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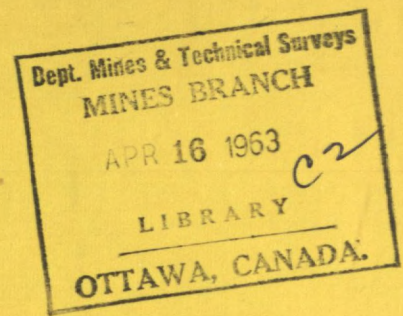
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INFRA-RED ABSORPTION BY
COLOURING MATTER IN
NATURAL WATERS

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MINERAL PROCESSING DIVISION

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INFRA-RED ABSORPTION OF COLOURING
MATTER IN NATURAL WATERS

by

John Ungar*

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ABSTRACT

A type of ion exchange chromatography was employed to extract organic colouring matter from natural waters. Infra-red spectroscopy of the extracts in KBr discs showed them to be markedly similar to organic matter studied by other workers using different extraction procedures. Such groups as hydroxyl, C=C, C=O, carboxyl and CH were present. Further studies using the described extraction technique as well as the direct measurement of infra-red spectra of aqueous direct solutions are recommended.

RÉSUMÉ

L'auteur a utilisé un certain type de chromatographie par voie d'échange ionique afin d'extraire les matières colorantes organiques des eaux naturelles. La spectroscopie à l'infrarouge des matières extraites contenues dans des disques de KBr a démontré qu'elles ont une ressemblance très prononcée avec les matières organiques étudiées par d'autres chercheurs qui ont utilisé des procédés différents d'extraction. L'auteur y a remarqué la présence de divers groupes: hydroxyle, C=C, C=O, carboxyle et CH. L'auteur recommande de poursuivre les recherches en recourant au procédé d'extraction qu'il décrit ainsi que la mesure directe de spectres infrarouges de solutions directes aqueuses.

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INTRODUCTION

One of the more useful tools in identifying and studying colour and/or organic matter in natural waters is the infra-red spectrograph. Not only is the infra-red spectrum useful in quantitatively estimating the amount of organic matter present, but it is also helpful in elucidating the structure since various structural and functional groups have characteristic absorption bands. For example, Sallee and associates (1) have described a referee method for the determination of alkyl benzene sulphonates in water by measuring the infra-red absorption of an extract at wavelengths of 9.6 and 9.9 microns. Iogansen (2) found that saturated hydrocarbons show characteristic bands in the frequency range 720 to 780 cycles cm^{-1} and noted that the non-branching chains of these compounds could be subdivided into five structural groups according to the length of their chains of methylenic groups. Edwards and his co-workers (3) demonstrated the use of infra-red spectra for characterising naturally-occurring organic pigments by determining and analysing the infra-red spectra of some twenty different 1:4 benzoquinones. In the water pollution field the U.S. Public Health Service has included infra-red spectroscopy in its methods for detecting organic pollutants (4).

Fuchs and Kohler (5) observed that in the infra-red absorption spectra there were marked similarities between water-soluble humic acids obtained from various brown coals and water-soluble lignins. Fuchs (6) considered that this suggested the presence of condensed ring systems. Hissel (7), in Belgium, published an infra-red spectral curve for a sample of "humic acids" which he obtained by absorbing organic matter on activated carbon, eluting with alkali, and precipitating the product with acid. Frisch and Kunin (8) eluted organic matter from fouled strong base anion exchange resins with brine and determined the infra-red spectra of the material thus recovered. Rice (9) also studied the infra-red spectra of coloured matter from waters causing fouling of ion exchange resins. Recently Black and Willems (10) reported studies on the extraction and identification of colour from several U.S. surface waters. Shapiro (11) concentrated and separated the colouring matter by solvent extraction or freezing, but has also studied other methods of extraction.

Since the so-called "humic acids" causing colour in waters of surface origin are considered a mixture of various vegetable degradation products, there is a tendency for infra-red absorption bands to be rather wide and for portions to be indefinite because one constituent masks another's spectrum. Some inorganic compounds, if present in the concentrate, tend to confuse the spectrum, since the overall concentration of organic colouring matter is very small.

EXPERIMENTAL WORK

Malartic River water, which has a very high colour (200-500 Hazen units, with a permanganate oxygen consumption of about 35 ppm), was sand-filtered and a portion was passed through a hydrogen ion exchange resin. After careful rinsing and preparation of the sulphonated polystyrene bead resin, hydrogen ion exchange did not significantly affect the amount of organic matter present, as evidenced by oxygen consumed and by ultra violet absorption tests (12).

Residues of the sand-filtered (A) and of the sand-filtered and hydrogen ion exchanged waters (B) were prepared by evaporation over a boiling water bath, and their infra-red spectral curves were obtained. The precipitate formed after several months' storage of composite samples of the highly coloured Mattagami River water was recovered by filtration and dried, and the infra-red spectrum of the resulting residue (C) was also obtained.

A few experiments were also carried out to study the usefulness of ion exchange resins in concentrating colouring matter from waters. It had previously been observed (13) that weak base anion exchange resins do remove organic colouring matter from waters when demineralization is carried out by the two-bed system; therefore, about 16 litres of Malartic River water was de-ionized through a series of two columns containing, respectively, a strongly acidic and a weakly basic bead resin. The anion exchanger was subsequently eluted and the organic matter collected as three separate eluate fractions.

After some 80 bed volumes of the water had been treated in the columns, the anion exchange resin was rinsed with distilled water (2 bed volumes) and eluted with 1.5 bed volumes of 20 per cent NaCl solution to yield a dark-brown eluate. A further rinse of 0.5 bed volume of distilled water was added to the previous eluate. Evaporation to dryness of a large volume of this composited eluate gave a residue D whose infra-red spectrum in KBr disc was then obtained. Another aliquot of this composite eluate was acidified and treated with barium chloride solution. The resulting precipitate of barium sulphate removed some colouring matter. The infra-red spectra of the dried co-precipitate (E) was also obtained.

The bed of weak base resin, after elution with brine and rinsing, was removed from the column, drained, and placed in a 500-ml conical flask; 1.5 bed volumes of concentrated hydrochloric acid were added, and the resin was allowed to contact the acid for several hours, with intermittent shaking. Considerable effervescence occurred upon addition of the acid, when the free-base active groups of the resin were neutralized. After soaking, the resin was washed with distilled water on a filter, and the filtrate and washings were evaporated to dryness. Two distinct residues resulted from the evaporation: a brown flaky material on the sides of the evaporating dish (F),

and a whitish, apparently crystalline solid on the bottom of the dish (G). These two residues were separated as carefully as possible and studied by infra-red spectroscopy.

The filtrate and washings from the first acid elution gave a bright yellow, clear solution; no such colour was obtained by acid treatment of unused resin. The near infra-red spectra of this first acid eluate and the above dark-brown brine eluate were also obtained.

The used resin was again placed in the conical flask and soaked for several hours, with intermittent shaking, in 1.5 bed volumes of fresh, concentrated hydrochloric acid. No effervescence occurred with this second acid elution, but the resulting yellow solution was decanted and evaporated to dryness as before. Once again two distinct residues, brown flakes (H) and white crystals (I), were obtained. These two residues were again separated as well as possible and their infra-red spectra obtained.

RESULTS AND DISCUSSION

Table 1 (page 6) is a summary of the findings of the infra-red spectra of all residues studied. The plus symbol (+) indicates a peak in the absorption graph and the probable presence of an organic grouping. Also included in Table 1, for comparison, are some infra-red data obtained by other workers on colouring matter extracted from natural waters.

Residues A and B

Residue A (in KBr disc, 0.51 per cent sample concentration) and residue B (in KBr disc, 0.53 per cent sample concentration) gave fairly wide absorption bands. A includes all the inorganic compounds in the water, while B should be free of such except possibly some traces of silica. These two residues show similar curves, except that B has a peak at a wavelength of 3.15μ which is either absent or masked in A. The peak at 2.95μ in both curves could be due to water or to hydroxyl ion; this peak was still present but much feebler when the residue A curve was repeated in "Nujol" mull. No positive C-H absorption at about 3.4μ is apparent in either residue. The peak at 3.15μ in the B curve could be due to bonded OH or NH. The peak in both curves at 6.2μ may be due to water and its slope may mask the absorption of the C=C double bond. This peak is also present in the "Nujol" mull of Residue A.

Residue B also shows a distinct peak at 5.82μ which is not present in A; this is considered indicative of a C=O group from carboxyl, aldehyde or ketone.

The broad band of both residues around 7.1μ could be due to carboxyl ion; some C-H absorption may be masked by the band.

It is considered that the broad band about 8μ , noted in both residue curves, is partly due to silica and/or sulphate.

Residue C

The precipitate from the Mattagami River water C (in KBr disc, at 0.55 per cent sample concentration) shows a somewhat similar curve to that of residue A above, except that it also has a distinct, if not large, C-H absorption peak at 3.45μ . C does not, however, show the extra peaks at 3.15μ and 5.82μ found with Residue B, and the "carboxyl" absorbance at 7.1μ is significantly less than in A or B.

It is important to realize that Residue C did not contain all the organic matter, but only that which had precipitated, whereas in Residues A and B most of the organic colouring matter had been collected by evaporation. Also, Residue C contained no crystalline material, according to X-ray diffraction study.

Residue D

The Residue D from the brine eluate (in KBr disc at 2.32 per cent sample concentration) shows a sharper peak at 2.9μ than does B; it is more like Residue A. Once again, none of the peaks found at 3.15μ and 5.82μ in B are found in D. A step in the D curve is noted at $5.9 - 6.0 \mu$ with a peak at 6.15μ , rather than the peak at 6.2μ found in A and B.

Instead of the rather broad band at 7.1μ found in B, D shows a narrower band about $6.85 - 6.9 \mu$ and a very sharp peak in the range 7.23 to 7.25μ . This may be caused by methyl groups, e.g. methoxyl.

The broad band ascribed to silica and/or sulphate in A and B is much narrower in D, and culminates more sharply around 8.9μ . A very distinct peak is noted at about 11.8μ , as well as a very sharp but small peak at 9.32μ ; the former could be due to a variety of organic groups, or to a trace of nitrate.

Residue E

The E curve shows a number of peaks, but is not conclusive probably because of the masking effects of the barium sulphate. Near infra-red spectra of NaCl eluates before and after barium sulphate precipitation showed, by peaks at 1.65 , about 1.35 and 1.15μ , that differences in the raw eluate solution and the solution after BaSO_4 precipitation are only caused by differences in chemical concentration of the same solute.

Residues F and G

Curves of the Residues F and G from the first acid eluate are considerably different, which indicates that fractionation of naturally occurring humic acids in waters by ion exchange chromatography, using weak base bead resins, is a distinct possibility.

Near infra-red spectra of the first HCl eluate (in solution) and of the brine eluate (in solution) are found to be quite different: the brine eluate has peaks about 1.05, 1.27, 1.50 and 1.77 μ , while the acid eluate has peaks at 1.17 and 1.40 μ . This seems to indicate that further fractionation took place with acid treatment.

Residues H and I

The Residues H and I from the second acid eluate are found to be much like Residues F and G from the first acid eluate. Residues H and F are almost identical, but I and G differ in that I has a broad band between 2.8 and 3.5 μ instead of the two peaks at 2.95 and 3.3 μ present in G.

COMPARISON OF INFRA-RED ABSORBANCE CURVES

Table 1 includes some infra-red data on coloured waters, reported by Hissel (7) and Frisch and Kunin (8).

Hissel's curve was obtained on KBr discs, using humic acids recovered from river water by absorption on a column of activated carbon, elution with sodium hydroxide, and precipitation with acid. Hissel claimed that infra-red spectra showed that drying the residue at 100°C did not alter its characteristics. His curve shows broad bands rather similar to those obtained with the sample of hydrogen ion exchanged Malartic River water (Residue B). The bands around the hydroxyl stretching frequency give the curve a rather different shape that may be due to Hissel's elution with strong alkali. Hissel admitted the probable existence of CH aliphatic, OH, C=O, C=C, and CH aromatic groups.

The curves of Frisch and Kunin were obtained by brine elution of coloured matter from fouled strong base anion exchange resins (in KBr disc, 0.5 per cent solids). One is a curve of the residue of the raw eluate and the other the curve of the residue of the de-ionized eluate. The raw eluate curve has sharper peaks. Frisch and Kunin indicated that, for the raw eluate, 2.95 μ is the OH stretching frequency and 3.4 μ the CH frequency; absorption at 8.8 μ is ascribed to sulphate, and between 9.9 and 10.5 μ to silica.

A study of Table 1 shows that there are a number of similarities between the various curves obtained in Canada, Belgium, and the United States, indicating that, even though they were obtained by different techniques and from different waters, the samples are generally compounds or mixtures of similar type.

TABLE 1
Infra-red Absorbance Peaks of Coloured Water Residues

Wave length (μ)	Approx. frequency (cycles cm ⁻¹)	Possible grouping present	Filtered Malartic River water Residue A	Filtered hydrogen ion exchanged Malartic River Residue B	Precipitate from Marragami River water. Residue C	Brine eluate from resin after B. Residue D	D acidified and BaSO ₄ precipitate. Residue E	First HCl eluate from resin after brine elution D.		Second HCl eluate from resin after D (F & G).		Hissel ⁷	Frisch & Kunin ⁸			
								Dark residue F	White residue G	Dark residue H	White residue I		Raw eluate residue	Deionized eluate residue		
2.95	3400	Hydroxyl or water	+	+	+	+		?	+	} Broad bands	} Broad bands	-	+	+		
3.0	3350		-	-	-	-						+	-	-		
3.1	3230	-	-	-	-		?	-				-	+	-		
3.12	3200	} Bonded OH or NH	-	-	-	-								+	-	-
3.15	3180		-	+	-	-									-	-
3.3						-		+	+							
3.45	2900	CH	-	-	+							+	+	+		
3.6-3.95	2780-2530		-	-	-							-	-	+		
4.15-4.2	-				-	-		+	+							
5.1-5.15					-	-		+	-				+			
5.2	1925		-	-	-	-						-	+	-		
5.82	1720	CaO	-	+	-	-						-	-	-		
5.85	1710		-	-	-	-						+	-	+		
6.07	1650		-	-	-	-						-	-	-		
6.1	1640		-	-	-	-		+	+			-	-	+		
6.2	1615	Water, CaC	+	+	+							-	-	-		
6.3	1590		-	-	-							-	+	-		
6.85						+		?	-			-	+	-		
7.0	1430		-	-	-	-						-	-	-		
7.1	1410	Carboxyl	+	+	+							-	-	-		
7.15	1400		-	-	-				?			-	-	+		
7.23-7.25						+		?	+			-	-	-		
7.30	1370		-	-	-	-						-	+	-		
7.8-7.9						?		-	-			-	-	-		
8.0	1250		?	?	?							+	-	-		
8.0-11.0								Broad bands, no distinctive peaks				-	-	-		
8.8	1148		?	?	?			?	?			-	+	-		
9.52	1050		?	?	?							+	-	-		
9.6	1042		?	?	?							-	-	+		
9.9	1010											-	-	-		
to												-	+	-		
10.5	953		-	-	-							-	+	-		
11.3	885		-	-	-							-	-	-		
11.8								Broad bands, no distinctive peaks				-	-	-		
11.8-12						+		+	+			-	+	-		
12	833		-	-	-							-	+	-		

+ Peak in absorption.
? Inflection or vague indication.
- No absorption peak noted.

SUMMARY

This study showed that a marked similarity exists between the organic colouring matter obtained by a type of ion exchange chromatography and organic matter extracted by other means and studied by other workers.

The technique outlined in this report for removal of organic matter is considered worthy of further study, particularly to classify coloured waters from various sources.

This study showed also that the organic colouring matter extracted from Canadian waters is of a similar nature to that found in waters in the United States and Europe by other workers.

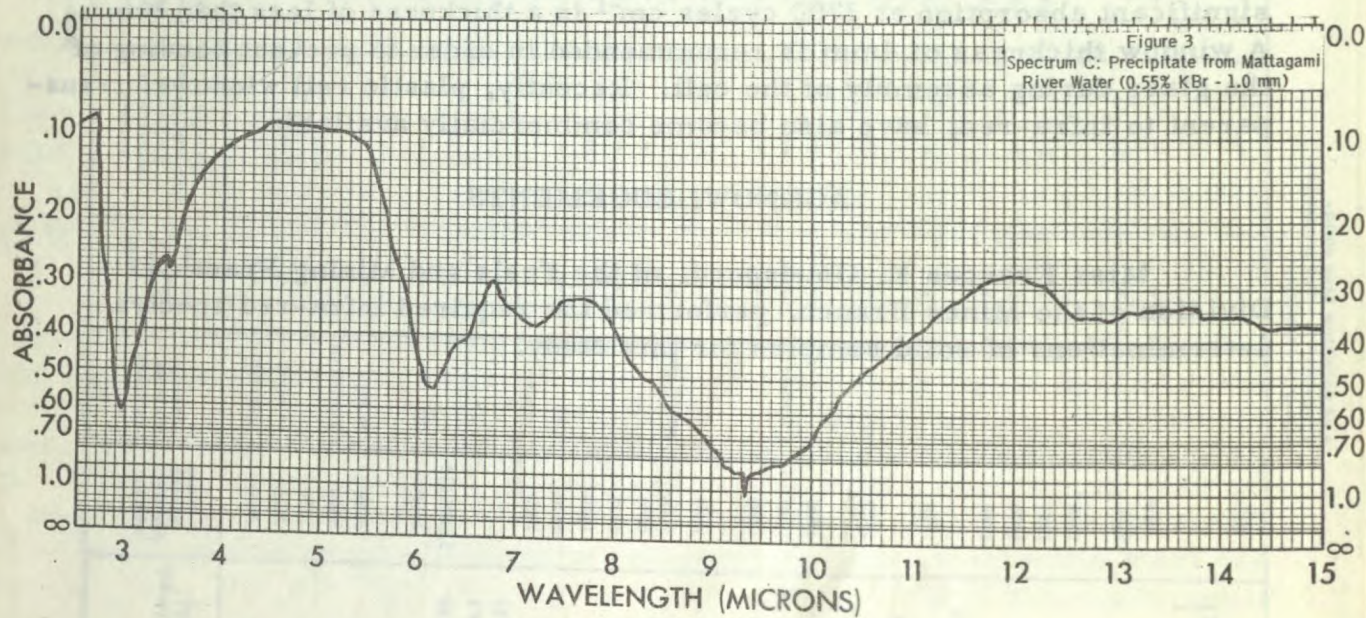
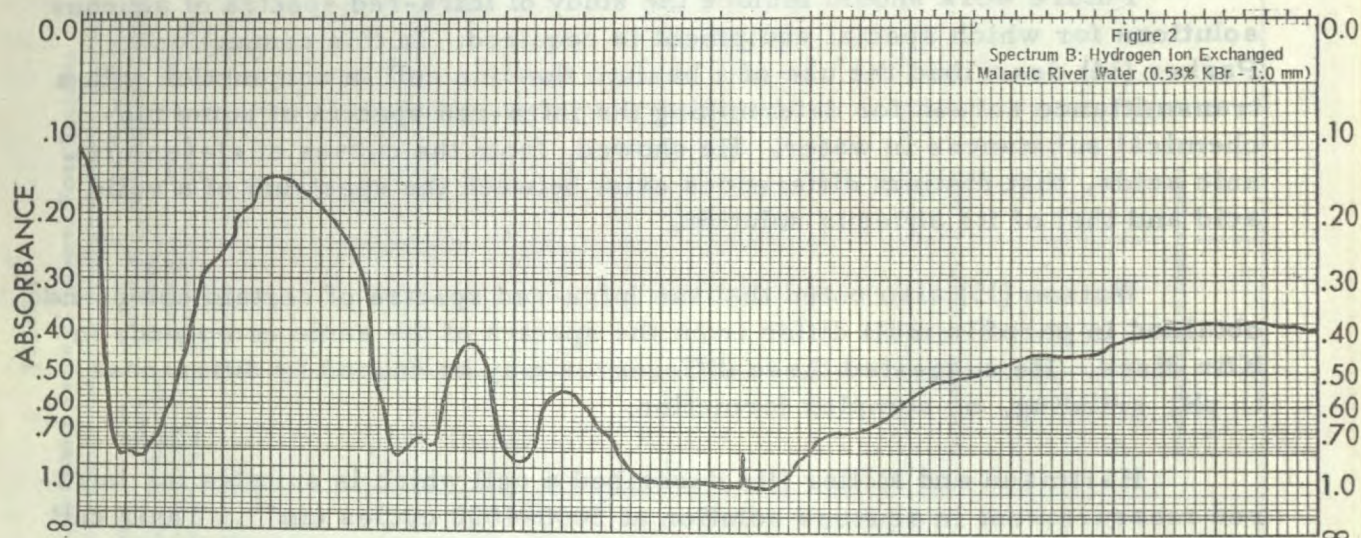
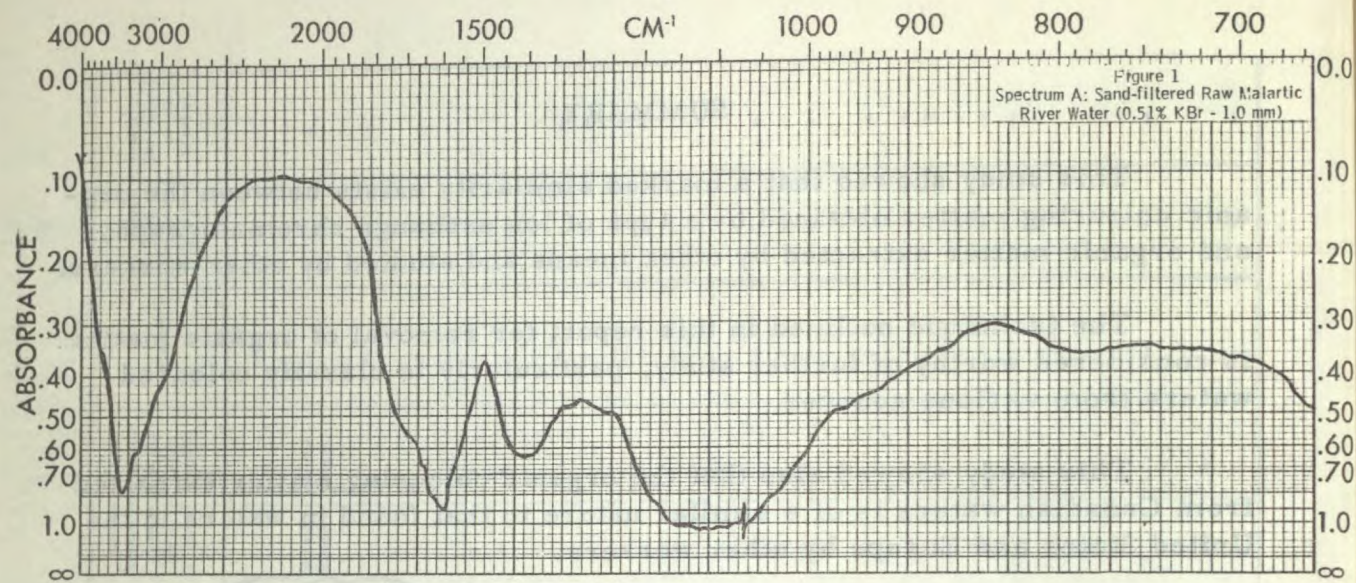
Future work should include the study of infra-red spectra of aqueous solutions for which special equipment is required. In this connection Parker (14) described the use of a barium fluoride cell in conjunction with a transmittance screen for determining the infra-red spectra of some biochemical substances in water. He showed, from the curves of eleven organic acids, that distinct differences exist between the spectrum of a solid acid and that of its aqueous solution.

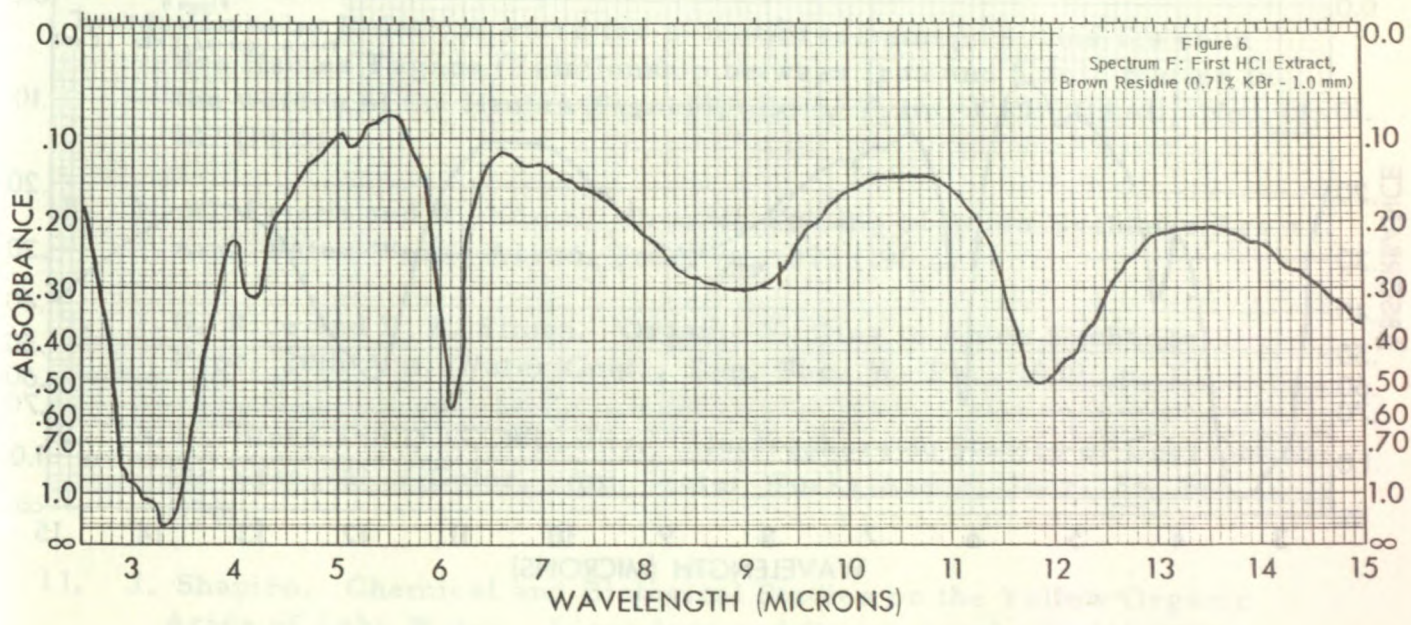
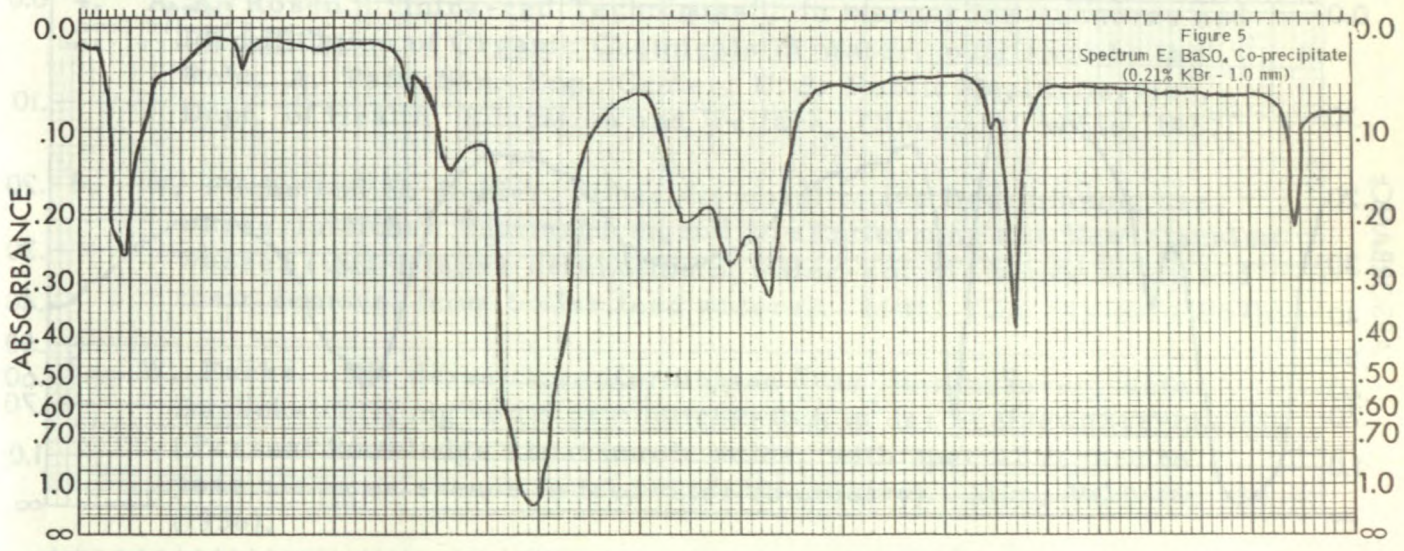
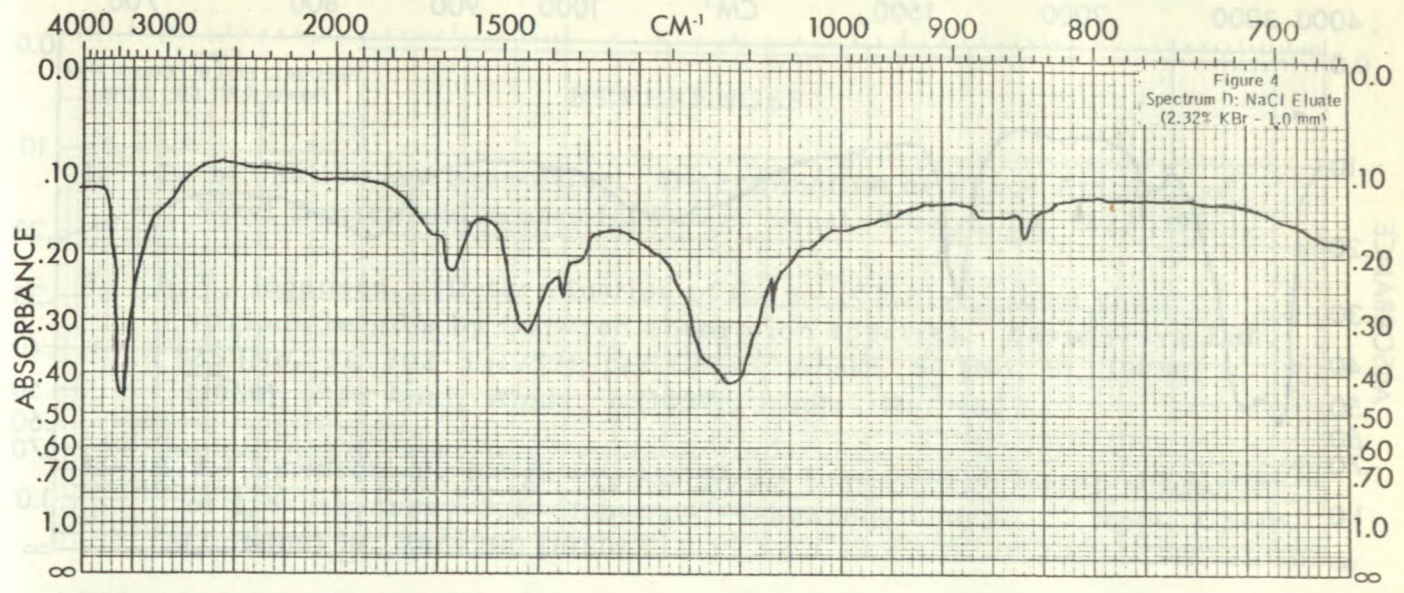
Watson (15) also noted that the infra-red spectra of certain compounds obtained in paraffin mull differ from the spectra of the same compounds in KBr discs. He suggested these differences may be caused by differences in pH, grinding, or complex formation.

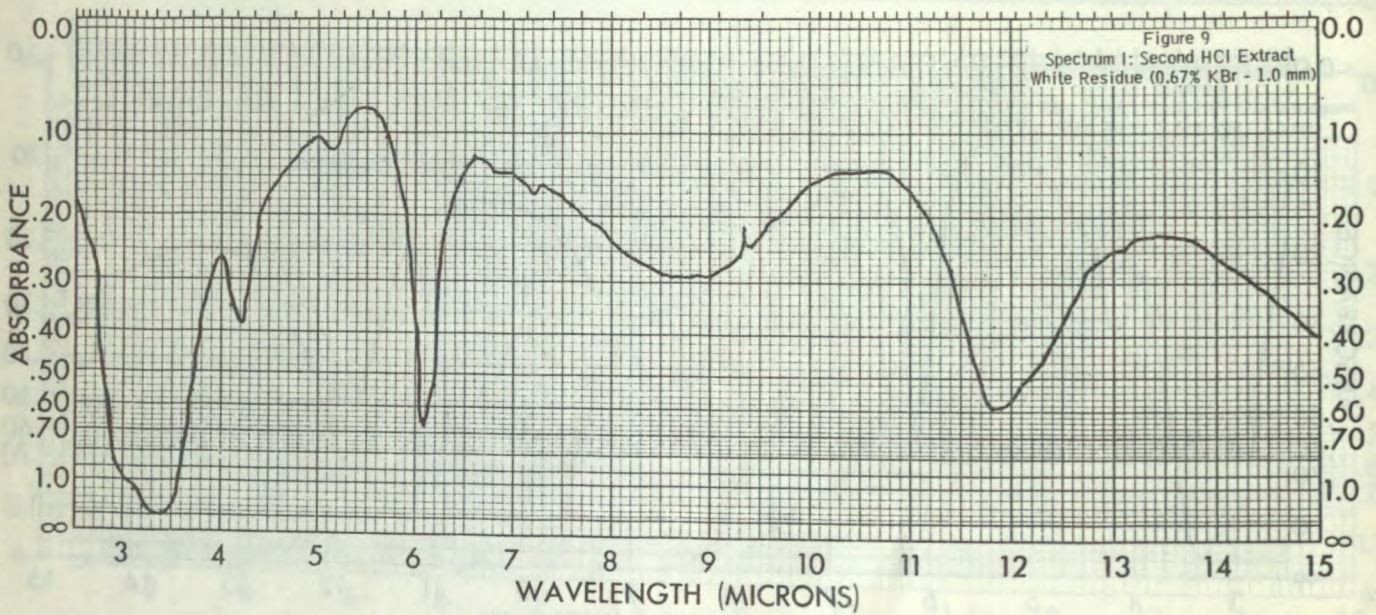
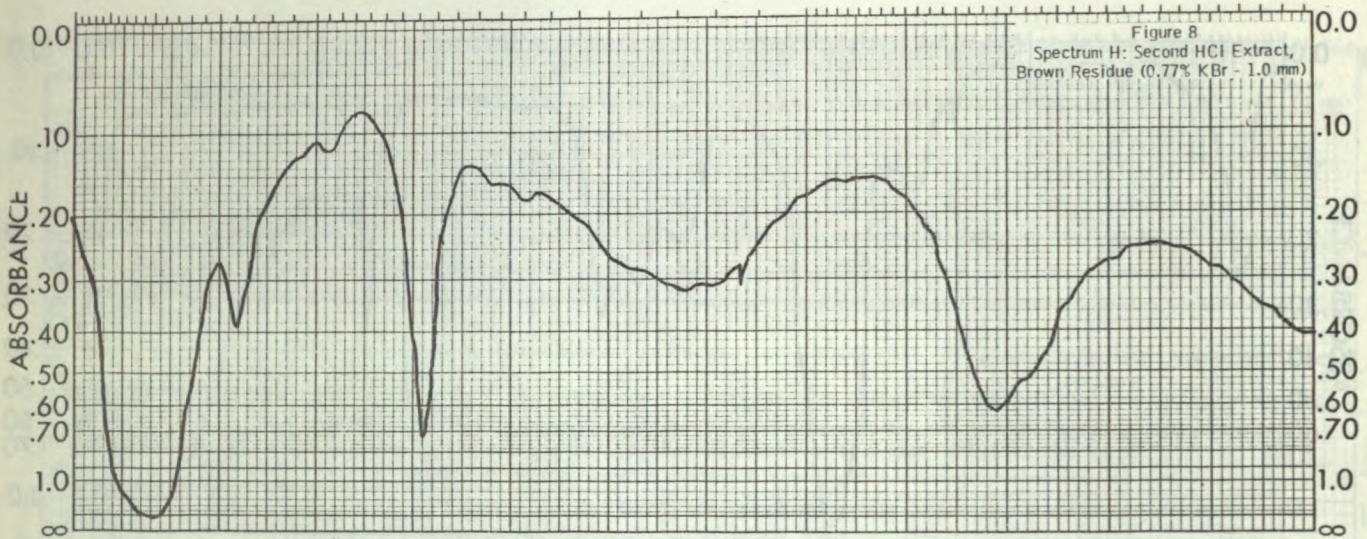
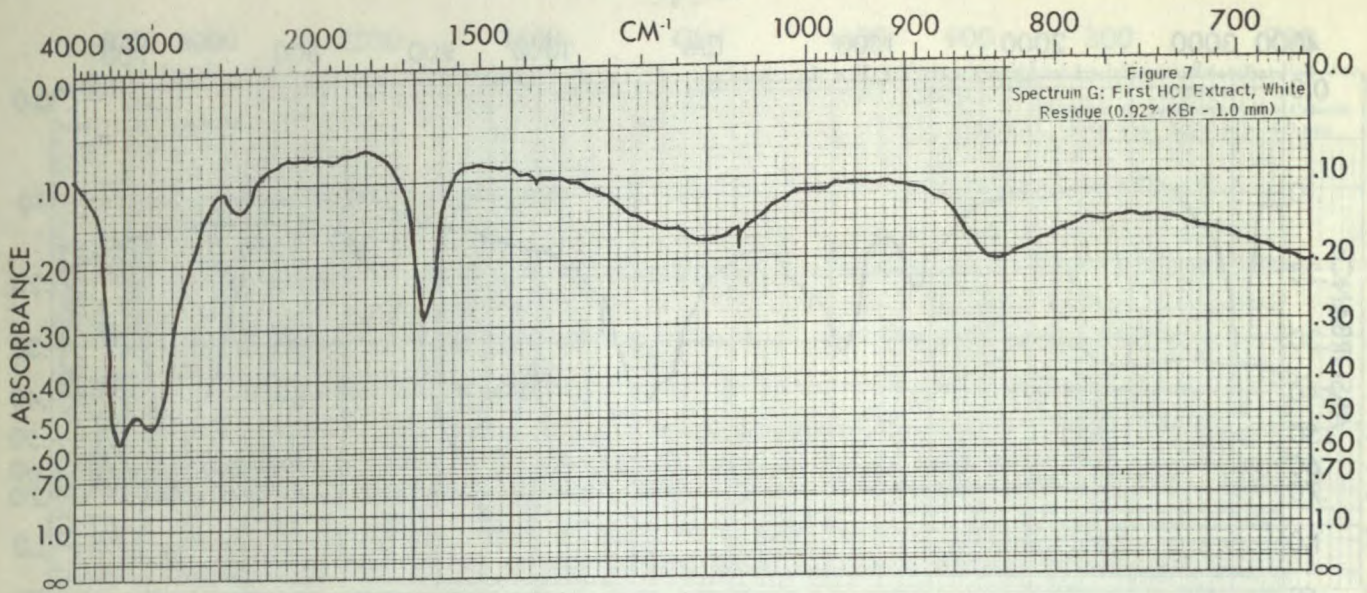
Hartmann and Miller (16) described a cell which is suitable for infra-red measurement in aqueous solution at 3000-4000 cycles cm^{-1} . Their cell has windows of a special quartz glass (Infrasil I) that does not show any significant absorption at 3700 cycles cm^{-1} in a thickness of less than 10mm. A window thickness of 4mm is recommended in order to prevent bending of the glass during assembly of the cell. Recently, plastic cell windows, transparent to infra-red, have also become commercially available.

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Miss Frances E. Goodspeed, of the Fuels and Mining Practice Division of the Mines Branch, performed the required infra-red spectra determinations of solid samples for this study.







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