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SEPARATION AND CHARACTERIZATION OF COAL-DERIVED LIQUIDS

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by

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Coal is a fuel whose full potential has not yet been exploited in spite of the fact that liquid hydrocarbons have been produced from coal for nearly two centuries. Currently, processes of conversion to liquid fuels are being developed in several countries that will depend on coal as a major source of energy in the near future. Analyses of products of coal liquefaction is needed to assess process efficacy, to understand conversion mechanisms with the purpose of optimizing liquid yields and to control product quality.

Coal-derived liquids (CDL) are very complex mixtures of widely different, predominantly aromatic compounds. A prerequisite for efficient chemical characterization of coal liquids is separation into fractions enriched in chemically similar species. Fractionation is achieved by taking advantage of either the different solubilities of components in solvents or applying chromatographic methods based on sorption, steric exclusion or ion exchange effects.

Development of coal liquefaction technology has also created a need for additional analytical methodology. In many cases, chemical characterization of CDL has borrowed heavily from the petroleum industry, using modifications of routine analytical techniques or modern spectrophotometric procedures.

This paper reviews methods of separation and characterization of CDL which covers the main developments in this expanding area in the last ten years. A reference guide (Table 1) for the separation and characterization of specific constituents of CDL is also included.

SEPARATION METHODS

There is a variety of methods used for the separation and characterization of components in CDL. Separation into compound types or according to functional groups has to be performed prior to characterization by means of instrumental techniques.

Solvent Extraction

Solvent extraction is commonly used as a means of fractionation and characterization of coal-derived products based on solubility in pentane, benzene and pyridine. The asphaltene fraction is operationally defined as benzene-soluble and pentane-insoluble and the preasphaltene fraction as pyridine or THF soluble and benzene-insoluble (1,2,3). Schweighardt et al. (4-7) have utilized this technique to separate CDL into pentane, benzene and THF soluble fractions. They suggest that their method could provide a guide to the development of a standard separation analysis of coal-derived material. Other investigators (8-11) have also used a liquid fractionation scheme to study the viscosity of CDL. Schwager et al. (12-15) used pentane, benzene, propane and carbon disulfide to fractionate CDL. Brown and others (16) and Taylor et al. (17) separated coal-derived asphaltenes (CDA) from acidic components by precipitation of the basic material from a toluene and benzene solution with dry HCl gas, according to the procedure of Sternberg et al. (18). Maekawa and co-workers (19) fractionated CDL by successive extraction with n-hexane, benzene and pyridine prior to analysis by nuclear magnetic resonance (NMR).

In a search for a standard method for determination of asphaltene in CDL, Schultz et al (20) compared results from five different methods based on solvent separation. Steffgen et al. (21) separated CDA by solvent fractionation with benzene and toluene.

Liquid Chromatography

The standard methods for hydrocarbon-type analysis of petroleum distillates and their processing products cannot be applied directly to CDL because of differences in the nature of the components. Farcasiu (22,23) developed an alternative scheme based on separation of fractions of different chemical functionality using sequential elution of the fractions from silica gel. Schiller and others (24-28) separated solvent-refined and liquefaction products of coal into saturates, aromatics and polar hydrocarbons with neutral alumina prior to gas chromatographic-mass spectral analysis (GC-MS). Other authors (29-31) used chromatographic methods based on ion-exchange, coordination and adsorption properties to separate saturates, aromatics and polar fractions from CDL.

Shultz (32) utilized a similar procedure to separate nitrogenous compounds with further fractionation by preparative thin layer chromatography (TLC) before GC-MS analysis. White (33) separated light oil from coal liquids by fluorescent indicator adsorption chromatography (FIA) and analyzed the fractions by GC-MS, infrared (IR) and Raman spectroscopy. Similarly, Ruberto et al. (34) fractionated the distillates from coal liquefaction products into saturates, aromatics and olefins by the FIA method. The saturate fraction was analyzed by GC-MS and the aromatic fraction investigated by proton nuclear magnetic resonance (PMR). According to these authors coal liquids can be analyzed by modifying the methods normally used for petroleum products.

In other studies (5,35) the heavy oil fractions obtained by solvent extraction were fractionated by the SARA method (saturates, aromatics, resins and alphas) and the fractions analyzed by GC-MS. Schweighardt et al. (4,36) described the separation of coal-liquids into fractions using a combination of solvent extraction and silica gel column chromatography prior to analysis by instrumental techniques.

Heavy coal hydrogenation products have been separated (37,38) into saturate, monoaromatic, diaromatic and polyaromatic polar fractions using gradient elution through dual-packed (silica gel-alumina) adsorption columns according to the technique described by Hirsch et al. (39).

Callen et al. (40) used gradient elution chromatography on alumina to separate solvent-refined coal (SRC) products from different coals into well-defined fractions. They reported recoveries of over 90%. The distribution of heteroatoms N, O and S within the chromatographic cuts was also examined. Other investigators (11,12,15,41) further separated the solvent extraction fractions of CDA by solvent elution chromatography on silica gel. They used benzene, diethyl ether and tetrahydrofuran (THF) in sequence. A method of separation of alkylphenols from CDL was developed by Schabron et al. (42) using silica gel open-column chromatography. The mobile phases used were n-hexane-toluene (96:4), chloroform saturated with HCl and chloroform-ether saturated with HCl respectively. Further separations were performed using high-performance liquid chromatography (HPLC). Lumpkin et al. (43) separated coal-liquids into saturates, aromatics and polar materials by clay-gel adsorption chromatography according to the ASTM-D-2007 method.

Gel Permeation Chromatography and Vapour Pressure Osmometry

Gel permeation chromatography (GPC) has been extensively used for preparing specific cuts of petroleum and coal-liquid fractions. It separates molecules according to their size in solution. Gel permeation chromatography gives the molecular weight distribution of SRC but provides very little information about the chemical nature of the products. Although GPC is not a complicated technique to use, problems of adsorption and calibration have been reported (44). Molecular size separation of various CDL fractions using GPC was studied by quantitative proton and carbon-13 Fourier transform NMR by Wootton et al. (45-49), and Welsh et al. (50). Yokoyama and others (51-53) separated the hexane-soluble oil from hydrogenated coal by liquid chromatography using silica gel columns. Further separations of these saturate and aromatic fractions as well as asphaltenes were performed by GPC and the fractions analyzed by NMR spectroscopy. Coleman et al. (54) separated the THF-soluble SRC into fractions by GPC and examined metals by flameless atomic absorption spectroscopy. Bockrath et al. (10,11,55) described the molecular weight distribution of CDA fractions by GPC.

A preparative quantitative separation of THF and chloroform-soluble SRC has been demonstrated (56-58) employing GPC and three column packings: a styrene-divinyl benzene packing (Bio-Beads S-X4), a cross-linked poly (N-acryloylmorpholine) polymer (Enzacryl Gel K-1) and a modified alkylated dextran (Sephadex LH-20). The percent recovery using Bio-Beads packing was greater than 95%. This technique (59) was also used to separate asphaltene and oil samples into fractions.

Molecular weight distributions of solubilized coal products from reductive alkylation were investigated by Ignasiak et al (60) using GPC. Determinations of molecular weight by GPC and vapor pressure osmometry (VPO) were also correlated (61,62) on SRC fractions. It was found that VPO gives a more precise and convenient measurement of molecular weights than GPC.

Molecular weights of asphaltenes and preasphaltenes were obtained by GPC and VPO (3) in a study related to the viscosity of CDL. Coal liquids from different sources were separated by GPC using THF and toluene as eluent (63). The separation was performed on a styragel column and the fractions analyzed by GC-MS. Dooley et al. (37) used GPC for further separation prior to MS analysis of the aromatic fraction from hydrocarbon-type separation on dual packed columns.

Quantitative correlation analyses of the degree of association of CDA was described for the first time by Lee and others (64) using VPO. The analyses of five CDA by this method was reported.

High Performance Liquid Chromatography

HPLC has been applied to liquid hydrocarbons mostly for separation of the polyaromatic compounds. HPLC is a highly effective method for separating individual compound species in coal liquefaction products according to their polarity or type of functional group.

Prather et al. (65) used HPLC to characterize products during hydrogenation/hydrodesulfurization of the creosote oil used as hydrogen donor in coal liquefaction. Twelve major components were separated on a preparative scale and identified by IR spectroscopy. Hurtubise et al. (66) developed an HPLC method to determine naphthalene and tetralin in coal-derived solvents.

They also identified several polyaromatic hydrocarbons by comparing HPLC and fluorescence spectroscopy data with the rates of flow (R_f) on TLC.

Other authors (67) used HPLC to separate component peaks from GPC fractions. Dark et al. (44,68) fractionated CDL into saturate, aromatic, and polar fractions by means of HPLC and analyzed the fractions with an interfaced quadrupole mass spectrometer. Separation of alkylphenols from CDL by HPLC has been investigated using several bonded phase columns (42,69).

Phenolic compounds were identified in HPLC fractions by comparison of their retention volumes, ultraviolet (UV) and fluorescence spectroscopy data with those for pure compounds.

Thin Layer Chromatography

TLC has not been used extensively in the hydrocarbon industry because of the increasing popularity of HPLC. The activity in TLC quantitation is mainly of fluorescent colored or quenched spots. Schweighardt et al. (36) reported the use of different TLC sprays for CDL. Quantitation is made by comparison of spot intensities with reference samples.

Farcasiu (23) reported R_f of nitrogenous and phenolic model compounds. Schweighardt and co-workers (4,36) analyzed fractions obtained from CDL by separation on silica gel column, by TLC and thin layer electrophoresis on silica gel, alumina and cellulose plates. Chromatograms were developed with specific spray reagents for active functional groups e.g. OH, C=O, -N=, NH, NH_2 . The distribution of functional groups in different fractions of CDL is described. Analysis of alkylphenols by TLC was investigated by Schabron et al. (42,69). Phenols were detected using ferricyanide-ferric chloride spray reagent. Other researchers (2,70) have described the analysis of asphaltenes and their basic acidic fractions by TLC, to confirm the information obtained from IR analyses. Six spray reagents were used for the detection of functional groups observed by IR spectroscopy.

Gas Liquid Chromatography

Separation by GLC is possible only for volatile components, which limits its efficacy for the separation of heavy fractions of CDL.

Utilization of GLC interfaced with a mass spectrometer should provide a powerful method of characterization. (See Mass Spectrometry section under Characterization Methods).

Inverse-phase chromatography involving the use of asphaltenes as column packing was investigated by Funk (71). A conclusion of his study suggests that nonvolatile hydrocarbons such as CDL can be separated by inverse-phase chromatography.

An overview of the application of GC-MS in CDL analysis is presented in the mass spectrometry section.

CHARACTERIZATION METHODS

Fluorescence and Ultraviolet Spectroscopy

Fluorescence spectroscopy has the potential to be used as a powerful analytical technique for the characterization of CDL which are mainly constituted of polyaromatic hydrocarbons. Alkyl substituents have a small effect on the fluorescence spectra which implies that the results of analysis are expressed in terms of the number of aromatic ring system rather than individual compound identification. Very little has been published on the use of fluorescence spectroscopy to identify aromatic compounds or ring numbers in CDL.

Kershaw (72) reported the identification of twelve polyaromatic ring systems in coal liquids by comparing their fluorescence excitation and fluorescence emission spectra with those of standard hydrocarbons. He used adsorption chromatography on silica gel to separate oil into fractions prior to spectroscopic measurements.

Fluorescence spectra of GPC fractions have been investigated by Hathaway et al. (67). Other researchers (42) utilized UV and fluorescence spectroscopies for the identification of phenols from liquid chromatographic fractions. Fluorescence excitation and fluorescence emission as well as absorption data of alkylphenols were reported.

Fluorescence spectroscopy combined with GPC or HPLC appears to be very promising for obtaining spectroscopic information on isolated unknown components.

Infrared Spectroscopy

IR spectroscopy offers considerable promise for the identification of functional groups, especially in polar material. Fourier-transform infrared (FTIR) spectroscopy has opened new possibilities for characterization of coal liquid products because of the greater sensitivity compared with conventional IR.

Hathaway et al. (67) examined GPC fractions by FTIR. IR spectra of the trimethylsilyl derivatives of CDA and coal liquefaction bottoms were examined by Schweighardt et al. (6) and Gould et al. (73) respectively. Pentane- and benzene-soluble fractions of CDA obtained by solvent extraction were analyzed by IR (10,11,55). The spectra indicated the presence of phenolic and nitrogenous material. Near IR and PMR techniques have been used to study the interactions (hydrogen-bonding) of two asphaltenes, and their acidic and basic components, with the model compound o-phenylphenol (17). Schwager and others (41) analyzed silica gel chromatographic fractions for hydroxyl oxygen and pyrrolic nitrogen by IR. Farcasiu et al. (22) and Painter et al. (74) fractionated SRC by the method described by Farcasiu (23) and analyzed the fractions by FTIR. Phenols, pyrrolic nitrogen compounds, ketones and ethers have been found.

Toluene- and pentane-soluble oils from upgraded coal liquids were studied by IR (75) for phenolic and pyrrolic groups.

Basic and acidic fractions of asphaltenes separated by HCl precipitation were investigated by IR spectroscopy (70,76). Phenols, furans and pyrrolic compounds have been detected. The chromatographic fractions separated from CDL by ion-exchange, coordination and adsorption chromatography have been analyzed by IR spectroscopy (31). The CDA acidic and basic fractions as well as their trimethylsilyl derivatives were also investigated using IR spectroscopy by Brown et al. (16). Makabe and others (77) described the IR analysis of the acidic components obtained by alkali-alcohol treatment of coal. Aromatic ring number was also examined by PMR.

Nuclear Magnetic Resonance

NMR spectroscopy provides a convenient method for the determination of the aromatic content of complex hydrocarbon mixtures (78,79). The technique consists essentially of integrating the peak areas of the aromatic protons and the side chain protons. Carbon-13 magnetic resonance (CMR) is another technique that has been applied to CDL to obtain information about the molecular structure and composition. Saturate, monoaromatic, diaromatic and polyaromatic polar fractions obtained from dual packed silica gel-alumina chromatography were examined by Pugmire et al. (38,80) using CMR. Retcofsky et al. (81-84) and Cantor (85) have used CMR to obtain structural information and study the aromaticity of CDL. Fourier-transform CMR has been applied for the first time to coal liquids by Bartle et al. (86,87) and Maekawa et al. (88). A combination of PMR and CMR have been used for structural characterization of heavy oils from coal by Yokoyama et al. (51-53) and Maekawa et al. (19). Other researchers (89) showed that computer-assisted molecular structure construction provides a general and systematic means of elucidating structures of coal-derived products. This technique utilizes elemental analysis, NMR spectra and molecular weight data to determine the allowable combinations of functional groups constituting the structure.

Model hydroaromatic hydrocarbons were studied using CMR by Seshadri et al. (90) and Joseph et al. (91). Carbon-13 chemical shifts of these hydrocarbons are reported. Similarly, other groups (92) examined model compound mixtures and coal liquid extract by CMR.

An original PMR method was used by Schweighardt et al. (5,6) and Schwager et al. (14,41) for the characterization and quantitation of hydroxyl groups in CDL, and asphaltenes, by formation of their trimethylsilyl derivatives (93,94). The accuracy of the method is %5%.

A method for carbon-hydrogen aromatic/aliphatic distribution analysis of silica gel chromatographic fractions by NMR has been described (36,95). Bockrath and Coworkere (10) examined CDA fractions obtained by solvent extraction by NMR. Wooton (47-49) and Dorn (96) have separated SRC by GPC and the fractions were analyzed by NMR.

Ruberto et al. (97,98) examined structural aspects of sub-bituminous coal from solvation studies with hydrogen donor solvents. In their study they utilized PMR, IR and other analytical techniques.

Heavy products of coal pyrolysis have been separated by GPC into THF soluble fractions and examined by NMR (99). Coal liquids from five major processes have been fractionated into five fractions by solvent extraction and analyzed by PMR for the percentage of aromatic protons by Schwager et al. (12-14). The results were compared to those obtained by x-ray diffraction method. Fractions from gradient elution chromatography on alumina have been examined by NMR (40) to gain insight into the chemical nature of the various fractions. IR spectroscopy was used to identify the functional groups present therein. Zilm et al. (100) described a study on a comparison of CMR spectra of solid coals and their liquid hydrogenation products. Chemical shifts of representative samples were reported. Three distillate fractions from high volatile bituminous coal liquefaction have been studied by NMR (101), and the number of rings determined for each fraction. Toluene-insoluble, asphaltene and heavy oil fractions from CDL were analyzed by PMR for proton distribution (102). Comparative solubility studies of solvent refined liquids (SRL) and SRC in organic solvents has been investigated by PMR and other analytical techniques (103,104). Saito et al. (105) reported sym-triazine to be excellent solvent for CMR measurements. This compound was as effective as pyridine for solvation of SRL and SRC but did not absorb in the regions of interest (5-60 and 90-160 ppm). Sym-triazine would appear to be an adequate solvent for the study of preasphaltene by CMR.

Basic and acidic fractions of asphaltenes separated by HCl precipitation have been analyzed by PMR (70). Acid groups in CDL have been quantitated by means of NMR spectroscopy as their acetyl derivatives (106). Recently, characterization of organic functional groups in SRC using ^{19}F NMR spectroscopy was reported (107). This method does not give information about the structure as PMR and CMR but it permits to obtain information about the functional groups bonded to the hydrocarbon backbone.

Mass Spectrometry

Mass spectrometry (MS) offers a unique capability to characterize CDL. Coal liquids would be too complex to be analyzed by electron-impact ionization mode (EI) of MS because of excessive fragmentation of the molecules. This difficulty can be circumvented by using chemical ionization (CI) and low ionization voltage mode. Low volatility presents another problem in MS analysis. This problem can be alleviated by utilizing field ionization (FI) or field desorption (FD) modes which give information on the molecular ions of most organic molecules (108). These techniques have been used for the characterization of low volatile compounds in complex mixtures such as asphaltenes and hexane-soluble oils from coal liquefaction (109). Hathaway et al. (67) analyzed GPC fractions by EI-MS. Similarly GPC fractions were examined by Philip et al. (63) using GC-MS. Numerous phenolic and aromatic compounds were identified. Bodzek et al. (70) and Anbar et al. (110) examined coal liquefaction products by FI-MS and concluded that molecular weight profiles obtained by this technique are more informative than those obtained by GPC. Fourteen structural types were found (111,112) in coal liquefaction products using high-resolution, low ionizing voltage mass spectrometry.

Separation into compound types by adsorption chromatography on alumina column was performed by Schiller et al. (24-28) and the aromatic fraction analyzed by GC-MS. Akhtar et al. (113) and Sharkey and others (114,115) examined heavy oil and asphaltene from solvent separation by combined gas chromatography mass spectrometry. Aromatic and thiophenic compounds were identified. Lumpkin et al (43) described the analysis of chromatographic fractions of CDL for compound type by MS. White et al. (116) described the analysis of volatile polar organics in untreated by-product waters from coal conversion processes. Identification of individual compounds was reported using GC-MS and confirmed by spiking with pure compounds. Other researchers (117) developed a GC-MS method of analysing indoles and quinolines in CDL. Hazlett et al. (118) studied the mechanism of coal liquefaction by means of GC-MS. The analysis of basic nitrogen compounds (pyridine, aniline-type compounds) separated by HCl precipitation from coal liquefaction products has been investigated by White et al. (119) and Schweighardt et al. (5) and 23 compounds were identified using GC-MS.

Electron Spin Resonance Spectroscopy

Electron spin resonance spectroscopy (ESR) is a useful technique to study free radicals in coal. The latter appear to play a prominent role in the mechanism of coal liquefaction. There is limited information in the literature on free radicals of CDL. The structure of free radicals has been examined in SRC and CDA by ESR spectroscopy (41,120,121,122). Measurements of the g-values in SRL and SRC samples have been reported by Woolsey et al. (103).

Atomic Absorption Spectroscopy, X-ray Diffraction and X-ray Fluorescence Analysis

Atomic absorption (AA) spectroscopy is a popular technique for the analysis metal elements in coal liquefaction products. Coleman et al. (54,123) examined twelve metallic elements from SRC via flameless atomic absorption spectroscopy. An x-ray diffraction method was employed (15,41) to determine the crystalline parameters of CDA and its chromatographically separated components.

Prather et al. (124) analyzed quantitatively 17 elements in SRC by x-ray fluorescence. This method provides a sample analysis within an hour. Previous methods required over two hours per sample.

CONCLUSIONS

The development of separation and chemical characterization methods has allowed significant progress in understanding conversion mechanisms of coal to liquids. The critical compilation of these methods would also help the analyst to have an overview necessary for improving existing methods or developing new ones.

Future developments in this field will involve a combination of different applications or techniques e.g. fractionation and analysis by HPLC or coupling fluorescence spectroscopy with HPLC for the separation and characterization of aromatic compounds. Improvement in the separation of the highly complexed compound mixtures in CDL by liquid chromatography will depend on the development of new sorbents with higher selectivity for various compound types.

The use of NMR for the analysis of CDL has been thoroughly investigated. This technique will have extensive application in the study of compound-type or derivatized functional groups. The search for more effective solvents will improve the applicability of NMR in this field.

The combination of separation and analytical methods used in coal, petroleum and polymer chemistry will play an important role in the development of coal liquefaction technology.

Table 1 Key for separation and characterization
of coal-derived liquids based on
compound types

Compound type	Separation method	Characterization method	References
Saturate	A,B,E	-	4
	A,B,E	PMR	36
	A,C	PMR,CMR	19
	B	-	31
	B	CMR	38
	B	PMR	23
	B,C	PMR,CMR	51,52,59
	B,C	MS,PMR	37
	B,F	MS	28,34,35,43
	B,F	MS,IR,PMR	33
	C	CMR,PMR	48,49
	C,F	CMR,PMR	53
	C,F	MS	63
			*
Aromatic	A	MS	109
	A	PMR	14
	A	IR,CMR	83
	A,B,E	-	4
	A,B,E	PMR	36
	A,C	PMR,CMR	19
	B	-	31
	B	FS	72
	B	CMR	38
	B	PMR	23
	B	PMR,UV	97
	B	PMR,MS	98
	B,C	MS,PMR	37
	B,C	PMR	52
	B,C	PMR,CMR	51,59

Table 1 (Cont'd.)

Compound type	Separation method	Characterization method	References
	B,F	MS	28,29,43
	B,F	MS,PMR,VPO	34
	B,F	MS,PMR,IR	33
	C	CMR,PMR	48,49,53
	C,D	IR,UV,MS,FS	67
	C,F	MS	63
	D	IR	65
	D	MS	44,68
	D,E	MS	109
	-	CMR	90,91,92
	-	CMR,PMR	80,85,89
Nitrogen	A	IR	10,75
	A,B	IR	11,41
	A,B,E	-	4
	A,B,E	PMR	36
	A,B,F	MS	5
	A,E	IR,MS	70
	A,E	IR,PMR	16
	A,F	MS	119
	B	IR	31,74
	B	IR,CMR,PMR	40
	B,D,E	-	42
	B,E	PMR	23
	B,F	MS	26,29,32
	B,F	IR,MS,PMR	33
	F	MS	116,117
	-	FMR	107
	-	CMR,PMR	106

Table 1 (Cont'd.)

Compound type	Separation method	Characterization method	References
Oxygen	A	IR, PMR	6, 14, 17
	A	IR	10, 75
	A	IR, CMR, PMR	1
	A, B	IR, CMR, PMR	22
	A, B	IR, PMR	11, 41
	A, B	IR, MS	9
	A, B, E	-	4
	A, B, E	PMR	36
	A, B, F	MS, PMR	5
	A, E	IR, PMR	16
	A, E	IR, MS	70
	A, E	IR	2
	B	IR	31, 74, 97
	B	IR, CMR, PMR	40
	B, D, E	UV, FS	42
	B, E	PMR	23
	B, F	IR, MS, PMR	33
	B, F	MS	26, 29
	C, F	MS	63
	D	MS	44
	F	MS	116
	-	FMR	107
	-	CMR, PMR	89, 106
	-	IR	73, 77
Sulfur	A	MS	70
	A, F	MS	113, 115
	B	EA	40
	B, F	MS	43
	F	MS	116

Table 1 (Cont'd.)

Compound type	Separation method	Characterization method	References
Asphaltene	A	PMR, VPO	97
	A	IR, CMR, PMR	1
	A	VPO	34, 64
	A	-	7, 20, 21, 113
	A	CMR	84
	A	PMR	13, 14, 102
	A	IR, PMR	6, 17, 75
	A	X-RAY, VPO	13
	A	GPC, VPO	3
	A	GPC, PMR	10
	A	ESR	122
	A	MS	32, 108, 110
	A, B	IR, CMR, PMR	22
	A, B	IR, MS	9
	A, B	X-RAY, PMR	12
	A, B	IR, UV	15
	A, B	IR	74
	A, B	IR, VPO, PMR, X-RAY	41
	A, B	CMR, PMR	40
	A, B, C	IR, VPO	11
	A, C	CMR, PMR	51, 53
	A, C	CMR	59
	A, C	IR	55
	A, C	MS	24
	A, C	PMR	52
	A, E	IR, PMR, MS	70
	A, E	IR, PMR	5, 16
	A, E	PMR	36
	A, E	IR	2
	A, E	-	4
	A, F	MS	115

Table 1 (Cont'd.)

Compound type	Separation method	Characterization method	References
Metal	A	MS	115
	A,B	AA	12
	A,C	AA	54
	-	X-RAY	124
	-	M	125

CAPTIONS

Legend for Table 1

Separation Methods

- (A): solvent extraction
- (B): liquid chromatography
- (C): gel permeation chromatography
- (D): high pressure liquid chromatography
- (E): thin layer chromatography
- (F): gas liquid chromatography

Characterization Methods

- (AA): atomic absorption
- (CMR): carbon magnetic resonance
- (EA): elemental analysis
- (ESR): electron spin resonance
- (FS): fluorescence spectroscopy
- (FMR): fluorine magnetic resonance
- (GPC): gel permeation chromatography
- (IR): infrared spectroscopy
- (M): Mossbauer spectroscopy
- (MS): mass spectrometry
- (PMR): proton magnetic resonance
- (UV): ultraviolet
- (VPO): vapour pressure osmometry

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