength range. Calibration at 20000, 33000, and 34000 cm^{-1} caused a value too low at 43000 cm^{-1} . Using amino acids, many of which absorb in the ultraviolet range, it was found that above 36000 cm^{-1} measurements were erratic. This behaviour was attributed to saturation of the photomultiplier tube power supply. The spectroscopic analysis of metalloporphyrins in crude oil was not affected by this non-linearity in the ultraviolet region, since only the visible bands of the metalloporphyrins were of interest for quantification.

Optimized fractions of an Athabasca crude were isolated using a homologous series of alkane solvents which increased linearly in polarizability. The total nitrogen content was measured on each fraction using elemental analysis and compared to results obtained from a quantification using MCD spectroscopy. The highest content of metalloporphyrin was found in the basic fractions of the n-pentane extract. In addition, it was observed that the metalloporphyrin content was a linearly increasing fraction of the total nitrogen content, reaching a maximum at the n-hexane extract. A decrease in the nitrogen content, as determined by MCD spectroscopy, for the fraction extracted with n-heptane was attributed to interferences in the MCD spectrum, caused by the complex nature of this particular fraction.

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**A man is a small thing, and the night is very large
and full of wonders.**

- Lord Dunsany

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I. INTRODUCTION

Since the crude oil price shocks of the early 1970's, petroleum companies have attempted to increase the extraction efficiency of marketable products from heavy oils, oil shales, tar sands, and bitumens. Heavy oil typically has high levels of impurities such as sulphur, nitrogen, nickel, and vanadium and is rich in the polyaromatic compounds which react to form coke during refinery processing.

In order to process heavy oils into environmentally acceptable products, it is important to, characterize the refinery feedstock with respect to the impurities present, eliminate these impurities from the feed, and monitor the decontamination for efficiency. These steps provide the knowledge of feedstock compounds necessary to optimize refining steps, avoid fouling of processing equipment, and reduce vehicular toxic emissions which contribute to acid rain. For optimization, a feedback process needs to be implemented whereby an impurity analysis is performed and processing adjusted accordingly. At present, most refineries make no attempt to analyze the feedstock for the components contained within the crude oil. Simple analytical tests are performed on the crude and these, combined with empirical correlations, are used to evaluate the crude oil as a feedstock. In order to meet modern product requirements a better knowledge of the chemical composition of crude

petroleum is needed. This is achieved not only through research into the compounds found in petroleum but by obtaining knowledge of the original source compounds and the conditions they have experienced. This provides insight into the range of possible chemical reaction pathways available to given petroleum precursors.

The combined requirements for rapid, convenient and accurate analysis of heavy metals and nitrogen impurities in crude oils suggests the need for a spectroscopic technique on optimized fractions of the crude petroleum. One such technique is magnetic circular dichroism (MCD - see Appendix A).

Magnetic circular dichroism is an appropriate technique for detection of many compounds in crude petroleum due to its sensitivity to aromatic systems and its insensitivity to interferences.^{1,2} MCD is particularly sensitive to the large aromatic chromophore present in porphyrins and metalloporphyrins, capable of detecting 7 ng/mL.³ Polarized light is scattered randomly from particles in a sample, with respect to polarization, and therefore affects the signal-to-noise ratio of the spectrum but not the quantitative data about the concentrations. The differential absorbance signal recorded follows Beer's law even when derived from turbid samples and therefore allows rapid quantification of the porphyrin in heterogeneous samples. A longer scan can

¹ Goldbeck, R.A., *Acc. Chem. Res.*, 21(3), 95, (1988).

² Michl, J., *Tetrahedron*, 40(20), 3845, (1984).

³ Lambert, J.B., Shurvell, H.F., Verbit, L., Cooks, R.G., and Stout, G.H., *Organic Structural Analysis*, Macmillan Publ. Co., Inc., pp. 400, (1976).

increase the S/N ratio without affecting the Beer's law relationship. This is an improvement over quantification by absorption spectroscopy^{4,5} because of the easy peak identification and lack of background interference.

MCD measurements can be performed on optimized fractions or fractions in which porphyrins have been preferentially concentrated. These can be determined by systematic fractionation with hydrocarbon solvents of increasing molecular weight. At the same time, the relationship of total nitrogen to metalloporphyrin can be determined so that the MCD metalloporphyrin result can also indicate total nitrogen impurities.

I. A. GENESIS OF PETROLEUM

Crude petroleum is the legacy of marine plants and animals. Though an inorganic origin was once postulated from abiogenic methane, it is now generally accepted as fact that the large accumulations of petroleum found throughout the world are of biogenic origin.⁶

The original organic matter contained in the sediment is contributed from all the bacteria, phytoplankton, zooplankton (especially foraminifers and

⁴ Funk, E.W. and Gomez, E., *Anal. Chem.*, **49**, 972, (1977).

⁵ Barbooti, M.M., Said, E.Z., Hassan, E.B., and Abdul-Ridha, S.M., *Fuel*, **68**, 84, (1989).

⁶ Lijmbach, G.W.M., 9th World Pet. Congress, **2**, 357, (1975).

certain crustaceans), and higher plants present in the original ecosystem.⁷ This has been shown convincingly by experiments which analyze the mixture produced after heating bacteria for different lengths of time. The resulting component distribution profile resembles that of a marine oil.⁶ However, additional quantitative data on the natural associations of organisms, their chemical compositions and the quantity and types of compounds deposited are needed before more detailed models of diagenesis can be postulated.

Most organisms are composed of essentially the same groups of biochemical constituents; these are proteins, lipids, carbohydrates and lignin in higher plants. Proteins, polymers composed of amino acids, account for most of the nitrogen compounds in organisms. Carbohydrates are among the most abundant constituents of plants and include individual sugars and their polymers. Lipids are compounds which are soluble in hydrocarbons but insoluble in water, or alternatively, compounds which yield fatty acids upon hydrolysis. Lipids are ubiquitous in biological systems and are suspected to be the main source of most petroleum hydrocarbons. Lignin and tannin are wide-spread in the plant kingdom and are important geochemically because of their aromatic structures. Aromatic compounds are not usually synthesized in animals.

The transformation of these biochemicals to oils can be postulated to have occurred in two steps: (1) selective accumulation and mechanical

⁷ Long, R., Chemistry of Asphaltenes, in *Advances in Chemistry Series*, 195, 17, (1981).

compaction of certain components in the original organic matter followed by; (2) conversion of the organic material in the source bed. Selective accumulation and mechanical compaction happen in deposits by chromatography, fractions accumulate horizontally according to mass and volatility. The transformation of the organic material occurs over millions of years by various chemical reactions caused by temperature, pressure and interaction with pore waters.⁸

The formation of source rocks begins with the accumulation of organic matter in sedimentary environments. These environments are usually low in oxygen or have high sedimentation rates. There, bacteria aerobically or anaerobically break down the organic matter into amino acid residues and other organic molecules including resins and waxy materials. Compaction forces the solubilized organic matter from the mud into adjacent rocks or back into the water column thereby producing the source bed for the oil, usually shale. Increased lithostatic pressure causes oil migration into adjacent pore spaces.

Maturation of the crude oil results in a slow cracking of the organic compounds present due to increased temperatures caused by greater overburden. This process converts the biochemicals to a large variety of hydrocarbons from dissolved gases to solid paraffin waxes up to sixty carbons in length. Different crudes contain different concentrations of these

⁸ Whittaker, A.H. and Dyson, P., *Oil & Gas J.*, 78(36), 260, (1980).

hydrocarbons and other compounds, and this results in some crudes being more valuable than others.

The premium oils contain a high percentage of saturated hydrocarbons. Heavy oils, in contrast, have relatively lower concentrations of low molecular weight hydrocarbons and higher concentrations of impurities.

The oil used in this study is an Alberta surface crude, the source rocks of which lie up to 500 km west of the actual oil field. There are at least 10 different sources of oil in the Western Canada Sedimentary Basin which may contribute to this oil field. As a result, the Alberta crude's properties have been altered along the migration pathway by interaction with oils derived from other source rocks, in situ water washing and biodegradation in the Tar Sands over the last 30 million years.

I. B. COMPOSITION AND IMPURITIES

Characterization and analysis of crude oils are of particular importance for Canada since this country currently produces 200 000 barrels of synthetic crude per day from tar sands and has one of the largest in-place reserves of heavy oil in the world. However, crude petroleum is a complicated, ill-defined mixture of organic and organometallic substances. The chemical nature of the heavier ends of crude petroleum is still largely unknown, despite the extensive

Figure I. 1. Hydrogen-Carbon mole ratio for petroleum feedstocks, coals, residual oils and premium products. Data from various sources.

studies on these materials.^{9, 10, 11, 12, 13} Though the basic elemental composition and functionalities are known, knowledge of their structural and associative properties is more vague. This is due to the difficulties in isolating pure components from these heavy fractions.

However, the classification of crude petroleums remains important for determining the optimum process conditions for refining and for assessing the relationship between oils, their migration routes and source rock conditions. In general, the dominant physical and chemical properties of the crude must be known to maximize yields of desired products.

Refiners currently use various methods to classify crudes prior to processing such as: viscosity, specific gravity, cloud point, and carbon residue. These tests are used to define the quantity and chemical composition of successive distillate fractions and to predict possible future problems associated with the crude petroleum. An alternative classification, which is used to group compounds with similar chemical properties, discriminates the

⁹ Hodgson, G.W., *Bull. Amer. Ass. Petrol. Geol.*, 38(12), 2537, (1954).

¹⁰ Bunger, J.W. and Cogswell, D.E., Chemistry of Asphaltenes, in *Advances in Chemistry Series*, 195, 219, (1981).

¹¹ Nguyen, S.N. and Filby, R.H., in *Metal Complexes in Fossil Fuels*, ACS Symp series 344, pp. 385, (1987).

¹² Fish, R.H., Reynolds, J.G., and Gallegos, E.J., in *Metal Complexes in Fossil Fuels*, ACS Symp series 344, pp. 332, (1987).

¹³ Speight, J.G. and Moschopedis, S.E., Chemistry of Asphaltenes, in *Advances in Chemistry Series*, 195, 1, (1981).

various structural types of hydrocarbons found in petroleum: alkanes, cycloalkanes, aromatics, and heteroatom compounds.¹⁴ This second classification requires greater analytical capabilities than more conventional testing procedures but could permit much more efficient control of refining processes.

Problems in refinery processing of heavy oil fractions are encountered because these fractions are hydrogen deficient (low H/C ratio), due to the high concentrations of high molecular weight compounds and impurities. These high molecular weight compounds are not easily used as fuels and are more valuable after being "cracked" or reduced to lower molecular weights.

A quantification of the levels of compounds considered to be impurities is necessary to prevent contamination of the processing system and of the final products. The impurities interfere with this refining process by adversely affecting catalyst activity and selectivity.

Catalytic cracking originally depended on natural clays and synthetic amorphous silica-alumina as catalysts. In the early 1960's the introduction of porous zeolites revolutionized the cracking catalyst field. These zeolitic cracking catalysts permitted increased selectivity, activity and stability characteristics over the old amorphous catalysts. However, these characteristics are adversely affected by the deposition of the metallic

¹⁴ Tissot, B.P. and Welte, D.H., *Petroleum formation and Occurrence*, 2nd ed., Springer-Verlag, part IV, chap. 2, (1984).

impurities present in raw crude oils at the part per million level and rapid, routine analysis has not been developed for these contaminants.

I. B.1. METALS

Metal impurities including vanadium and nickel, accumulate on catalyst particles. The main effect of nickel contamination is the enhancement of undesirable reactions with no net loss of activity. In contrast, vanadium deposits affect both the selectivity and the activity.^{15, 16} X-ray diffraction patterns indicate vanadium deposits as a sulphide which causes changes in catalyst pore structure and has autocatalytic activity on hydrodemetallization.¹⁷

Current avenues of research in this area involve passivation of metals through the addition of certain antimony compounds¹⁸ and the use of catalysts specifically selected to be resistant to the effects of deposited vanadium and nickel.

¹⁵ Branthaver, J.F., in *Metal Complexes in Fossil Fuels*, ACS Symp. series 344, pp. 189, (1987).

¹⁶ Rankel, L.A. and Rollmann, L.D., *Fuel*, 62, 44, (1983).

¹⁷ Asaoka, S., Nakata, S., Shiroto, Y., and Takeuchi, C., in *Metal Complexes in Fossil Fuels*, ACS Symp. series 344, pp. 275, (1987).

¹⁸ Dale, D.H. and McKay, D.H., *Hydrocarbon Process.*, Sept., 97, (1977).

I. B.2. NITROGEN

Nitrogen containing impurities in crude petroleum also react with the acid cracking catalysts in various ways adversely affecting their activity.¹⁹

The heteroatom compounds are concentrated in the resin and asphaltene fractions of crude petroleum.¹³ These fractions are operationally defined as the pentane soluble/propane insoluble and pentane insoluble portions of crude petroleum, respectively. Both fractions contain high concentrations of undefined high molecular weight moieties, composed primarily of polycyclic aromatic compounds rich in heteroatoms. The heteroatom and metal contaminants are usually present in crude petroleum as components of complex molecules which are essentially hydrocarbon in character. Heavy oils like that of the Athabasca tar sands can contain up to 1% N, 2% O, 5% S and 150 ppm of vanadyl porphyrins.^{20, 21} The type of crude (ie. tar sand, conventional oil, etc.) influences the production method which in turn can affect the distribution of nitrogen functional groups.²² Many of these nitrogen compounds also foul reforming catalysts and cause the formation of gums and tars during storage

¹⁹ Dorbon, M., Ignatiadis, I., Schmitter, J.M., Arpino, P., Guichon, G., Toulhoat, H., and Huc, A., *Fuel*, **63**, 565, (1984).

²⁰ Strausz, O.P., *The Chemistry of the Alberta Oil Sand Bitumen, Oil Sands*, 156, (1977).

²¹ Yen, T.F., in *The Role of Trace Metals in Petroleum*, Ann Arbor, (1975).

²² Holmes, S.A., *AOSTRA J. Res.*, **2**, 167, (1986).

of liquid fuels.²³

Nitrogen occurs in two broad types in crude petroleum, non-basic and basic (Figure I.2). The basic nitrogen fraction is responsible for much of the reported deleterious effects associated with the nitrogen found in petroleum.²⁴ This fraction consists of a complex mixture of alkylmonoazaarenes including alkyl substituted pyridines, quinolines, benzoquinolines, acridines and phenanthridines.^{25, 26, 27, 28}

Non-basic nitrogen compounds consist of indoles, carbazoles, benzocarbazoles and pyrrole derivatives.^{21, 26} Nitrogen acting as a donor in metal complexes can also be placed in this category.

Non-porphyrin metal chelates have not been isolated or characterized as have the metalloporphyrins but there is evidence that some of these compounds contain nitrogen donors.^{12, 29}

²³ Ford, C.D., Holmes, S.A., Thompson, L.F., and Latham, D.R., *Anal. Chem.*, **53**, 831, (1981).

²⁴ Somogyvari, A., Jeffries, R., and Zanzotto, L., *Prep. Am. Chem. Soc. Div. Pet. Chem.*, **35**, 453, (1990).

²⁵ Schmitter, J.M., Vajta, Z., and Arpino, P.J., *Adv. Org. Geochem.*, **12**, 67, (1979).

²⁶ Frakman, Z., Ignasiak, Y., Montgomery, D., and Strausz, O., *AOSTRA J. Res.*, **3**, 131, (1987).

²⁷ Schmitter, J.M., Garrigues, P., Ignatiadis, I., Arpino, P.J., et al, *Org. Geochem.*, **6**, 579, (1984).

²⁸ Haines, W.E., Cook, G.L., and Dinneen, G.U., *7th World Pet. Congress*, **9**, 83, (1987).

²⁹ Reynolds, J.G., Biggs, W.R., and Bezman, S.A., in *Metal Complexes in Fossil Fuels*, ACS Symp. series 344, pp. 205, (1987).

Name	Molecular Formula Molecular Weight	Molecular Structure
pyrrole	C_4H_4NH (67)
indole	C_8H_7NH (117)
carbazole	$C_{12}H_9NH$ (167)
pyridine	C_5H_5N (79)
quinoline (benzo[b]pyridine)	C_9H_7N (129)
isoquinoline (benzo[c]pyridine)	C_9H_7N (129)
acridine	$C_{13}H_9N$ (179)
phenanthridine	$C_{13}H_9N$ (179)

Figure I. 2. Some families of nitrogen compounds found in Crude Petroleum.

Studies have shown that metallo-nonporphyrins encompass a larger molecular weight range than metalloporphyrins, represent most of the metal containing compounds in many crudes, and are generally more polar than metalloporphyrins. Electron spin resonance spectroscopy indicates that metallo-nonporphyrins do not usually contain a metal complexed to four nitrogens.³⁰

In addition, petroleum nitrogen compounds are of concern because they form harmful NO_x combustion products³¹ which contribute to acid rain, present health and environmental problems due to their possible carcinogenic and mutagenic actions, play a role in the promotion of asphalt oxidation³², and may provide new insight into petroleum genesis and aging (see Appendix B).

Control of these compounds must occur during refining. Therefore, familiarity with the refinery process is essential in understanding the usefulness of monitoring for nitrogen compounds in petroleum refinery streams.

³⁰ Dickson, F.E. and Petrakis, L., *Anal. Chem.*, **46**, 1129, (1974).

³¹ Ismagilov, Z.R. and Kerzhentsev, M.A., *Catal. Rev.-Sci.Eng.*, **32**, 51, (1990).

³² Branthaver, J.F., Nazir, M., Petersen, J.C., et al, *Liq. Fuels Tech.*, **2**, 67, (1984).

I. C. PROCESS CONTROL

In general, refinery flow consists of several processing steps beginning with crude distillation. The crude oil is heated in a furnace and charged to an atmospheric distillation tower, where it is separated into various distillate fractions. Bottom residues from this procedure are further distilled at low pressure and separated into vacuum gas oil and pitch. The vacuum gas oil is mixed with a hot recirculating catalyst in the fluid catalytic cracking unit (FCCU) for conversion into lower boiling compounds.

Light hydrocarbons from FCCU gas are piped to the alkylation unit to form a high octane gasoline blending component called alkylate. Prior to shipping, various grades of gasoline are created by blending streams produced in the various processing units.

Major process variables are controlled automatically by a sophisticated computer control system. This system monitors conditions in the processing units, tank inventories, and it controls blending conditions.

Certain refining processes have been specifically designed to remove nitrogen and metal compounds from the crude so that usable products are obtained efficiently. In heavy synthetic crudes, both the metal and nitrogen impurities tend to be removed by the coking process producing the pitch fraction. Continuous analysis is needed to confirm that these impurities do not proceed to later refining stages.

I. D. PROCESSING OF IMPURITIES

Since organonitrogen compounds are generally more kinetically inert than sulphur compounds, nitrogen removal requires more severe operating conditions than does desulphurization. Therefore, any treatment which reduces nitrogen to satisfactory levels will effectively remove excess sulphur.

If the initial coking does not completely remove these impurities, upgrading processes in the form of denitrogenation and desulphurization can be used to rid the feed of contaminants containing nitrogen and sulphur. Upgrading to remove nitrogen compounds as well as oxygen, sulphur and halides is accomplished in general by high pressure hydrogenation or hydrotreating. This process mixes the feed with a hydrogen rich gas stream at moderate temperatures over a metal-oxide catalyst to produce H_2S , NH_3 , saturated hydrocarbons and free metals.

Hydrodenitrogenation occurs simultaneously with hydrodesulphurization during hydroprocessing. Both processes vary in effectiveness depending on the nature of the feed and the specific decontamination methods employed. Severe

inhibitory effects of nitrogen-containing compounds on the catalytic removal of sulphur have been reported.³³ Another author reports the selective removal of several heterocyclic nitrogen compounds from oil by bacteria.³⁴ Kinetic experiments of the catalytic hydrodenitrogenation of pyridine³⁵ and carbazole³⁴ show that the reaction intermediates of these processes are dependant upon the catalyst. These techniques and experiments hold promise for the future but are not currently suitable as a means of commercially removing nitrogen.

In each case a technique which could rapidly monitor for organic nitrogen and metal complexes would be necessary. This would allow the very specific process control required for monitoring the inflow and outflow of impurities from the FCCU and hydrotreating units. To do this however it is necessary to identify marker compounds representative of the nitrogen impurity levels. Since they are readily detected, candidates for this role are the azaarenes in acid or metal substituted forms.

³³ Nagai, M., Masunaga, T., and Hana-oka, N., *Energy & Fuels*, **2**, 645, (1988).

³⁴ Aislabie, J. and Atlas, R.M., *Fuel*, **69**, 1155, (1990).

³⁵ Kim, K.L., Chung, N.H., and Choi, K.S., *Korean J. Chem. Eng.*, **4**, 61, (1987).

I. E. HYPOTHESIS

The dangers of nitrogen oxides in the atmosphere as well as the deterioration in selectivity and activity of cracking catalysts by nitrogen and nitrogen-metal impurities necessitates efficient methods of removing these compounds from crude petroleum. These methods have been developed but no on-line monitoring system is available to detect their effectiveness as normal processing takes place. As air pollution standards become stricter and markets get increasingly competitive, nitrogen accountability will become more important.

A large proportion of the nitrogen and metals in crude oils is in the form of stable azaarenes and metalloporphyrins. Jackson and Decora,³⁶ have performed pyrolysis studies on plant pigments, which include the metalloporphyrin compounds chlorophylls a, b and c, and have shown that the resulting distributions of nitrogenous products compare favourably with the array of nitrogen containing compounds found in a natural shale-oil. This suggests that the catagenic thermal breakdown of metalloporphyrin structures result in azaarenes. In addition, observations from the reaction sequence of metalloporphyrins during upgrading refinery processes show that geoporphyrins are degraded quickly when exposed to air, H₂S, H₂, or heat. Peripheral double bonds are first hydrogenated on the porphyrin, followed by

³⁶ Jackson, L.P. and Decora, A.W., U.S. Bureau of Mines, RI 8018, (1975).

fragmentation of the ring into polypyrroles, and metal removal.^{37, 38} While these conditions cannot be directly related to those that exist beneath the surface, there are similarities and underground there is a much longer residence time. H_2S is produced as a by-product of sulphur-reducing bacteria acting on sulphate ions dissolved in formation waters.²⁰ Catalysts are present in the form of clays, minerals and metal ions and, in addition, the overburden produces elevated temperatures and pressures.³⁹

Taken together, this evidence suggests that there could be a reliable relationship between some of the chemical properties of a crude petroleum: the metalloporphyrin content, total nitrogen content, total metal content; and some of the physical characteristics: age of the crude, geographic location, depth of burial and migration effects.

The determination of some of these characteristics may be sufficient to calculate other properties. The metalloporphyrin signal can be used as a marker for the total nitrogen content since the metalloporphyrin chromophore is easily detected spectroscopically using MCD and therefore has the potential for rapid analysis and process control under refinery conditions.

³⁷ Rankel, L.A., *Metal Complexes in Fossil Fuels*, ACS Symp. series 344, pp. 257, (1987).

³⁸ Hung, C.W. and Wei, J., *Ind. Eng. Chem. Proc. Des. Dev.*, **19**, 250, (1980).

³⁹ Venuto, P.B. and Habib, E.T., *Catal. Rev.- Sci. Eng.*, **18**(1), 1, (1978).

II. MCD CALIBRATION

II. A. INTRODUCTION

Magnetic circular dichroism is typically used to gain information about electronic excited states, their symmetries, angular momenta, electronic splittings and their vibrational-electronic interactions. In this respect it is complementary to absorption spectroscopy. An MCD spectrum gives information not available from an absorption spectrum for two reasons: (1) a transition buried under a stronger transition can appear or become more visible if the magnetic differential intensity $\Delta A/A$ is much larger for the weaker transition or if it is of opposite sign; and (2) if $\Delta A > \Delta A_{\min}$ but $A < A_{\min}$ where $\Delta A_{\min}$ and $A_{\min}$ are the minimum ΔA and A signals detectable. In particular, for present purposes, MCD has also been used in analytical chemistry to quantify porphyrins in many environments such as lunar dust and to determine the concentration of urinary porphyrins.^{40,41}

The application of MCD to the determination of metalloporphyrins in crude petroleum is based on: (1) its sensitivity to small amounts of porphyrin; (2) its

⁴⁰ Hodgson, G.W., Peterson, E., Kuenvolden, K.A., Bunnenberg, E., Halpern, B., and Ponnampuruma, C., *Science*, **167**, 763, (1970).

⁴¹ Kalman, S.M., Barth, G., Linder, R.E., Bunnenberg, E., and Djerassi, C., *Anal. Biochem.*, **52**, 83, (1973).

freedom from interferences caused by other substances; and (3) the characteristic shape of the metalloporphyrin MCD bands.

II. A.1. Instrument

The outline of the instrument used to obtain the MCD data is shown in Figure II.1. The light from a 150-W xenon lamp passes through a double beam monochromator followed by a beamsplitter which sends 20 percent of the radiation to a reference channel. The remaining light goes through a linear polarizer and then a photoelastic modulator, the last element in the optic array. The modulator transforms the radiation into left and right circularly polarized light. The applied electric field creates in the crystal an alternating linear birefringence, whose sign and magnitude depend on the instantaneous value of the modulation voltage. The circularly polarized light then passes through the sample cuvette which is placed in a uniform magnetic field oriented such that the field is parallel to the propagation direction of the beam of circularly polarized light. The transmitted radiation is detected by the photomultiplier. Absorption by the sample gives rise to a small 50 kHz alternating current signal which exits from the pre-amplifier and which is fed to a phase lock amplifier which also receives the reference signal from the photoelastic modulator. The lock-in amplifier discriminates the 50 kHz signal from noise at different frequencies and registers the circular differential

FIGURE II.1 MCD Optical Block Diagram

absorbance (ΔA).

An analog-digital converter is then used to plot the information in real-time on a personal computer. The spectrum can also be stored digitally and/or printed.

II. A.2. Spectral Characteristics

Several different effects are grouped under this category: the emission spectrum of the xenon lamp, the roll off of the monochromator and the polarizers, and the non-linearity of the photomultiplier tube.

To maintain constant energy throughput of the system most spectrophotometers vary the amount of incident light by altering the slit width. This system runs at constant slit width to maintain a constant energy band pass, and the intensity throughput is kept constant by altering the photomultiplier tube voltage. The photomultiplier power supply can provide a maximum of 900 volts and it is possible with relatively opaque samples to exceed the dynamic range of this correction circuit and encounter non-linearity in the spectral response. Figure II.2 illustrates the relationship between the photomultiplier tube voltage and output at different slit widths obtained with this instrument.

II. A.3. Software

There are several important parameters associated with the energy axis of any spectrophotometer. These are resolution, which refers to the size of the energy window at any point, the speed with which this window moves across the spectrum and the absolute calibration of the energy axis.

In early spectrophotometers the spectral scan was performed in terms of wavelength. This set a precedent which is unfortunately still followed today in most modern spectrophotometers. There are several reasons why an energy scale should be used in preference to a wavelength scale.

Energy is inversely proportional to the wavelength, therefore band shapes can be severely distorted when plotted with respect to wavelength. This distortion prevents Gaussian or Lorentzian curve fitting of these bands. In addition, band shifts on an energy scale properly reflect constant energy shifts at the molecular level. Lastly and perhaps most importantly, when an energy scale is used, band positions can be mapped directly onto traditional molecular energy calculations. The spectroscopic wavenumber scale has no direct significance to the molecule in this context, but the SI kJmol^{-1} unit is directly interpretable on a bond strength scale.

Intimately related to the concept of energy resolution is time and time constants, that is, the time spent gathering data through a certain energy window. The time constant chosen for a given spectrum must complement the

response time of the instrument and the conditions of the spectrum. This is best achieved by coupling the time resolution to the energy window via a feedback loop thereby giving a direct connection to absorption at any given energy.

Before attempting to characterize the performance of an analytical instrument it must first be shown to be "well-behaved". Being well-behaved, means, that the instrument produces reproducible intensities with satisfactory signal-to-noise ratios and has a relatively flat baseline when there is no sample in the sample holder. It is presumed that the other components of the instrument all behave according to specifications.

In addition to giving reproducible results, the instrument must be controlled in a manner which maximizes the information gathering rate of the electronics while it minimizes the noise in the spectrum. This means coupling many of the operating parameters of the instrument through feedback mechanisms in either hardware or software domains. This results in a complex system in which the operation of components is highly inter-related, requiring well defined criteria of performance to obtain optimized data gathering.

The rate of movement of the energy window across the spectrum in this instrument is controlled by feedback from the slope of the spectrum. As the controlling software detects an increase in the slope of the signal from the lock-in amplifier, indicating a peak is being scanned, the energy scan increment is

reduced below control values. Time resolution or the amount of time (or number of points, or both, depending on the time constant) the software gathers data from the energy window, is controlled by feedback from the signal-to-noise ratio. In this manner the two-level feedback control program spreads spectrum noise throughout the scan.

II. B. EXPERIMENTAL

There is no established protocol for the calibration of a magnetic circular dichroism spectrophotometer. Several existing methods rely upon the values of the differential extinction coefficients of cobalt hexahydrate and potassium ferricyanide. These methods do not provide a calibration over the entire wavelength range.

The important aspects of MCD calibration are to (1) calibrate the energy axis of the instrument, (2) calibrate the sensitivity in CD mode, (3) calibrate the sensitivity in MCD mode, and (4) to check for sensitivity degradation in the magnetic field.

Though accurately known wavelength sources exist, it can be troublesome to disturb the alignment of the instrument lamp in order to check for mercury or iron lines with atomic lamps. In most laboratories, periodic testing of visible spectroscopic instrumentation is carried out using holmium

oxide glass. These calibration standards have been condemned for polarized spectroscopy because localized differences in density, refractive index, or absorption coefficient can affect the polarization of the light having a potentially large impact on the intensity value. However, the energy of absorption is constant over time and is independent of further strain introduced into the glass standard.

CD calibration should be carried out over the entire wavelength range to obtain meaningful readings.⁴² Using the apparatus shown in Figure II.1 with the magnet off, the CD spectra of four accepted standards were measured. These compounds were (1R)-10-Camphorsulfonic acid, Δ -(-)-tris(ethylenediamine) cobalt(III) iodide, D-Pantolactone, and Epiandrosterone. These compounds show large Cotton effects over the range 20000-46000 cm^{-1} .

Camphorsulfonic acid was obtained from Aldrich, D-Pantolactone and Epiandrosterone were purchased from Sigma (lot # 75F-0722 and 57F0626 respectively). The cobalt complex was synthesized following a modified procedure by Broomhead.⁴³ Data listed in Table II.1 report literature CD values from several authors as well as results obtained from this study.

⁴² Schippers, P.H. and Dekkers, P.J.M., *Anal. Chem.*, **53**, 778, (1981).

⁴³ Broomhead, J.A., Dwyer, F.P., and Hogarth, J.W., *Inorg. Syn.*, **6**, 183, (1960).

II. B.1. Synthesis of $\Delta(-)$ -tris(ethylenediamine) cobalt(III) iodide

The composition of an ethylenediamine sample was assessed using methyl orange as the indicator to titrate 1.0 mL of an ethylenediamine sample using 1.00 M hydrochloric acid. The sample of ethylenediamine used was found to be 94.7% (w/v) ethylenediamine. To a filter flask fitted with a rubber stopper and an air inlet tube was added 20.5 mL of 94.7% (w/v) ethylenediamine and 50 mL of distilled water. This mixture was cooled on ice while 10 mL of 12 M hydrochloric acid was added followed by a solution of 28.2 g of cobalt(II) sulfate in 50 mL of distilled water and some activated charcoal. A current of air was allowed to pass through this mixture for 3.5 hours.

Sample	this work		literature ^{45, 47, 48}	
	Energy (cm ⁻¹)	Intensity (mV)	Energy (cm ⁻¹)	Intensity ($\Delta\epsilon$), Lmol ⁻¹ cm ⁻¹
CD:				
EpiAndrosterone	32868	121.20	32895	3.30
Cobalt complex	20302	121.30	20367	1.80
CamphorSulfonic acid	34168	92.32	34364	2.37
Pantolactone	42834	-5.96	45454	-4.88
MCD:				
Co(H ₂ O) ₆ ²⁺	19607	-1.365	20200	-7.86 × 10 ⁻⁷

Table II.1. CD and MCD of the Standard Solutions

Afterwards the pH of the mixture was adjusted to 7 by adding a drop of ethylenediamine. The mixture was then heated on a steam bath for twenty minutes, cooled, the charcoal filtered off, and washed with water.

Barium-d-tartrate was prepared by mixing barium chloride 2-hydrate (24.4 g) and sodium potassium tartrate 4-hydrate (28.2 g) at 90°C, cooling, filtering, and washing with warm water.

The resulting barium-d-tartrate was added to the above mixture and heated in a water bath with mechanical stirring for 45 minutes. A lilac coloured, pasty precipitate (BaSO_4) was filtered off and washed with 30 mL of hot water. The orange filtrate was rotary evaporated to a volume of 60 mL.

Crystallization of (+)-tris(ethylenediamine)cobalt(III) chloride d-tartrate 5-hydrate was allowed to proceed overnight. This product was then filtered, washed with 100 mL of 40% ethanol-water, and recrystallized from approximately 40 mL of hot water. The recrystallized product was washed with 40% ethanol-water followed by 95% ethanol-water. The crystals were air dried to give a yield of 17.1 g or 25%. Throughout the procedure there was substantial physical loss.

In order to synthesize the dextro iodide isomer the chloride d-tartrate obtained was then dissolved in 40 mL of hot water. A small amount (0.5 mL) of concentrated ammonium hydroxide was added and the mixture stirred. At this point a solution of 35 g of sodium iodide in 15 mL of hot water was added. The iodide began crystallizing immediately and was placed in an ice bath to

obtain complete crystallization. The crystals were washed with 30% NaI, ethanol, and acetone respectively. Yield of the powdery, orange dextro-tris(ethylenediamine)cobalt(III) iodide monohydrate was 17.4 g or 30%

II. B.2. Calibration Compounds

(1R)-10-Camphorsulfonic Acid

Optical rotation:

measured: $[\alpha]^{25}_D = +20.2^\circ$; literature: $[\alpha]^{25}_D = +20.8^\circ$ ⁴⁴

The compound was purified by recrystallization twice from ethyl acetate and dried at room temperature in a vacuum dessicator.

CD:

$\lambda_{\max} = 290 \text{ nm}$

Measurements were performed on a $11.35 \times 10^{-3} \text{ M}$ solution in distilled water using a 1 cm path length quartz cell, time constant = 1 second and a spectral quality of 3.

D-Pantolactone

Optical rotation:

measured: $[\alpha]^{25}_D = -51.9^\circ$; literature: $[\alpha]^{25}_D = -50.7^\circ$ ⁴⁵

CD:

$\lambda_{\max} = 220 \text{ nm}$

Measurements were performed on a $4.24 \times 10^{-3} \text{ M}$ solution in distilled water using a 1 cm path length quartz cell, time constant = 1 second and a spectral quality of 3.

⁴⁴ Gillen, M.F., and Williams, R.E., *Can. J. Chem.*, **53**, 2351, (1975).

⁴⁵ The Merck Index, 11th edition, ed. Budavari, S., Merck & Co., (1989).

Epi-Androsterone**Optical rotation:**

measured: $[\alpha]^{25}_D = +87.2^\circ$; literature: $[\alpha]^{25}_D = +83.9^\circ$ ⁴²

CD:

$\lambda_{\max} = 304 \text{ nm}$

Measurements were performed on a $4.70 \times 10^{-3} \text{ M}$ solution in dioxane (spectrograde Aldrich) using a 1 cm path length quartz cell with time constant = 1 second and spectral quality of 3.

Cobalt Complex: $[\text{Co}(\text{en})_3]\text{I}_3 \cdot \text{H}_2\text{O}$ **Optical rotation:**

measured: $[\alpha]^{25}_D = +85.1^\circ$; literature: $[\alpha]^{25}_D = +91.0^\circ$ ⁴⁷

The complex was recrystallized twice from hot water, no change in rotation was observed.

CD:

$\lambda_{\max} = 490 \text{ nm}$

Measurements were performed on a $18.5 \times 10^{-3} \text{ M}$ solution in distilled water in a 1 cm quartz cell with time constant = 1 second and spectral quality of 3.

II. C. RESULTS

The relationship between slit width, energy and photomultiplier tube voltage was investigated (Figure II.2). For various slit widths, the photomultiplier tube voltage was measured as a function of energy. The conditions for this scan were a spectral quality of 1 and a time constant of 1 second.

The baseline behaviour of the available MCD instrument was recorded by running the instrument with no sample present (Figure II.3). The deviation

from a perfectly flat baseline is slight in the dynamic range needed for analysis. Full scale deflection is 2×10^{-7} ΔA units. This however, is not an absolute limit since the baseline can be digitally subtracted.

The level of sensitivity of the instrument was measured by plotting the signal-to-noise ratio versus $\log \Delta A$ for cobalt hexahydrate at 20000 cm^{-1} (Figure II.4). This method is similar to the method used by Policke⁴⁶ and the Japan Spectroscopic Company Ltd. The points were obtained by varying the concentration of cobalt hexahydrate from 10^{-1} M to 10^{-5} M . The slit was kept steady at 1.0 mm and the time constant was fixed at 1.0 s. The spectrum signal-to-noise ratio was defined as the average spectral signal divided by the standard deviation of the signal over some interval. Extrapolation of the curve to a signal-to-noise ratio of 1 yields a sensitivity limit of approximately $1 \times 10^{-7} \Delta A$.

The initial circular dichroism calibration curve was constructed using the four compounds listed in Section II.B.2. Attempts were made to find other suitable compounds but the four used are particularly useful due to their large differential absorption signals. In order to test the purity of the compounds their absorption spectra and rotation of plane polarized light were measured.

The CD calibration was checked using literature values for the MCD of cobalt hexahydrate⁴⁷ which is also shown in Figure II.5. The scan was

⁴⁶ Policke, T.A., *Ph.D. Thesis*, North Carolina State University, (1989).

⁴⁷ Kaden, T.A., Holmquist, B., and Vallee, B.L., *Inorg. Chem.*, **13**(11), (1974).

performed with the magnet on and off to observe any possible degradation of the signal.

All compounds showed a signal-to-noise ratio of at least ten and constant intensity over repeated scans several weeks apart.

Figure II.2.

Photomultiplier tube voltage of the MCD instrument in Figure II.1 versus energy at different slit widths. Errors are within the dimensions of the plotted points.

Figure II.3.

Baseline with no sample in the sample holder of the instrument in Figure II.1. Full scale deflection is $2 \times 10^{-7} \Delta A$.

Figure II.4. MCD sensitivity curve as a function of the S/N ratio versus $\log(\Delta\lambda)$ for various concentrations of $\text{Co}(\text{H}_2\text{O})_6^{2+}$.

Figure II.5.

Calibration curve for the MCD spectrophotometer in Figure II.1. The graph plots lock-in amplifier voltage against peak intensity ΔA . Errors are within the dimensions of the plotted points.

II. D. DISCUSSION

Several papers have detailed the difficulties encountered when calibration of a circular dichrometer is performed using only one compound.^{48,49} In the latter reference, in a survey of a large number of CD spectrophotometers, after calibration at 291 nm, the spectrophotometers gave readings differing by up to 25% at 222 nm and 491 nm. This comparative method of calibration does however seem to be better than the non-comparative absolute methods.

Absolute calibration of CD spectrophotometers can proceed by three main paths. The first method is indirect and theoretical in nature, it involves a study of the signal processing of the various components of the CD.⁴⁹ The second route uses optical filters of known ellipticity. This method is limited by the accuracy to which the ellipticity of the filters is known. In addition the strains which exist in solids can cause localized differences in absorption coefficients, which can have a large effect on the polarization of the light. The position of the photoelastic modulator as last in the optic array is designed to avoid this problem. The third method of absolute calibration utilizes the Kramers-Kronig relations which allow the exact calculation of a CD spectrum from an ORD curve provided the ORD is known over the entire wavelength

⁴⁸ Tuzimura, K., Konno, T., Meguro, H., Hatano, M., Murakami, T., Kashiwabara, K., Saito, K., Kondo, Y., and Suzuki, T.M., *Anal. Biochem.*, **81**, 167, (1977).

⁴⁹ Davidsson, Å. and Norden, B., *Spectrochimica Acta*, **32A**, 717, (1976).

range. Though absolute ORD data is obtained relatively easily, the ORD curve corresponding to a particular CD band is only partially due to that band. Background rotation from other CD transitions also contribute.

Comparative calibration was undertaken in this study using first a coarse calibration of the CD using compounds with large differential absorption and then a fine adjustment using the MCD measurement of a well-known MCD standard. The resulting calibration curve is shown in Figure II.5.

Pantolactone ($\lambda_{\text{max}} = 220 \text{ nm}$) has an intensity reading approximately 15 times too small. A lower than expected intensity value in this region of the spectrum is apparently quite common in CD instruments. Some authors have explained this as a small static birefringence in the modulator which interferes with the CD measurement.⁴² Using amino acids (many of which absorb in this region) to test the extent of the problem it was found that it exists up to about 285 nm and generally reduces the intensity of any peaks in this below this value.

L-Tryptophan contains the indole chromophore and exhibits absorption in the 260 - 290 nm region. Three positive dichroic peaks centred at 291, 281, and 272 nm are reported.⁵⁰ A study listing these bands as unresolved has also been published.⁵¹ Legrand and Viennet⁵² give circular dichroism data for a

⁵⁰ Myer, Y.P. and MacDonald L.H., *J. Amer. Chem. Soc.*, **89**, 7142, (1967).

⁵¹ Verbit, L. and Heffron, P.J., *Tetrahedron*, **23**, 3865, (1967).

⁵² Legrand, M. and Viennet, R., *Bulletin de la Société Chimique de France*, no. 121, 679, (1965).

variety of amino acids and list the intensity of this band at $0.35 \text{ Lmol}^{-1}\text{cm}^{-1}$.

Similarly L-Histidine and L-Phenylalanine were also examined. L-Histidine contains the imidazole chromophore and has a positive Cotton effect at 214 nm with an intensity of $+2.70 \text{ Lmol}^{-1}\text{cm}^{-1}$ at pH 7. L-Phenylalanine shows a number of weak Cotton effects in the 260 nm region associated with the symmetry forbidden $\pi\text{-}\pi^*$ transition of the aromatic ring. In addition there is a positive Cotton effect centred at 218 nm with an intensity of $+3.0 \text{ Lmol}^{-1}\text{cm}^{-1}$.⁵³

The measured spectrum of L-Tryptophan showed no peaks in the region 200 - 300 nm in contrast to a reported weak intensity peak at 266 nm.

The CD spectrum of L-Histidine shows a positive Cotton effect at 240 nm with an intensity of $\Delta\epsilon = 2.1 \times 10^{-3} \text{ Lmol}^{-1}\text{cm}^{-1}$. This peak is red-shifted 25 nm. In addition the magnitude of the response is three orders of magnitude too small.

The spectrum of L-Phenylalanine instead of having a peak at 218 nm has one at 228 nm and the peak intensity is about two orders of magnitude too small.

Literature values show Pantolactone peaks at 220 nm with $\Delta\epsilon = -4.90 \text{ Lmol}^{-1}\text{cm}^{-1}$.⁴² Using the spectrum obtained in this study the peak is red-shifted to 233 nm and is only three percent of its reported magnitude.

To recapitulate, the compounds studied which had Cotton effects in the

⁵³ Goodman, M. and Toniolo, C., *Biopolymers*, **6**, 1673, (1968).

210 to 270 nm range have two distinct characteristics when measured with our instrument. The peaks are red-shifted anywhere from 10 - 25 nm and they are greatly reduced in intensity.

This behaviour points to a problem in the ultra-violet which becomes less severe towards the visible region. This is probably caused by a non-linear response of the photomultiplier as a result of saturation effects. These saturation effects of the photomultiplier power supply exist in the high energy region of the spectrum (see Figure II.2). Above 285 nm the instrument measurements agreed with literature values. The red shifting of peaks in this high energy region suggests there may be misaligned components inside the monochromator.

These problems, which do not exist in a new instrument built in this laboratory, are confined to the near ultraviolet. Since the present research uses transitions in the visible region, they have no effect on the spectra and results obtained in this study.

III. ANALYSIS OF ORGANIC NITROGEN COMPOUNDS

III. A. INTRODUCTION

Crude oil is a heterogeneous mixture of many components. It is most likely that the impurities are distributed unequally throughout these components. Thus to determine whether porphyrin concentrations can be used to analyze for total nitrogen and heavy metals, these distribution patterns must be found. It is possible that preferential concentration of porphyrins could then be exploited in designing a rapid analysis procedure for process control which is based on the minimum possible sample preparation.

III. A.1. Fractionation of Crude Oils

Boiling point is used as the basis for fractionation in crude petroleum refining, but on a laboratory scale, separations based on solubility in alkane solvents or chromatography are more practical. Early separation schemes relied on extraction of components by soxhlet using solvents such as dichloromethane or tetrahydrofuran, but due to the instability of some nitrogen compounds to air, light and high temperature, this method has been supplanted by other techniques.

Current laboratory methods of crude oil fractionation favour chromatography. The use of chromatography in crude petroleum separation was first introduced by Munday and Eaves for the separation of organic acids and bases, and pyrrolic nitrogen compounds in crude petroleum.⁵⁴ The development of resins designed specifically for large organic molecules in non-aqueous media made this method popular for petroleum analysis.^{55, 56, 57}

While analysis of simple chromatographic fractions containing bulk quantities of compounds seems primitive, it is a very useful method when examination of the basic compounds in crude petroleum is desired.

The initial separation of crude petroleum into an asphaltene and maltene fraction is defined operationally. The classical definition for asphaltenes is that they are soluble in benzene but insoluble in n-pentane, whereas maltenes are soluble in both benzene and n-pentane. Asphaltenes however, can also be classified by the particular paraffin used to precipitate them from the benzene soluble portion of the feed. Corbett and Petrossi have shown that the yield of n-alkane insolubles depend upon the carbon number

⁵⁴ Munday, W.A. and Eaves, A., 5th World Pet. Congress, Section V, Paper 9, (1959).

⁵⁵ Webster, P.V., Wilson, J.N., and Franks, M.C., *Anal. Chim. Acta*, **38**, 193, (1967).

⁵⁶ Jewell, D.M., Weber, J.H., Bunger, J.W., Plancher, H., and Latham, D.R., *Anal. Chem.*, **44**, 1391, (1972).

⁵⁷ Bunger, J.W., *Shale oil, Tar sands, and related fuel sources*, Advances in Chemistry Series 151, 121, (1976).

Figure III. 1. The effect of solvent carbon number on the generation of precipitate from an Arabian light atmospheric residuum - 100/1 (v/w).⁶⁷

of the precipitating n-alkane (Figure III.1.).⁵⁸ The amount of precipitate decreases with higher carbon number n-alkane solvents until it reaches n-heptane where there is very little difference in the amount of precipitate between n-heptane and heavier n-alkanes. The additional precipitate from lower carbon number solvents is comprised of less polar material of higher molecular weight and more polar material of lower molecular weight.⁷

Another powerful chromatographic technique for the separation of petroleum fractions is high performance liquid chromatography. This technique allows flexibility in the types of solvents and columns employed, avoids high temperatures and has good resolution. With peak isolation methods and the ability to couple the HPLC to an element selective technique such as GFAAS or structure determination methods, HPLC is a primary tool in the identification and quantification of components.

III. A.2. Metalloporphyrin Analysis

Many methods of isolation and separation exist for geoporphyrins and nitrogen compounds found in fractions of crude petroleum. The selection of any one method is dependant upon the goals of the research and the limitations these goals impose upon the method.

Nitrogen concentrations have, until recently been detected in samples

⁵⁸ Corbett, L.W., and Petrossi, U., *Ind. Eng. Chem. Prod. Res. Dev.*, **17**, 342, (1978).

using the well-known Kjeldahl technique. In this technique the sample is oxidized in hot sulfuric acid, during which the nitrogen is converted to ammonium ion. This process does not preserve the original species but reduces most of the organic nitrogen compounds to ammonia after addition of an excess of strong base. Many compounds, particularly stable azaarenes, are not reliably detected by this technique unless special precautions are followed. More recently ICP/MS methods have been introduced which are faster, but these techniques are also destructive.

Metalloporphyrins, due to their value as biological markers, have received more attention from analytical chemists than other components of crude petroleum. Metalloporphyrins are often closely associated with other aromatic heterocyclic nitrogen compounds in crude oils. These compounds, like metalloporphyrins, span a range of basicities and therefore similar separation techniques can be used on them (see Appendix B). Metalloporphyrins, due to their diversity and the complexity of the petroleum matrix, are not concentrated in any one fraction during either precipitation with n-alkane solvents or ion-exchange procedures. To determine their form various approaches are available.

Methods used to characterize porphyrins include the analysis of bulk porphyrins using various methods such as uv/vis and mass spectrometry of chromatographic concentrates, speciation of single porphyrins by HPLC

separation^{59,60} and peak isolation followed by structure determination by high field NMR,^{61,62} X-ray diffraction,⁶³ GC/MS of derivatized porphyrins^{64,65} and tandem mass spectrometry (MS/MS).⁶⁶ Electron spin resonance has been used to determine that vanadium in the +4 oxidation state is bonded to sulfur in petroleum.⁶⁷ This is inferred from the ligand- g_0 value which is a function of the electron-donating ability of the heteroatom coordinated to the vanadium. These data show that in some chromatographic fractions the environment around the vanadyl entity is not the porphyrin ligand system (VON_4).

Many detailed investigations of the base fractions in petroleums have

⁵⁹ Barwise, A.J.G., *Metal Complexes in Fossil Fuels*, ACS Symp. Series. 344, pp. 100, (1987).

⁶⁰ Sundararaman, P., *Anal. Chem.*, 57, 2204, (1985).

⁶¹ Ocampo, R., Callot, H.J., and Albrecht, P., *J. Chem. Soc., Chem. Commun.*, 198, (1985).

⁶² Chicarelli, M.I., Kaur, S., and Maxwell, J.R., in *Metal Complexes in Fossil Fuels*, ACS Symp. Series 344, pp. 40, (1987).

⁶³ Storm, C.B., Krane, J., Skjtene, T., Telnaes, N., Branthaver, J.F., and Baker, E.W., *Science*, 223, 1075, (1984).

⁶⁴ Marriott, P.J., Gill, J.P., and Eglinton, G., *J. Chromatography*, 249, 291, (1982).

⁶⁵ Marriott, P.J. and Eglinton, G., *J. Chromatography*, 249, 311, (1982).

⁶⁶ Johnson, J.V., Britton, E.D., Yost, R.A., and Quirke, J.M., *Anal. Chem.* 58, 2204, (1986).

⁶⁷ Dickson, F.E. and Petrakis, L., *Anal. Chem.*, 46, 1129, (1974).

been conducted.^{68, 69, 70} HPLC coupled with GFAAS or ICPE^{71, 72, 73} detectors have revealed the complex nature and ubiquity of these compounds in the different components of crude petroleums. The strong bases present in petroleum appear to be largely azaarenes, many of which have been fully characterized, together with some metalloporphyrins. Progress in analytical methodology is making higher molecular weight azaarenes amenable to quantification. In addition, many analytical techniques are being applied to the identification of these compounds. Fluorescence analysis and the Shpol'skii effect, as well as GC/MS, are being used for the speciation of azaarenes in petroleum.

Ion exchange is still used as a separation technique for nitrogen compounds in crude petroleum since it provides a very simple method for the enrichment of these compounds. Silica gel, gel permeation and size exclusion chromatography are also all used for the separation of petroleum

⁶⁸ Uden, P.C., Carpenter, A.P., Hackett, H.M., Henderson, D.E., and Siggia, S., *Analyt. Chem.*, 51, 38, (1979).

⁶⁹ Jewell, D.M., Yevich, J.P., and Snyder, R.E., ASTM STP 389, Am. Soc. testing Mats., 363, (1965).

⁷⁰ McKay, J.F., Weber, J.H., and Latham, D.R., *Anal. Chem.*, 48(6), 891, (1976).

⁷¹ Fish, R.A. and Reynolds, J.G., *Trends Anal. Chem.*, 7, 174, (1988).

⁷² Fish, R.A., Komlenic, J.J., and Wines, B.K., *Anal. Chem.*, 56, 2452, (1984).

⁷³ Reynolds, J.G. and Biggs, W.R., *Acc. Chem. Res.*, 21, 319, (1988).

components.^{74, 75}

Gas chromatography (GC) offers another method of analysis. However, the basicity of some of these compounds can cause irreversible column adsorption and column bleed. GC/MS is an extremely powerful technique for both separation of the many isomers present and identification of the specific structures through fragmentation patterns but is susceptible to some of the same column problems as GC. Preparation of petroleum samples for GC/MS analysis is arduous and precludes GC/MS as an on-line detection system.

None of these investigative experimental methods however, are suitable for routine on-line quantification of impurities due to the extensive sample preparation required.

III. A.3. Heavy Metal Analysis

Analytical detection of metals in crude petroleum samples is not straight forward due to the complex petroleum matrix. This matrix also makes demetallation difficult since destruction of the particle aggregates is necessary as well as removal of the metal ion. Quantitative studies on the efficiencies of demetallation have rarely been mentioned in the literature but need to be performed. For present purposes however, demetallation is not essential.

⁷⁴ Hall, G. and Herron, S.P., *Chemistry of Asphaltenes*, Advances in Chemistry Series 195, 137, (1981).

⁷⁵ Gratzfeld-Hüsgen, A., *LC-GC*, 7(10), 837, (1989).

Preliminary studies have shown that most of the heavy metals are found in the nitrogenous impurities. More specifically the metals lighter than iron are usually found in the fossilized porphyrins. Thus, an analysis for porphyrins is coincidently an analysis of these metals.

III. B. EXPERIMENTAL

The bitumen sample was obtained by the Clark hot water extraction process from the Athabasca tar sands in Alberta, Canada. The tar-bearing sand was digested with benzene for 24 hours and filtered through a sintered glass funnel and the benzene removed by rotary evaporation.

This material was used as the starting material for subsequent separation into fractions. Elemental analysis of the material for C, H, and N and MCD spectra were taken to aid in the characterization of the starting material.

III. B.1. Fractionation

The filtered crude sample was initially divided into five fractions pentane, hexane, and heptane asphaltenes, resins and a deasphalted oil fraction.

Several 50 g samples of the crude bitumen were digested in 2 litres of n-pentane (Caledon). The asphaltene fraction, defined as the insoluble portion of a 40:1 (v/w) mixture of n-pentane with the bitumen, comprised approximately 30% of the original sample depending on the digestion time with the n-pentane, the n-pentane soluble or maltene fraction comprised 65%.

Once obtained the asphaltenes were further separated by analogous treatment with n-hexane (Caledon) and n-heptane (Caledon) to give exclusively n-pentane asphaltenes, n-hexane asphaltenes and n-heptane asphaltenes. The n-pentane asphaltenes contained material which was insoluble in n-pentane but soluble in n-hexane. The n-hexane asphaltenes contained material insoluble in n-hexane but soluble in n-heptane. The final asphaltene fraction, n-heptane asphaltenes, contain compounds which were insoluble in n-heptane.

Maltenes were divided into a resins and deasphalted oil fraction by mixing the maltenes with propane 25:1 (v/w) in a flask cooled to dry ice temperatures. During this procedure the flask was agitated violently to avoid the formation of clumps of resinous material. Afterwards, the solid resins were filtered and washed with propane. The deasphalted oil fraction was obtained from the propane solution by allowing the propane to evaporate which resulted in an orange viscous liquid.

All fractions except for the hexane asphaltenes were then further separated into acids, bases, saturates, and aromatics.

Samples of the bitumen fractions were dissolved in cyclohexane and

treated to columns containing Amberlyst 15 cation exchange resin (sulfonic acid form, from Rohm and Haas). This resin was particularly suited for the analysis due to its large pore structure and stability in non-aqueous solvents. The column was eluted to remove non-reactive material with 4 bed volumes of cyclohexane. Retained bases were eluted with benzene, benzene-methanol azeotrope, and benzene-methanol-isopropylamine azeotrope. The resulting basic samples were stored in amber vials under nitrogen gas at room temperature for future analysis.

The non-basic fraction was redissolved in cyclohexane and added to Amberlyst 29 anion resin (OH^- , from Rohm and Haas).

Retained acids were eluted with 5% acetic acid-95% benzene and stored for further analysis.

The non-basic, non-acidic fraction was rotary evaporated to remove cyclohexane and redissolved in dichloromethane and coated to Davisil, Silica gel (150 Å) from Aldrich Co.. After evaporation of the dichloromethane the coated silica was dry-packed into a column and treated with 3 bed volumes of cyclohexane to remove the saturates, followed by benzene-methanol azeotrope to elute the aromatic fraction. The experimental scheme for the separation of the crude petroleum into various fractions is seen in Figure III.2. and Figure III.3.

III. B.2. Analysis of Fractions

UV/VIS Spectra:

Absorption spectra were obtained on a Lambda 4b Perkin-Elmer uv/vis spectrophotometer in benzene solution utilizing a 1 mm path length cell.

MCD Spectra:

MCD spectra were taken on a custom-built MCD spectrophotometer (Fig. II.1). All spectra were taken in benzene solution using 1 cm path length quartz cells, a 1 mm slit, a time constant of 1 second and a spectral quality between 5 and 8.

Spectral Quality is a parametre which controls the selection of data points and ultimately affects the signal-to-noise ratio. Low intensity peaks require a high spectral quality for better resolution.

GC:

Preliminary GC work was performed on a Varian 3400 gas chromatograph equipped with a 1045 Split/Splitless injection system, a 30 m, DB 5 capillary column, and a thermionic specific detector.

GC/MS:

Exploratory GC/MS was performed on a Varian system using a DB 5 column emerging into a 70 V ion trap mass spectrometer. Temperature programs usually employed were a steep ramp at 20 °C to a final column temperature of 300 °C.

Elemental Analysis:

Elemental analysis was carried out on certain samples for carbon, hydrogen, and nitrogen by Canadian Microanalytical Service Ltd..

Figure III.2.

Experimental Scheme for separating the asphaltene fractions from the bitumen.

Figure III.3.

Experimental scheme for separating the maltene fractions from the bitumen.

III. B.3. Synthesis of Metalloporphyrin

No general method for the synthesis of metalloporphyrins exists due to problems with solubility, the lability of the metalloporphyrin, the stability of the metal carrier and the donor strength of the solvent. However, certain specific methods have given high yields of product.

A similar procedure to that of Buchler was used to synthesize vanadyl tetraphenylporphine (VOTPP).⁷⁶

TPP (0.2005 g) (Aldrich: 16,099-7) was dissolved in 50 mL of a chloroform-methanol azeotrope (69 mole percent chloroform) and added to a solution of 0.2509 g of vanadyl sulfate hydrate (Aldrich: 23,370-6) in 50 mL of the same azeotrope. The solution was refluxed for 3 hours after which excess methanol was added to force the metalloporphyrin out of solution. The crystalline product was filtered and washed with water. The yield of the crude product was 70%. During refluxing and prior to filtering the mixture was shielded from light to avoid decomposition. Absorption spectra of the starting material versus the reaction product showed a reduction in intensity of the Soret band and a change from a four band structure to two bands in the 18000 - 20000 cm^{-1} range.

The crude product was purified by dissolving it in trichloroethylene,

⁷⁶ Buchler, J.W., et al, *Liebigs Ann. Chem.*, 745, 135, (1971).

filtering and chromatographing on an alumina column.⁷⁷ Elution with additional trichloroethylene resulted in a brownish effluent. A green band remained on the column which when eluted with acetone proved to be unreacted tetraphenylporphine (TPP). Evaporation of trichloroethylene gave a dark violet solid, which was recrystallized from chloroform-methanol to give a final yield of 58%.

A stock solution of the product, VOTPP, was used to create solutions of 2.43×10^{-6} M, 4.68×10^{-7} M, 1.90×10^{-8} M, and 9.55×10^{-9} M in benzene, which were used to make a calibration curve relating the Soret and Q band peak heights to the quantity of VOTPP.

III. B.4. Total Metal Content

The total metal content of the bitumen sample can be determined by using an element selective technique on portions of the crude. Demetallation is usually used in order to quantify the amount of porphyrin. For this purpose, the method has drawbacks since usually one-third of the original porphyrins are lost.⁷⁸ However, as a method of quantifying the total metal content, demetallation using strong acid is expected to have high yields.

⁷⁷ Vaughan, G.B., Tynan, E.C., and Yen, T.F., *Chem. Geol.*, 6, 203, (1970).

⁷⁸ Barwise, A.J.G. and Whitehead, E.V., *Advances in Organic Chemistry, Physics and Chemistry of the Earth*, 12, ed. Douglas, A.G. and Maxwell, J.R., Pergamon Press, (1980).

A 40 g sample of the crude petroleum to be demetallated was mixed with 150 mL of 85% phosphoric acid and heated to 180°C in an oil bath for several hours. It was then poured onto cracked ice and treated with 150 mL of 5% HCl.

Graphite furnace AAS indicated that there were no detectable limits of vanadium or nickel in the aqueous phase. The procedure was then repeated with sonication for 1, 2 and 6 hours in an attempt to break up the aggregate particles. This procedure did not aid in detecting vanadium or nickel in the crude samples.

III. C. RESULTS

Vanadyl porphyrin (VOP) concentrations, in grams VOP per gram of fraction (C), were calculated from absorption spectra using this equation,⁵

$$C = \frac{A \times M.W.}{\epsilon l} \times 100(\text{wt } \%)$$

where A is the absorbance of the VOP solution at 570 nm; ϵ is the molar extinction coefficient of VOP, $2.9 \times 10^4 \text{ Lmol}^{-1}\text{cm}^{-1}$; M.W. is the molecular weight of petroleum vanadyl porphyrin (510 gmol^{-1}); l is the path length and m is the concentration of the fraction being measured in g/L.

Q-bands used to determine the metalloporphyrin concentrations from

MCD spectroscopy were for the most part extremely intense with a signal-to-noise ratio in excess of 100. A few samples however, had much lower signal-to-noise ratios and they are identified by their low (close to zero) porphyrin contents.

Table III.1 lists the recovery yields after fractionation of the crude as well as the porphyrin content of each fraction.

Table III.3 shows the results from elemental analysis of several fractions.

The weight percent porphyrin was calculated from the spectra using the calibration formula from Figure III.5. Beer's law relationships exist between the differential absorbance values of the Q and B bands and their concentrations. The MCD response of vanadyl tetraphenylporphyrin (VOTPP) was used as a standard with which to calibrate the experimental signals. The results were,

$$\text{Q-band:} \quad \text{porphyrin (g/L)} = \frac{\Delta A - 3.0228 \times 10^{-6}}{0.01930}$$

$$\text{B-band:} \quad \text{porphyrin (g/L)} = \frac{\Delta A - 2.7577 \times 10^{-7}}{0.01332}$$

where ΔA is the differential absorbance of the appropriate transition.

The nitrogen content plotted in Figure III.8 was determined from the MCD Q-band metalloporphyrin content by multiplying by the fraction of nitrogen contained in VOTPP.

Bitumen	Recovery as Percent of Bitumen	Fraction	Recovery as percent of Fraction	Porphyrin Content		
				MCD Q band	MCD B band	Absorption 570 nm
	%		%	wt %	wt %	wt %
Deasphalted Oil	34 ± 3			0.17 ± 0.02	0.22 ± 0.02	0.37 ± 0.01
		Weak Bases	8 ± 1	0.14 ± 0.2	0.13 ± 0.01	0.54 ± 0.08
		Medium Bases	9 ± 1	0.13 ± 0.02	0.00	0.9 ± 0.1
		Strong Bases	1.0 ± 0.1	0.00	0.00	3.5 ± 0.4
		Acids	7 ± 1	0.00	0.00	0.12 ± 0.01
		Saturates	69 ± 12	0.00	0.28 ± 0.03	0.23 ± 0.03
		Aromatics	7 ± 1	0.00	0.00	0.75 ± 0.08
Resins	35 ± 3			2.87 ± 0.09	2.69 ± 0.03	0.77 ± 0.01
		Weak Bases	3.0 ± 0.2	4.2 ± 0.1	0.00	0.9 ± 0.1
		Medium Bases	15 ± 1	3.9 ± 0.1	0.00	1.9 ± 0.2
		Strong Bases	7 ± 1	1.58 ± 0.05	0.00	2.2 ± 0.2
		Acids	21 ± 3	0.39 ± 0.05	0.40 ± 0.04	0.9 ± 0.1
		Saturates	0	0.00	0.00	0.00
		Aromatics	54 ± 10	0.41 ± 0.05	0.52 ± 0.08	4.1 ± 0.4
Pentane Asphaltenes	4.0 ± 0.1			5.5 ± 0.2	0.00	1.19 ± 0.01
		Weak Bases	15 ± 1	8.3 ± 0.2	1.65 ± 0.02	1.45 ± 0.01
		Medium Bases	23 ± 1	6.8 ± 0.2	3.13 ± 0.03	2.5 ± 0.3
		Strong Bases	4.0 ± 0.2	4.7 ± 0.6	0.00	3.1 ± 0.3
		Acids	52 ± 5	0.010 ± 0.001	0.06 ± 0.01	0.20 ± 0.02
		Saturates	<1	0.00	0.00	0.00
		Aromatics	<1	0.00	0.00	0.00
Hexane Asphaltenes	1.0 ± 0.1			10.23 ± 0.03	2.28 ± 0.02	1.20 ± 0.01
Heptane Asphaltenes	19 ± 1			1.85 ± 0.06	0.00	5.8 ± 0.6
		Weak Bases	32 ± 2	0.99 ± 0.03	0.00	6.4 ± 0.7
		Medium Bases	14 ± 1	3.9 ± 0.1	2.90 ± 0.03	2.5 ± 0.3
		Strong Bases	7.0 ± 0.4	2.51 ± 0.08	0.00	3.0 ± 0.3
		Acids	6 ± 1	1.0 ± 0.1	0.84 ± 0.09	3.5 ± 0.4
		Saturates	28 ± 4	0.00	0.53 ± 0.06	0.52 ± 0.06
		Aromatics	12 ± 2	4.1 ± 0.1	4.24 ± 0.04	0.82 ± 0.09

Table III.1.

Percent recovery and porphyrin content of petroleum fractions and sub-fractions

Sample Description	C (%)	H (%)	H/C Ratio	N (%)	N/C Ratio
bitumen	70.7 ± 0.7	9.9 ± 0.1	1.67 ± 0.04	0.37 ± 0.01	0.004 ± 0.0002
malenes	80.6 ± 0.8	8.18 ± 0.08	1.21 ± 0.02	1.13 ± 0.03	0.012 ± 0.001
asphaltenes	82.5 ± 0.8	10.7 ± 0.1	1.55 ± 0.04	0.29 ± 0.01	0.003 ± 0.0001
oil fraction	84.8 ± 0.8	10.5 ± 0.1	1.48 ± 0.02	0.15 ± 0.01	0.002 ± 0.0001
medium-basic oil	86.4 ± 0.7	8.91 ± 0.09	1.80 ± 0.04	0.88 ± 0.02	0.0114 ± 0.002
saturate oil	86.6 ± 0.9	11.5 ± 0.1	1.80 ± 0.04	< 0.1	< 0.001
acids oil	82.8 ± 0.5	7.85 ± 0.08	1.73 ± 0.04	1.43 ± 0.03	0.023 ± 0.002
resins	83.1 ± 0.8	9.8 ± 0.1	1.40 ± 0.02	0.44 ± 0.01	0.004 ± 0.001
weakly basic resins	82.4 ± 0.8	8.37 ± 0.08	1.21 ± 0.02	0.85 ± 0.02	0.009 ± 0.001
medium-basic resins	71.9 ± 0.7	8.49 ± 0.08	1.41 ± 0.02	0.99 ± 0.03	0.012 ± 0.001
strongly basic resins	81.4 ± 0.8	9.21 ± 0.09	1.35 ± 0.02	1.49 ± 0.04	0.016 ± 0.002
resin acids	55.8 ± 0.8	7.03 ± 0.07	1.50 ± 0.04	0.92 ± 0.03	0.014 ± 0.002
resin aromatics	78.8 ± 0.8	8.07 ± 0.08	1.22 ± 0.02	1.17 ± 0.03	0.013 ± 0.001
pentane asphaltenes	81.9 ± 0.8	9.09 ± 0.09	1.32 ± 0.02	0.76 ± 0.03	0.008 ± 0.001
weakly-basic pentane asphaltenes	79.3 ± 0.8	7.94 ± 0.08	1.19 ± 0.02	0.81 ± 0.03	0.009 ± 0.001
medium-basic pentane asphaltenes	68.2 ± 0.7	7.80 ± 0.08	1.36 ± 0.02	1.00 ± 0.03	0.013 ± 0.001
hexane asphaltenes	80.7 ± 0.8	8.53 ± 0.09	1.26 ± 0.02	0.96 ± 0.03	0.010 ± 0.001
heptane asphaltenes	80.2 ± 0.8	7.94 ± 0.08	1.18 ± 0.02	1.20 ± 0.04	0.013 ± 0.001
weakly-basic heptane asphaltenes	79.3 ± 0.8	7.53 ± 0.08	1.13 ± 0.02	1.35 ± 0.04	0.015 ± 0.002
medium-basic heptane asphaltenes	48.5 ± 0.5	6.13 ± 0.06	1.51 ± 0.03	0.77 ± 0.03	0.014 ± 0.002
strongly basic heptane asphaltenes	78.0 ± 0.8	8.14 ± 0.08	1.24 ± 0.02	1.44 ± 0.04	0.016 ± 0.002
heptane saturates	84.7 ± 0.8	11.3 ± 0.1	1.58 ± 0.04	< 0.1	< 0.001
heptane acids	71.3 ± 0.7	7.72 ± 0.08	1.29 ± 0.02	1.02 ± 0.03	0.012 ± 0.001
heptane aromatics	79.0 ± 0.8	9.25 ± 0.09	1.39 ± 0.02	0.57 ± 0.02	0.008 ± 0.001

Table III.2.

Elemental Analysis results for Carbon, Hydrogen and Nitrogen isolated from fractions of an Athabasca crude petroleum.

Figure III.4. Relationship between the static average electric polarizability volume of groundstate molecules and the number of carbons in the alkane extraction solvents.

Figure III.5.

Calibration curve for quantification of porphyrin. Both curves use VOTPP as a model petroporphyrin. Errors are within the dimensions of the plotted points.

Figure III.6.

Amount of porphyrin based on the porphyrin Q band as a function of petroleum fraction. Errors listed in Table III.1.

Figure III.7. Total porphyrin content across all isolated fractions as determined from the MCD of the Q band. The nitrogen content increases linearly from the propane to n-hexane extract.

Figure III.8. Comparison of the total nitrogen content of various fractions determined by elemental analysis and the nitrogen content based on the MCD of the metalloporphyrin Q band. Errors listed in Tables III.1 and III.2. Abcissa fractions related by polarizability (Figure III.4).

Figure III.9. Base, acid and aromatic separation based on their respective metalloporphyrin concentrations in alkane extracts.

III. D. DISCUSSION

An evaluation of the utility of magnetic circular dichroism (MCD) in determining the quantity of metalloporphyrin and its relationship to other nitrogenous compounds in crude petroleum is made. The quantification was determined by relating the MCD peak-to-trough amplitude of the Q_{660} band of samples of an Athabasca tar sands crude to calibration values.

The sample was separated into groups which correlate with distillate fractions normally found in a refinery. Within each fraction, sub-fractions were collected based on their acidity or basicity. Each sub-fraction was characterized by means of MCD and Absorption spectroscopy. Elemental analysis was also performed on selected fractions. GC/MS and GC/TSD (thermionic specific detector - sensitive to nitrogen and phosphorous) were performed only on preliminary fractions due to fraction acidity and basicity and the inadequacy of certain reference compounds.

III. D.1. Nature of Crudes

The petroleum used in this study was probably generated during the late Cretaceous (65-85 million years ago) and therefore probably has not yet reached its equilibrium distribution point. As a result any chemical analysis represents only a snapshot of the degradative chemical reaction pathway. However, certain conclusions can be drawn by considering the standard

enthalpy of formation data listed in Table III.3. One of the metalloporphyrin species which has been identified in crude petroleum are the etioporphyrins. These are more stable than the azaarenes in the demetallated state and it is expected that metallation will stabilize these compounds further. If enough energy is added to the refining process to hydrogenate the metalloporphyrins, it would, based on this thermodynamic data, be enough to hydrogenate the other organic nitrogen compounds present.

Name	Molecular Formula	Standard Enthalpy of Formation (kJ/mole) ΔH_f (298.15 K)
pyrrole	C_4H_5N	63.1
indole	C_8H_7N	86.7
carbazole	$C_{12}H_9N$	125.1
pyridine	C_5H_5N	100.2
isoquinoline	C_9H_7N	144.5
acridine	$C_{13}H_9N$	200.9
phenanthridine	$C_{15}H_9N$	148.9
21H,23H-porphin	$C_{22}H_{14}N_4$	-1106.9
etioporphyrin I	$C_{22}H_{20}N_4$	-25.2
etioporphyrin II	$C_{22}H_{20}N_4$	1.6
octaethylporphyrin	$C_{38}H_{46}N_4$	-183.2

Table III.3. Standard enthalpies of formation at 298.15 K for some organic heterocycles⁷⁹ found in crude petroleum

⁷⁹ Pedley, J.B., Naylor, R.D., and Kirby, S.P., *Thermodynamic data of Organic Compounds*, 2nd ed., Chapman and Hall Ltd., (1986).

Therefore any technique which monitors for metalloporphyrin, such as MCD, is in effect tracking one of the the most stable nitrogenous compounds in a crude petroleum.

III. D.2. Fractionation

Figure III.4 illustrates the linear relationship between the carbon number of the alkane extraction solvent and its polarizability volume. Longer chain solvents have a larger polarizability volume and are therefore able to extract "softer" species. This is the chemical relationship which exists between fractions extracted with a homologous series of alkane solvents. As both the polarizability and the carbon number increase, the nitrogen content and N/C ratio of the extracted fractions also increases (Table III.1). This indicates that the nitrogen is associated with soft species, such as aromatic systems, and that these systems are extracted with higher molecular weight alkane chains.

Table III.1 lists the recovery of each fraction as a percentage of the original bitumen as well as the recovery of each sub-fraction as a percentage of each fraction. There is an increasing yield of the total basic sub-fractions from the low molecular weight alkane extraction solvent to the highest molecular weight solvent. The other sub-fractions experience maxima at one of the intermediate extraction solvents. Acids are the largest percentage sub-fraction in the pentane asphaltenes while the saturates and aromatics are the

largest in the deasphalted oil (propane) and resin fractions (butane), respectively. The pentane and hexane asphaltenes represent a small percentage of the original bitumen sample.

III. D.3. Calibration and Quantification

The MCD spectrum of a crude fraction typically consisted of six peaks grouped together to form the Q band, these included the intense A-term origin ($Q_{0,0}$) which was used in the quantification. At higher energy, in some fractions, the B band (also an A term) was present as well. Unlike the absorption maxima the MCD peaks were superposed on flat baselines in all cases except for extremely dilute samples.

The exact positions and intensities of these bands in both Absorption and MCD spectroscopy vary according to the particular metal incorporated and the nature and distribution of the side chains. The Absorption spectra of petroleum fractions show strong absorption over the range 400 - 550 nm with a shoulder at 570 nm, corresponding to the existence of vanadyl porphyrin. The shoulder due to nickel porphyrin at 550 nm was not always evident due to its relatively low concentration in the extract.

The MCD of metalloporphyrins like their absorption spectra varies depending on the chromophore symmetry. The presence of A terms in the MCD spectrum indicate the effective electronic symmetry of the

metalloporphyrin is D_{4h} . MCD spectra obtained from each fraction are contained in Appendix C.

In the absorption spectra of metalloporphyrins, there are two visible bands between 16700 cm^{-1} and 20000 cm^{-1} separated by about 1250 cm^{-1} . The lower energy band is the electronic origin $Q_{0,0}$ of the lowest energy excited state. The higher energy band at 18415 cm^{-1} is denoted $Q_{1,0}$ and is composed of several vibrations. In addition to the B bands at 25000 cm^{-1} there are the N, L, and M bands to the blue of the B bands. Like the B bands, these bands are usually obscured under strong UV absorbing species in the petroleum.

The calibration curves constructed from the VOTPP results and shown in Figure III.5 were based on the peak heights of both the $B_{0,0}$ and the $Q_{0,0}$ bands. The Soret or B band is intense in the absorption spectra and generally appears between 380 and 420 nm. with a molar ellipticity (ϵ_M) from $2 - 4 \times 10^6\text{ M}^{-1}\text{cm}^{-1}$.⁸⁰ The much less intense Q bands in absorption spectra are observed in the visible region between 500 and 600 nm. The $Q_{0,0}$ band represents the lowest energy excited singlet state. Since it involves a much larger magnetic moment, this band yields a much more intense MCD signal than the B band.

Other components of crudes do not severely affect the quantification using the MCD Q band. The B band in contrast was observed less clearly in some of the derived fractions (see Table III.1). These fractions contain a large

⁸⁰ Gouterman, M., in *The Porphyrins*, Vol. III, Physical Chemistry, Part A, chap. 1, edited by Dolphin, D., Academic Press, (1978).

proportion of basic compounds which absorb in the ultra-violet and near visible and therefore they may obscure the excited state B transition relative to that of the Q band.

The quantification of the amount of metalloporphyrin in the crude petroleum sub-fractions was accomplished using vanadyl tetraphenylporphyrin (VOTPP) as the calibration petroporphyrin. While VOTPP is slightly larger than most petroporphyrins it was chosen because vanadyl petroporphyrin derivatives are often the most abundant species present in heavy crudes.

III. D.4. Metalloporphyrin Detection

The weight percents of porphyrin in each fraction based on this calibration are recorded in Table III.1. The porphyrin content measured from the B and Q bands are in agreement for most fractions. The basic fractions are most affected by obscured B term intensities for the predicted porphyrin contents.

The metalloporphyrins are found to be distributed throughout all the collected fractions except the deasphalted oil fraction (Figure III.6) which is the fraction of the crude petroleum lowest in nitrogen content. When the porphyrin content, as determined using MCD of the fraction Q bands, is plotted against the carbon number of the solvent, a maximum is revealed for the fraction isolated using hexane. These hexane asphaltene compounds

which were soluble in n-hexane but insoluble in n-heptane.

If these data are then compared to the percent total nitrogen content as determined by elemental analysis (Figure III.8), it is observed that the detectable metalloporphyrins decrease in the heptane fraction. Another interesting fact to note is the linearity with which the total nitrogen content increases in fractions progressively isolated with a homologous series of alkane solvents. The ratio between total nitrogen and nitrogen detected using MCD decreases steadily until it reaches 0.96 for the hexane asphaltenes whereupon it increases again for the heptane fraction.

This increase at the heptane fraction could be caused by several possibilities. The first is that the linear relationships are coincidental and there is no reason why the metalloporphyrin content as determined by MCD should be a marker for the total nitrogen. This does not mean that the linear relationships are not real, just that there is another explanation.

The second and third reasons are that either the metalloporphyrin content is experimentally too low or that the nitrogen content is experimentally too high. The possibility that all the metalloporphyrins had already been extracted from this fraction is rejected based on the significant metalloporphyrin content of the heptane asphaltene sub-fractions.

The nitrogen content was determined by the Kjeldahl technique, which tends to give low results, not high, when used on nitrogen containing aromatic heterocycles.

The nitrogen content from MCD measurements of the metalloporphyrin Q-band however, could be low for the following reasons.

The heptane fraction was not as strictly operationally defined as the hexane, pentane and other fractions. For example, the hexane fraction contained compounds soluble in n-hexane but insoluble in n-heptane, whereas the heptane fraction included all compounds soluble in n-heptane including any potential octane or nonane fractions. Therefore the heptane fraction should be expected to contain a wider variety of complex species. Since the MCD signal, like any spectroscopic method, is a summation of all the signals of the components in the mixture which respond to that particular frequency, it is not unexpected that this net response does not accurately reflect the porphyrin content.

The low value recorded due to the complex nature of the heptane fraction can also be seen by comparing the results obtained from the fractions to those obtained from their sub-fractions. If this is done it is found that in all cases, the fraction totals **underestimate** the porphyrin content as compared to the sub-fraction totals (Table III.1).

III. D.5. Porphyrin Partitioning

In general, the porphyrins are concentrated in the basic groups of each fraction, as is apparent from Table III.1. Considering the sub-fractions

together, each sub-fraction category, bases, acids and aromatics are isolated primarily by a different solvent. This is evident from Figure III.9 which plots sub-fraction porphyrin totals against the carbon number of the solvent. The pentane extract contains bases, the hexane extract contains primarily aromatics and the heptane extract is composed largely of acids.

This effect is significant since it demonstrates that each extraction solvent dissolves a certain group of components that is distinct from what a different solvent would extract. For example, porphyrins are associated with the aromatic fraction of a n-hexane cut and are also associated with the bases of a n-pentane cut. This partitioning behaviour could be useful if a certain group of compounds need to be investigated.

IV. CONCLUSIONS

Monitoring the nitrogen content of refinery outflow streams is critical for reducing acid rain and reducing the attrition rate of petroleum cracking catalysts.

Magnetic circular dichroism spectroscopy has shown that by monitoring the metalloporphyrin content of crude petroleum fractions it can account for a significant fraction of the total nitrogen content of a crude.

Analysis of petroleum fractions reveals that there is a differential distribution of metalloporphyrins. This distribution suggests a correlation to the total nitrogen content of a given fraction. Using this relationship, on-line analysis by MCD of a crude petroleum feedstock in a refinery setting could provide an effective method of tracking refining progress in terms of hydrodenitrogenation and hydrodemetallation.

Additional work with metallo-nonporphyrins, with fractions isolated using higher carbon number alkane solvents, and with several different crude petroleum samples may further define this relationship.

APPENDICES

Appendix A. Magnetic Circular Dichroism

Two types of light can be distinguished, polarized and unpolarized. Polarized light is represented by a vector whose magnitude and orientation change in a related manner as the phase of the light varies. When the amplitude varies and the orientation is constant the light is plane polarized.

This plane polarized light can be regarded as the resultant of beams of right and left circularly polarized light which are conterminal. The right and left circularly polarized light beams are enantiomorphs of one another, and will interact differently with a given enantiomorph of a dissymmetric molecule. Upon interaction with the molecule, the plane of polarization of the light is rotated. This rotation of the plane of polarization can be measured and constitutes the circular dichroism.

Both circular dichroism and magnetic circular dichroism are based on the difference in the molar absorptivity for left and right circularly polarized light. The differences in the two techniques stem from their origins.

Circular dichroism is caused by small inherent structural dissymmetries

in the molecule or its environment. Magnetic circular dichroism is the consequence of normal longitudinal Zeeman effect interactions, and as a result can characterize symmetry and angular momentum properties of the ground and excited states of an atom. The shape and magnitude of MCD are strongly affected by degeneracies and near-degeneracies in electronic energy levels associated with the degree of rotational symmetry experienced by electrons of the chromophore and, through spin-orbit coupling, by degeneracies due to spin. Magnetically induced optical activity is frequency dependant and is proportional to the applied field.

The Faraday effect is only subtly related to natural optical activity. In natural optical activity, the chiral field perturbing the chromophore is within the molecule itself and therefore has a fixed geometrical relation to the chromophore no matter what the orientation of the molecule. In magnetic optical activity, the external magnetic field acts as the perturbing force on the electronic states of the chromophore and as a result the mcd may not directly represent the molecular geometry of the molecule. Some studies performed with carbonyl compounds indicate that MCD is highly sensitive to the molecular geometry of these compounds.

The magnetic field can induce three types of effects in a transition to manifest CD. These effects have been denoted A, B, and C terms. Consider first a transition from a ground state to some excited state. If circularly

Figure A.1. Transitions involving degenerate initial or degenerate final states result in an A term.

Figure A.2. C terms occur when a transition takes place from a degenerate ground state to a non-degenerate excited state. The greater intensity lcpl transition is due to a Boltzmann population effect.

polarized light is used, two transitions, each caused by the absorption of left and right circularly polarized light occur at the same energy, resulting in no net CD. If the excited state of this transition is degenerate the applied magnetic field splits it into equal higher and lower energy levels by the Zeeman effect. These magnetically differentiated transitions differentially absorb left and right circularly polarized light with equal intensity but of opposite sign (Figure A.1). If these lineshapes are superimposed the result is a Faraday A term, which appears as a symmetrical biphasic signal crossing the axis at λ_{max} .

A different lineshape results when a transition takes place from a degenerate groundstate to a non-degenerate excited state. As before each split transition differentially absorbs circularly polarized light resulting in bands of opposite sign. Transitions from the lowest energy level however, have a greater intensity due to a greater Boltzmann population. The resultant MCD spectrum is called a Faraday C term (Figure A.2). Faraday C terms are inversely proportional to the absolute temperature.

A Faraday B term is similar in appearance to a C term but shows no temperature dependence. The B term is ubiquitous in the MCD spectra of organic compounds and arises from the magnetically induced mixing of energy levels that are not degenerate.

Appendix B. Azaarenes and Metalloporphyrins in Crude Petroleum

B. 1. Azaarenes

The observation of monoazaarenes in crude petroleums has been well documented.^{81,82} Compounds with as many as four rings have been detected,³⁷ and with the synthesis of pentacyclic azaarenes as reference compounds new discoveries are likely.

The basic skeleton of metalloporphyrins is porphin (Figure B.1.(i)), an unsubstituted porphyrin, which is formed from four pyrrole rings linked together into a ring through their 2- and 5- positions by four methine bridges. The subunit, pyrrole, is a relatively stable aromatic five-membered heterocycle. Though it is a secondary amine, pyrrole is not strongly basic because of its aromatic structure. It is, however, quite reactive to electrophilic substitution

⁸¹ Garrigues, P., De Vazelhies, R., Ewald, M., and Jousset-Dubien, J., *Anal. Chem.*, **55**, 138, (1983).

⁸² Schmitter, J.M., Ignatiadis, I., and Arpino, P.J., *Geochim. Cosmochim.*, **47**, 1975, (1984).

at the positions alpha to the nitrogen atom and tends to form dimers, trimers and higher condensation products.⁸³

When four pyrroles are cyclized to create a porphyrin, an 18 π electron aromatic resonance system is formed. The reactivity of the pyrrole nuclei in porphin is reduced due to the increased aromatic character and because the reactive 2- and 5- positions are occupied.

Porphyrins are widely distributed in nature and can occur in the free form or as metal chelates.

The progenitors of most azaarenes remain unknown as do their diagenetic pathways but several authors have presented interesting hypotheses.

The occurrence of carbazole derivatives in petroleum has been correlated to plant alkaloids containing an indole nucleus. Snyder observed that the lack of benzo[b]carbazoles in crude petroleum matched the natural preference of plants for angular over linear annelated structures and thus suggested that petroleum benzocarbazoles originated from plant alkaloids.⁸⁴ However, Schmitter notes that the overall distribution of carbazole derivatives is very similar among all petroleums, and seems to be independant of the distribution of alkaloids in the plant kingdom. He also points out that by and large, plant alkaloids are very complex, labile and incorporate more than one nitrogen atom

⁸³ Paquette, L.A., *Principles of Modern Heterocyclic Chemistry*, W.A. Benjamin Inc., N.Y., (1968).

⁸⁴ Snyder, L.R., *Nature*, 205, 277, (1965).

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(ie. not monoazaarenes). Upon degradation these alkaloids are unlikely to form large dibenzocarbazole derivatives. Therefore the authors favour a mechanism whereby ammonia or other low molecular weight amines condense around compounds such as 1,4-diketones,^{85, 86} leading to pyrrole derivatives which may then form the indole nucleus. Once formed these compounds are very stable and despite processing may appear in the final product.

Azaarenes are a major source of NO_x upon combustion of fuels carrying these impurities.⁸⁷

Nitrogen oxides are formed by three mechanisms during fossil fuel combustion,

- (1) thermal nitrogen formed by a radical chain mechanism,

where M is any molecule that can act as an energy transfer agent.

⁸⁵ Katritzky, A.R. and Lagowski, J.M. (eds.), in *Heterocyclic Chemistry*, Wiley, New York, pp. 142-159, (1960).

⁸⁶ Dorbon, M., Schmitter, J.M., Garrigues, P., Ignatiadis, I, Ewald, M., Arpino, P., and Guiochon, G., *Org. Geochem.*, 7(2), 111, (1984).

⁸⁷ Bartok, W., Crawford, A.R., and Skopp, A., *Chem. Eng. Progr.*, 67, 64, (1971).

- (2) prompt nitrogen oxides formed in rich hydrocarbon flames via interaction of N_2 with hydrocarbon radicals,

- (3) fuel NO_x formed by oxidation of nitrogen containing hydrocarbons.

and,

- (4) the overall reaction for the combustion of fossil fuels which produces NO_x (NO and NO_2) in the following equilibrium,³¹

The equilibrium of NO_x forms is dependant on the content of nitrogen in fuel, the air-fuel equivalence ratio, and temperature and is only slightly dependant on the type of nitrogen-containing compounds.

Most countries have air quality standards for NO_x due to their negative impact on the environment.³¹ NO_x formed from human activities is a

significant percentage of the world total and can be more dangerous than natural sources since it is concentrated in certain regions.

Methods of control for thermal NO_x such as decreasing the flame temperature and lowering preheat air temperature are not effective for fuel NO_x . Hence, delicate process control is required since methods of NO_x regulation may reduce one mechanism of NO_x formation at the expense of another.

B. 2. Metalloporphyrins

A small portion of the total nitrogen content and total metal content in crude petroleum is present in the form of metalloporphyrins.²¹

The biogenic origin of metalloporphyrins was first postulated by Treibs.⁸⁸ Treibs proposed that the sedimentary metalloporphyrin vanadyl-DPEP was the degradation product of chlorophyll a through a series of chemical reactions.

Chlorophyll a in addition to chlorophyll b are the two major types of green pigments obtained from green plants. Both of these pigments are derivatives of chlorin (7,8-dihydroporphyrin).

With Treib's discovery the concept of biological markers was born. These are compounds which can be correlated with their original biological precursor due to the survival of their carbon skeleton through geologic time.

⁸⁸ Treibs, A., *Justus Liebigs Ann. der Chemie*, 517, 172, (1935).

The potential information content of petroporphyrins is high, due to the influence of environmental conditions on the original source compounds. Yet, there are still many aspects of the geochemical evolution of the petroporphyrins which are not understood.

Chlorophyll and hemes represent the tetrapyrroles existing in the biomass; these constitute relatively simple porphyrins. Highly modified tetrapyrrolic structures of bacterial origin such as vitamin B₁₂ and sirohemes are also present, but in much smaller amounts. Chlorophylls are quantitatively the most significant tetrapyrrole.

In most crudes, porphyrins occur in homologous series of etio, desoxophylloerythroetio(DPEP), benzo-etio, benzo-DPEP, and tetrahydrobenzo-DPEP(THBD) usually complexed with divalent nickel and vanadyl (VO^{2+}) (Figure B.1).

Metallation and demetallation are governed by the stability of the metalloporphyrin. The absence of the original ferrous complexes is likely due to removal of iron in anaerobic sulphur-rich environments as the highly stable pyrite (FeS_2). The predominance of nickel and vanadium porphyrins over other metalloporphyrins in sedimentary environments has been rationalized by taking into account four factors: the abundance of the metal, the speciation of the metals, and the thermodynamic and kinetic stability of the complexes. When all these factors are considered, there are four metalloporphyrin complexes which could possibly be widespread in this environment. These are

Figure B.1. Porphin Skeleton (i), Probable precursor chlorophyll molecules of metalloporphyrins (ii,iii,iv), and the common vanadyl metalloporphyrins found in crude oils.

V^{4+} , Ni^{2+} , Ga^{3+} , and Cu^{2+} porphyrins.⁸⁹ Gallium porphyrins have been detected in coals along with iron[III] and manganese[III] porphyrins.⁹⁰ The presence of these high oxidation state ions supports the belief that coals are formed under more oxic conditions than crude oils and oil shales.

The other reactions leading to DPEP are consistent with the knowledge that the marine depositional environment is reducing, thereby activating the keto, vinyl and phytyl double bond on chlorophyll *a*. It has been observed that the mineral matrix acts as a catalyst in the formation of petroleum.⁹¹ Its effects on metalloporphyrin stability and formation are unknown.

Researchers, recognizing that nickel and vanadium are the dominant metals in both porphyrin and non-porphyrin chelates, have conjectured that the non-porphyrin complexes may in fact be metalloporphyrin degradation products.²¹ The distribution of nitrogenous products in a natural shale oil resembled the distributions obtained from pyrolysis studies on plant pigments. This experiment suggests that some of the nitrogen compounds in petroleum could be generated by the thermal degradation of pre-existing nitrogen compounds in addition to those generated by bacterial metabolic activity or the theorized ammonia condensation mechanism described in Section B.1.

⁸⁹ Quirke, J.M.E., in *Metal Complexes in Fossil Fuels*, ACS Symp. series 344, pp. 75, (1987).

⁹⁰ Filby, R.H. and Van Berkel, G.J., *Metal Complexes in Fossil Fuels*, ACS Symp. series 344, pp.2,(1987).

⁹¹ Whittaker, A.H. and Dyson, P., *Oil & Gas J.*, 78(37), 156, (1980).

Appendix C. MCD Spectra

Spectral Conditions:

Depending on the opacity of the sample the slit width was varied from 0.5 to 1.5 mm. The spectral quality number used was usually 3 or 5 depending on spectrum noise. The time constant was 10 seconds for petroleum samples.

Figure C.1

MCD spectrum of the deasphalted oil fraction

Figure C.2 MCD spectrum of the deasphalted oil weak bases fraction

Figure C.3 MCD spectrum of the deasphalted oil medium bases fraction

Figure C.4 MCD spectrum of the deasphalted oil strong bases fraction

Figure C.5 MCD spectrum of the deasphalted oil acids fraction

Figure C.6 MCD spectrum of the deasphalted oil saturates fraction

Figure C.7 MCD spectrum of the deasphalted oil aromatics fraction

Figure C.8 MCD spectrum of the resin fraction

Figure C.9 MCD spectrum of the resin weak bases fraction

Figure C.10 MCD spectrum of the resin medium bases fraction

Figure C.11 MCD spectrum of the resin strong bases fraction

Figure C.12 MCD spectrum of the resin acids fraction

Figure C.13 MCD spectrum of the resin aromatics fraction

Figure C.14 MCD spectrum of the pentane asphaltene fraction

Figure C.15 MCD spectrum of the pentane asphaltene weak bases fraction

Figure C.16 MCD spectrum of the pentane asphaltenes medium bases fraction

Figure C.17 MCD spectrum of the pentane asphaltene strong bases fraction

Figure C.18 MCD spectrum of the pentane asphaltene acids fraction

Figure C.19 MCD spectrum of the hexane asphaltene fraction

Figure C.20 MCD spectrum of the heptane asphaltene fraction

Figure C.21 MCD spectrum of the heptane asphaltene weak bases fraction

Figure C.22 MCD spectrum of the heptane asphaltene medium bases fraction

Figure C.23 MCD spectrum of the heptane asphaltene strong bases fraction

Figure C.24 MCD spectrum of the heptane asphaltene acids fraction

Figure C.25 MCD spectrum of the heptane asphaltene saturates fraction

Figure C.26 MCD spectrum of the heptane asphaltene aromatics fraction

Appendix D. CD Spectra

Figure D.1

CD spectrum of Pantolactone

Figure D.2

CD spectrum of Camphorsulfonic Acid

Figure D.3

CD spectrum of Epiandrosterone

Figure D.4 CD spectrum of tris(ethylenediamine) Cobalt(III) iodide

Figure D.5

CD spectrum of L-phenylalanine

Figure D.6

CD spectrum of L-tryptophan

Figure D.7

CD spectrum of L-histidine

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