



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

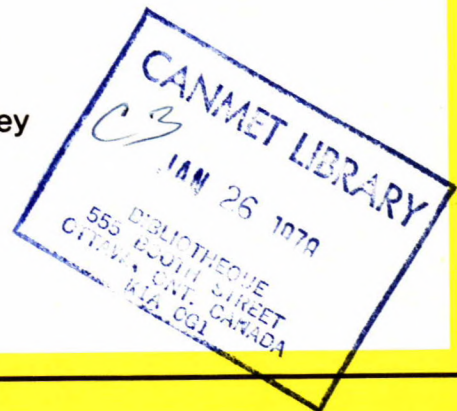
Centre canadien
de la technologie
des minéraux
et de l'énergie

324
22 (21)
212 TC

SEPARATION OF NITROGENOUS MATERIALS FROM BITUMEN AND HEAVY OILS

H. Sawatzky, S.M. Ahmed, A.E. George and G.T. Smiley

MAY 1977



ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
CANMET REPORT 77-10

© Minister of Supply and Services Canada 1977

© Ministre des Approvisionnements et Services Canada 1977

Available by mail from:

En vente par la poste:

Printing and Publishing
Supply and Services Canada,
Ottawa, Canada K1A 0S9

Imprimerie et Édition
Approvisionnement et Services Canada,
Ottawa, Canada K1A 0S9

CANMET
Energy, Mines and Resources Canada,
555 Booth St.,
Ottawa, Canada K1A 0G1

CANMET
Énergie, Mines et Ressources Canada,
555, rue Booth
Ottawa, Canada K1A 0G1

or through your bookseller.

ou chez votre libraire.

Catalogue No. M38-13/77-10
ISBN 0-660-01572-2

Price: Canada: \$1.00
Other countries: \$1.20

N° de catalogue M38-13/77-10
ISBN 0-660-01572-2

Prix: Canada: \$1.00
Autres pays: \$1.20

Price subject to change without notice.

Prix sujet à changement sans avis préalable.

SEPARATION OF NITROGENOUS MATERIALS
FROM BITUMEN AND HEAVY OILS

by

H. Sawatzky*, S.M. Ahmed**, A.E. George* and G.T. Smiley***

ABSTRACT

Separation of nitrogenous compounds and associated polar materials from deasphalted Athabasca bitumen has been studied by modified API-USBM procedures. A pumping system was used and small fractions were collected to follow the extent of the separations. It was found that only limited elution or extraction of the ion exchange resins was required compared with the exhaustive extractions of the unmodified method.

The amounts of so-called "neutral nitrogen compounds" that elute from the ion exchange resins with pentane and cyclohexane depend on the degree of extraction. These neutral nitrogenous materials are concentrated in the tail of the pentane and cyclohexane eluates and can be further concentrated by the same procedure as the type separations. It appears that this is more desirable than the use of methods involving complexing with ferric chloride because polynuclear hydrocarbons are also removed by the ferric chloride.

Some applications of the method have been made. Cold Lake bitumen, Lloydminster and Medicine River oils were studied. A heavy oil product from a severely hydrocracked Athabasca bitumen was also investigated. The fractions separated from Athabasca bitumen and its hydrocracked products were examined by infrared spectrometry. The main points of interest were the practically complete decarboxylation of carboxylic acids and the apparent large increase in carbazoles and indoles during hydrocracking.

* Research Scientists, ** Chemist and *** Technologist, Research on Bituminous Substances Section, Synthetic Fuel Research Laboratory, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

SEPARATION DES SUBSTANCES AZOTEES DES BITUMES
ET DES PETROLES LOURDS

par

H. Sawatzky*, S.M. Ahmed**, A.E. George* et G.T. Smiley***

RESUME

La séparation des composés azotés et des matériaux polaires associés du bitume désalphalté de l'Athabasca a été étudiée à l'aide des méthodes de l'API-USBM, modifiées. Un système de pompage a été utilisé et de petits échantillons ont été recueillis afin de suivre la mesure dans laquelle s'effectuaient les séparations. On a trouvé que seule une élution ou une extraction limitée des résines échangeuses d'ions était requise, en comparaison aux extractions intensives que requière la méthode API-USBM non modifiée.

Les quantités de soi-disant "composés azotés neutres" qui éluent des résines échangeuses d'ions avec le pentane et le cyclohexane dépendent du degré d'extraction. Ces matériaux azotés neutres se concentrent dans les queues des éluats de pentane et de cyclohexane et peuvent être davantage concentrés par la même méthode comme les séparations type. Il semble qu'il soit plus souhaitable d'utiliser cette méthode que celles qui comportent la formation de complexes avec le chlorure ferrique, car les hydrocarbures polynucléaires sont également retirés par le chlorure ferrique.

Certaines applications de cette méthode ont été faites. Le bitume de Cold Lake et les pétroles de Lloydminster et de Medicine River ont été étudiés. Un produit de pétrole lourd tiré d'un bitume de l'Athabasca, ayant subi un intense hydrocraquage a également été étudié. Les fractions séparées du bitume de l'Athabasca et ses produits d'hydrocraquage ont été analysés par spectrométrie en infrarouge. Les principaux points d'intérêt étaient la décarboxylation presque complète des acides carboxyliques et l'augmentation notable apparente des carbazoles et des indoles au cours de l'hydrocraquage.

* Chercheurs scientifiques, ** Chimiste et *** Technologue, Section de la recherche sur les matières bitumineuses, Laboratoires de recherche sur l'énergie, Centre canadien de la technologie de l'énergie et des minéraux, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Abstract	i
Résumé	ii
Introduction	1
Experimental Apparatus and Resin Preparation	2
Procedure	3
Results and Discussion	5
The Fate of Nitrogenous Material During Hydrocarbon-type Separation	5
Separation on Ion-Exchange Resins	7
Ion-Exchange Resin Chromatography on Other Cretaceous Bitumens and Oils	16
Infrared Spectroscopy	17
Conclusions	19
References	20

INTRODUCTION

The separation, concentration and investigation of the nitrogenous components in bitumens and heavy oils is of considerable importance in petroleum recovery and processing. These components together with the associated polar compounds, can cause the oils and bitumens to adhere strongly to the sand, clay or rock surfaces of the reservoirs, including the tar sands, which would adversely affect secondary and tertiary recovery of conventional oils. They are also responsible for the emulsion problems encountered in the hot water separation process of bitumen from sand. These components also deactivate the catalysts in upgrading processes (1).

The Department of Energy, Mines and Resources is concerned with all these problems, particularly those pertaining to refining. Research on the chemical nature of these nitrogenous and polar components could lead to better solutions of the recovery and processing problems involved. The separation of these components is not only an initial requirement for the chemical investigation but it might also lead to an economically feasible process for their removal prior to refining. The nitrogenous and associated polar materials might be useful additives as binders for briquetting, form coking, or to improve certain qualities of asphalts.

The hydrocarbon-type separation of the heavy fraction of petroleum was studied in the American Petroleum Institute (API project 60) (2). This entailed a pretreatment with both anion and cation exchange resins, followed with ferric chloride to preclude the interference of nitrogenous material with the hydrocarbon separation. The material retained by the anion- and cation-exchange resins was referred to as acidic and basic compounds respectively although it was suggested that much of the retention would be due to association rather than ionic bonding.

A modification to the API-USBM procedure was developed at CANMET which deletes these initial ion exchange separations but uses additional steps to obtain more composition information and alleviate difficulties caused by the polar materials in the sample (3).

The hydrocarbon-type separation apparatus was adapted to ion exchange resins.

EXPERIMENTAL

Apparatus

Use was made of the same modified apparatus as for the compound-type separations (Figure 1) (3). It has two columns to contain the two types of ion exchange resins, connected initially in series and then operated separately. Glass columns and gravity flow alternatives were also tried.

Samples

1. Athabasca bitumen
2. Heavy oil product of hydrocracked Athabasca bitumen (LHSV-1, temperature 460°C, pressure 13.89 MPa)

All samples were deasphalted with 20 volumes of pentane.

Preparation of Resins(a) Anion-Exchange Resin

Amberlyst A-29 resin was washed four times with a methanolic HCl solution (10% volume aqueous HCl in methanol) and then rinsed with distilled water until the washings were neutral to litmus paper. The resin was activated with a methanolic hydroxide solution (10% by weight potassium hydroxide in methanol) and again washed with distilled water until the washings were neutral to litmus paper. Final preparation of the resin was made by 24-hour Soxhlet extractions with each of the following solvents: methanol, benzene, and pentane. The resin was then dried for 24 hours at 40°C in a vacuum oven(4).

(b) Cation-Exchange Resin

Amberlyst A-15 was washed four times with a methanolic hydroxide solution (10% by weight potassium hydroxide in methanol) then rinsed and extracted with methanol in a Soxhlet extractor. The resin was activated by adding it slowly to a stirred solution of 10% by volume aqueous HCl in methanol (Caution - exothermic reaction). The resin was then washed with distilled water until the washings were neutral to litmus paper. Final preparation was made by 24-hour Soxhlet extraction of the resin with each of the following solvents: methanol, benzene, and pentane. The resin was then dried for 24 hours at 40°C in a vacuum oven(4).

Procedure

The columns were packed with 46.0 g and 56.0 g of anion- and cation-exchange resins respectively (Figure 1). About 25 g of deasphalted bitumen samples were dissolved in the least amount of initial solvent and introduced to the system via the separatory funnel, followed immediately by the train of solvents listed in Table 1.

TABLE 1

<u>Volume of Eluents</u>	
<u>Eluents</u>	<u>Volume (ml)</u>
Columns in Series	
Pentane	360
Cyclohexane	220
Anion Exchange Resin Column	
Benzene	220
Benzene-40% Methanol	120
Benzene-20% Acetic Acid	160
Cation Exchange Resin Column	
Benzene	120
Benzene-40% Methanol	80
Benzene-37% Methanol-8% Isopropyl Amine	140

The solvents were pumped through the system at 2.0 ml/min. Using an automatic fraction collector, 20.0-ml fractions of the eluates were collected, and the solvents were evaporated according to previous procedure (3).

In initial studies the work of J.W. Bunger was closely followed, using large diameter glass columns and gravity flow (5). Although the resins were not exhaustively extracted, the added time in resin preparation and the large volume of resins, solvents and samples did not improve the separation achieved previously.

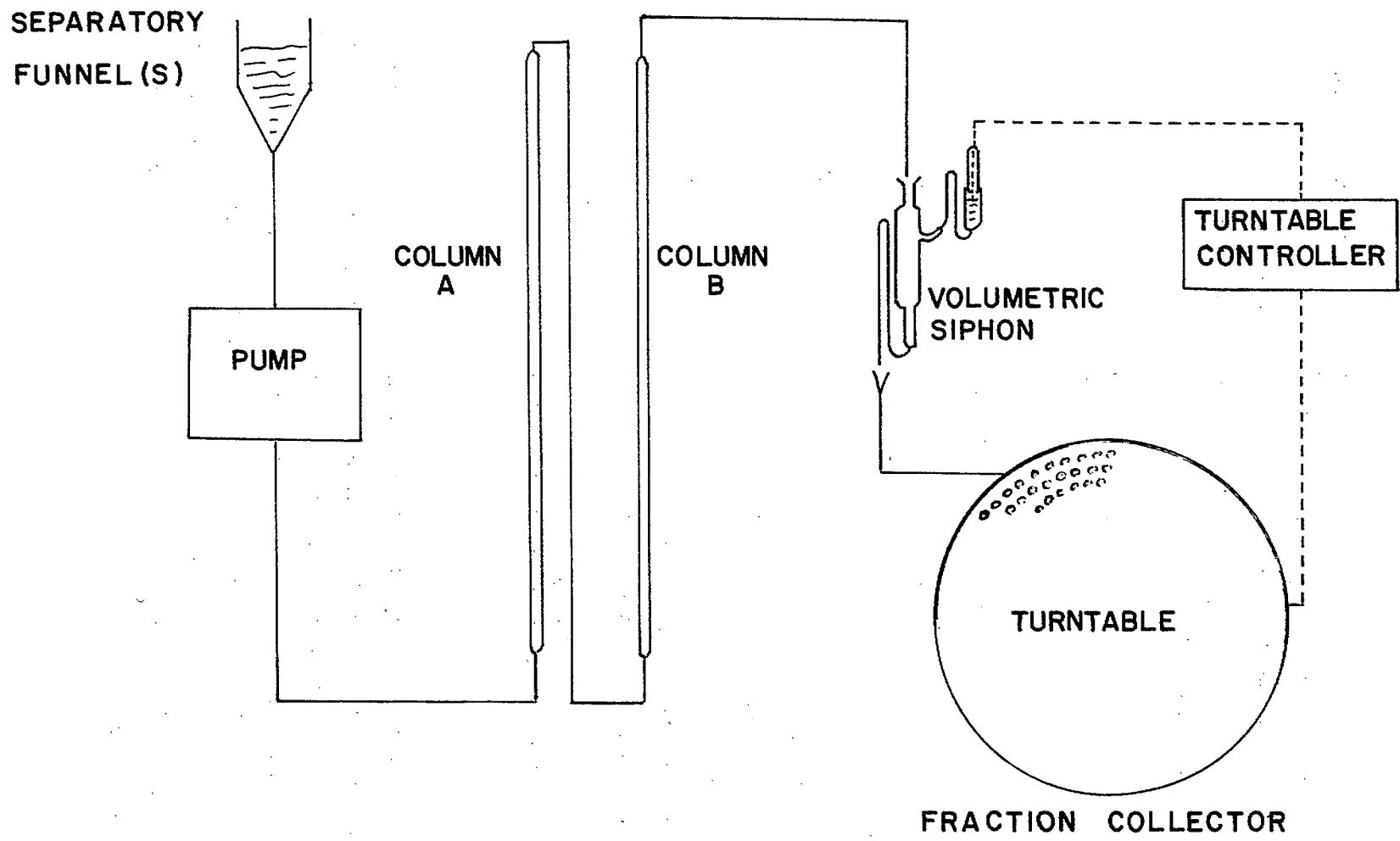


FIGURE 1. Ion-Exchange Chromatography System

RESULTS AND DISCUSSION

The Fate of Nitrogenous Material During Hydrocarbon-Type Separation

To simplify fractionation in the API-USBM method, the samples were treated with both anion- and cation-exchange resins before the hydrocarbon-type separation. A comparison was made at CANMET of the separation of deasphalted Athabasca bitumen with and without prior treatment with anion- and cation-exchange resins using the modified hydrocarbon-type analysis method as shown in Figures 2 and 3, respectively (3). The ion-exchange resins removed 26.9% of the sample, and about 94.0% of the nitrogen content. The chromatogram of the deasphalted Athabasca bitumen was treated previously with ion-exchange resins and showed a slight reduction in the material eluted by benzene from 16.4% to 15.3% (Figure 3). The polar mixture eluate was reduced from 26.3% to 6.3%, and the pyridine peak was eliminated. Reduction in the benzene eluate, which probably consists mainly of polynuclear aromatic hydrocarbons, could be due to the retention of some of these hydrocarbons on the ion-exchange resins (4).

It is interesting to note that the basic nitrogen fractions, as separated by the ion-exchange resins from the deasphalted Athabasca bitumen, total 7.96% while the eliminated pyridine peak accounts for 7.62% of the sample. Thus, the pyridine fraction seems to consist of the basic nitrogen compounds. These compounds are strongly sorbed on the acidic silica and alumina adsorbents and require hot pyridine for their removal. The material in the polar mixture fraction appears to be dominated by the acidic and neutral nitrogen compounds. The portion of 6.3% in this fraction is probably due to neutral polar material not removed by the ion-exchange resins.

The nitrogen content of material separated during compound-type distribution of both the deasphalted bitumen and a hydrocracked bitumen is listed in Table 2.

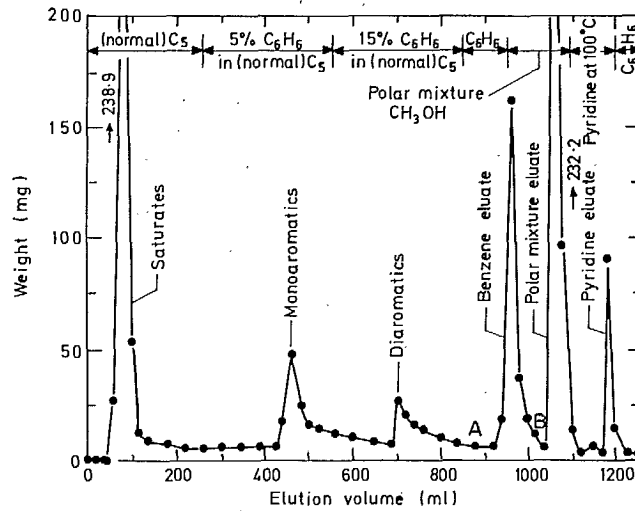


FIGURE 2 Liquid-solid Chromatographic Separation of Deasphalted Athabasca Bitumen

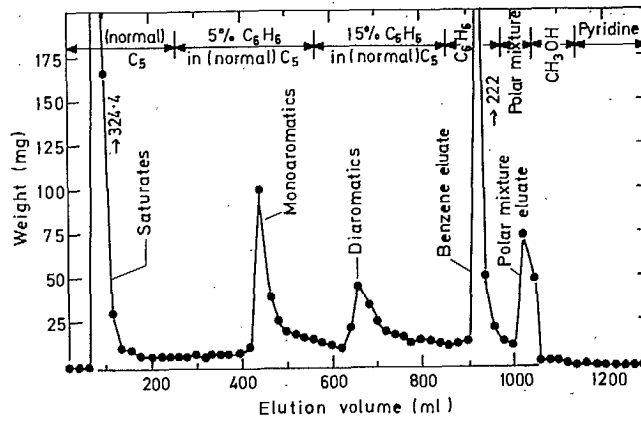


FIGURE 3 Liquid-solid Chromatographic Separation of Deasphalted Athabasca Bitumen (anion and cation resin-treated)

TABLE 2

Nitrogen Concentration in the Hydrocarbon-Type Eluates

	Deasphaltened Bitumen	Hydrocracked* Bitumen
Fraction A**	0.065	0.017
Polynuclear Aromatics (Benzene Eluate)	0.180	0.080
Fraction B**	0.280	0.180
Polar Mixture Eluate	0.700	1.800

* LHSV 1, 460°C

** See Figure 2

The nitrogenous material is concentrated in the polar fractions, whereas the polyaromatics have less nitrogen content. The separation is better in lighter samples. This could be attributed to steric hindrance effects in the higher molecular weight unprocessed bitumen.

Separation on Ion-Exchange Resins

An ion-exchange separation of deasphalted Athabasca bitumen is shown in Figure 4. The initial portion of the chromatogram shows the separation obtained during elution with pentane and cyclohexane, when the ion-exchange resin columns were in series and the pumping system was used. The use of cyclohexane speeds up the elution of the tailing pentane eluate. The remainder of the chromatogram has two series of three peaks each, that were obtained when the columns were eluted separately by benzene, 60% benzene-40% methanol mixture, and finally with 80% benzene-20% acetic acid mixture, in the anion-exchange resin column; and with benzene, 60% benzene-40% methanol mixture, and finally with 55% benzene-37% methanol-8% isopropyl amine mixture, in the cation-exchange resin column.

Table 3 gives the accumulative percentage of total nitrogen in the fractions collected from the ion-exchange columns. The amount of nitrogenous components increases gradually up to and including fraction 10, which represents 63.6% of the sample eluate but contains only about 2.8% of the total nitrogen in the sample. As the elution continues much more nitrogen is eluted in a relatively smaller portion of the sample. About 5% of the total nitrogen is contained in the fractions eluted with the pentane and cyclohexane solvents, which represent 75% of the total sample. The nitrogen

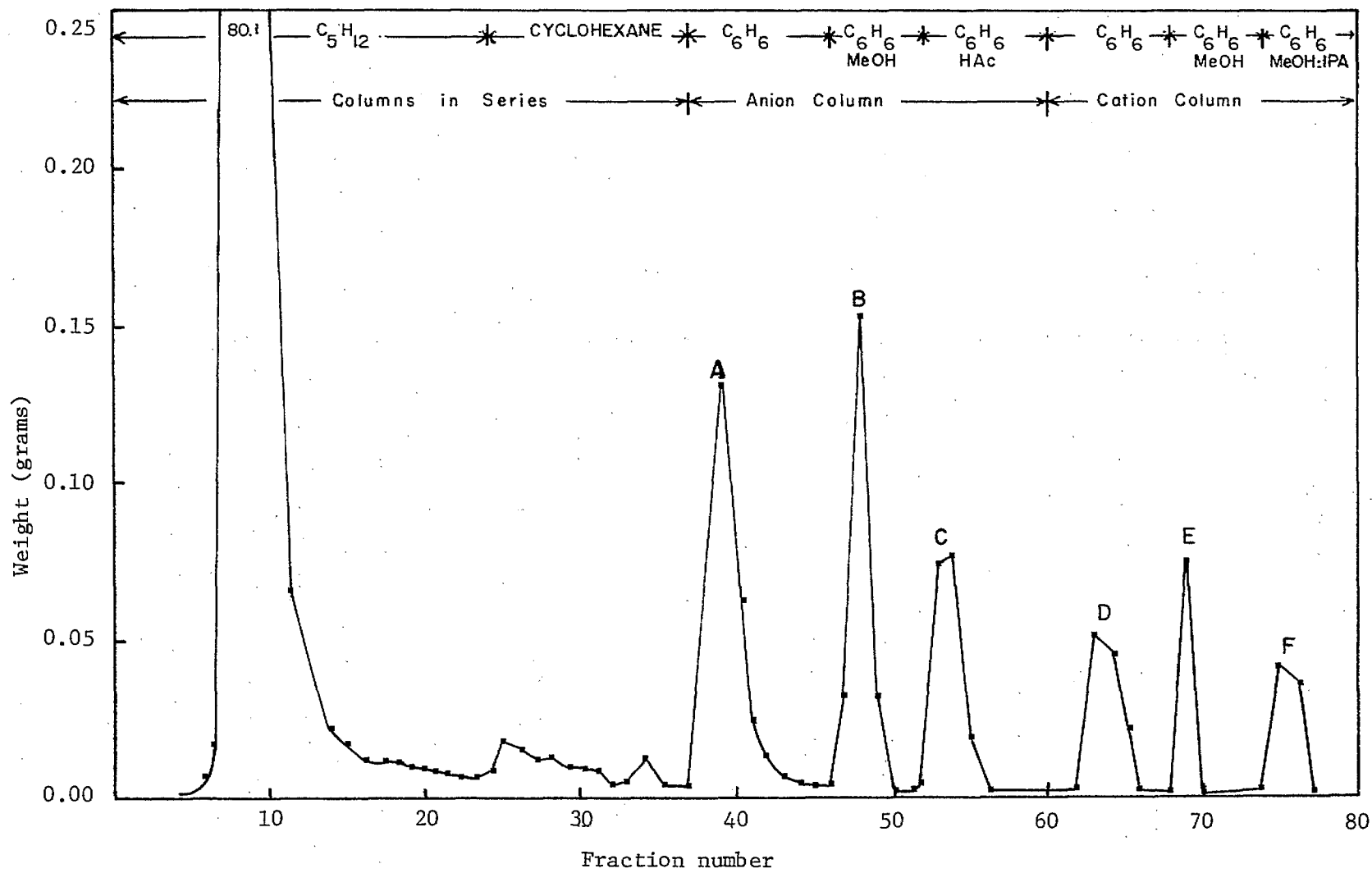


FIGURE 4. Liquid Chromatographic Separation of Deasphalted Athabasca Bitumen

components in these eluates are considered as neutral nitrogen compounds (4). Other laboratories have carried out exhaustive extractions by recycling solvents (4,5). The additional nitrogen material obtained by recycling solvents would be components eluting in peaks A and D (Figure 4). These

TABLE 3

Accumulative % of Total Nitrogen

Fraction Number	Accumulative % N	Accumulative Wt % of Fractions
8	0.86	42.60
9	1.85	57.32
10	2.82	63.64
11	3.65	66.16
12	4.41	67.42
13	5.10	68.69
14	5.60	69.19
15	6.14	69.44
16-24 combined	8.90	71.46
25-30 "	12.06	73.48
31-36 "	14.60	74.24
37-45 "	41.90	82.32
46-49 "	60.20	87.89
52-55 "	70.60	92.17
63-65 "	77.60	96.21
69-70 "	84.10	98.23
75-76 "	100.00	100.00

laboratories treated extracted pentane and cyclohexane eluates with ferric chloride on Attapulugus clay or cellulose to remove the nitrogen-containing components. Ferric chloride is not totally selective and forms complexes with some polynuclear aromatic hydrocarbons.

Some of the material separated on ion-exchange resins were examined by rechromatography on the dual silica-alumina column used for hydrocarbon-type separation. The combined fractions 7, 8 and 9 in Figure 4, representing 57% of the total sample, contain less than 2% of the nitrogen and show the following compound-type distribution as listed in Table 4.

TABLE 4

Weight Per Cent Compound-Type Distribution

(Combined fractions 7, 8 and 9)

<u>Compound-Type</u>	<u>Wt %</u>
Saturated hydrocarbons	31.8
Mononuclear aromatic hydrocarbons	21.9
Dinuclear aromatic hydrocarbons	17.5
Polynuclear aromatic hydrocarbons	16.6
Polar material	12.2

The polar material content is high. This fraction would include aliphatic sulphides and possible oxidation products formed during sample handling.

The combined fractions 10-36 consisting of the pentane eluate tail and the cyclohexane eluate represent 16.9% of the total sample and 12.8% of the total nitrogen. Results of the compound-type analysis are shown in Table 5.

TABLE 5

Weight Per Cent Compound-Type Distribution

(Combined fractions 10-36)

<u>Compound-Type</u>	<u>Wt %</u>
Saturated hydrocarbons	8.6
Mono- and dinuclear hydrocarbons	12.0
Polynuclear aromatic hydrocarbons	41.8
Polar material	36.1

The proportions of saturates, mono- and diaromatic-hydrocarbons decrease with progressive elution, while the polynuclear aromatic hydrocarbons and polar materials become more prominent.

The remaining fractions were combined and subjected to type analysis. These fractions are mostly polar or basic materials. It was found that 7.0% of the combined fractions A to F is of the polynuclear aromatic type. This represents 1.34% of the total sample.

The effect of sample size on the separation is listed in Table 6.

TABLE 6

Effect of Sample Size on the Distribution of Resin-Separated Fractions

	A*	B**
Oil to Resin Ratio	4:102	41:208
Recovery, wt %	97.4	97.0
Pentane Eluate, wt %	73.3	73.0
Cyclohexane Eluate, wt %	2.7	5.4
Eluate from Anion Exchange Resin		
Benzene, wt %	8.0	7.8
Benzene-Methanol, wt %	5.5	2.4
Benzene-Acetic Acid, wt %	4.3	3.5
Eluate from Cation Exchange Resin		
Benzene, wt %	2.4	4.5
Benzene-Methanol, wt %	2.0	1.8
Benzene-Methanol-Isopropyl Amine, wt %	2.0	1.6

* Using pumping system

** Using glass columns under gravity

The column with the lower sample to resin ratio holds back more material in the anion exchange resin.

As shown in Table 7, removal of most of the nitrogen does not significantly affect the sulphur content of the sample.

TABLE 7
Relationship between Nitrogen and Sulphur Contents
in the Resin-Separated Fractions

	Wt % of Eluate*	% N	% Referred to Total Nitrogen	% S
Pentane Eluate	73.0	0.02	5.7	4.0
Cyclohexane Eluate	5.4	0.46	8.8	6.3
Eluate from Anion-Exchange Resin				
Benzene	7.8	1.26	34.5	7.2
Benzene-Methanol	2.4	1.28	10.8	5.8
Benzene-Methanol-CO ₂	2.7	0.34	3.2	3.4
Benzene-Acetic Acid ²	0.8	2.95	8.4	5.6
Eluate from Cation Exchange Resin				
Benzene	4.5	0.64	10.2	7.8
Benzene-Methanol	1.8	0.92	6.0	5.8
Benzene-Methanol-Isopropyl Amine	1.6	2.14	12.2	3.3

* This is the same material as described in Table 6, using glass columns. The sample had 0.25% N and 4.26% S.

The nitrogen distribution in the main eluates of a severely hydro-cracked heavy oil(6,7) is shown in Table 8.

TABLE 8

Weight Per Cent Distribution of Nitrogen in Eluates of Hydrocracked Heavy Oil
(Recovery 98.2%)

	Wt % of Eluate	% N	% of Total N
Pentane Eluate	82.7	0.02	2.5
Cyclohexane Eluate	2.4	0.70	2.5
Eluate from Anion Exchange Resin			
Benzene	7.2	5.29	58.0
Benzene-Methanol	1.2	5.57	10.1
Benzene-Methanol-CO ₂	0.2	-	-
Benzene-Acetic Acid	0.1	-	-
Eluate from Cation Exchange Resin			
Benzene	2.0	2.07	6.3
Benzene-Methanol	0.4	-	-
Benzene-Methanol-Isopropyl Amine	1.9	7.32	21.0

Separation improves with decrease in molecular weight. Pentane eluted 82.7% of the material and this eluate contained only 2.5% of the total nitrogen. The acidic material has been almost completely eliminated. Fractions of the hydrocracked sample have a much higher nitrogen content than those of the unprocessed bitumen due to cleavage of hydrocarbon components from the nitrogenous compounds, which concentrates the nitrogenous groups.

To ascertain the amount of material retained by both columns, a 2.54-g acid fraction collected from the anion resin was introduced to the cation column. The results are listed in Table 9.

TABLE 9

Liquid Chromatography of Acid Fraction on Cation Exchange Resin

Eluate	Wt % Recovery
Cyclohexane	28.74
Benzene	19.69
60:40 Benzene-Methanol	18.50
55:37:8 Benzene-Methanol-Isopropyl Amine	1.97
Total	68.90

From these data 31.1% of the acidic fraction is retained on the cation resin. This retained material represents 3.2% of the 25.0-g initial bitumen charge to the resin columns.

An investigation was made on the extent of nitrogen removal due to ion-exchange resin treatment from a coker kerosene. Coker kerosene (nitrogen content 415 ppm) was pumped through the columns without dilution. Figure 5 shows that even after 700 ml of the coker kerosene had passed through the columns, over 75% of the nitrogenous material was retained by the resins.

A similar experiment was conducted with an asphaltene sample. The asphaltenes (25 g) were dissolved in 350 ml of benzene and washed through the columns with an additional 400 ml of benzene. The resins were then subjected to washing with other solvents to remove the retained material. Table 10 shows that only 20.4% of the asphaltenes was retained on the resins.

TABLE 10

Separation of Asphaltenes on the Resins

	% of Material Removed
Benzene Eluate	79.6
Eluate from Anion Exchange Resin	
Benzene-5% Methanol	6.1
Benzene-5% Acetic Acid	3.9
Eluate from Cation Exchange Resin	
Benzene-5% Methanol	3.5
Benzene-5% Isopropyl Amine	5.5

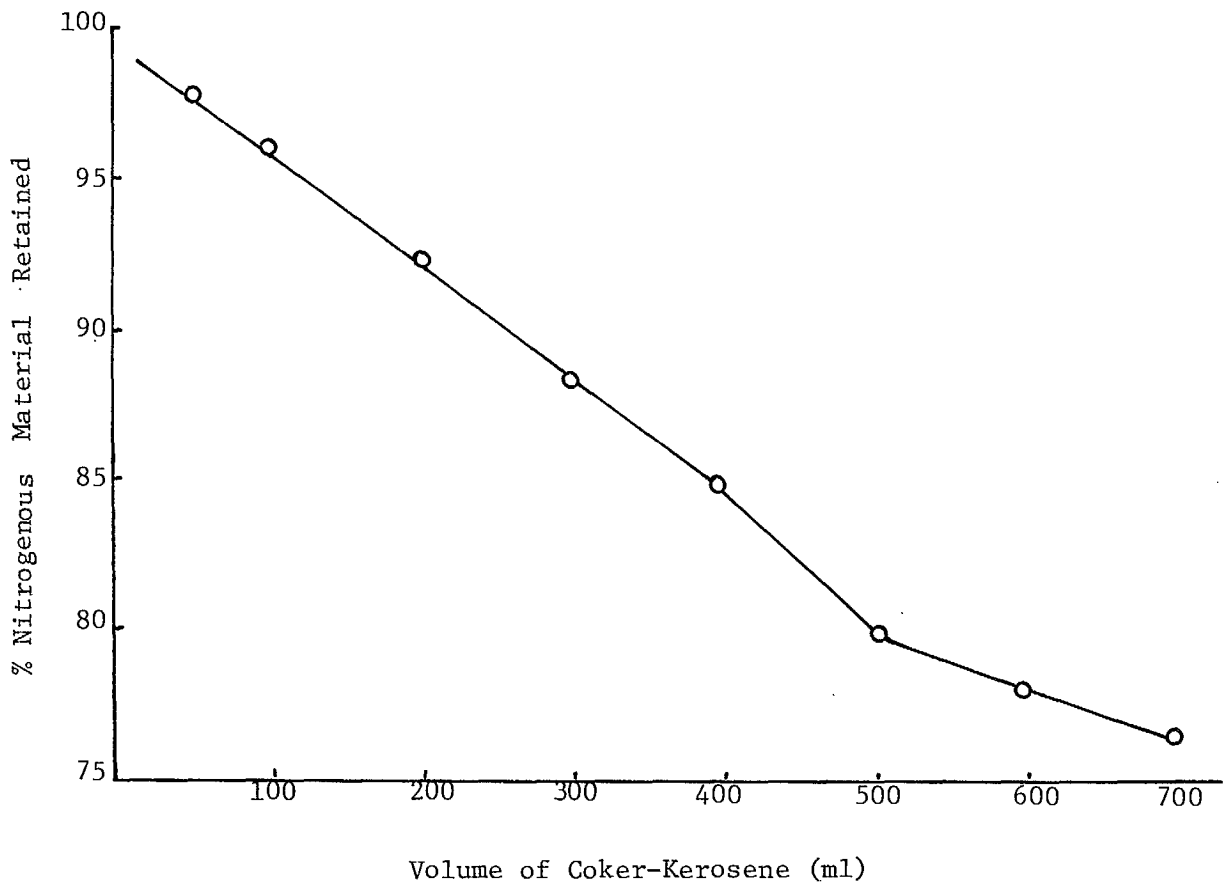


FIGURE 5. Removal of Nitrogenous Material from a Coker Kerosene on Ion-Exchange Resins

On a smaller sample of 5.5-g asphaltenes, 37.5% was retained on the resins.

Ion-Exchange Resin Chromatography on Other Cretaceous Bitumens and Oils

Ion exchange chromatography was performed on some bitumens and oils from the Alberta Basin. A 100.0-g sample was distilled up to 250°C to remove the light ends. The distillation residue, boiling above 250°C, was deasphalted with pentane. The deasphalted residue was then subjected to ion-exchange chromatography. The results are given in Table 11.

The Medicine River oil is one of the most mature Cretaceous oils in the Alberta Basin and contains the least nitrogenous and polar materials. The acids, materials displaced by CO₂ and by acetic acid, and the strong bases, displaced by amines, decrease respectively in Athabasca, Cold Lake, Lloydminster and Medicine River Oils (8).

TABLE 11

Ion Exchange Chromatography of Alberta Basin Bitumen and Oils

	Wt % of Total Sample			Medicine River
	Athabasca	Cold Lake	Lloydminster	
Cyclohexane Eluate	4.32	2.16	2.62	0.37
Eluate from Anion Exchange Resin				
Benzene	6.23	5.44	6.16	1.34
Benzene-Methanol	1.92	0.92	1.00	0.16
Benzene-Methanol-CO ₂	2.15	0.61	0.30	0.40
Benzene-Acetic Acid	0.65	0.24	0.32	0.40
Eluate from Cation Exchange Resin				
Benzene	3.62	3.04	2.68	0.66
Benzene-Methanol	1.49	1.35	0.62	0.24
Benzene-Methanol-Isopropyl Amine	1.29	1.02	0.58	0.10

Infrared Spectroscopy

The materials treated with ion-exchange resins were analyzed by infrared spectroscopy in methylene chloride solutions in the regions of 3400-3600 cm^{-1} and 1650-1800 cm^{-1} . In the 1650-1800 cm^{-1} region there is an insignificant peak around 1700 cm^{-1} in all the fractions which could be attributed to amides or other carbonyl groups (Figure 6).

The most interesting fractions are the acids displaced from the anion-exchange resins with carbon dioxide and acetic acid. The material displaced by the former has absorption characteristics similar to an aliphatic carboxylic acid, such as stearic acid. The latter adsorbs similarly to aromatic carboxylic acids. Benzoic acid shows similar adsorption. The corresponding fractions were practically absent in the hydrocracked sample. Thus, hydrocracking appears to cause practically complete decarboxylation.

In the 3400-3600 cm^{-1} region (Figure 7) the only prominent peaks appear to be due to carbazoles and/or indoles. The benzene-methanol eluates from the anion-exchange resin chromatography of the hydrocracked fractions gave the most prominent peaks. There is a peak which is common to the benzene eluate of the cation-exchange resins and the cyclohexane eluate with the columns in series. This peak is also observed in the absorption of Athabasca bitumen feed with traces of it in the cyclohexane eluate, and in the benzene-methanol eluate from the anion-exchange resin. The benzene eluate from this resin gives a larger peak. The bitumen feed has much less carbazoles than the hydrocracked material.

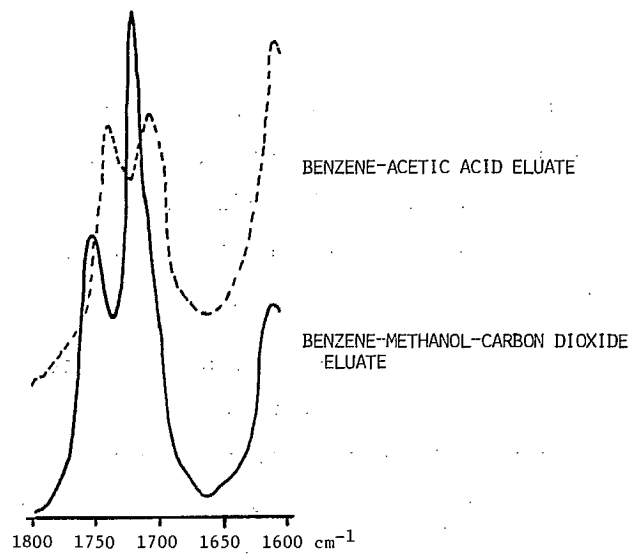


FIGURE 6 Infrared Spectra of Athabasca Bitumen Acids

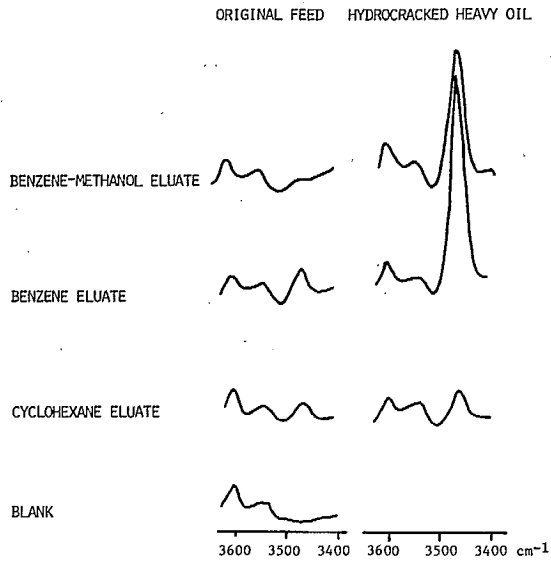


FIGURE 7 Athabasca Bitumen; Infrared Spectra of Eluate from Anion Exchange Resin

CONCLUSION

In this modified API-USBM procedure for separating the nitrogenous compounds and associated polar materials, most of the "neutral nitrogen compounds" were obtained in the tail portions of the pentane and cyclohexane eluates. This precluded the cumbersome treatment with ferric chloride. Further concentration could be obtained by chromatography on a dual silica-alumina column.

The polar materials retained on the ion-exchange resins after the pentane and cyclohexane elutions, were removed quantitatively by minimum amounts of eluents. The exhaustive extractions are unnecessary and undesirable.

The application of this modified procedure to the study of thermal hydrocracking products of the Athabasca bitumen indicated a substantial increase in the carbazoles and indoles content during hydrocracking.

REFERENCES

1. Mills, G.A., Boedeker, E.R. and Oblad, A.G. "Chemical characterization of catalysts"; J. Amer. Chem. Soc.; v. 72, pp 1554-1559, April 1950.
2. Hirsch, D.E., Hopkins, R.L., Coleman, H.J., Cotton, F.O. and Thompson, C.J. "Separation of high-boiling petroleum distillates using gradient elution through dual-packed (silica gel-alumina gel) adsorption columns"; ACS Preprints, Div. Petrol. Chem., Boston, pp A65-A74, April 9-14, 1972.
3. Sawatzky, H., George, A.E., Smiley, G.T. and Montgomery, D.S. "Hydrocarbon-type separation of heavy petroleum fractions"; Fuel; v. 55, pp 16-20; January 1976.
4. McKay, J.F., Cogswell, T.E. and Latham, D.R. "Analytical methods for the analysis of acids in high-boiling petroleum distillates"; ACS Preprints, Div. Petrol. Chem., Los Angeles; pp 25-35; March 31 - April 5, 1974.
5. Bunger, W.J. "Characterization of a Utah tar sand bitumen"; Advances in Chemistry Series, v. 151, pp 121-136; 1976.
6. Merrill, W.H., Logie, R.B. and Denis J.M. "Pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; Mines Branch Report R-281; 1973.
7. Pruden, B.B. and Denis, J.M. "Heat of reaction and vaporization of feed and product in the thermal hydrocracking of Athabasca bitumen"; CANMET Laboratory Report ERP/ERL 76-66 (R); 1976.
8. Montgomery, D.S., Clugston, D.M., George, A.E., Smiley, G.T., Sawatzky, H. "Investigation of oils in the western Canada tar belt"; "Oil sands fuel of the future"; Ed. L.V. Hills, published by Canadian Society of Petroleum Geologists, Calgary, Alberta, pp 168-183; September 1974.

CANMET REPORTS

Recent CANMET reports presently available or soon to be released through Printing and Publishing, Supply and Services, Canada (addresses on inside front cover), or from CANMET Publications Office, 555 Booth Street, Ottawa, Ontario, K1A 0G1;

Les récents rapports de CANMET, qui sont présentement disponibles ou qui ce seront bientôt, peuvent être obtenus de la direction de l'Imprimerie et de l'Édition, Approvisionnement et Services, Canada (adresses au verso de la page couverture), ou du Bureau de Vente et distribution de CANMET, 555 rue Booth, Ottawa, Ontario, K1A 0G1:

- 77-9 Filtration - Filters and filter media; H.A. Hamza;
Cat. No. M38-13/77-9, ISBN 0-660-01174-3; Price: \$2.00 Canada, \$2.40 other countries.
- 77-11 Ozonation for destruction of cyanide in Canadian gold mill effluents - A preliminary evaluation; G.I. Mathieu;
Cat. No. M38-13/77-11, ISBN 0-660-01171-9; Price: \$1.50 Canada, \$1.80 other countries.
- 77-12 Pit slope manual - Chapter 3 - Mechanical properties; M. Gyenge and G. Herget;
Cat. No. M38-14/3-1977, ISBN 0-660-00994-3; Price: \$3.50 Canada, \$4.20 other countries.
- 77-13 Pit slope manual - Chapter 4 - Groundwater; J. Sharp, G. Ley and R. Sage;
Cat. No. M38-14/4-1977, ISBN 0-660-01006-2; Price: \$3.25 Canada, \$3.90 other countries.
- 77-15 Pit slope manual - Chapter 8 - Monitoring; G. Larocque;
Cat. No. M38-14/8-1977, ISBN 0-660-01012-7; Price: \$3.50 Canada, \$4.20 other countries.
- 77-22 Pit slope manual - Supplement 2-3 - Geophysics for open pit sites; G. Herget;
Cat. No. M38-14/2-1977-3, ISBN 0-660-00991-9; Price: \$2.50 Canada, \$3.00 other countries.
- 77-36 Thermal hydrocracking of Athabasca bitumen: Effect of recycle-gas purity on product yields and qualities; A.M. Shah, B.B. Pruden and J.M. Denis;
Cat. No. M38-13/77-36, ISBN 0-660-01172-7; Price: \$1.25 Canada, \$1.50 other countries.
- 77-38 Comparison of notch-ductility and weldability of three high-strength structural steels; W.P. Campbell;
Cat. No. M38-13/77-38, ISBN 0-660-01217-0; Price: \$2.00 Canada, \$2.40 other countries.
- 77-39 The environmental cracking susceptibilities of three high-strength alloy steels; G.J. Biefer;
Cat. No. M38-13/77-39, ISBN 0-660-01242-1; Price: \$1.00 Canada, \$1.20 other countries.
- 77-42 Maturation studies on Canadian east coast oils; H. Sawatzky, A.E. George, R.C. Banerjee, G.T. Smiley and D.S. Montgomery;
Cat. No. M38-13/77-42, ISBN 0-660-01206-5; Price: \$1.00 Canada, \$1.20 other countries.
- 77-44 Thermal hydrocracking of Athabasca bitumen: Steady-state effects on product yields and qualities in the absence of scrubbing of the recycle gas; A.M. Shah, B.B. Pruden and J.M. Denis;
Cat. No. M38-13/77-44, ISBN 0-660-01241-3; Price: \$1.00 Canada, \$1.20 other countries.
- 77-45 Exploratory corrosion tests in the Canadian Arctic; G.J. Biefer;
Cat. No. M38-13/77-45, ISBN 0-660-01416-5; Price: \$1.00 Canada, \$1.20 other countries.
- 77-46 Comparison of coke produced in different CANMET coke ovens: Part 1: 12- and 18-inch oven coke strengths; W.R. Leeder and J.T. Price;
Cat. No. M38-13/77-46, ISBN 0-660-01194-8; Price: \$1.25 Canada, \$1.50 other countries.
- 77-49 Effect of elevated temperatures on compressive strength, pulse velocity and conversion of high alumina cement concrete; D.H.H. Quon and V.M. Malhotra;
Cat. No. M38-13/77-49, ISBN 0-660-01436-X; Price: \$2.25 Canada, \$2.70 other countries.
- 77-50 A comparative study of Fe catalysts, ZnCl₂ catalysts and ZnCl₂ - Promoted Fe catalysts for hydrocracking of Athabasca bitumen; W.A.O. Herrmann, L.P. Mysak and K. Belinko;
Cat. No. M38-13/77-50, ISBN 0-660-01218-9; Price: \$0.75 Canada, \$0.90 other countries.
- 77-51 Analysis of reactor samples collected during thermal hydrocracking of Athabasca bitumen; K. Belinko and J.M. Denis;
Cat. No. M38-13/77-51, ISBN 0-660-01245-6; Price: \$1.00 Canada, \$1.20 other countries.