

INFRARED SPECTROSCOPIC CHARACTERIZATION OF SLUDGES AND SLUDGE EXTRACTS: COMPARISON OF SEVERAL MILD EXTRACTION PROCEDURES

W. V. GERASIMOWICZ, D. M. BYLER, AND E. G. PIOTROWSKI

Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Philadelphia, Pennsylvania 19118

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ABSTRACT

Using Fourier-transform infrared (FTIR) spectroscopic techniques, we examined a series of whole sewage sludges and extracts obtained from the various samples. Sludges were fractionated by three different, chemically mild techniques: (1) direct solvent extraction, (2) two-phase ether/water extraction in which the pH of the aqueous layer was adjusted from 1.5 to 11.5, and (3) dry-column chromatography. The FTIR spectra provide a qualitative assessment of the types of constituents and functional groups found in the sludges and extracts. The spectra also allow a comparison of the differences and similarities of both the whole and fractionated samples.

INTRODUCTION

Disposal of sewage sludge by application to agricultural land is receiving increasing attention throughout the United States. Amending soil with municipal sludge has been demonstrated to be advantageous in certain cases and hazardous in others. Valuable plant nutrients, when present in sludge, can enhance soil fertility and produce higher crop yields (Sabey et al. 1977; Hinsley et al. 1977). By contrast, a major concern in using sludge on cropland is the presence of heavy metals or organic pollutants, derived largely from industrial effluents that reach the sewage treatment plants. Elevated levels of toxic metals may cause plant injury and soil toxicity, reduce harvests, and allow undesirable elements to enter the food chain (Webber 1972; Chaney et al. 1978). Furthermore, soil microorganisms are known to influence metals in natural systems (Summers and Silver 1978; McBride and Wolfe 1971). Microbiological and ecological changes are affected by metal pollution, and such factors must be considered against the ability of bacteria to transform nontoxic substances derived from sludge into useful energy sources for themselves.

Characterization of the sludge must be a primary consideration for a full understanding of such properties as micronutrient solubility and heavy metal transport in the soil. Insight gained

in such areas would be highly informative with regard to the delineation of optimum conditions for sludge disposal and the choice of disposal sites. The fate of the inorganic components during the decomposition of sewage sludge in soil is probably linked to the organic matter in the system that is capable of forming metal complexes.

As a consequence of the intimate relationship between organic components of the sludge and natural processes occurring in the environment to which the sludge is added, knowledge concerning the composition and properties of such complex, heterogeneous mixtures is necessary. The mode of action of the organic matter present in these systems will be reflected not only as a function of the quantity, but also as a function of its quality.

Extraction of sludge and its fractionation by harsh treatment with strong acids and bases may result in chemical alteration of the species present in the samples. Studies have borne out this possibility in the case of humic and fulvic substances that were isolated from soil systems by such means (Grant 1977; Dereppe et al. 1980). Such possibilities must be considered in the study of analogous sludge systems presented here. Otherwise, the actual effects of individual components, be they organic or inorganic, may be modified or lost altogether in terms of inter-

actions that occur naturally in the whole sludges.

Therefore, initial studies have been designed to permit a qualitative analysis of functional groups present in selected sludges and sludge extracts by means of Fourier-transform infrared (FTIR) spectroscopy. Extractions of sludges were carried out by relatively mild, nondegradative techniques. Similarities and differences seen in the FTIR spectra of sludge extracts obtained from a specific sludge by the several extraction methods are discussed, along with the effectiveness of the extraction procedures. Comparisons are also made of the variability of the chemical nature of the whole sludge (as determined by FTIR) obtained from different cities in the United States.

Infrared spectroscopy is a useful, nondestructive method for qualitatively characterizing complex mixtures. Indeed, a number of reports include infrared spectra of humic or fulvic substances extracted from sludges and soils (Stevenson and Goh 1971; Boyd et al. 1979, 1980). To our knowledge, however, no one has heretofore attempted to use this technique to help characterize either whole sludges or their aqueous and organic extracts.

EXPERIMENTAL PROCEDURE

Materials

Sludges

Samples of several representative municipal sludges—Baltimore sludge (S1), Baltimore compost (C1), and City #9 sludge (S2)—were kindly provided by R. L. Chaney of the U.S. Department of Agriculture, Beltsville Agricultural Research Center, Beltsville, Maryland. (City #9 is Chaney's pseudonym for a small Pennsylvania city whose identity, by prior agreement, must remain undisclosed.) The sludges were treated by the primary and secondary treatment facilities of the two cities designated. The compost was prepared according to the Beltsville method of the U.S. Department of Agriculture (Epstein 1977).

S1, C1, and S2 were lyophilized and then ground in a porcelain ball mill for 3 days to obtain homogeneous, powdered samples. Ball-milling did not affect the metal content of the sludges. The powders were stored under refrigerated conditions until required for use.

Solvents

Methylene chloride, methanol, and diethyl ether were all reagent grade and used without further purification (J. T. Baker Chemical Co., Phillipsburg, New Jersey 08865).¹

Chromatographic column

The column was glass, 30 mm i.d., and 30 cm long with a drip tip 8 mm i.d., 5 cm long; it was prepared by a local glassblower.

Column packing

The packing consisted of granular anhydrous, reagent grade sodium sulfate (J. T. Baker Chemical Co., Phillipsburg, New Jersey) and Celite 545 (Fisher Scientific Co., King of Prussia, Pennsylvania 19406).

Methods

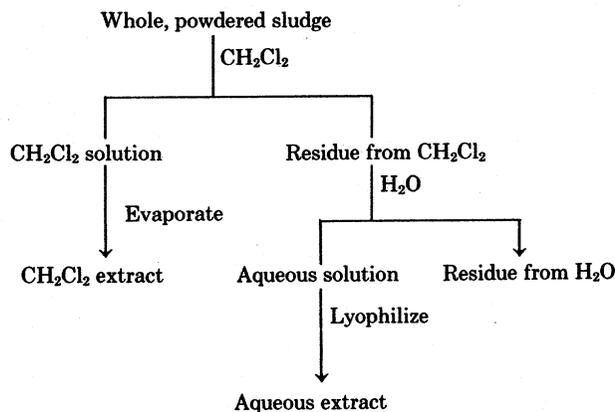
Extraction procedures

Three different procedures were used to extract various sludge fractions. Relative efficiencies were determined qualitatively to evaluate the advantages and disadvantages of each.

Method 1. Samples of S1, S2, and C1, 25 g each, were extracted by shaking for approximately 24 h with 150 ml of methylene chloride in stoppered flasks. Each solution was filtered. The solvent was removed under reduced pressure. This procedure was repeated with 150-ml aliquots of fresh CH₂Cl₂ each day until no further extractable materials could be obtained in the nonpolar solvent (as determined by the weights of materials obtained from the solvent phase). This stage was usually terminated after six extractions. The greasy materials extracted by methylene chloride were combined and examined by FTIR. The CH₂Cl₂-insoluble residues that remained were then serially extracted with water. Ten-gram samples of the remaining material were shaken with 75 ml of water for 24 h. The aqueous solution was filtered and lyophilized. This procedure was repeated with 75-ml aliquots of water until no further extractable material could be obtained (as determined by the weights of material obtained from the solvent phase). This stage was usually terminated after six aqueous extractions. The aqueous ex-

¹ Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

tracts were also examined by FTIR. A simplified schematic representation of this extraction procedure is shown below



Method 2. Ten-gram samples of S2 were placed in five, glass-stoppered flasks. One hundred milliliters of water was added to each. The pH of each sample was adjusted with dilute hydrochloric acid or dilute sodium hydroxide until values of 1.5, 3.7, 7.6, 9.2, and 11.5 were reached. Two hundred-milliliter aliquots of diethyl ether were added to each of these mixtures, resulting in a two-phase ether-water system. These were periodically shaken for 24 h, and the ether layers were then drawn off and filtered. After each extraction, the pH of the aqueous portions was checked and adjusted, if necessary (particularly at the high and low pH extremes), to the values stated above. The extractions were repeated with 200-ml aliquots of fresh diethyl ether until no further extractable materials could be obtained in the nonpolar solvent (as determined by the weights of material obtained from the solvent phase). This step was terminated after five extractions. The residues obtained after removal of solvent from the ether layers corresponding to a particular pH were combined and examined by FTIR. The water-soluble solids extracted at each pH were also spectroscopically studied upon removal of the solvent.

Method 3. A dry-column extraction procedure was employed to fractionate S2 only. This procedure has been used previously in the extraction of various components from meat samples (Maxwell et al. 1980; Marmer and Maxwell 1981). We present one example of the application of this technique to the extraction of sludge

samples. A glass-wool plug was inserted into the tip of the chromatographic column. Two grams of Celite 545 was added to the column and the

material was pressed down with a tamping rod to provide a firm base. Five grams of the sludge was weighed out into a porcelain mortar. Twenty grams of anhydrous Na_2SO_4 was added to the sludge, and the mixture was ground with a pestle until the material was reduced to a powder. Fifteen grams of Celite 545 was added to this mixture, which was ground again until a free-flowing powder was formed. The mixture was quantitatively transferred with a stainless steel spoon and a powder funnel to the previously prepared column. The powder was moderately tamped into place to obtain a uniform bed. The column bed was wetted with CH_2Cl_2 and isocratically eluted with 150 ml of the solvent. After this step was completed and the fraction was collected, the bed was subsequently eluted with 150 ml of 3:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ to extract more polar materials left behind in the previous step. The solvents were removed from the various fractions which were then subjected to FTIR analysis.

Fourier-transform infrared spectra

All infrared spectra were run from 4000 to 400 cm^{-1} on a Nicolet 7199 Fourier-transform infrared spectrometer at $\sim 4 \text{ cm}^{-1}$ resolution. The spectrometer was equipped with a Globar source, a Ge/KBr beamsplitter, and a TGS detector. Prior to Fourier transformation, each interferogram was zero-filled once and then multiplied by the Happ-Genzel apodization function. Spectra of the whole powdered sludges and the solid materials from the aqueous phases were run as

KBr pellets with approximately a 1:200 weight ratio of sample to KBr. The organic extracts typically gave greasy materials when solvents were removed. Spectra were taken of thin films of these extracts smeared between KBr plates.

Atomic absorption metal determinations

Copper, iron, calcium, and cadmium concentrations were determined by standard means for S2 and various extracts obtained therefrom through measurements on a Perkin-Elmer 5000 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Extraction methods

The relative organic content of the sludges was determined by ashing techniques (Table 1). This table also includes the relative distribution of various carbon-containing groups as estimated from ^{13}C NMR solid-state studies, which are the subject of another paper (Piotrowski et al. 1983). The total percentage of sludge extracted by the various methods described is listed in Table 2. Exhaustive extraction of S1, C1, and S2 by methylene chloride in Method 1 shows that from 1 to 7% of the total weight of the sludge sample was extracted by this nonpolar solvent. These values represent approximately 3 to 15% of the total organic material present in the whole sludges when considered as a function of their organic content, as stated in Table 1. The amount of organic matter extracted from each of the sludges is variable, and no systematic correlation between percentage of organic content of the sludge and percentage of total organic extract is evident. Similarly the fraction of each sludge subsequently extracted by water under Method 1 indicates that variations also exist in the amount of material that

TABLE 1
Relative carbon distribution in the sludges as determined by ^{13}C (CPMAS) NMR

Sample	% organic content ^a	Relative composition by ^{13}C (CPMAS) NMR ^b
S1	45	R ~ CARB > C=O > AR
C1	37	R ~ CARB ~ C=O ~ AR
S2	49	R ~ CARB > C=O > AR

^a Estimated by ashing.

^b Relative quantities of carbon atoms within a given sludge. R = unsubstituted alkyl carbon; CARB = carbohydrate; C=O = carbonyl; AR = aromatic.

TABLE 2
Total percentage of material extracted from sludge by various procedures

		Solvent medium	
Method 1		CH_2Cl_2	H_2O
S1		6.8	2.0
C1		1.4	2.7
S2		3.2	5.5
Method 2		ether	H_2O
S2	pH = 1.5	3.8	15.4
S2	pH = 3.7	3.1	6.7
S2	pH = 7.6	2.4	3.9
S2	pH = 9.2	2.1	5.8
S2	pH = 11.5	2.0	6.9
Method 3		CH_2Cl_2	$\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (3:1, vol/vol)
S2		6.10	3.99
S2		6.50	4.23
S2		6.03	4.15
S2		6.41	3.90

can be solubilized in aqueous media. Thus, extraction of sludge is not completely dependent upon the quantity of organic or inorganic materials comprising the sludge matrix. Rather, the results suggest that the quantity and type of material extractable from a sludge by a particular solvent system are markedly dependent upon the chemical nature of the constituent and its environment within the whole sludge. Such results are not inconsistent with the variable nature of sludges and the differences in composition of materials obtained from different treatment facilities. To make realistic comparisons, sludges should be treated individually and comparisons of extracts should be limited to fractions of an individual sludge.

Thus, in extraction Methods 2 and 3 the focus is only on S2. This sludge was chosen because its relative organic content was highest among the samples examined, and because the central focus of this paper primarily concerns organic functional group analysis of the sludges by FTIR.

Extraction of S2 across a pH gradient, as carried out in Method 2, results in differing quantities of material being solubilized at the different pHs and in the two solvent phases. Particularly noteworthy are the data at pH = 1.5. More material was extracted at this acidic pH into both the aqueous and ether layers than at other pH values. In sludge, certain inorganic

and organic components are present as metal salts. Protonation of functional groups and release of metal ions into solution could therefore result in enhanced release of sludge constituents from the overall sludge matrix. The solubility of such components is therefore increased, and, as a result, greater concentrations of materials are found in both the aqueous and ether phases. As the alkalinity of the aqueous phase is increased, decreased yields are seen in the ether phases. As organic salts form or are stabilized as a function of increasingly basic media, solubility in the ether layer diminishes. Only nonpolar, ether-soluble constituents, such as hydrocarbons, would be extractable at the higher pHs. The data presented above follow these trends.

As the pH increases, the percentage of the total sludge extracted into the aqueous layers decreases over the middle pH ranges and increases again at the more basic levels. This behavior is consistent with certain inorganic salts being quite soluble at both low and high pH, but not at intermediate values near neutrality. For example, in a moderately basic environment, most metal hydroxides are highly insoluble. At relatively high concentrations of hydroxide anion (pH > 9), however, formation of moderately soluble, negatively charged polyhydroxy complex ions may occur. Such a trend is reflected by the decrease in the amount of S2 solubilized in the aqueous phase at pHs around 7 relative to the solubility of the sludge observed in more acidic media. Relative to the amount of S2 extracted at pH ~7, a subsequent increase in the solubility of its components in the water layer is noted at pH = 9.7, with a further increase at pH = 11.5.

Examination of the fractions obtained from the aqueous layers of this pH gradient extraction method by atomic absorption analysis indicates that Cu^{+2} , Fe^{+3} , Ca^{+2} , and Cd^{+2} were present in larger amounts at the lower pHs (Table 3). Metal concentration decreased markedly across the neutral pH region and, with the exception of Cu^{+2} , further decreased as the pH approached 11.5. Realizing that the data for the extraction of metals presented here are for the case of a specific sludge from a single experiment, one may nonetheless infer that the amendment of land with sludges containing various metals will affect soils in different ways. Soil acidities vary from region to region, and, as such, these data

TABLE 3
Distribution of selected metals extracted from S2 into the aqueous layer by Method 2

pH	Percentage of the total metal present in S2 extracted into aqueous layer			
	Fe	Ca	Cd	Cu
1.5	4.16	39.96	51.53	28.32
3.7	<0.01	20.82	28.69	2.22
7.6	0.01	4.44	0.74	3.58
9.2	0.31	0.46	1.05	11.29
11.5	0.31	0.11	0.79	4.12
Metal in S2 (dry-weight basis), ppm	18 300	34 900	224	1980

corroborate generally accepted ideas that the potential transport and retention of metal ions added to soils is probably a direct function of the acidity of the soil itself. Thus, the sludge was maximally extractable under acidic conditions, with a decrease as neutrality was approached. A noticeable increase, however, in total extractable components in the aqueous phase was then seen at the upper pH values. More specific detail concerning the inorganic and organic groups associated with these fractions is discussed below under FTIR spectroscopic analysis.

The dry-column extraction (Method 3) offers interesting potential with respect to fractionation and analysis of sewage sludge. The data in Table 2 show the results of extracting four samples of S2; the percentage of total sludge extracted was experimentally consistent from run to run. Furthermore, the total amount of material extracted by this method was as much as or comparably more than seen in the tedious procedures of Methods 1 and 2. (Maxwell and his colleagues found similar trends in relative extraction efficiencies in their studies of meats (Maxwell et al. 1980; Marmer and Maxwell 1981).) This dry-column technique requires approximately 2 h as opposed to several days or a week needed in the other two cases. Extraction Method 3 is also safer in that the handling of sludge is limited and minimized. Furthermore, the solvents employed here are noncarcinogenic and relatively inexpensive.

Thus, the data at hand imply that the dry-column extraction of sewage sludge is more efficient than conventional direct extractions and is cost-effective. Additional work is being conducted to establish optimal solvent ratios, tem-

peratures, and conditions that might enhance this method and permit routine usage of this technique in the analysis of sludges.

FTIR spectroscopic analysis

In this study, FTIR spectroscopy served as the qualitative tool to characterize three different whole sludges and various extracts obtained from them. Because of the inherent complexity of these mixtures, we certainly cannot identify individual component compounds with this technique alone. Nonetheless, FTIR spectroscopy can serve to define some of the major classes of substances and chemical groups that comprise these heterogeneous matrices.

Whole sludges

Turning first to the whole sludges: the IR spectra of S1, S2, and C1 show, not surprisingly, more similarities than differences (Fig. 1). In every case, there are strong, broad absorptions due to the stretching of hydrogen-bonded hy-

droxyl groups (including those of water) centered at $\sim 3440\text{ cm}^{-1}$. Bending vibrations of adsorbed H_2O also contribute to another feature near 1640 cm^{-1} (Colthup et al. 1975; Bellamy 1975; Nakamoto 1978). On the high-frequency side of the former absorption are a pair of sharp bands (about 3620 and 3700 cm^{-1}) that probably result from isolated, non-hydrogen-bonded hydroxyls of claylike minerals, such as kaolin (van der Marel and Beutelspacher 1976).

Silica (SiO_2) and other silicates appear to be major inorganic constituents. Silica itself produces weak, but sharp, features about 800 , 780 , 690 , 510 , and 460 cm^{-1} (van der Marel and Beutelspacher 1976). In addition, these species all strongly absorb $\sim 1080\text{ cm}^{-1}$ and contribute to the intense, broad, overlapping band system found between 950 to 1250 cm^{-1} . Other inorganic substances that have intense absorptions in this same region, and whose presence in sludge is likely, include sulfates and phosphates (Table 4).

Alkyl groups (both methyl and methylene)

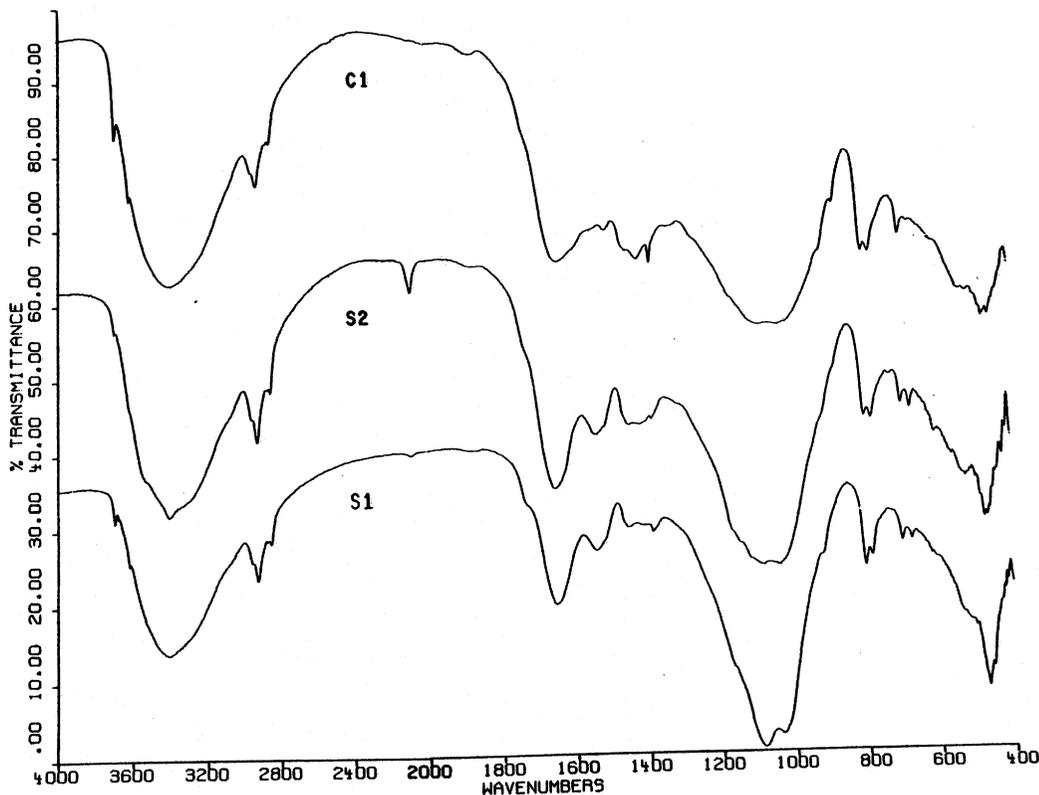


FIG. 1. FTIR spectra of whole powdered sludges.

TABLE 4
Major infrared absorptions of selected inorganic ions^a

Group	Approximate band position, cm ⁻¹
Ammonium (NH ₄ ⁺)	3300–3030 vs, ^b 1430–1390 s
Carbonate (CO ₃ ²⁻)	1495–1410 s, 880–960 m, ~710 w
Nitrate (NO ₃ ⁻)	1405–1350 vs, ~830 m, 720–690
Phosphate (PO ₄ ³⁻)	1020 s, v. broad, 570 m
(HOPO ₃ ²⁻)	3400 m, 1170–1120 m, 1080 s, 970 s, 870 s
((HO) ₂ PO ₂ ⁻)	3500–3400 m, 1300–1250 s, ~1170 s, 1050 s, 970 vs, 910 m, 890 s
Sulfate (SO ₄ ²⁻)	1160–1080 s, ^c 680–610 m-w ^c

^a Based on Bellamy (1975) and Nakamoto (1978).

^b Relative intensities: vs = very strong, s = strong, m = medium, w = weak.

^c In the solid, more than one band is often observed.

TABLE 5
Major infrared absorptions of selected functional groups^a

Group	Band position, cm ⁻¹
Alkyl —CH ₃	2960, 2870, 1460–1440, 1385–1375
—CH ₂ —	2925, 2850, 1485–1445, 750–720
Aryl —CH—C—C— Monosubstituted	~1600, ~1500, 1450, 770–730, ~700
Carbonyl —C=O Ester	1750–1740
—C=O Ketone	1725–1705
Alkoxy —C—O— Ester	1300–1150
—C—O— Alcohol, ether	1150–1050
Carboxylate —COO ⁻	1610–1550, 1400–1300
Hydroxyl —OH Hydrogen-bonded	3550–3200 (broad), 1410–1260
Amino —NH, —NH ₂ Hydrogen-bonded	3300–3200 (broad), 1650–1550
—NH ₃ ⁺ Hydrogen-bonded	3130–3030 (broad), 1640–1610, 1550–1485, ~800
Amide H O Hydrogen-bonded	3320–3270, 3180–3140, 1680–1630, 1570–1515,
—N—C—	1310–1270, ~700 (broad)
Water HOH Absorbed, hydrated	~3450 (broad), ~1640, 600–500 (broad)

^a Based on Colthup et al. (1975) and Bellamy (1975).

constitute a significant part of the organic fraction of the whole sludges. The absorption bands due to the CH stretching vibrations between 2850 to 2960 cm⁻¹ make this particularly evident (Table 5 and Fig. 1). Alkoxy moieties (single-bonded —C—O—) from such compounds as alcohols, carbohydrates, esters, and ethers very likely contribute to the broad, amorphous feature between 950 to 1250 cm⁻¹. A shoulder at about 1735 cm⁻¹ most likely represents the presence of carbonyl groups (—C=O).

The band observed at ~1650 cm⁻¹ seems too intense relative to the broad absorption at 3400 cm⁻¹ to be due solely to the HOH bending mode of water (Fig. 1). Amides (polypeptides) also absorb in this region. These facts, plus the observation of features ~3300 and between 1520 to 1540 cm⁻¹, lead us tentatively to conclude

that such species are present. (Based on their IR data, Boyd et al. (1980) concluded that amides were present in their humic acid extracts from Chicago sludge and sludge-treated soils.) Based on the presence of other characteristic bands (Table 5) observed in the 1350 to 1700 cm⁻¹ region (Fig. 1), amino and carboxylate groups (perhaps as amino acids) may also be components of whole sludges.

Despite the general similarities in the appearance of these three spectra, sufficient differences in detail are apparent so that even the untrained eye can distinguish between the spectra of the three different sludge samples. In the middle frequencies (especially 1300 to 1750 cm⁻¹), one observes that sludges S1 and S2 fall into one class, while the compost C1 clearly exhibits separate characteristics. For example, the former

two sludges absorb noticeably more strongly at 1545 cm^{-1} than does C1, the compost (Fig. 3).

Aqueous extracts

Now we compare the spectra of the various extracts studied with one another and with the spectra of the whole sludges. Spectral differences are now more readily apparent with respect to the specific sludge investigated. Even more obvious, however, are the changes found when the method of extraction or the polarity of the solvent is altered.

In general, as might be expected, spectra of materials extracted by solvents of different polarity display the greatest distinctions from one another and from the spectra of the original whole sample. Water, the most polar solvent employed in these studies, obviously gives extracts containing rather large amounts of soluble (predominantly ionic) inorganic species (Figs. 2, 3, 4). Organic substances are much less evident

in these solutions than in the less polar organic media or even in the whole sludges. Nevertheless, weak features between 2850 to 2960 cm^{-1} do betray the presence of modest numbers of CH bonds.

A strong band $\sim 1120\text{ cm}^{-1}$, along with weaker peaks sometimes seen between 600 and 700 cm^{-1} (Figs. 2, 3, 4), implies that sulfate ion is probably an important inorganic component of the aqueous extracts. The absorptions observed between 1000 to 1250 cm^{-1} are too complex to be due solely to this ion, however. Alkoxy (single-bonded $-\text{C}-\text{O}-$) groups of water-soluble carbohydrates or other polyhydroxyl species also absorb between 1050 to 1150 cm^{-1} . Thus, such materials are likely components of these extracts. Carboxylate groups probably contribute to the two bands near 1600 and 1400 cm^{-1} ; amides, amino groups, or both also seem to be likely possibilities, for there are significant absorptions around 3250 and 1650 to 1600 cm^{-1} .

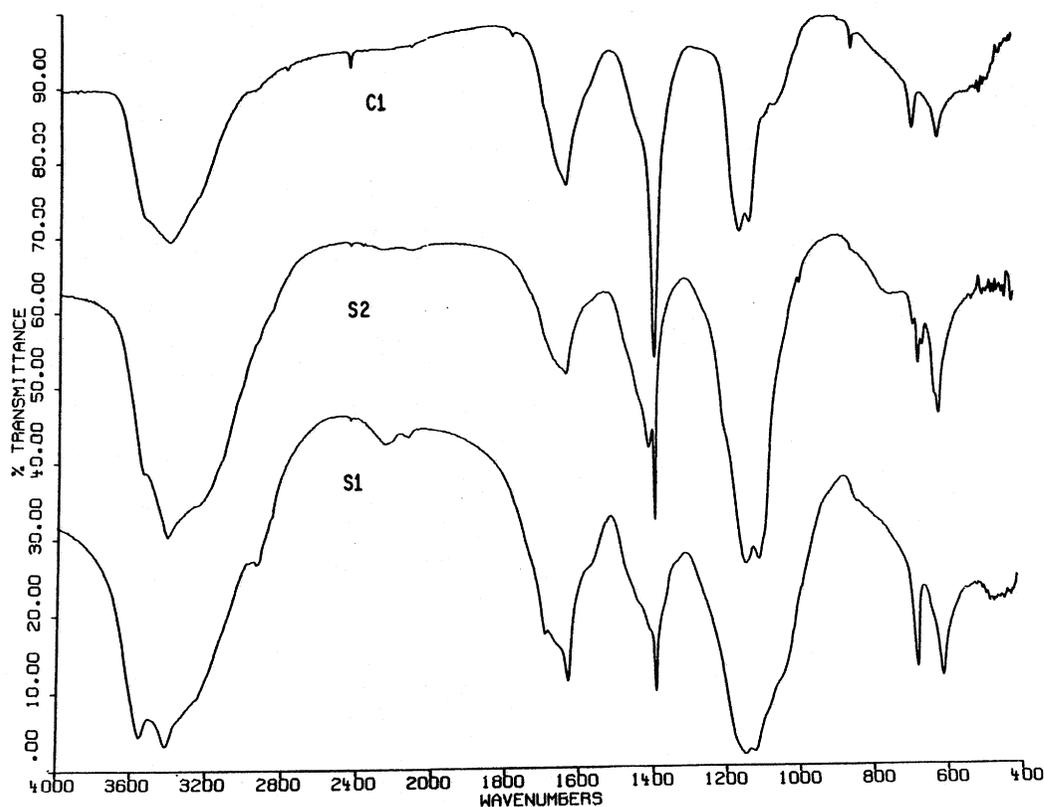


FIG. 2. FTIR spectra of the first aqueous extracts obtained from the sludges by Method 1.

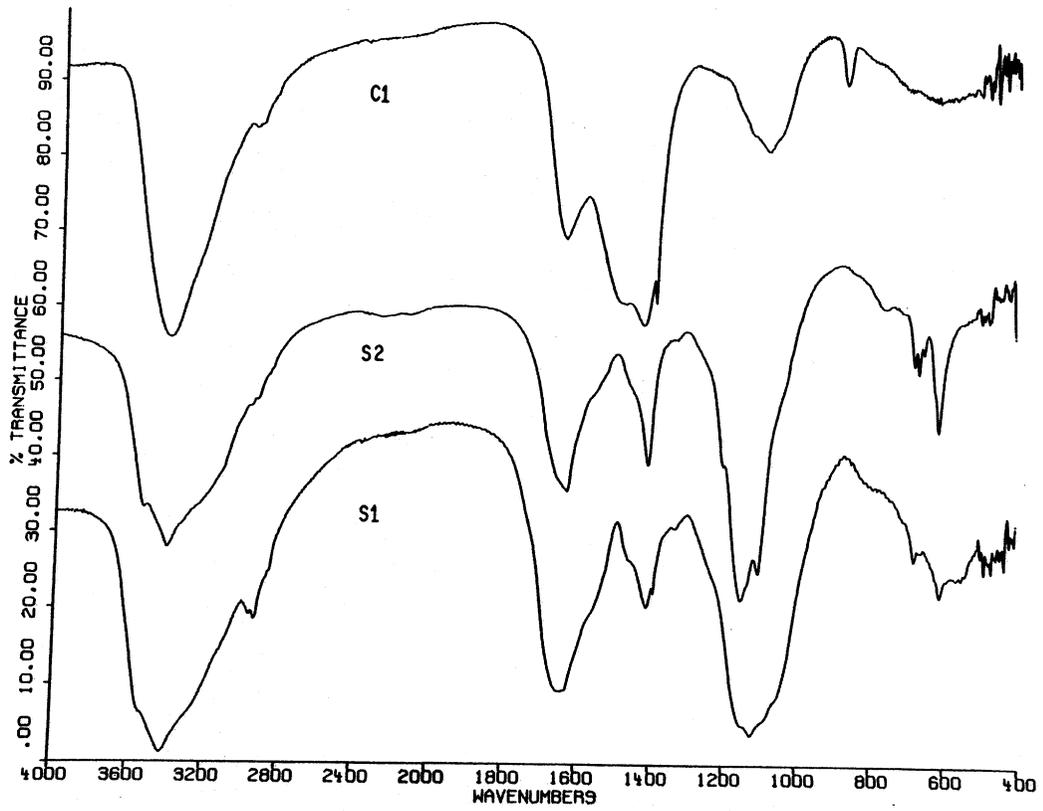


FIG. 3. FTIR spectra of the fourth aqueous extract obtained from the sludges by Method 1.

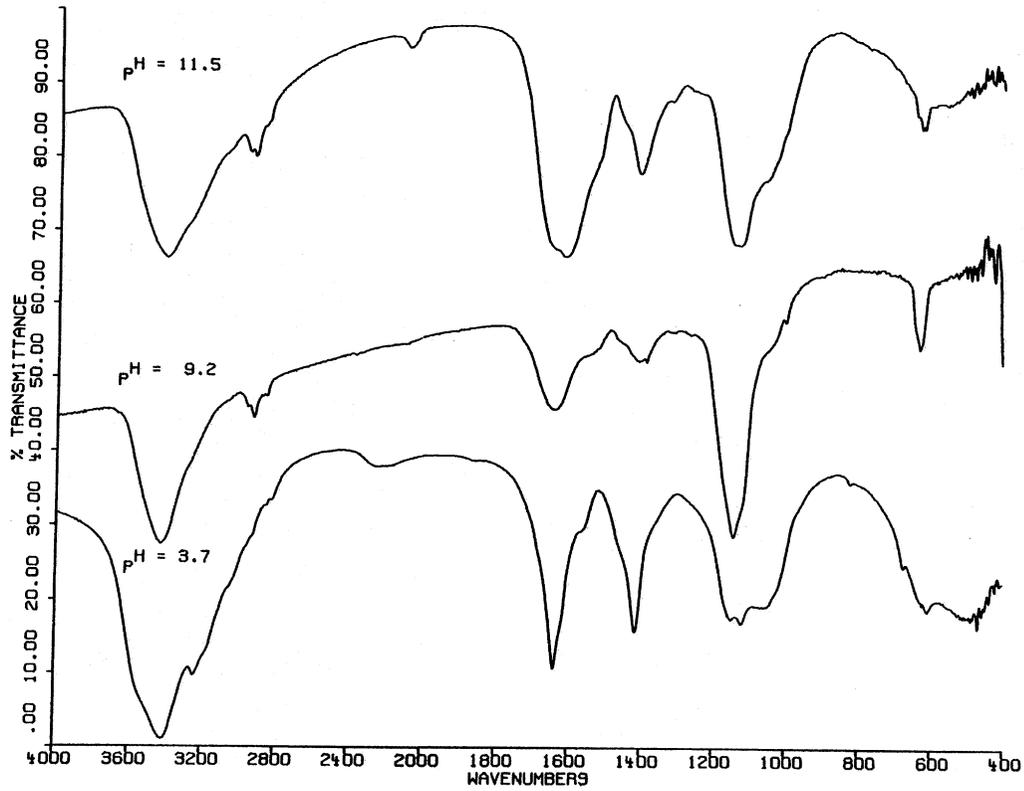


FIG. 4. FTIR spectra of residues from the aqueous layer of the ether-water extraction of S2.

Of the remaining prominent peaks in these spectra, several are attributable to other, simple inorganic ions including NO_3^- and NH_4^+ (Table 4).

The spectra of materials from the first aqueous extract of Method 1 (Fig. 2) differ noticeably from those of the water-soluble solutes obtained from later extracts (e.g., extract 4, shown in Fig. 3). In general, soluble inorganics are most evident in the early extracts. The broad absorptions of the organic ions and molecules are more prominent in the latter ones. (Compare Figs. 2 and 3.) Again, as for the whole sludges, the spectra of substances from the initial extracts of the two sludges S1 and S2 bear greater resemblance to one another than they do to spectra of matter extracted from compost C1,

particularly between 1300 and 1500 cm^{-1} and near 700 cm^{-1} (Fig. 2). By contrast, fraction 4 of all three sludges exhibits noticeable differences from one to another (Fig. 3).

Comparison of the spectra of the mixtures of water solubles recovered by the direct extraction procedure (Method 1) with those of the substances extracted by the two-phase ether-water technique (Method 2) at a series of different pHs (Fig. 4) provides additional interesting variations. Although the spectral regions having prominent bands are similar for both types of extracts, the two-phase procedure gave significantly greater relative amounts of organic CH-containing material, particularly at pH greater than 7.0. (Note the greater intensity of the bands in the 2850 to 2960 cm^{-1} region.) The extracts

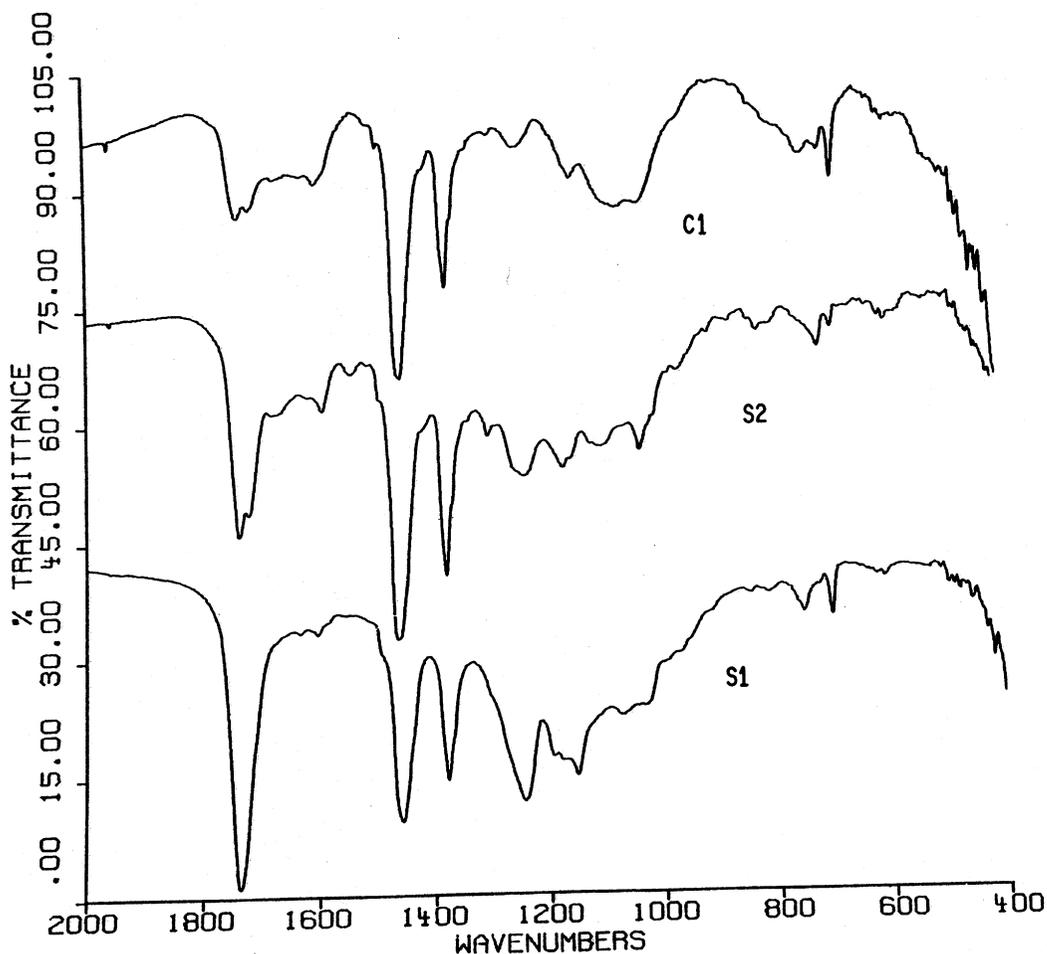


FIG. 5. FTIR spectra of CH_2Cl_2 extracts of whole sludges obtained by Method 1.

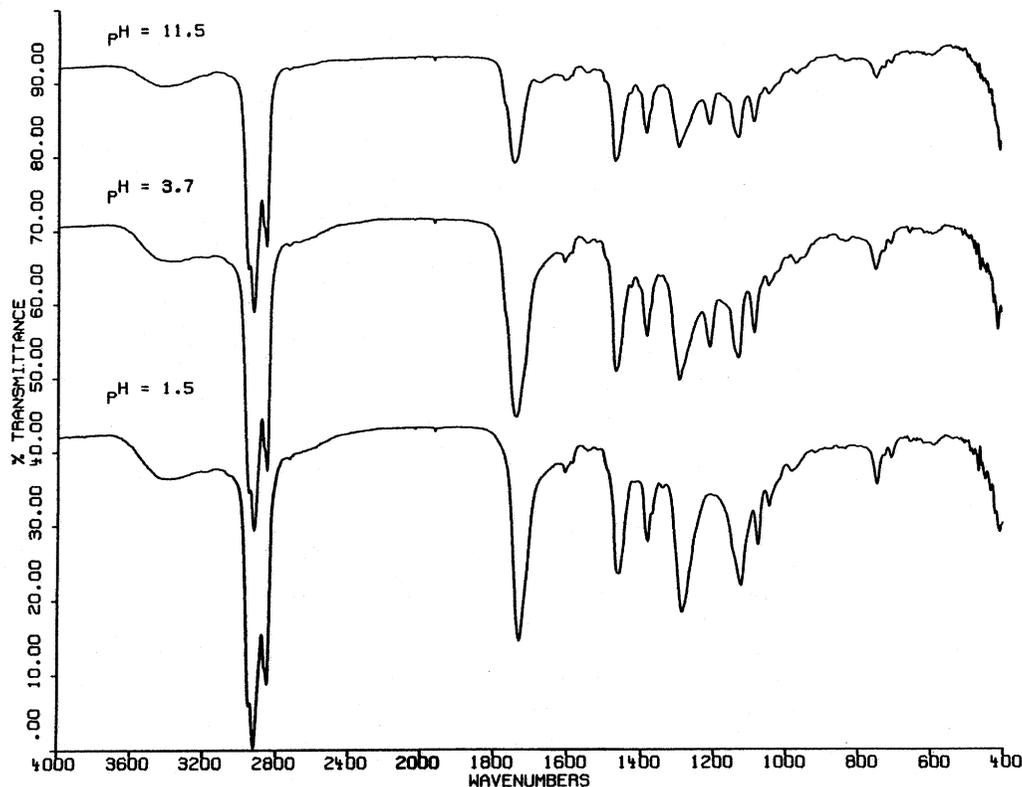


FIG. 6. FTIR spectra of residues from ether layer of ether-water extraction of S2.

at basic pH also show evidence of small amounts of ketonic, carbonyl-containing substances, for there are distinct shoulders about 1720 cm^{-1} on the moderately strong band at 1650 cm^{-1} . Another noticeable difference in the spectra from Method 2 is the absence or low relative intensity of the sharp band at 1385 cm^{-1} assigned to the NO_3^- ion.

Organic extracts

Proceeding now to the spectra of materials extracted by the organic solvents, we find that the strongest bands in every instance (Figs. 5, 6, 7) are those near 2900 cm^{-1} associated with the carbon-hydrogen stretching modes of both methyl and methylene groups. (Methyne CH stretching vibrations generally produce much weaker absorptions overlapping with bands produced by the other two types. Methyne modes are thus not readily distinguished in complex infrared spectra.) Prominent bands near 1380 and 1460 cm^{-1} in all of these spectra are associated with CH_3 and CH_2 bending motions.

These corroborate the presence of alkyl groups in significant quantities.

In the region between 1700 and 1770 cm^{-1} , one expects bands due to the vibration of carbonyl ($-\text{C}=\text{O}$) moieties. All the spectra of the organically extracted materials show a band between 1730 and 1735 cm^{-1} . These bands probably represent esters. In addition, some spectra clearly display a second absorption between 1710 and 1720 cm^{-1} , which is probably due to ketones. The absence of features between 2700 and 2500 cm^{-1} and at 1480 and 1300 cm^{-1} , characteristic of carboxylic acid dimers, leads us to conclude that such species are not present in these extracts in appreciable quantities. All samples from the ether layer of the two-phase extraction (except those at $\text{pH} < 3$) also exhibit another unresolved feature $\sim 1765\text{ cm}^{-1}$. Significantly, these carbonyl bands in our spectra always have a lower intensity than the alkyl CH stretching bands near 2900 cm^{-1} and sometimes have even less strength than the peaks of the alkyl bending vibrations at 1384 and 1460 cm^{-1} .

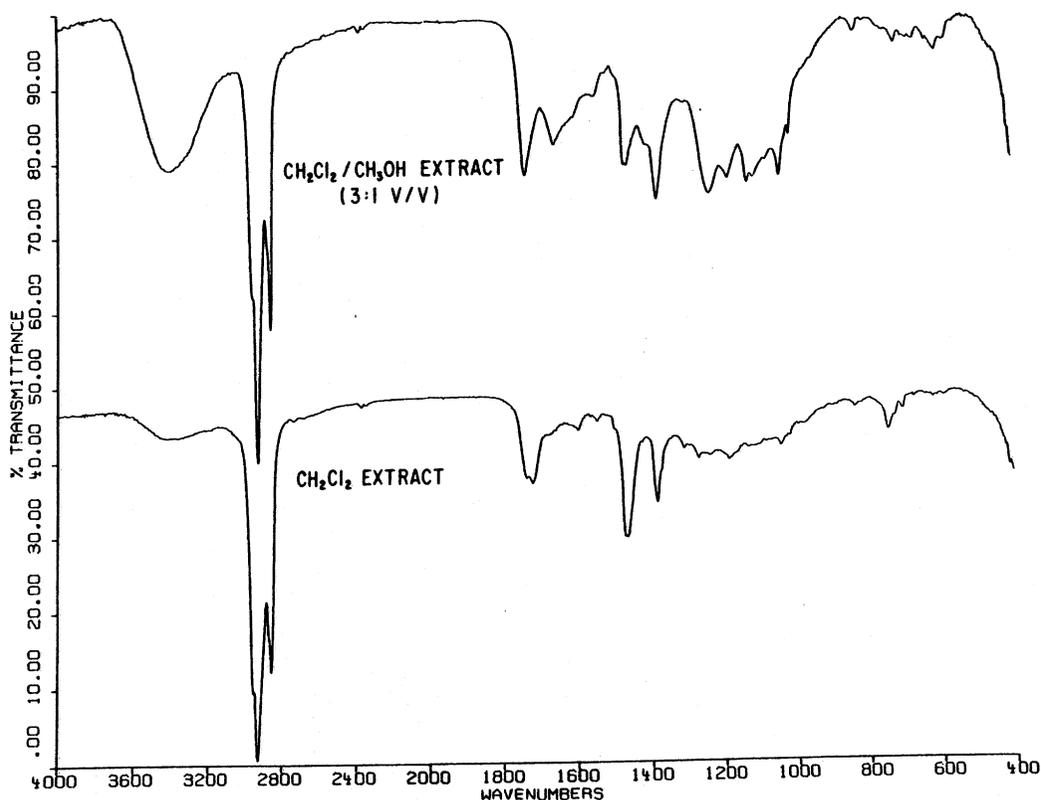


FIG. 7. FTIR spectra of S2 extracted with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 3:1 (vol/vol) and with pure CH_2Cl_2 on a "dry" celite column.

Because carbonyl bands are inherently much stronger than carbon-hydrogen bands, we may surmise that the ratio of CH bonds to carbonyl groups is much greater than unity in these complex mixtures.

The sharp band near 700 cm^{-1} and other weak features between 730 and 770 cm^{-1} (Figs. 5, 6, 7) betray the presence of a small proportion of monosubstituted aryl groups. Weak bands, sometimes visible at about 1495 to 1500 and 1600 cm^{-1} , lend further credence to this assumption. Based on the observed intensities of these peaks relative to those of the alkyl groups (1380 , 1460 , and 2850 to 2960 cm^{-1}), the direct CH_2Cl_2 extraction (Fig. 5) yields the largest ratio of aromatic to aliphatic organic species.

In the same spectra of the organically soluble material, broad, low-intensity bands between 1000 to 1100 cm^{-1} indicate that alkoxy C—O bonds (alcohols or ethers) are present in small quantity. The broad absorption near 3450 cm^{-1} may also be due in part to the hydroxyl groups of alcohols.

Additional features found between 1100 to 1300 cm^{-1} probably result from various species already identified as present in these extracts on the basis of bands observed in other regions. For example, the single-bonded C—O functionality of esters exhibit bands located in this spectral region. The exact position of these absorptions varies greatly depending on the structure of the ester. Strong bands also arise between 1120 to 1250 cm^{-1} , when branching of the hydrocarbon chains yields secondary, tertiary, and quaternary carbons.

CONCLUSIONS

FTIR spectroscopy, combined with mild extraction procedures, provides a relatively non-destructive probe into the nature of municipal sewage sludges. Of the three extraction methods discussed in this paper, the dry-column procedure may, in general, prove to have the greatest potential for the fractionation of such complex mixtures. This method affords the analyst an efficient technique that is rapid, simple, safe,

and cost-effective. The dry-column extraction of S2 with CH_2Cl_2 resulted in approximately twice as much material being extracted as seen for the same solvent by Method 1. The cause of this increase in total extractables is probably related to the dispersion of the sludge in the celite/ Na_2SO_4 column bed. Such dispersion results in an increased surface area for the sludge particles and therefore enhanced exposure to the eluting solvent. This phenomenon is currently under investigation, and further comment at this time would be premature.

We cannot yet identify specific constituents of sewage sludges or their various extracts, but by FTIR spectroscopy we now have good evidence for stating which major organic functional groups are present. Thus, the water-soluble fractions exhibit absorption bands attributable to alkyl ($-\text{CH}_2-$ and $-\text{CH}_3$), hydroxy ($-\text{OH}$), and alkoxy ($-\text{C}-\text{O}-$) groups, as well as bands assigned to carbonyl ($-\text{C}=\text{O}$) moieties, carboxylate groups ($-\text{COO}^-$), and N—H bonds. In addition, we can sometimes give a qualitative estimate of the relative quantities of important functional groups found in the different organic extracts. The FTIR spectra of these specific organic extracts generally exhibit the following trend: alkyl ($-\text{CH}_x$) > carbonyl ($-\text{C}=\text{O}$) > alkoxy ($-\text{C}-\text{O}-$) \gg aromatic ($-\text{CH}$). FTIR, therefore, may be used to profile whole sludges as well as certain extracts obtained from them.

The mixtures of materials extracted by non-polar solvents have a somewhat different composition from that of the total organic fraction of any whole sludge. NMR spectroscopic estimates (Table 1) corroborate this fact (Piotrowski et al. 1983; Pfeffer et al. 1983). The relative quantity of alkoxy groups, including carbohydrate-like materials, is much greater in the whole sludges than in the extracts from low-polarity solvents, because carbohydrates and related species have no appreciable solubility in dichloromethane and diethyl ether.

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REFERENCES

- Bellamy, L. J. 1975. The infrared spectra of complex molecules, 3rd ed., vol. 1. Chapman and Hall, London.
- Boyd, S. A., L. E. Sommers, and D. W. Nelson. 1979. *Soil Sci. Soc. Am. J.* 43:893-899.
- Boyd, S. A., L. E. Sommers, and D. W. Nelson. 1980. *Soil Sci. Soc. Am. J.* 44:1179-1186.
- Chaney, R. L., P. T. Hundmann, W. T. Palmer, R. J. Small, M. C. White, and A. M. Decker. 1978. Proc. national conference on composting of municipal residues and sludges. Information Transfer, Rockville, Maryland, pp. 86-97.
- Colthup, N. B., L. H. Daly, and S. E. Wiberley. 1975. Introduction to infrared and Raman spectroscopy, 2nd ed. Academic, New York.
- Dereppe, J. M., C. Moreaux, and Y. Debyser. 1980. *Org. Geochem.* 2:117-124.
- Epstein, E. 1977. *Compost Sci.* 18:5-7.
- Grant, D. 1977. *Nature* 270:709-710.
- Hinsley, T. D., R. L. Jones, E. L. Ziegler, and J. J. Tyler. 1977. *Environ. Sci. Technol.* 11:182-188.
- Marmer, W. N., and R. J. Maxwell. 1981. *Lipids* 16:365-371.
- Maxwell, R. J., W. N. Marmer, M. P. Zubillaga, and G. A. Dalickas. 1980. *Assoc. Off. Anal. Chem.* 63:600-603.
- McBride, B. C., and R. S. Wolfe. 1971. *Biochemistry* 10:4312.
- Nakamoto, K. 1978. Infrared and Raman Spectra of inorganic and coordination compounds, 3rd ed. Wiley-Interscience, New York.
- Pfeffer, P. E., W. V. Gerasimowicz, and E. G. Piotrowski. 1983. *Anal. Chem.* (*in press*).
- Piotrowski, E. G., K. M. Valentine, and P. E. Pfeffer. 1983. *Soil. Sci.* (*in press*).
- Sabey, B. R., N. N. Abgim, and D. C. Markstorm. 1977. *J. Environ. Qual.* 6:52-58.
- Stevenson, F. J., and K. M. Goh. 1971. *Geochim. Cosmochim. Acta* 35:471-483.
- Summers, A. O., and S. Silver. 1978. *Annu. Rev. Microbiol.* 32:637-672.
- van der Marel, H. W., and H. Beutelspacher. 1976. Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier, Amsterdam.
- Webber, J. J. 1972. *J. Water Pollut. Control Fed.* 71:404-413.