

PROJECT ADMINISTRATION DATA SHEET

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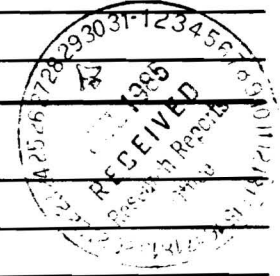
See Attached N/A Supplemental Information Sheet for Additional Requirements.

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Equipment: Title vests with None proposed or anticipated

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- ☐ None
- ☐ Final Invoice or Copy of Last Invoice
- ☐ Final Report of Inventions and/or Subcontracts- Sent Patent Questionnaire to P/I
- ☐ Government Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Release and Assignment
- ☐ Other

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COAGULANT RECOVERY FROM ALUM SLUDGES
AT NORTH AREA PLANT

by

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For

Bureau of Water
City of Atlanta

Submitted to

Williams, Russell, Johnson, Inc.
Jordan, Jones and Goulding, Inc.
A Joint Venture
Atlanta, GA

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Mr. Michael Roeder, Mr. J. Havash and Mr. M. Asim assisted in collection of data on sludge extraction, conditioning, thickening and dewatering. Dr. Maurizio Giabbai coordinated GC/MS analyses of sludge and extract samples while Ms. Zhanna Geskin and Ms. Isabel Escovar conducted analyses of trace metals.

CONCLUSIONS AND RECOMMENDATIONS

The recovery of aluminum from potable-water treatment sludges was examined using sulfuric acid extraction. Sludges from four treatment plants in metropolitan Atlanta using the Chattahoochee River as a source of raw water and alum as a primary coagulant were examined under controlled laboratory conditions. The following conclusions are based on the results of the experimental studies.

Alum sludges from the underflow of post-coagulation clarifiers at run-of-the-river plants had suspended solids (SS) concentrations which ranged from 51 to 179 g/L, or 5.1 to 17.9 percent solids. These concentrations were higher than conventional estimates would indicate, which was attributed to high solids loadings and the high density of turbidity particles. Treatment plants with presedimentation basins prior to coagulation had underflows with conventional suspended solids (SS) concentrations of 8-23 g/L.

Aluminum contents of sludges from the four treatment plants ranged from 47 g/kg SS to 102 g/kg SS, accounting for 4.7 to 10.2 percent of the dry mass of the sludge solids. Aluminum contents reflected both aluminum-hydroxide precipitates, formed in the coagulation process using aluminum sulfate, and aluminum oxides, contained in influent clays and suspended solids. Aluminum was the predominant metal in all sludges, although iron and manganese accounted for 4.0 to 5.7 percent and 0.13 to 0.46 percent of sludge dry mass, respectively.

Concentrations of trace metals, which are regulated in potable waters and which included arsenic, barium, cadmium, chromium, lead, mercury and selenium, ranged from 0.1 to 240 mg/kg SS in sludge samples. Concentrations of copper, nickel, tin and zinc ranged from 25 to 185 mg/kg SS.

Acidification of alum sludges was used to solubilize aluminum. Addition of sulfuric acid and depression of pH from near-neutral values to $\text{pH} \approx 4$ resulted in negligible solubilization of aluminum. Depression of pH from $\text{pH} \approx 4$ to $\text{pH} \leq 2$ resulted in solubilization of significant quantities of aluminum. Aluminum concentrations in clarified extracts with pH values between 2 and 4 increased linearly with decreasing pH. The extent of solubilization varied for each suspension and could not be effectively normalized using acid addition rates or suspended solids concentrations. The extent of solubilization was indicated to be directly related to the concentration of aluminum in aluminum-hydroxide precipitates. However, because of high levels of aluminum in raw-water suspended solids which could not be extracted by acid addition under ambient conditions, the relative amounts of aluminum-hydroxide could not be measured, contributing to the inability to normalize aluminum extraction data.

Acid application rates of 0.1 to 10 meq $\text{H}_2\text{SO}_4/\text{g}$ of SS, or 0.05 to 0.5 lb $\text{H}_2\text{SO}_4/\text{lb}$ SS, were used to extract aluminum concentrations of 600 to 3400 mg/L ($\text{pH} \leq 2$) or 12 to 60 mg Al/g SS. With the exception of one dilute sludge sample, all acid application rates were ≤ 0.1 lb $\text{H}_2\text{SO}_4/\text{lb}$ of suspended solids.

Acidification of alum sludges resulted in the release of organic matter from sludge solids. Acid addition rates up to 0.1 lb $\text{H}_2\text{SO}_4/\text{lb}$ SS produced soluble organic carbon concentrations of 580 mg/L to 3400 mg/L ($\text{pH} \leq 2$).

Commercial alum used at two plants contained aluminum at 55 to 60 g/L. Other metals included iron at 1845-2080 mg/L; tin at 155 mg/L; chromium at 40-78 mg/L; nickel at 44 mg/L; and manganese at 20 mg/L. Silver, cadmium, copper, mercury, lead, and zinc were contained at concentrations of 0.003-9 mg/L. The highest projected concentrations of regulated metals to be

contained in a potable water treated with commercial alum at an alum dose of 11 mg/L (Al = 1 mg/L) were silver = 4 ng/L, cadmium = 5 ng/L; chromium = 1.3 µg/L; mercury = 0.08 ng/L; and lead = 0.3 µg/L. All of these projected metal concentrations were less than 2.6 percent of the maximum contaminant levels (MCL) for regulated metals.

By comparison of trace-metal contents of sludges and commercial alum, it was concluded that commercial alum could be the major source of silver, chromium, nickel and tin in alum sludges. Commercial alum was a minor source of cadmium, copper, iron, mercury, manganese, lead and zinc in sludges, indicating that other chemical additives or influent raw-water solids were the major source of these metals.

Projected metal concentrations in coagulated waters using commercial alum or recovered coagulants at an equivalent alum dose of 11 mg/L indicated that recovered coagulants and commercial alum produced equivalent concentrations of silver, cadmium and chromium. Concentrations of mercury, lead, copper and zinc were higher for recovered coagulants, but none were at concentrations higher than 4 percent of current MCL values. Iron and manganese were the major metal contaminants for recovered coagulants with projected concentrations in coagulated waters of 0.04-1 mg/L and 0.033-0.12 mg/L, respectively. Iron, however, was considered to be as a contributing coagulant metal, unlike manganese which could result in increased requirements for preoxidants.

GC/MS scans resulted in the detection of no organic priority pollutants in recovered coagulants. Alum sludge samples contained chloroform at concentrations of 0.15-37.5 mg/kg SS. Trace concentrations (i.e., < 15 mg/kg SS) of benzene, toluene, chlorobenzene, 1,2-dichloroethane, 1,1,1-trichloroethane, anthracene, pyrene, and 2,4-dichlorophenol were detected in several sludge samples.

Recovered coagulants were shown to be effective in coagulating Chattahoochee River waters. Raw waters with an initial turbidity of 11-16 NTU were treated with recovered coagulants at equivalent alum doses of 5-10 mg/L (0.8-1.7 mg/L as Al) to achieve settled turbidities of \leq 0.6 NTU.

Acid-extracted sludge could be effectively thickened with polymer addition and dewatered to solids contents of 22 to 60 percent solids using a low-pressure (100 psi) recessed-chamber filter press. Lime conditioning and polymer conditioning were both established to be effective in enhancing sludge dewaterability. Lime conditioning produced firmer dewatered cakes with better handling properties. Polymer conditioning resulted in enhanced recovery of aluminum and in production of significantly lower quantities of sludge solids.

A coagulant recovery system was proposed for the North Area Plant which was compatible with the conventional, semi-batch filter-press system. The design water flow for the plant was 30 mgd with a sludge loading of 7000 lb/d (5 operational days/week). Sulfuric acid requirements of 325 gal/d were established with a required acid-storage capacity of 10,000 gal. Conditioning tanks designed for the conventional system were compatible with coagulant recovery. The volume of recovered coagulant to be produced ranged from 2030-5180 gal/d at an effective overall aluminum recovery of 63 percent, with the balance of the aluminum being contained in lime-conditioned residual sludge solids. Polymer conditioning of acid-extracted sludge resulted in an estimated overall aluminum recovery of 80 to 86 percent.

1. INTRODUCTION

At potable-water treatment plants, sludge solids are produced through removal of suspended and colloidal solids contained in influent waters and through precipitation of coagulant salts added to aid in removal of influent solids. Aluminum salts are common coagulants used in potable-water treatment. Polymeric aluminum hydroxides are highly gelatinous and add significantly to the volume of sludges produced in coagulation. Solubilization of aluminum-hydroxide precipitates by acidification would provide a means of reducing sludge volume and reclaiming a coagulant for reuse. Many factors determine the success of coagulant recovery at a plant. The primary focus of this research was to examine those process factors affecting the design of a coagulant recovery facility, with emphasis placed on (i) the chemical quality of the recovered coagulant and its impact on finished water quality and (ii) the handling and dewatering properties of acidified sludges in conventional filter-press systems.

2. MATERIALS AND METHODS

The research on aluminum recovery from alum sludges was conducted on sludge samples indicative of those projected for production at the North Area plant treating water withdrawn from the Chattahoochee River. Sludge samples were collected from four water treatment plants in the metropolitan Atlanta area currently treating water from the river. The procedures employed in the research are presented below.

SLUDGE SAMPLES

Sludge samples were collected manually from the underflow of post-coagulation clarifiers at the Chattahoochee River and Hemphill plants of the City of Atlanta, from the thickener underflow at the Quarles plant of the Cobb-County Marietta Water Authority and from the sludge blanket in the post-coagulation clarifier at the Candler plant of DeKalb County. All samples were taken as grab samples over a 0.5- to 2-h period at each plant and transported directly to the laboratory for analysis. Concerted efforts were made to collect sludge samples which had not been altered or conditioned in any way in a subsequent sludge treatment system. For example, lime conditioning prior to filter-press dewatering is practiced at three of the plants. Sample location points and collection procedures were established at these plants to assure that lime conditioning was avoided completely.

SLUDGE EXTRACTION

The extraction of aluminum under acidic conditions was done on a batch basis, typically using 0.2- to 2-L volumes in glass beakers stirred

intensively with Teflon bars or paddles. While glassware and materials placed in contact with sludge samples were rigorously cleaned prior to use, acid-washed glassware was not employed throughout to minimize trace-level contamination by metals and organic compounds. However, an intensive examination of trace metals and priority-pollutant organic compounds was conducted for sludge samples and acid extracts. In these acidic extractions, all glassware was baked for 12 h at 250-280°C prior to use. In addition, a blank extraction was conducted with distilled water for each extraction vessel to quantify any contamination attributable to glassware and chemical additives.

ANALYTICAL METHODS

Measurements of sludge samples were conducted using standard methods to establish their chemical and physical properties. Total, suspended and dissolved solids were performed in accord with Methods 209A and 209C of Standard Methods (APHA, 1985). Measurements of pH were performed using a combination electrode in accord with Method 423 of Standard Methods (APHA, 1985). Capillary Suction Time (CST) was measured on sludge samples using a Type 92/1 CST apparatus manufactured by Triton Electronics Limited (Essex, England). An 18-mm reservoir and Whatman No. 17 chromatography paper was used with the unit.

TOC measurements were made on filtered, acidic extracts with a Beckman Model 915 TOC instrument. Measurements of total carbon (TC) and total inorganic carbon (TIC) were used to establish TOC values. Humic substances in acidic extracts were measured by passing extracts through a 60-mL bed volume of XAD-8 resin. The resin was preconditioned with 3 bed volumes of 0.1 N NaOH, a sufficient volume of organic-free water to wash out residual

alkali and, finally, 3 bed volumes of 0.1 N HCl. A 40-mL sample volume was passed through the bed, followed by a 60-mL volume of 0.1 N HCl. Alkali at 0.1 N NaOH was then used to elute the humic substance fractions from the column, using TOC, ultraviolet absorbance at 254 nm and visible absorbance at 420 nm to monitor humic substances. Humic substances were expressed in terms of the concentration of TOC sorbed to and then eluted from the resin under alkaline conditions.

Analysis of metals in sludge samples and acidic extracts was conducted using a nitric acid digestion, according to Method 302D [Standard Methods, APHA (1985)]. Trace metal analyses were conducted using a Perkin Elmer Model 703 atomic absorption spectrophotometer with Methods 303A, C, E and F [Standard Methods, APHA (1985)] using standard addition procedures.

Sludge samples from the four water treatment plants were analyzed for trace organic priority pollutants. Of the total organic priority pollutants, 33 are classified as purgeables, as indicated in Table 2.1. The purgeable organic priority pollutants were stripped from water samples by means of the purge-and-trap method developed by Bellar and Lichtenberg (1973). A Hewlett-Packard purge and trap unit (Model 7675A), mounted on a Hewlett-Packard 5830A gas chromatograph, was connected to a glass capillary column and interfaced to a Finnigan 4023 mass spectrometry (MS), as described in detail elsewhere (DeWalle et al., 1981). Ultra-high-purity helium was employed as the purging gas. The trap consisted of a Tenax-GC (60-80 mesh) column. The operating conditions of the purge-and-trap-method were as follows: pre-purge time = 5 min; purging of water sample = 15 min; purging flow-rate = 20 mL/min; trap head desorption time = 10 min; and, heat desorption temperature = 200°C.

TABLE 2.1. EPA LIST OF 129 PRIORITY POLLUTANTS ANALYZED IN SLUDGE SAMPLES FROM WATER TREATMENT PLANTS

<u>Purgeables</u>	
Acrolein	1,2-Dichloropropane
Acrylonitrile	1,3-Dichloropropene
Benzene	Methylene chloride
Toluene	Methyl chloride
Ethylbenzene	Methyl bromide
Carbon tetrachloride	Bromoform
Chlorobenzene	Dichlorobromomethane
1,2-Dichloroethane	Trichlorofluoromethane
1,1,1-Trichloroethane	Dichlorodifluoromethane
1,1-Dichloroethane	Chlorodibromomethane
1,1-Dichloroethylene	Tetrachloroethylene
1,1,2-Trichloroethane	Trichloroethylene
1,1,2,2-Tetrachloroethane	Vinyl chloride
Chloroethane	1,2-trans-dichloroethylene
2-Chloroethyl vinyl ether	bis(Chloromethyl)ether
Chloroform	
<u>Base/Neutral Extractables</u>	
1,2-Dichlorobenzene	Butyl benzyl phthalate
1,3-Dichlorobenzene	Fluorene
1,4-Dichlorobenzene	Fluoranthene
Hexachloroethane	Chrysene
Hexachlorobutadiene	Pyrene
Hexachlorobenzene	Phenanthrene
1,2,4-Trichlorobenzene	Anthracene
bis(2-Chloroethoxy)methane	Benzo(a)anthracene
Naphthalene	Benzo(b)fluoranthene
2-Chloronaphthalene	Benzo(k)fluoranthene
Isophorone	Benzo(a)pyrene
Nitrobenzene	Indeno(1,2,3-c,d)pyrene
2,4-Dinitrotoluene	Dibenzo(a,h)anthracene
2,6-Dinitrotoluene	Benzo(g,h,i)perylene
4-Bromophenyl phenyl ether	4-Chlorophenyl phenyl ether
bis(2-Ethylhexyl)phthalate	bis(2-Chloroethyl) ether
Di-n-octyl phthalate	1,2-Diphenylhydrazine
Dimethyl phthalate	Hexachlorocyclopentadiene
Diethyl phthalate	N-Nitrosodiphenylamine
Di-n-butyl phthalate	N-Nitrosodimethylamine
Acenaphthylene	N-Nitrosodi-n-propylamine
Acenaphthene	bis(2-Chloroisopropyl) ether

TABLE 2.1 (Continued)

Acid Extractables

Phenol	p-Chloro-m-cresol
2-Nitrophenol	2-Chlorophenol
4-Nitrophenol	2,4-Dichlorophenol
2,4-Dinitrophenol	2,4,6-Trichlorophenol
4,6-Dinitro-o-cresol	2,4-Dimethylphenol
Pentachlorophenol	

Pesticides/PCBs Extractable

α -Endosulfan	Heptachlor
β -Endosulfan	Heptachlor expoxide
Endosulfan sulfate	Chlordane
α -BHC	Toxaphene
β -BHC	Aroclor 1016
δ -BHC	Aroclor 1221
γ -BHC	Aroclor 1232
Aldrin	Aroclor 1242
Dieldrin	Aroclor 1248
4,4'-DDE	Aroclor 1254
4,4'-DDD	Aroclor 1260
4,4'-DDT	2,3,7,8-Tetrachlorodibenzo-
Endrin	p-dioxin (TCDD)
Endrin aldehyde	

Neutral extractable, phenols, pesticides and PCB priority pollutants were extracted by means of a vapor-phase steam distillation extractor (DeWalle et al., 1981). GC analysis was performed on a Hewlett-Packard Model 5830A instrument interfaced to a Finnigan 4023 MS and equipped with capillary injector port. Zero-grade helium was used as carrier gas. The typical GC conditions were as follows: injector temperature = 250°C; injection mode = splitless (1-2 μ L); and, oven temperature program = 40°C (3 min) to 300°C at 10°C/min.

High-resolution capillary columns were prepared from soft glass tubing (121 cm x 6 mm O.D. x 4 mm I.D.) which was washed with detergent and rinsed with tap water, distilled water and acetone. A Shimadzu GDM-1 glass drawing machine was used to draw glass capillaries with 0.25 to 0.4 mm I.D. Approximately 30-40 m of each capillary tube was leached, dehydrated and deactivated by the persilylation method following the procedure outlined by Grob (1980). Hexamethyldisilazane (HMDS) and diphenyltetramethyldisilazane (DPTMDS) were purchased from Tridom-Fluka (Hauppauge, NY). The capillary columns were coated using the static method (Giabbai, 1978) by preparing a known amount of stationary phase to achieve a 0.15- to 0.25- μ m film thickness. SE-30, SE-52 and SE-54 (Applied Science Labs, State College, PA) were investigated as stationary phases. Each wall-coated column was conditioned under a low flow of carrier gas from 40°C to 300°C at a program rate of 1°C/min. Stock solutions of organic priority pollutants were purchased from Supelco (Bellefonte, PA).

MS identification and quantitation were performed on a Finnigan model 4023 mass spectrometer equipped with Incos Data System. The glass capillary column was directly coupled to the ionization source by means of fused-silica tube (40 cm x 0.1 mm I.D.). Ultra-high-purity helium was employed as

carrier gas. The mass spectrometer was operated under the following conditions: electron impact ionization mode; electron energy = 70 eV; electron multiplier = 1500 V; preamp sensitivity = 10^{-7} A/V; emission current = 0.4 mA; mass range = 41-500 a.m.u.; and scan rate = purgeables: 2 scans/sec; extractables: 1 scan/sec. Perfluorotributylamine (FC43) was used to initially tune the mass spectrometer; decafluorotriphenylphosphine (DFTPP) was subsequently used to check the acceptability of the tuned spectrometer.

Selected organic compound surrogates (i.e., organic compounds with physico-chemical properties similar to the organic priority pollutants under study) were used to monitor the performance of the analytical scheme for each sludge sample. The recovery range measured in this overall study are reported in Table 2.2.

TABLE 2.2. SURROGATE ORGANIC COMPOUNDS USED IN ANALYSIS
OF SLUDGE AND EXTRACT SAMPLES

Compound	Recovery Range (%)
<u>Purgeables</u>	
Bromochloromethane	70-110
1-Chloro-2-bromopropane	68-109
1,4-Dichlorobutane	81-114
<u>Acid/Neutral Extractables</u>	
Phenol-d ₅	33-83
Anthracene-d ₁₀	63-91
Perylene-d ₁₂	21-63

3. RESULTS AND DISCUSSION

ALUM SLUDGE SUSPENSIONS

Sludge suspensions were collected from four (4) water treatment plants in the metropolitan-Atlanta area using the Chattahoochee River as a raw-water source. Samples were obtained from the Chattahoochee and Hemphill plants of the City of Atlanta; the Candler plant of DeKalb County; and the Quarles plant of Cobb County-Marietta Water Authority. Characteristics of these suspensions are included in Table 3.1.

A total of six (6) samples were collected on five separate days in July and August from the Chattahoochee plant. The samples were collected from the underflow of the clarifier (immediately following the flocculation chamber) prior to discharge into the filter-press wet well to avoid contact with lime-treated filtrate frequently recycled into the wet well. These suspensions had suspended solids concentrations which ranged from 77.6 g/L to 235.9 g/L. These exceptionally high values were attributed, in part, to high sediment loadings and extended (although unquantified) retention times for the solids in the clarification basins. The pH of the suspensions ranged from 5.79 to 7.29 and CST (10 mm) values ranged from 139 sec to 678 sec.

Suspensions from the Hemphill plant were manually collected from the wet well at the underflow of the clarifiers, prior to pumping of the suspension to the thickener at the solids-handling facility. The suspended solids concentrations of the three samples ranged from 8.67 g/L to 120.3 g/L. Because of treatment of raw water in a presedimentation basin and the resulting reduction in the sediment load, it was not unexpected that the suspended solids concentrations of Hemphill sludges were, in general, lower

TABLE 3.1. CHARACTERISTICS OF ALUM SLUDGE SAMPLES COLLECTED
FOR ALUMINUM RECOVERY STUDIES

Sample	Suspended Solids (g/L)	pH	CST (10mm) (sec)	Filtrate Alkalinity (mg/L as CaCO ₃)
<u>CHATTAHOOCHEE</u>				
C-07-19-S	179.4	6.45	603	95.6
C-07-22-S	104.19	6.42	405	95.6
C-08-01a-S	142.9	5.79	289	-
C-08-01b-S	77.6	5.88	139	-
C-08-21-S	171.7	6.1	678	-
C-08-29-S	235.9	7.29	237	-
C-09-27-S	50.7	-	16.8*	-
<u>HEMPHILL</u>				
H-07-22-S	8.67	6.38	22	-
H-08-29-S	120.3	7.72	59.3	-
H-09-10d-S	23.5	7.2	23	-
<u>CANDLER (DEKALB)</u>				
D-08-01-S	10.85	5.95	61	-
<u>QUARLES (COBB)</u>				
Q-08-01-S	97.4	5.96	830	-
Q-09-18-S	103.7	6.8	311*	-
QW-09-16-S	-	-	-	-

*CST (18mm)

than those for the Chattahoochee plant. The pH of the Hemphill sludges ranged from 6.38 to 7.72, while CST (10 mm) ranged from 22 to 59 sec.

One suspension was collected from the Candler plant in DeKalb County. This sample was collected manually with a Van Dorn sampler lowered into sludge blankets contained in clarifiers. All samples were collected at or near the bottom of shallow sludge blankets. The suspended solids concentration of 10.85 g/L was reflective in part of the low sediment load on the basin, resulting from the use of a presedimentation basin, and of the sampling procedure employed. The pH of 5.95 was the lowest of any sample collected.

Three samples were collected from the Quarles plant of the Cobb County-Marietta Water Authority, but only two were examined in detail. The samples were collected from the underflow of a gravity thickener receiving sludge from clarifiers following the flocculation basins. The suspended solids concentrations were 97.4 g/L and 103.7 g/L for these samples and the pH values were slightly acidic.

The suspended solids concentrations of the underflows from clarifiers immediately following flocculation basins were exceptionally high for the Chattahoochee and Hemphill plants, ranging from 26 g/L to 235.9 g/L and averaging 111.5 g/L. These values were commonly much higher than the concentration range of 10-20 g/L frequently assigned to alum sludges for surface water plants. The samples collected from the Quarles plant were taken during a period when the thickener was not functional and the suspended solids values were assumed to be indicative of those from the clarifiers. The very dilute sample obtained from the Candler plant was attributed to the manner in which the sample was manually collected.

ACIDIC EXTRACTION OF SLUDGES

A total of six (6) sludge suspensions were examined intensively in this phase of the study. The suspensions were examined initially by making a series of acid additions to separate aliquots and monitoring selected parameters related to product quality and dewatering properties. Another series of samples was examined using intensive QA/QC procedures to monitor the quality of recovered coagulant solutions. The suspensions examined in the initial phase of acid addition are presented in Table 3.2. The three (3) suspensions from Chattahoochee (C) and the suspension from Quarles (Q) had high suspended solids concentrations (i.e., 97.4 g/L to 179.4 g/L), while those from the Hemphill (H) and Candler (D) plants were more dilute, allowing for some relative comparison of sludge concentration effects. The pH values of all suspensions were mildly acidic, ranging from 5.79 to 6.45.

Extraction Time

Addition of acid to an alum sludge in sufficient quantities to produce a highly acidic suspension (e.g, $\text{pH} \leq 3$) results in a sequence of dynamic reactions analogous to the reverse of those resulting in the formation of aluminum-hydroxide flocs. Stumm and O'Melia (1965) indicated that aluminum hydroxide has a minimum solubility at $\text{pH} \approx 5-6$. At pH values below this and immediately following the addition of acid, aluminum hydroxide reacts with the acid forming soluble aluminum polymerization and hydrolysis products [e.g., $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ and $\text{Al}(\text{OH})_2^+$]. These reactions are not instantaneous and a situation is created in which pH is dramatically depressed upon the addition of acid, followed by an increase in pH, due to the neutralization of H^+ ions by aluminum hydroxide and other species, until an equilibrium pH is achieved.

TABLE 3.2. CHARACTERISTICS OF ALUM SLUDGE SAMPLES FROM CHATTAHOOCHEE (C),
QUARLES (Q), HEMPHILL (H) AND CANDLER (D) PLANTS USED IN ACID
ADDITION STUDIES

Sample	Suspended Solids g/L	pH
C-07-19-S	179.4	6.45
C-07-22-S	104.19	6.42
C-08-01a-S	142.9	5.79
Q-08-01-S	97.4	5.96
H-07-22-S	8.67	6.38
D-08-01-S	10.85	5.95

To examine the extent of these variations, three sludge samples were extracted with acid at doses sufficient to depress initial pH to near 2.0. The initial acid addition and rapid mixing of the acid with the sludge suspensions was conducted over a 20-minute period at which time the initial pH was taken. Undoubtedly, the pH of a suspension was depressed below this value immediately after acid addition. However, providing adequate mixing and reaching a quasi-stable pH value which could be read reliably necessitated using a value taken at 20 minutes as the "initial" pH reading. This protocol was followed throughout the experimental study presented herein.

The data for evaluation of the effect of time on extraction kinetics are presented in Table 3.3. Acid doses of 199 meq/L (80 lb/10³ gal), 69 meq/L (28 lb/10³ gal) and 219 meq/L (90 lb/10³ gal) were added to sludges from the Chattahoochee, Candler and Quarles plants, respectively, resulting in normalized acid doses of 1.4 meq/g, 72 meq/g and 2.4 meq/g, on a unit suspended solids basis. The pH of the suspensions increased in a near-linear fashion, increasing by 0.5 to 0.6 pH units over the initial 11-h period, as shown in Figure 3.1. Over the next 17-h period, pH increased only slightly, i.e., 0.06 to 0.13 pH units, indicating the suspensions were near equilibrium conditions within an 11-h period. Concurrent with the elevation of pH, the concentration of solubilized aluminum was monitored, as presented in Figure 3.2. Aluminum concentration for the Candler sludge sample (D-08-01-S) remained relatively constant throughout the extraction period with an average concentration of 601 mg/L. The aluminum concentration for the Quarles sample (Q-08-01-S) decreased slightly for the initial 11-h period and increased approximately 25 percent at the 28-h measurement. The aluminum concentration for the Chattahoochee sludge sample increased slightly after 11 h and remained that value for the following 17-h period. With the exception of the

TABLE 3.3. EFFECT OF TIME ON CHARACTERISTICS OF ALUMINUM EXTRACT
FOR CHATTAHOOCHEE (C), CANDLER (D) AND QUARLES (Q)
SLUDGE SAMPLES

Sample	Time Hours	pH	Aluminum mg/L	TOC mg/L	Suspended Solids g/L
C-08-01a-S*	0.33	1.96	1500	1092	144.7
	7	2.51	-	835	144.8
	11	2.61	1680	900	142.9
	28	2.74	1660	702	138.9
D-08-01-S*	0.33	2.27	592	367	9.7
	7	2.71	647	407	9.6
	11	2.78	519	366	9.5
	28	2.84	647	342	9.5
Q-08-01-S*	0.33	2.25	1556	1739	90.9
	7	2.48	1500	1342	91.5
	11	2.75	1462	1251	91.1
	28	2.85	1906	1434	92.4

*Acid addition: C-08-01a-S = 199 meq/L; D-08-01-S = 69 meq/L;
Q-08-01-S = 219 meq/L.

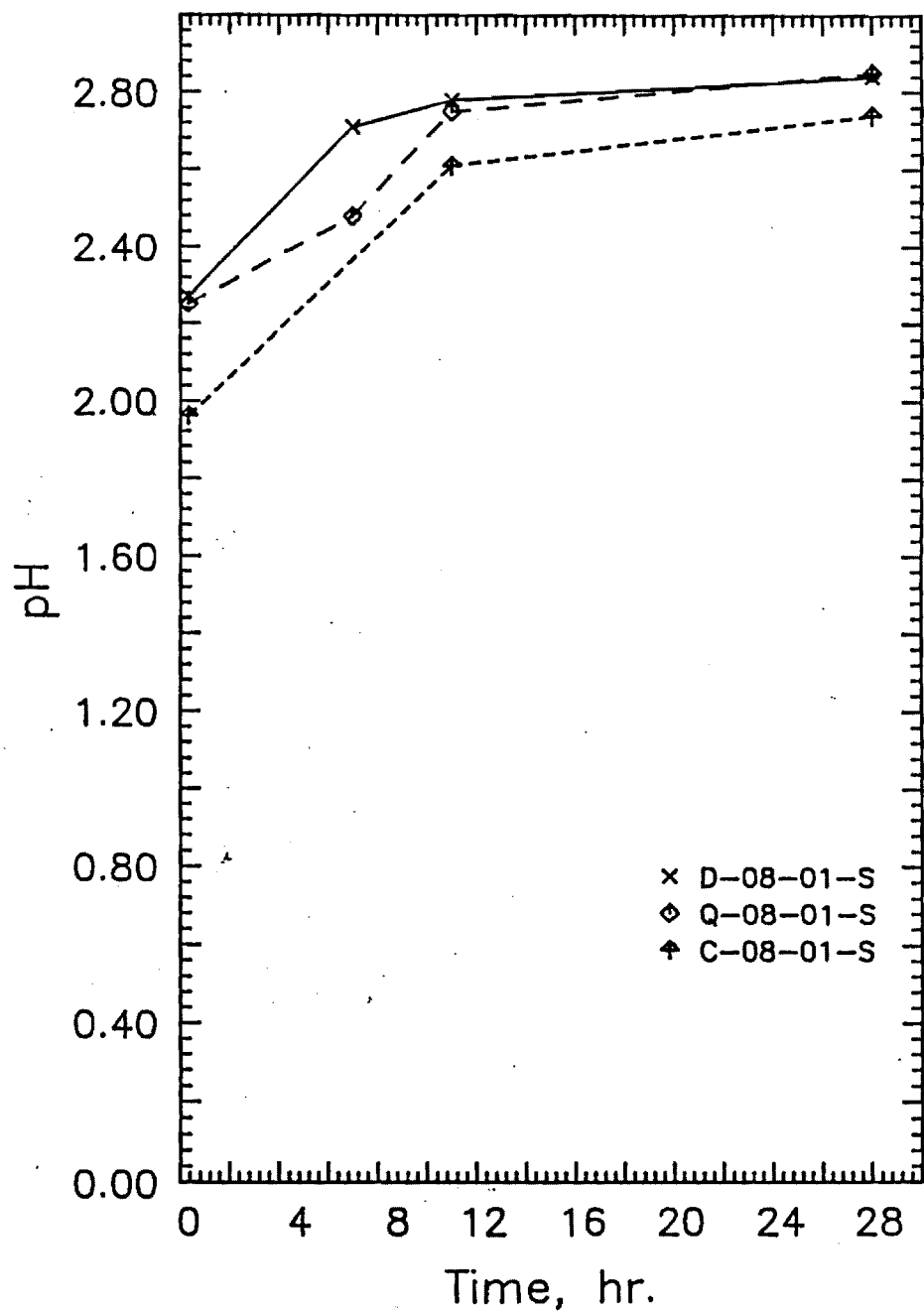


Figure 3.1. Variation in Suspension pH with Time Following Acidification of Three Sludge Samples.

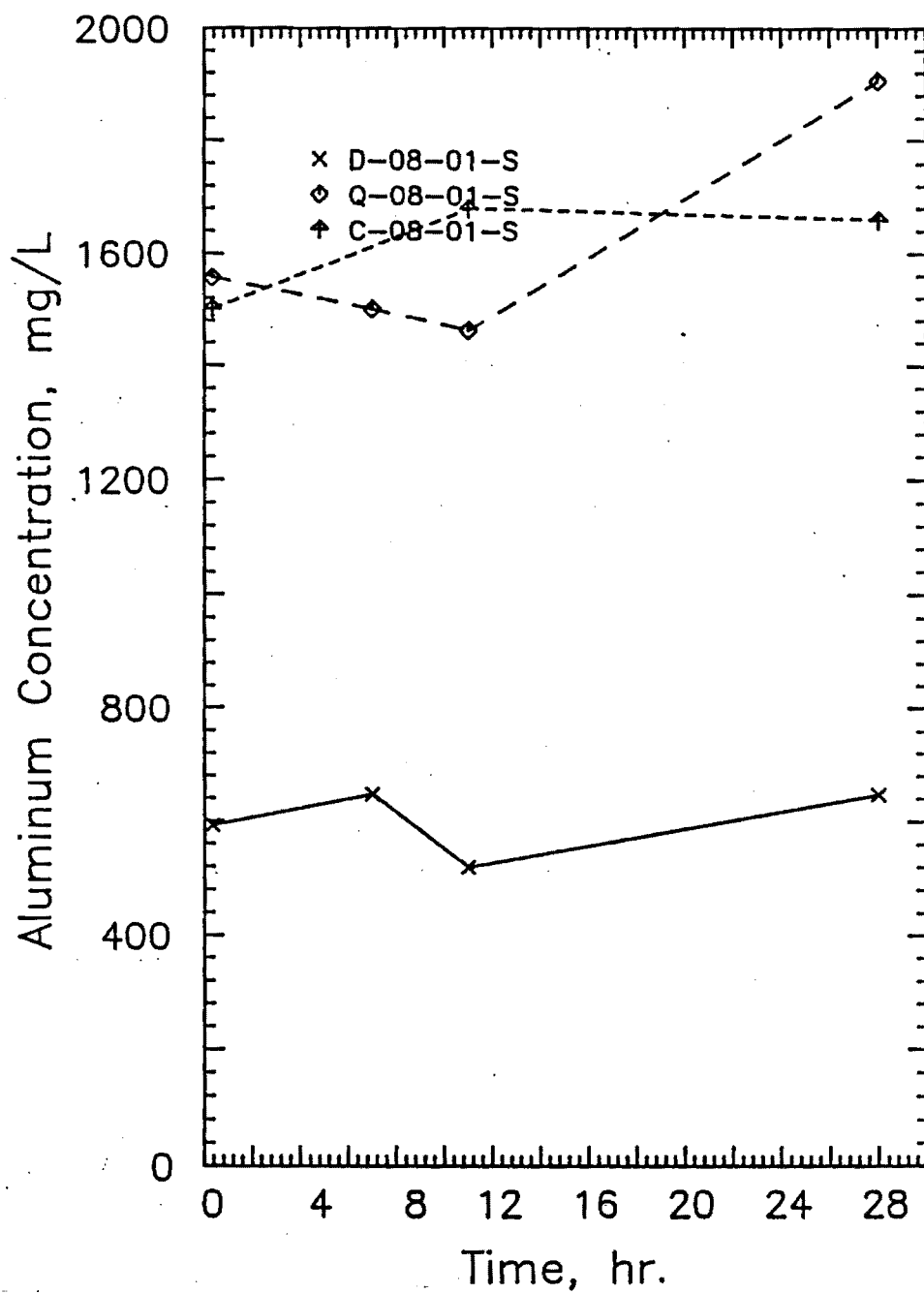


Figure 3.2. Variation of Soluble Aluminum Concentration with Time Following Acidification of Three Sludge Samples.

28-h concentration for Q-08-01-S, the data do not indicate any major change in aluminum concentration after the initial 20-minute extraction period.

Data for TOC concentrations as a function of extraction time are presented in Figure 3.3. The TOC concentration of the Candler sludge did not change with time and was similar to the response for aluminum concentration. The TOC concentration for the Quarles and Chattahoochee sludges decreased with time of extraction. The response for the Quarles sludge was similar to that noted for aluminum, i.e., an initial decrease followed by an increase after 28 h. Therefore, increased time of extraction may result in a decrease in TOC concentration, which could be attributable to acidic hydrolysis and oxidation of soluble organic matter, and the TOC concentration realized within the initial 20-minute period was indicative of the highest concentration achieved over the 28-h extraction period. Based on these studies, subsequent extractions were conducted for a 20- to 30-minute period to reach a pseudo-stable pH value and then examined for numerous parameters, as presented below.

Acid Addition and pH Variations

Initial studies were focused on addition of increasing quantities of acid to aliquots of sludge samples. Sulfuric acid doses ranged from 0 to 227 meq/L (0-94 lb $\text{H}_2\text{SO}_4/10^3$ gal) resulting in depression of suspension pH as indicated in Tables 3.4 and 3.5 and as shown graphically in Figure 3.4. Relatively low levels of acid addition were required to lower pH from near-neutral values to a pH of approximately 4. Below a pH of 4.0, the quantity of acid required to reach a set pH value varied dramatically. For example, at a final pH of 2.0, the Hemphill sludge required approximately 50 meq/L (21 lb $\text{H}_2\text{SO}_4/10^3$ gal), while the Quarles sludge required approximately 210 meq/L (87 lb $\text{H}_2\text{SO}_4/10^3$ gal). This variation was attributable in part to

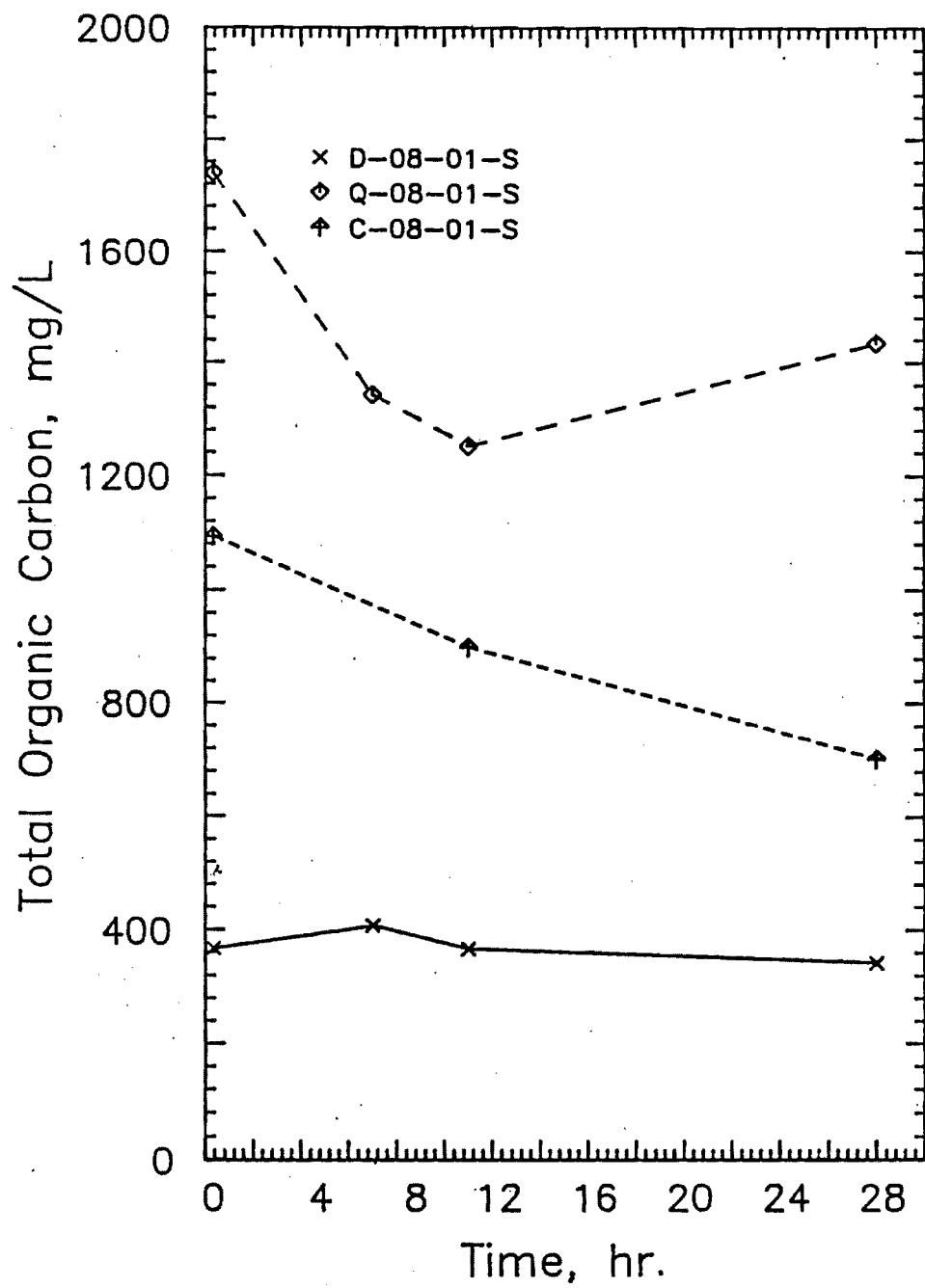


Figure 3.3. Variation of Soluble Organic Carbon Concentration with Time Following Acidification of Three Sludge Samples.

TABLE 3.4. EFFECT OF ACID ADDITION ON CHARACTERISTICS OF ALUMINUM EXTRACT FROM CHATTAHOOCHEE SLUDGE SAMPLES

Sample	Acid Addition meq/L	pH	Aluminum mg/L	TOC mg/L	CST (10 mm) sec
C-07-19-S	0.0	6.5	<5	101	-
	1.71	5.55	<5	79	-
	3.42	4.88	<5	77	-
	6.84	4.36	18	84	-
	13.11	3.66	396	319	-
	25.65	3.23	1432	378	-
	48.45	2.76	2043	332	-
	90.06	1.93	2654	856	-
C-07-22-S	0.0	6.5	14	139	-
	1.14	5.86	<5	110	-
	3.99	5.04	<5	115	-
	8.55	4.23	17	151	-
	17.67	3.58	660	372	-
	59.85	2.84	1452	688	-
	83.79	2.23	1750	856	-
	102.03	1.75	2016	836	-
C-08-01a-S	0.0	5.65	<5	55	360
	2	5.22	<5	60	295
	6	4.5	<5	65	331
	19.27	3.85	71	129	227
	59.34	3.44	773	294	354
	130.01	2.49	1629	372	731
	150.01	2.13	1343	823	-
	213.34	1.48	1722	1306	1089

TABLE 3.5. EFFECT OF ACID ADDITION ON CHARACTERISTICS OF ALUMINUM EXTRACT FOR HEMPHILL (H), QUARLES (Q), AND CANDLER (D) SLUDGE SAMPLES

Sample	Acid Addition meq/L	pH	Aluminum mg/L	TOC mg/L	CST (10 mm) sec
H-07-22-S	0.0	6.38	-	21	-
	0.34	6.03	9	15	-
	0.8	5.51	<5	13	-
	1.94	4.75	<5	13	-
	3.42	4.03	26	42	-
	9.69	3.55	726	187	-
	30.78	3.02	1232	315	-
	43.89	2.32	1205	378	-
	52.44	1.79	1538	380	-
Q-08-01-S	0.0	5.96	<5	208	-
	4.53	5.4	<5	181	1238
	11.53	4.61	3	177	895
	23.33	4.02	35	237	981
	103.34	3.36	960	555	1828
	126.67	2.94	1691	994	>1000
	193.34	2.16	3054	1241	>1000
	227.34	1.67	3436	1514	>1000
D-08-01-S	0.0	5.92	<5	24	66
	0.933	5.18	6	23	70
	11.5	3.91	60	112	92
	35.2	3.6	463	306	246
	46.33	2.89	510	354	304
	60.67	2.22	541	403	346
	110.34	1.81	566	368	475

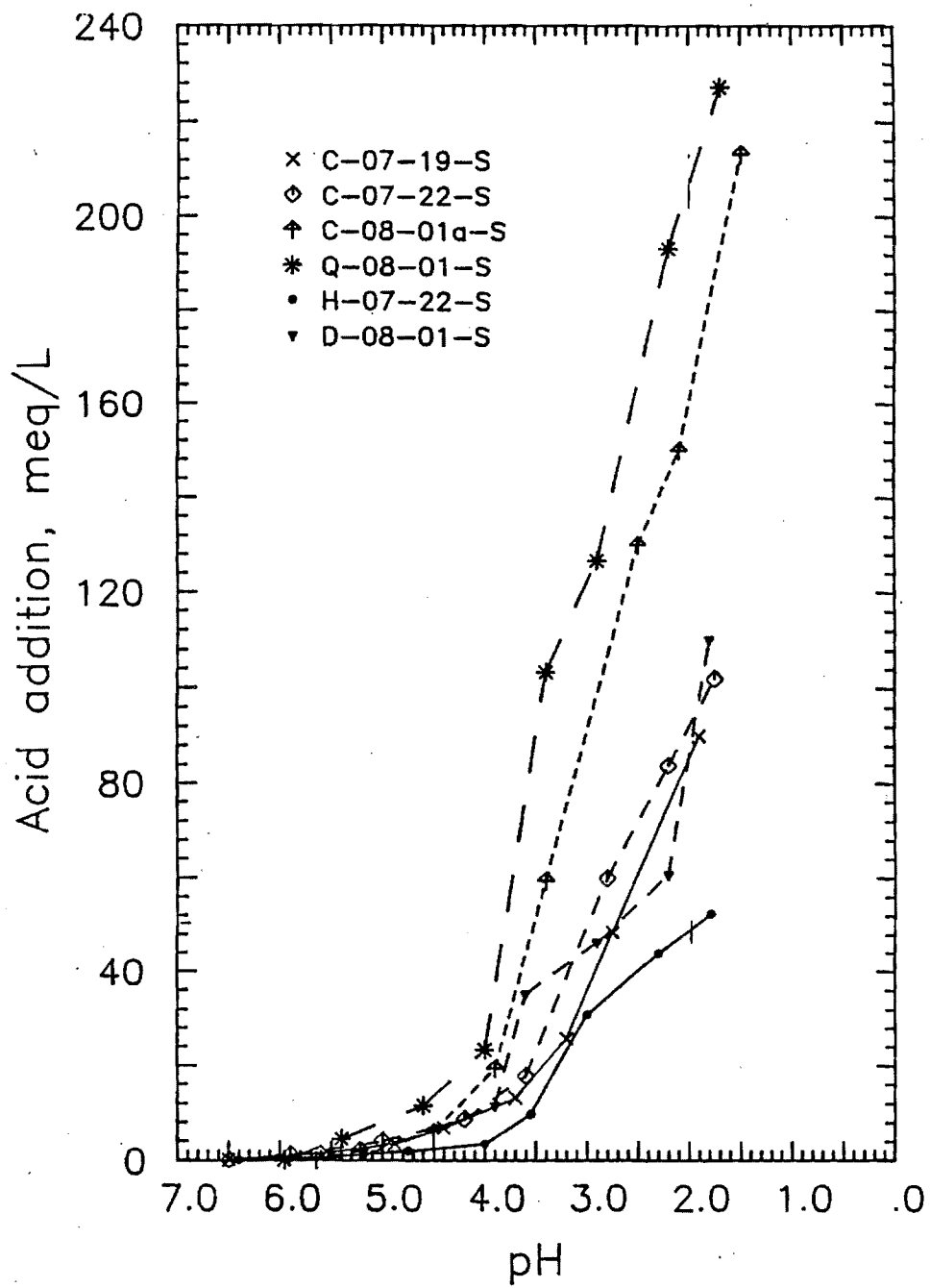


Figure 3.4. Acid Application Required to Reach Indicated pH Values for Six Sludge Samples.

the variation in the concentration of suspended solids in each of the suspensions. To account for this variation, acid addition data were normalized to suspended solids concentrations and are presented in Figure 3.5. With the exception of the Candler sludge (D-08-01-S), this resulted in a reduction in the scatter of the data with, for example, acid doses ranging from approximately 0.5 to 2.0 meq/g (24.5 to 98 lb $\text{H}_2\text{SO}_4/10^3$ lb SS) at a final pH of 2.0. The Candler sludge (D-08-01-S), however, required approximately 8 meq/g (392 lb $\text{H}_2\text{SO}_4/10^3$ lb SS) to reach a pH of 2.0. The quantity of acid required is dictated by reactions with the alkalinity and suspended matter of the water. At a soluble alkalinity of 100 mg/L as CaCO_3 , which is a reasonable approximation of the maximum value for raw water from the Chattahoochee River, the calculated acid requirement to reach a pH of 4 is 2 meq/L (0.8 lb $\text{H}_2\text{SO}_4/10^3$ gal). This acid requirement is negligible in comparison to the quantities required to reach a pH value of 2.0 and indicates, as expected, that the primary reactive species was suspended matter. The elevated acid requirement for the Candler sludge could be attributed to differences in sludge composition and aluminum content. For example, coagulant aluminum would appear as $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ in the initial sludge suspension and would require acid at a rate of 22.7 meq/g $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$. If lime (CaO) is used to increase alkalinity and if, as is typical, a portion is not solubilized upon addition in the coagulation process, it may appear in the sludge and would require acid at a rate of 35.7 meq/g CaO . Therefore, it is assumed that differences in the chemical composition of the Candler sludge produced the elevated acid requirement, although no confirmation of this was possible. The effects of acid addition on the pH of all but the Candler sludge are presented in an expanded plot in Figure 3.6. The acid requirements for the Hemphill and Quarles sludges were

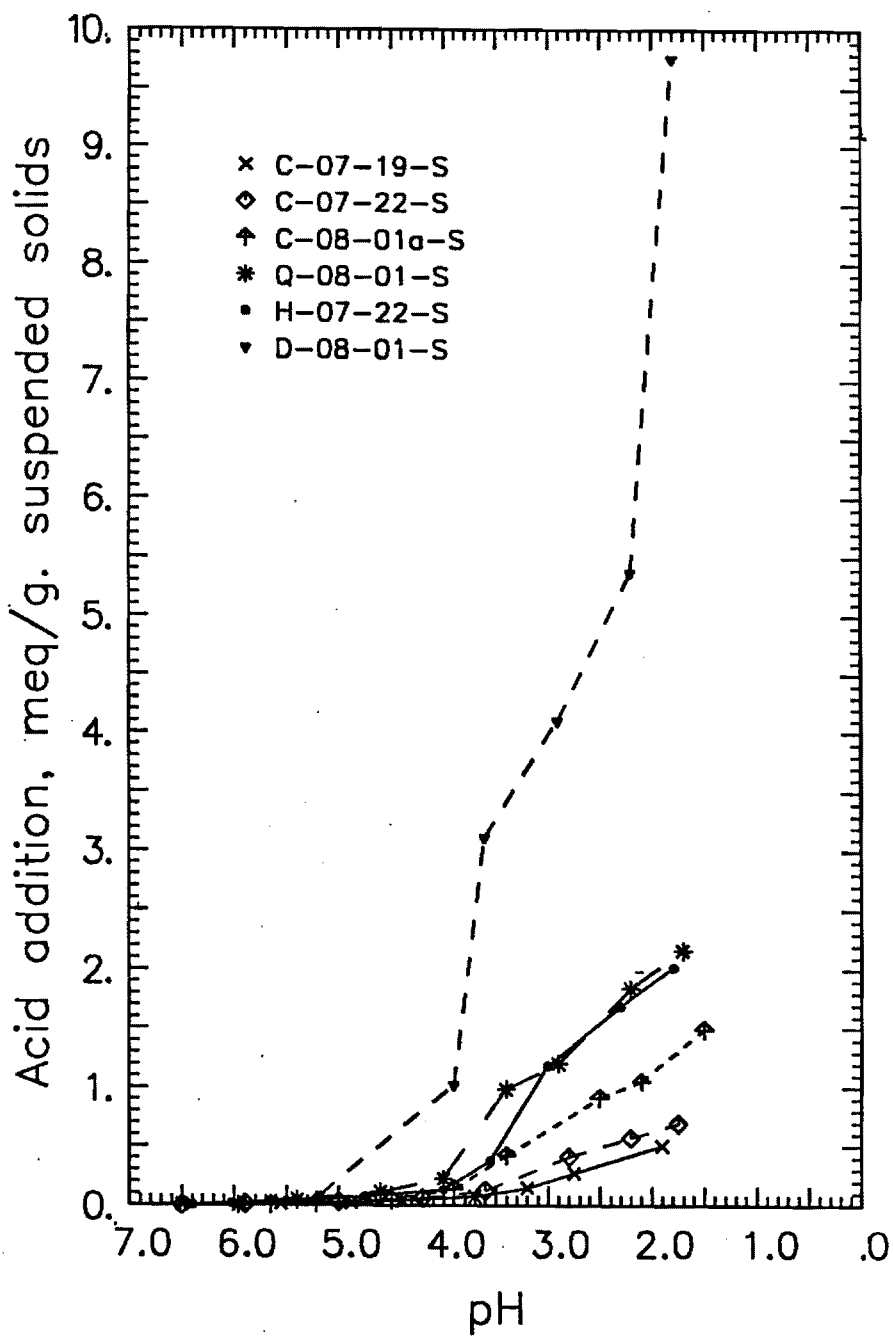


Figure 3.5. Normalized Acid Addition (meq/g) versus Suspension pH for Six Sludge Samples.

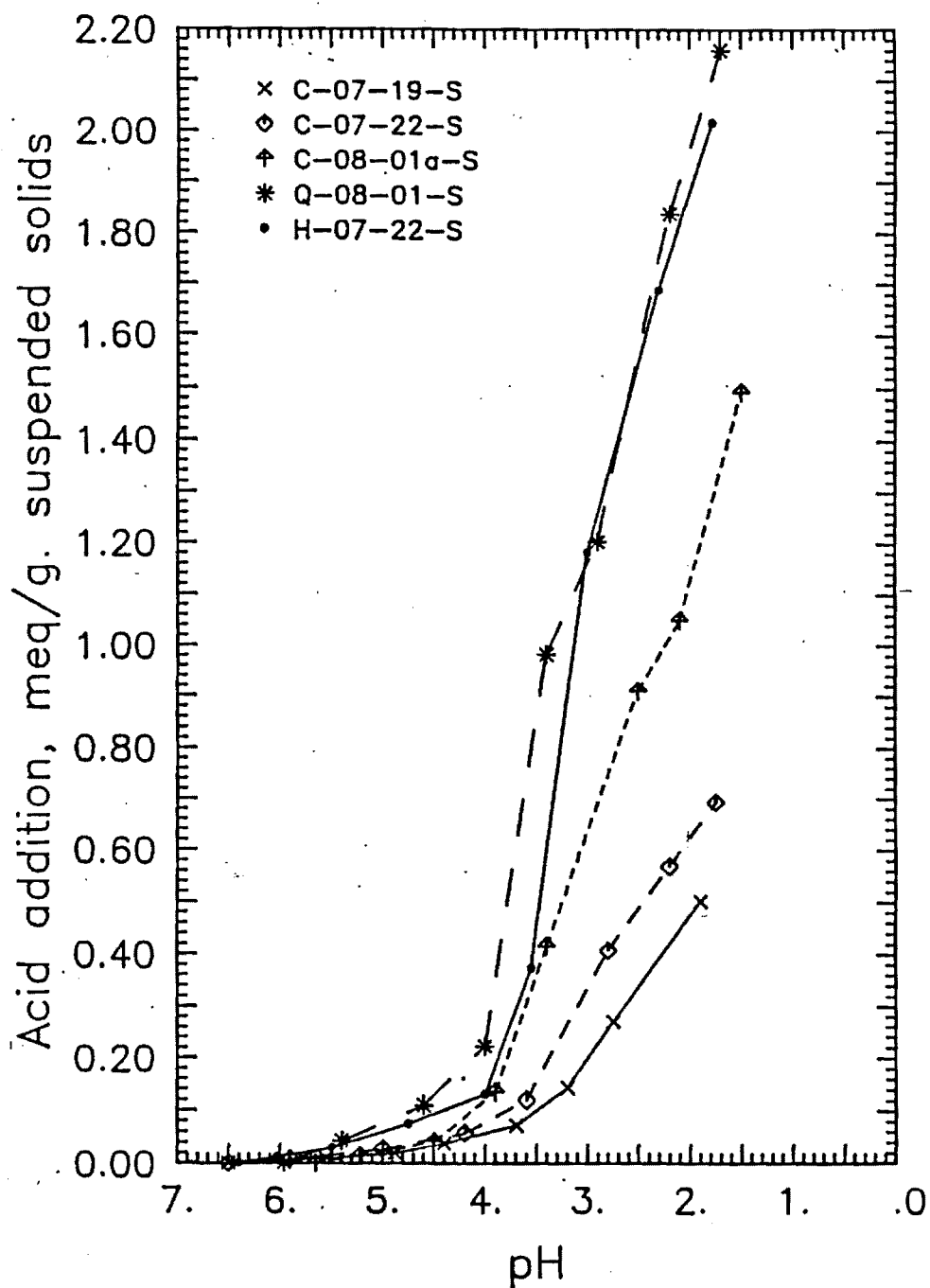


Figure 3.6. Expanded Plot of Normalized Acid Addition (meq/g) Versus Suspension pH for Five Sludge Samples.

virtually identical. In addition, those for the three Chattahoochee sludges, taken over a 14-day period, were less than those for the Hemphill and Quarles sludges and varied considerably. For example, at a pH of 2.0, acid addition rates for the Chattahoochee sludges were 0.47 meq/g, 0.62 meq/g and 1.11 meq/g (i.e., 23, 30 and 54 lb $H_2SO_4/10^3$ lb SS) indicating considerable variation in acid requirements or the extent of extraction.

Aluminum Extracted

Aluminum solubility increases as pH is depressed, thereby converting insoluble aluminum hydroxide into soluble aluminum hydrolysis and polymerization products and aluminum ions, all of which were measured and expressed herein as Al^{+3} . Data in Figure 3.7 for each of the extractions indicated that aluminum was virtually insoluble until pH was depressed below a value of approximately 4. At $pH < 4$, soluble aluminum increased in near linear fashion for all sludges until a plateau was reached for some of the sludges. At a $pH = 2$, aluminum concentrations of the extracts ranged from approximately 560 mg/L (D-08-01-S) to 3200 mg/L (Q-08-01a-S). The extract aluminum concentrations for the three Chattahoochee extracts at $pH = 2$ were 2480 mg/L (C-07-19-S); 1880 mg/L (C-07-22-S); and 1680 mg/L (C-08-01a-S).

The aluminum extracted was normalized to total suspended solids in the initial sample and is presented in Figure 3.8 as a function of pH. The three Chattahoochee sludges were virtually identical when examined in this manner, indicating that equivalent amounts of aluminum were extracted at pH values below 4. At a pH value of 2.0, for example, 12 to 14 mg of aluminum were extracted from each gram of suspended solids. These data indicated that the relative levels of extractable aluminum contained in the solids in each of the three Chattahoochee sludges were similar. Expressing the extracted aluminum as the aluminum hydroxide contained in the sludge.

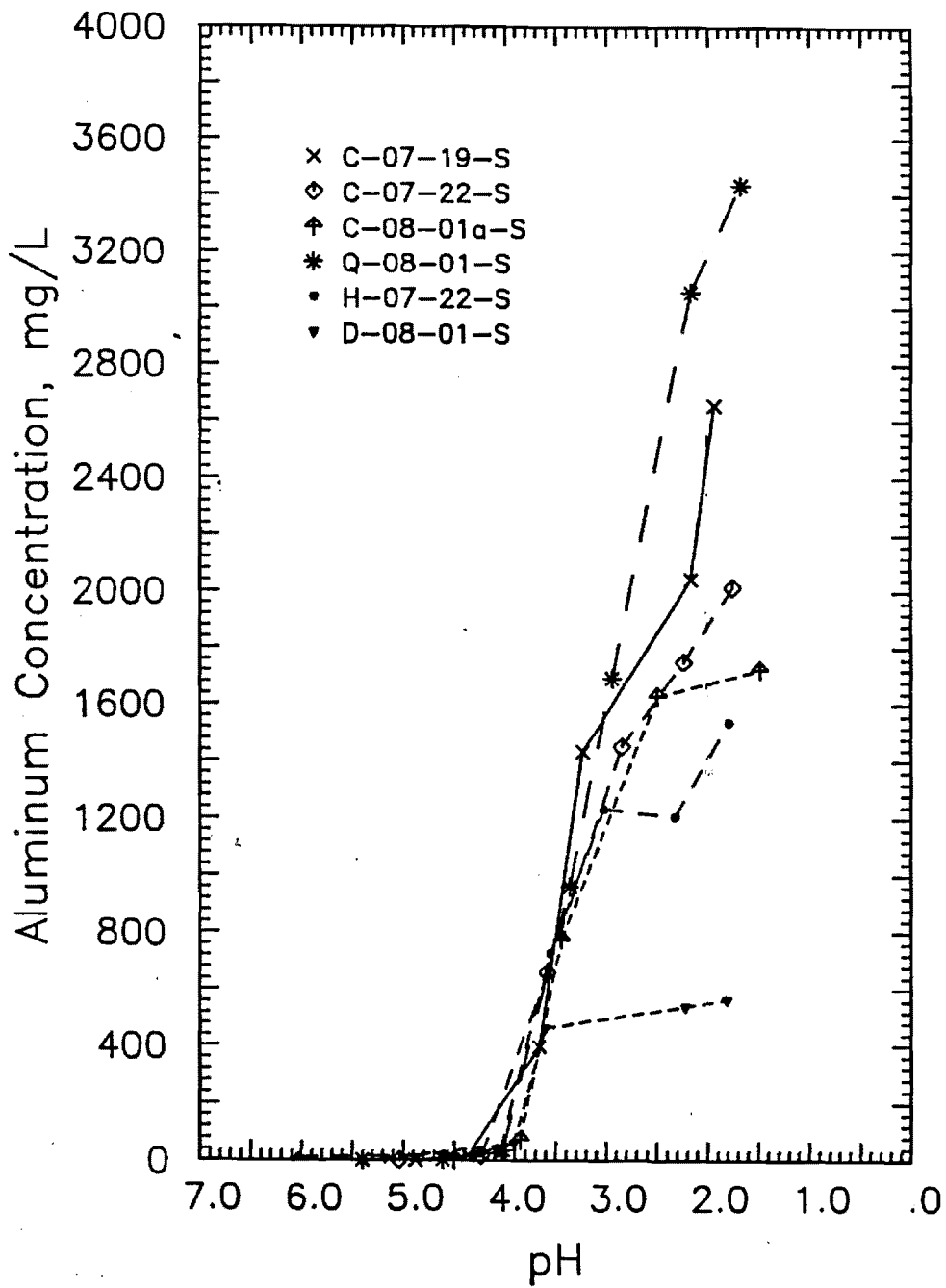


Figure 3.7. Soluble Aluminum Concentration Versus Suspension pH for Six Sludge Samples.

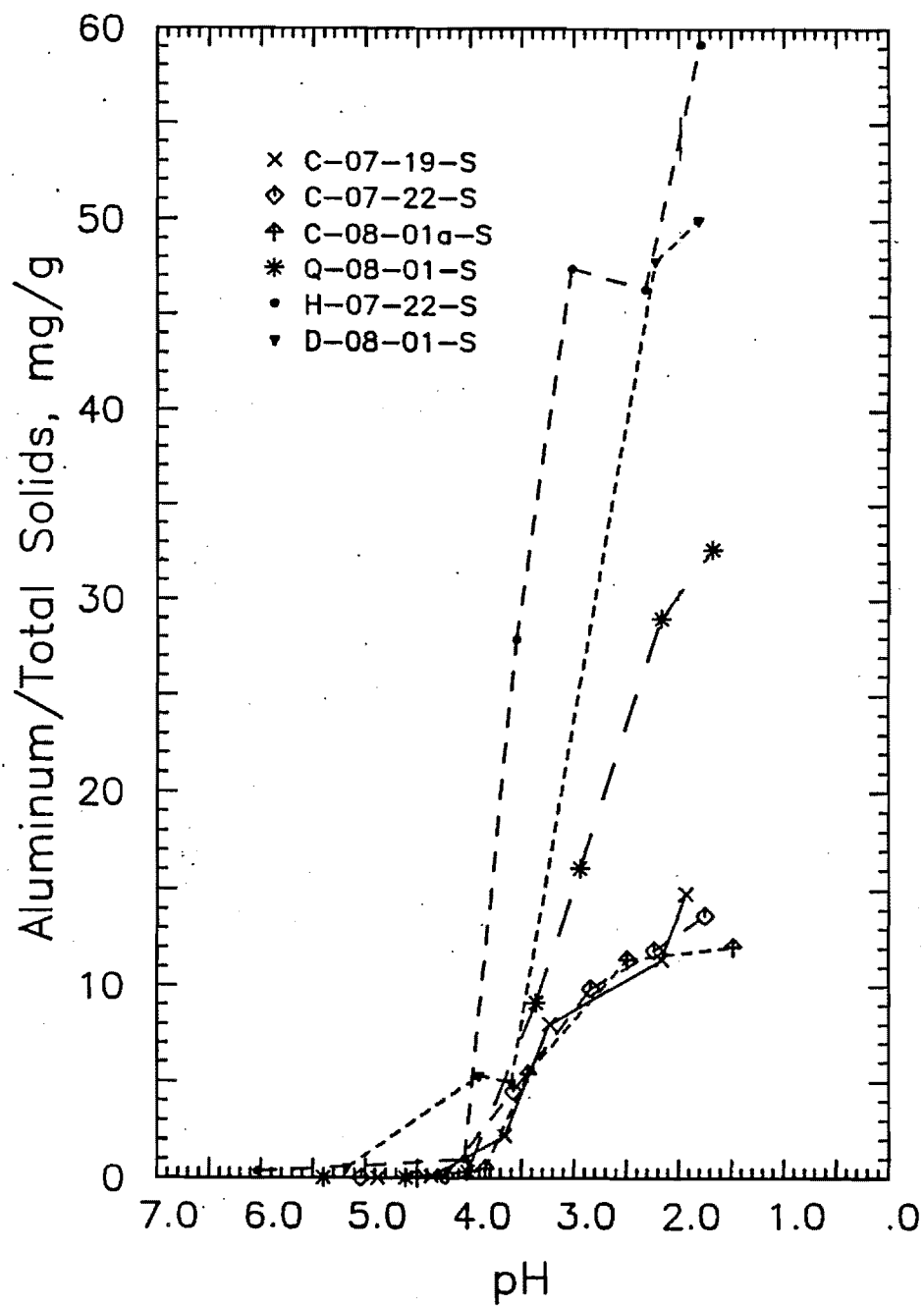


Figure 3.8. Normalized Aluminum Concentration Versus Suspension pH for Six Sludge Samples.

initially [i.e., $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$], this would indicate that only approximately 4.9 to 6.8 percent of the initial mass of the suspension was extracted. The three other suspensions had considerably higher levels of aluminum per unit mass of suspended solids than did the Chattahoochee samples. Using a reference pH of 2.0, the extracted aluminum values were approximately 30 mg/g (Q-08-01-S), 49 mg/g (D-08-01-S) and 54 mg/g (H-07-22-S) indicating that 15, 24 and 26 percent of the initial mass of suspended solids was aluminum hydroxide which was extracted. With the use of presedimentation basins or influent reservoirs to minimize the solids loading on the coagulation system at the Candler, Hemphill and Quarles plants, it is to be expected that the relative aluminum content of the sludges would be high, although data were not available to confirm this. The dramatic difference between the three samples from the Chattahoochee plant and the one from the Hemphill plant would appear to negate differences related to location of raw water intakes on the river, since both use the same pumping station to collect raw water. It is, therefore, apparent that there were significant differences in extractable aluminum content of the sludges examined and that sludges obtained from plants with presedimentation basins or reservoirs contained higher relative levels of aluminum.

Examination of extracted aluminum relative to acid addition indicated considerable variation occurred, as indicated in Figure 3.9. The data, however, indicate apparent plateaus for extracted aluminum for the Candler sludge (D-08-01-S) and one of the Chattahoochee sludges (i.e., C-08-01a-S). For the Candler sludge, acid addition above approximately 35 meq/L (14 lb $\text{H}_2\text{SO}_4/10^3$ gal) resulted in only slight increases in the quantity of aluminum extracted (i.e., 463 mg/L at 35.2 meq/L to 566 mg/L at 110.3 meq/L). The apparent plateau for Chattahoochee sample C-08-01a-S was reached at an acid

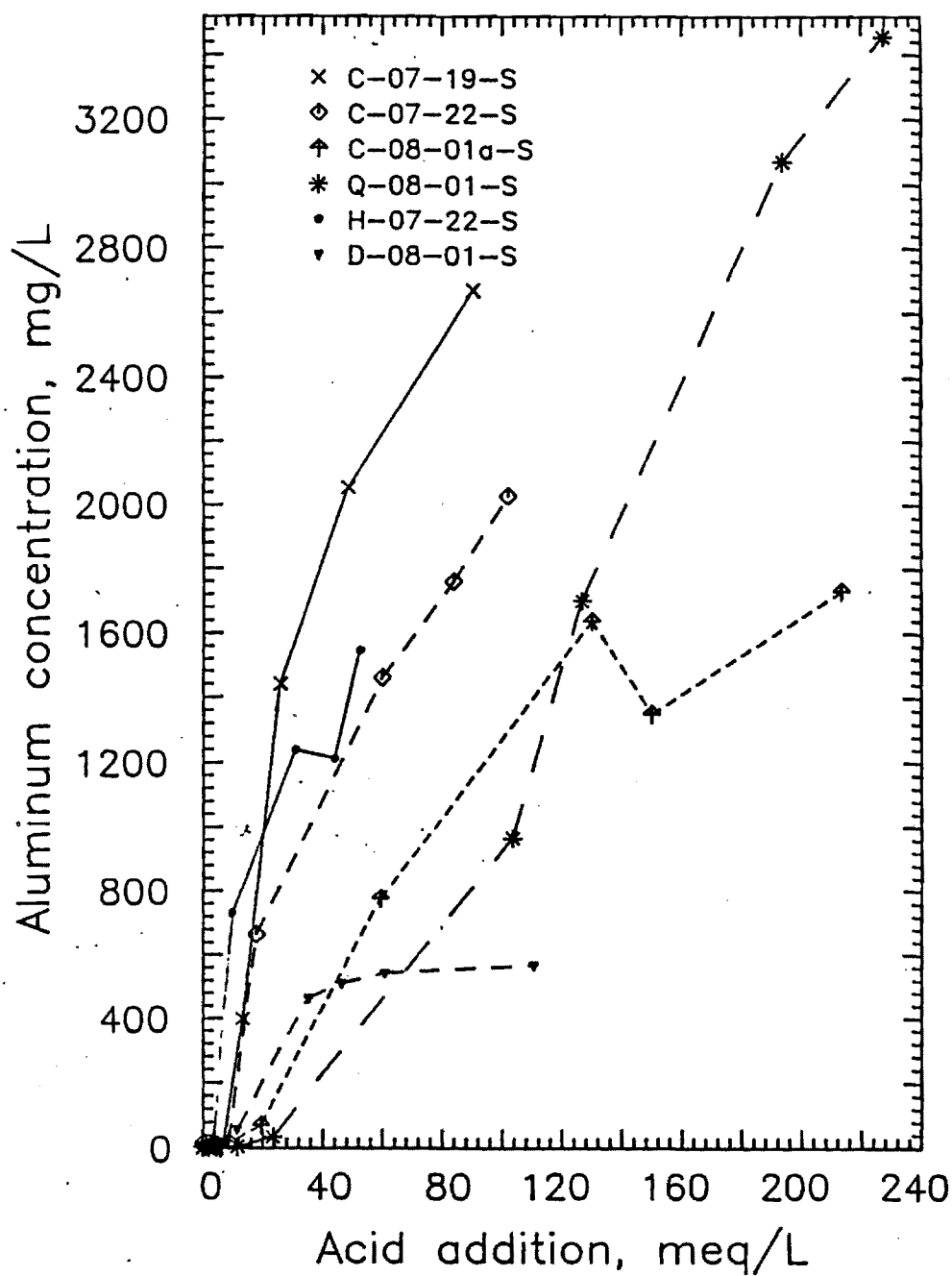


Figure 3.9. Soluble Aluminum Concentration Variation with Increased Level of Acid Addition.

dose of 130 meq/L ($54 \text{ lb H}_2\text{SO}_4/10^3 \text{ gal}$).

The variations in aluminum extracted at equivalent acid doses, based on suspended solids concentrations, are presented in Figures 3.10 and 3.11. As apparent from previous data, the Candler sludge had a high acid demand and a low level of extracted aluminum, creating a wide range of data in Figure 3.10. The data for the Candler plant were deleted and the remaining data are presented in Figure 3.11. This approach was not successful in normalizing the aluminum data because of the apparent variations in aluminum content of the suspended solids in each suspension. Development of a technique to measure or predict the easily extracted aluminum-hydroxide portion of a sludge suspension is therefore needed.

TOC Extracted

In addition to the extraction of aluminum, organic matter was extracted upon the addition of acid. As demonstrated in Figure 3.12, TOC concentrations of acid extracts increased in a manner similar to that of aluminum. That is, concentrations remained relatively constant until a pH of approximately 4.0 was reached and it then abruptly increased. Using a pH of 2.0 as a reference example, the TOC concentrations of the extracts ranged from 380 mg/L to 1348 mg/L, indicating that TOC and aluminum concentrations of the acid extracts were similar.

Examination of the TOC extracted per unit of suspended solids is illustrated in Figure 3.13. The three Chattahoochee sludges contained the lowest relative quantity of extracted organic matter with, for example, TOC equalling 4.4 to 6.6 mg/g or 0.44 to 0.64 percent of the suspended solids at a pH of 2.0. At this same example pH value, the other extracts contained TOC at values of 13-34 mg/g or 1.3 to 3.4 percent of the mass of the initial suspended solids in the sludge suspensions.

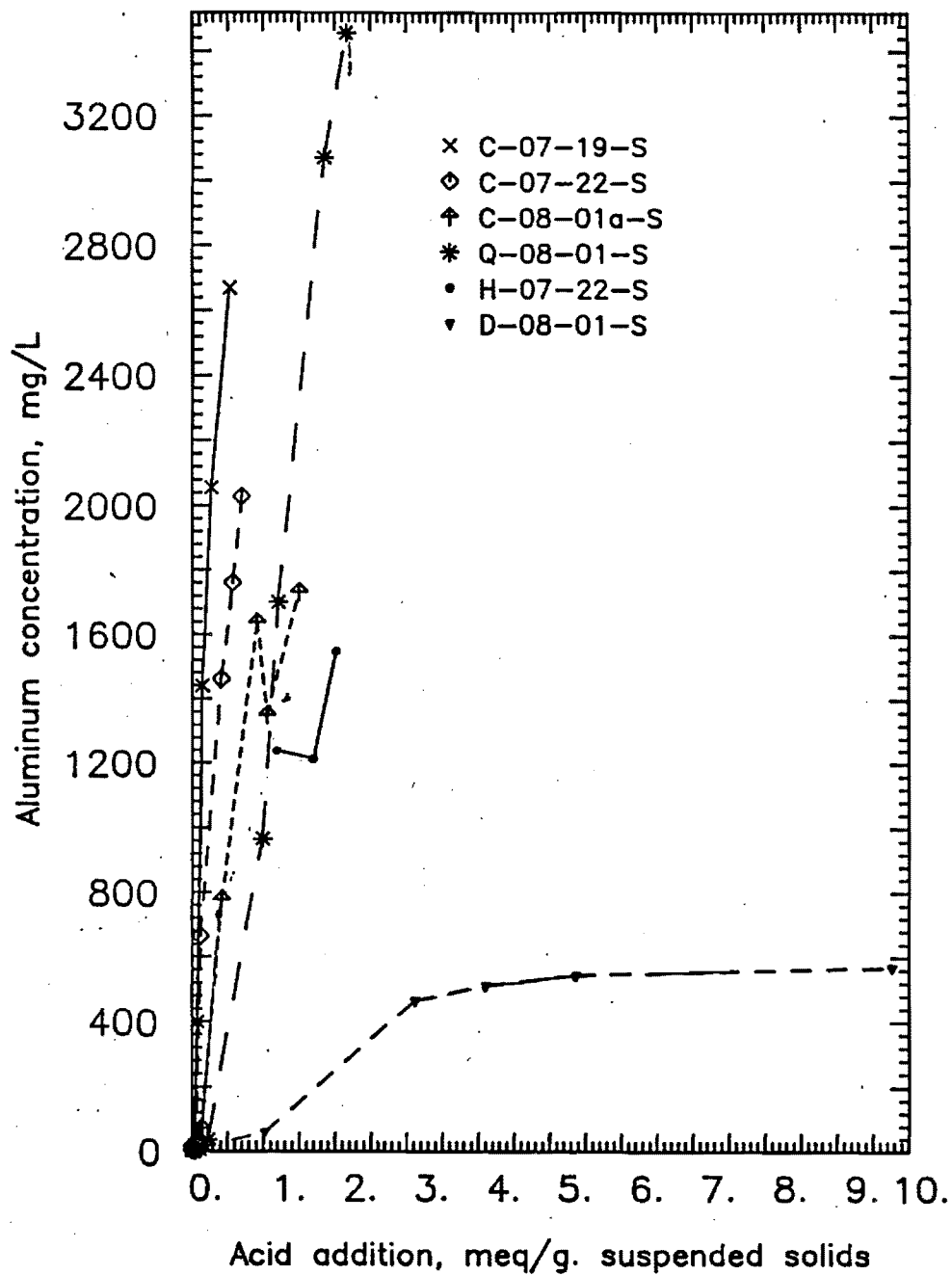


Figure 3.10. Soluble Aluminum Concentration Versus Normalized Acid Addition for Six Sludge Samples.

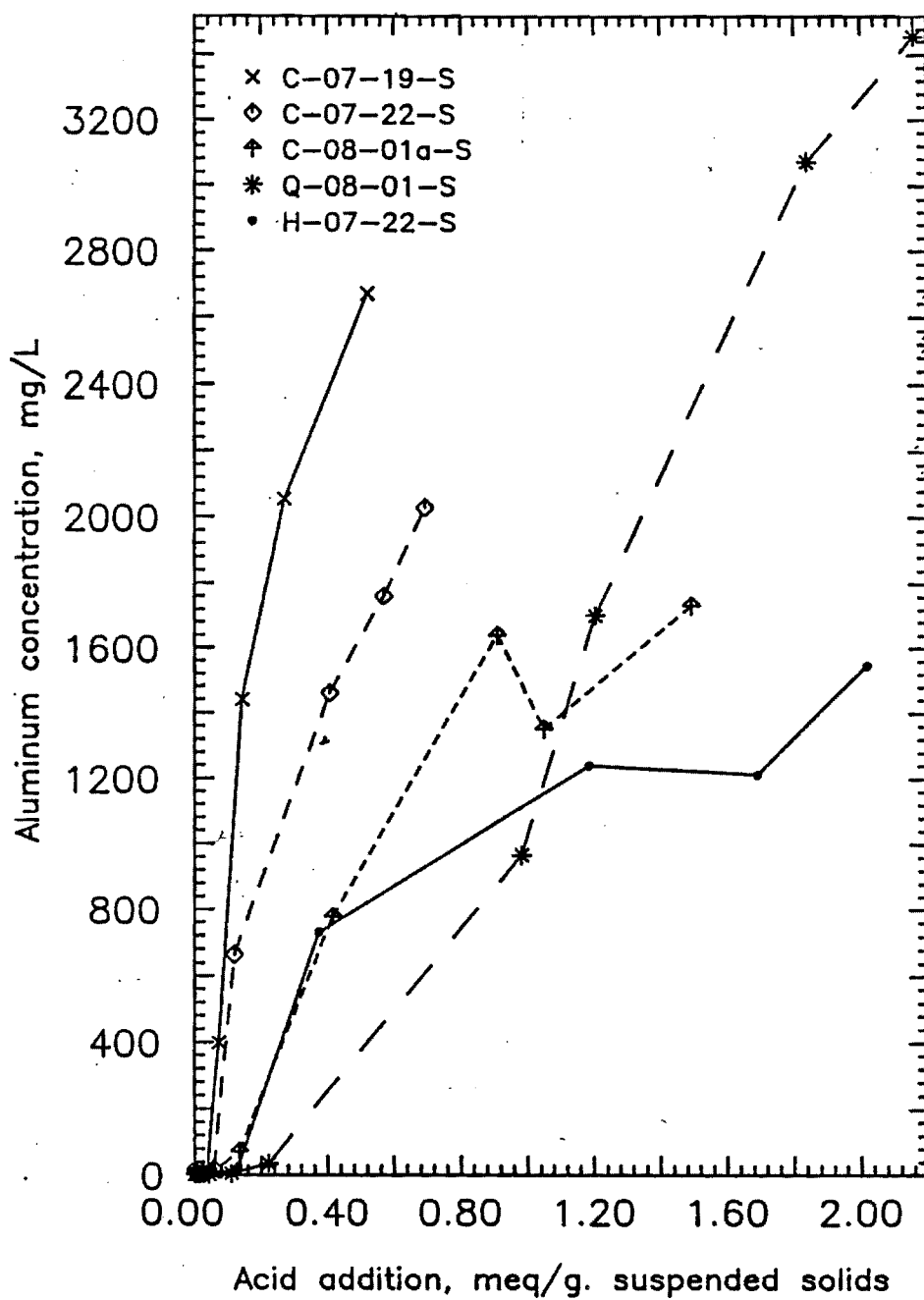


Figure 3.11. Expanded Analysis of Soluble Aluminum Concentration Versus Normalized Acid Addition for Five Sludge Samples.

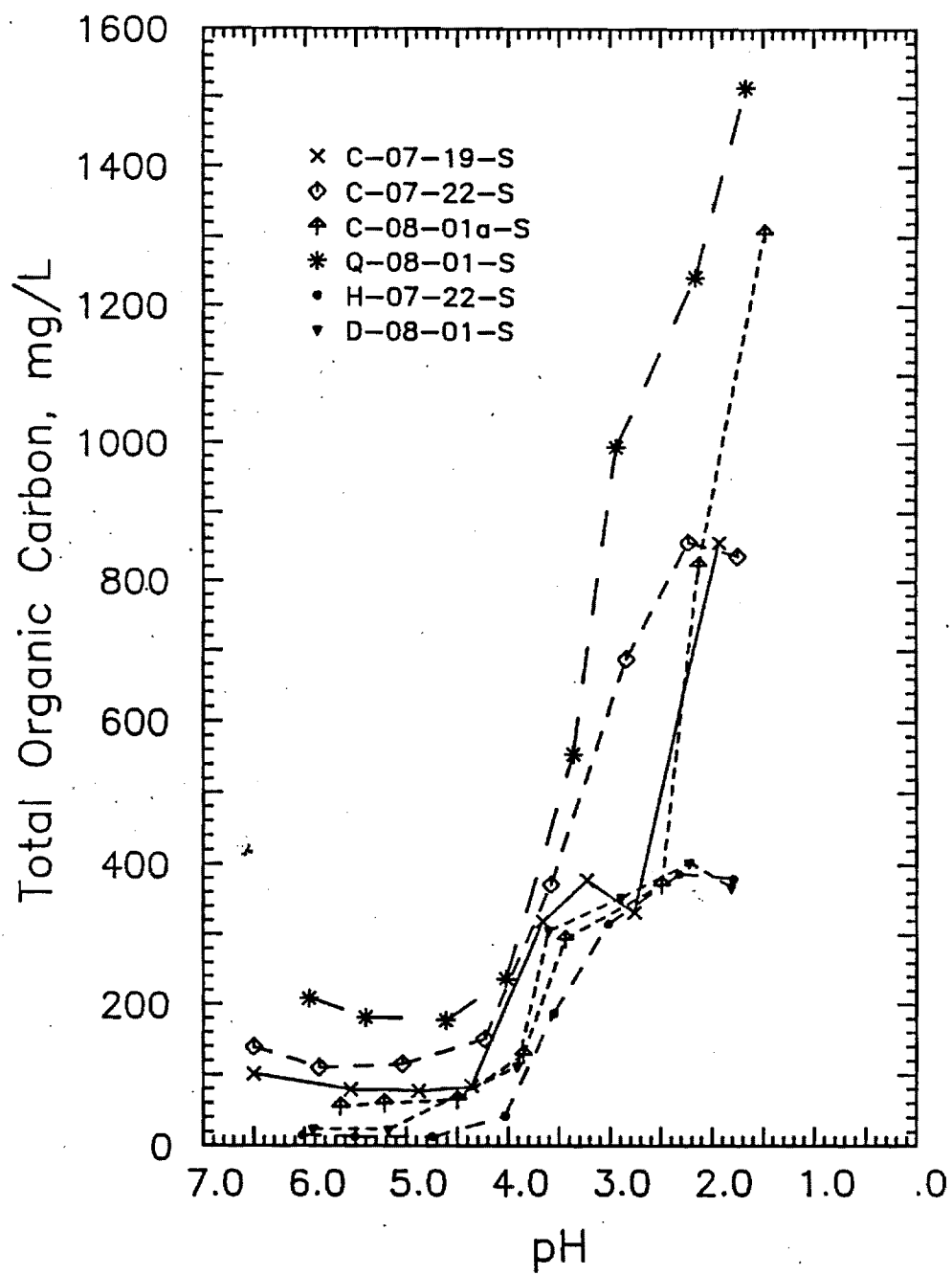


Figure 3.12. Soluble Organic Carbon of Six Acidified Sludge Samples Versus pH.

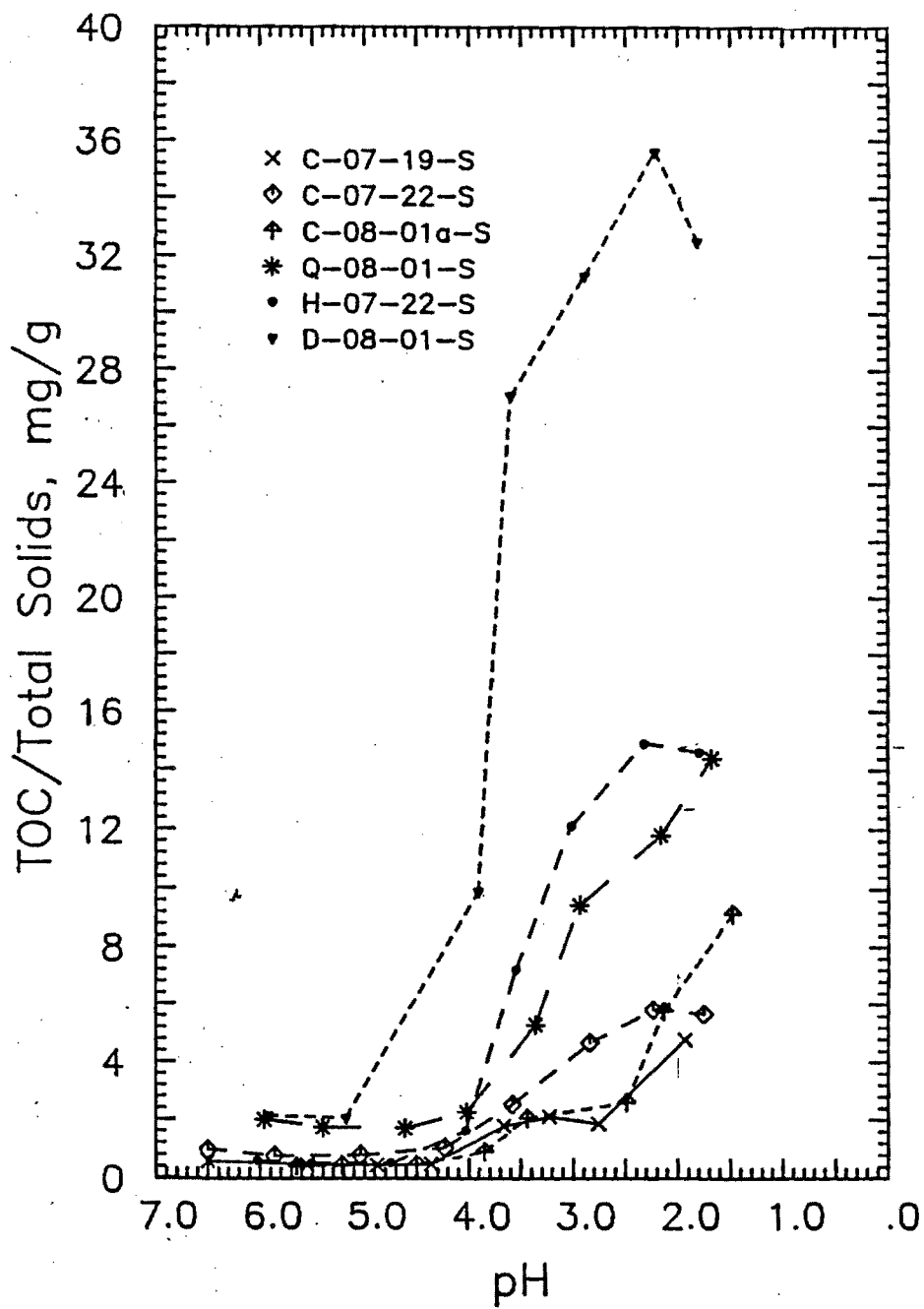


Figure 3.13. Normalized Organic Carbon Concentration Versus Suspension pH.

QUALITY OF SLUDGES AND ACID EXTRACTS OF SLUDGES

A series of extractions of sludge samples was conducted using acid-cleaned, baked glassware to establish the chemical quality of the extract solutions. Organic-free water blanks were carried through the procedures to detect any contamination attributable to equipment or chemicals (i.e., sulfuric acid) used in the study. In addition, aliquots of the initial sludges, previously collected and stored in the laboratory, were examined for chemical content, as were two samples of commercial alum obtained from the Chattahoochee and Candler plants.

Inorganic Constituents

Sludges, acidic extracts and alum samples were examined for aluminum content and the following metals for which a MCL value was established: silver, barium, cadmium, chromium, mercury and lead. Arsenic and selenium were not examined due to low concentrations detected in initial screening studies and the difficulty associated with their measurement as volatile hydrides. In addition, the following metals were examined due to their potential impact on product-water quality or coagulant effectiveness: copper, iron, manganese, nickel, tin and zinc.

Sludge Solids

The metallic composition of four sludge samples are presented in Table 3.6. The major metals were aluminum and iron, which accounted for between 4.7 to 10.2 percent and 3.9 to 5.6 percent, respectively, of the total suspended solids of the suspensions. If it is assumed that each metal was present as its hydroxide [i.e., $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ and $\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$], the two metals together would account for a total of 35 to 66 percent of the suspended solids, while aluminum hydroxide [$\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$] alone would account for 23 to 50 percent of the suspended solids. While it is unlikely

TABLE 3.6. TOTAL METAL COMPOSITION OF ALUM SLUDGE SAMPLES COLLECTED FROM CHATTAHOOCHEE (C), HEMPHILL (H), CANDLER (D) AND QUARLES (Q) WATER TREATMENT PLANTS

Metal	C-07-22		H-07-22		D-08-01		Q-08-01	
	mg/L	mg/kg SS	mg/L	mg/kg SS	mg/L	mg/kg SS	mg/L	mg/kg SS
Al - Aluminum	4904	47,068	885	102,076	831	76,590	5167	53,049
Ag* - Silver	0.024	0.23	0.004	0.46	.00275	0.25	0.014	0.14
Ba* - Barium	25	240	<20	-	<20	-	20	205
Cd* - Cadmium	0.011	0.106	.02	2.3	0.016	1.5	0.65	0.67
Cr* - Chromium	5.5	52.8	0.944	108.9	0.5	46.1	6.0	61.1
Cu - Copper	4.15	39.8	0.54	62.3	0.415	38.3	4.925	50.6
Fe - Iron	4158	39,908	490	56,517	518	47,742	4900	50,308
Hg* - Mercury	0.004	0.04	0.0017	0.20	0.0028	0.26	0.019	0.19
Mn - Manganese	249	2,390	40	4,614	39	3,594	125	1,283
Ni - Nickel	2.6	25.0	0.5	57.7	0.5	46.1	2.4	24.6
Pb* - Lead	6.1	58.6	1.45	167.2	0.56	51.6	6.85	70.3
Sn - Tin	10	92.17	<10	-	<10	-	10	102.7
Zn - Zinc	13	124.8	1.6	184.5	1.0	92.2	9.4	96.5

*Metals for which Maximum Contaminant Levels (MCL) are established for finished drinking water.

NOTE: Suspended solids concentrations for sludge samples: C-07-22 = 104.19 g/L; H-07-22 = 8.67 g/L; D-08-01 = 10.85 g/L; Q-08-01 = 97.4 g/L.

that a major portion of the iron would appear as a hydroxide or that all of the aluminum was present as its hydroxide, the above analysis serves to place the two metals in perspective relative to the suspended solids in the sludge samples. Manganese was the next most predominant metal, accounting for 0.13 to 0.46 percent (i.e., 1283 mg/kg to 4614 mg/kg) of the suspended matter.

Of the metals for which MCL values are established, barium, chromium and lead were contained at concentrations ranging from 0.5 mg/L to 25 mg/L and accounted for 0.0046 to 0.024 percent (i.e., 46.1 mg/kg to 240 mg/kg) of sludge suspended solids. Silver, cadmium and mercury were contained at substantially lower values, ranging from 1.6 µg/L to 24 µg/L. The remaining uncontrolled metals, copper, nickel, tin and zinc, were contained in concentrations ranging from 0.4 mg/L to 10 mg/L.

All of the metals examined accounted for 9.0 to 16.4 percent of the total suspended solids in the four sludge samples. Other metals and non-metallic components therefore accounted for a majority of the sludge solids and could be attributable to the broad array of materials contained in the influent raw water.

Acid Extracts of Sludge Suspensions

A total of six sludge samples were examined using strict procedures to assure for a minimal of sample contamination from other sources. The information in Table 3.7 indicates that the range of acid addition varied from 157 meq/L to 342 meq/L and that pH values of the extracts, 30 minutes after acid addition, ranged from 1.75 to 2.5. Four of the acid doses were typical of those employed previously, ranging from 1.4 meq/g SS to 3.5 meq/g SS. Two sludges (i.e., D-08-01-S and H-07-22-S) were dosed with elevated acid doses of 14.5 meq/g SS and 33.2 meq/g SS, respectively, and had .

TABLE 3.7. CHARACTERISTICS OF CLARIFIED SLUDGE EXTRACTS DEVELOPED
FOR TRACE ORGANIC AND INORGANIC ANALYSES

Sample	Date of Extraction	Acid Addition			pH	SOLIDS			
		meq/L	lbs	meq		Initial Sludge	Acidified Sludge		
			10 ³ gal	g SS		SS g/L	TS %	TDS %	SS %
C-07-19-S	8/21	338	144	1.9	2.36	179.4	18.59	2.76	15.83
C-07-22-S	8/23	227	96	2.2	2.51	104.2	-	-	-
C-08-01a-S	8/20	198	84	1.4	2.15	142.9	14.52	1.62	12.90
H-07-22-S	8/23	288	122	33.2	1.86	8.67	-	-	-
Q-08-01-S	8/23	342	145	3.5	1.95	97.4	11.32	2.5	8.82
D-08-01-S	8/23	157	67	14.5	1.72	10.85	1.88	0.79	1.09

All samples were clarified by centrifugation (2700 x g) and analysed.

correspondingly lower pH values.

Following extraction for a 30- to 45-minute period, the sludge suspensions were centrifuged (2700 x g) and the clarified centrate was examined for metal composition. The metal data are presented in Tables 3.8 and 3.9. The aluminum concentrations for the three Chattahoochee sludges ranged from 1250 to 1900 mg/L. Sludge sample C-08-01a was examined using a centrate sample and a filtered centrate sample. The aluminum concentrations for the two samples were very similar indicating no significant difference between the centrate and a filtered centrate, confirming that examination of centrates was sufficient to indicate the concentrations of soluble metals. After aluminum, the most predominant metal was iron, followed by manganese. All other metals were at concentrations < 5 mg/L, or less than 0.4 percent of the concentration of aluminum.

The aluminum concentrations for the clarified sludge extracts of the Hemphill, Candler and Quarles sludges ranged from 500 mg/L to 1800 mg/L. With these sludge extracts, iron and manganese were the predominant metals and all other metals were < 5 mg/L, as was indicated with the Chattahoochee sludges. The impact of these trace metals on product quality are to be examined in depth in a subsequent section.

Commercial Alum Samples

Two samples of commercial alum were obtained from feed lines or alum storage reservoirs at the Chattahoochee and Candler plants. The metal composition of these commercial-strength products is presented in Table 3.10. The aluminum concentrations were 55.05 g/L and 60.3 g/L for the samples. These concentrations are indicative of commercial strengths of 8.0 percent as Al_2O_3 and 8.8 percent as Al_2O_3 , respectively, for products with a density of 1300 kg/m³ (81 lb/ft³) and are well within the range of typical product

TABLE 3.8. METAL COMPOSITION OF CLARIFIED SLUDGE EXTRACTS COLLECTED BY ACIDIFICATION
OF CHATTAHOOCHEE (C) SLUDGE SAMPLES

Metal	C-07-19		C-07-22		C-08-01a		C-08-01a Filtered	
	mg/L	mg/kg SS	mg/L	mg/kg SS	mg/L	mg/kg SS	mg/L	mg/kg SS
Al-Aluminum	1,900	10,591	1,250	11,997	1,250	8,397	1,200	8,747
Ag*-Silver	0.0018	0.01	0.0011	0.011	0.0011	0.008	0.0033	0.023
Ba*-Barium	ND	-	ND	-	ND	-	ND	-
Cd*-Cadmium	0.002	0.01	0.01	0.096	0.0169	0.12	0.0165	0.12
Cr*-Chromium	2.78	15.5	1.71	16.4	2.67	18.7	1.07	7.5
Cu-Copper	1.67	9.3	2.70	25.9	2.28	15.9	1.33	9.3
Fe-Iron	1,885	10,507	1,208	11,594	490	3,429	458	3,205
Hg*-Mercury	0.0003	0.002	0.0014	0.013	0.0004	0.003	0.0033	0.023
Mn-Manganese	200	1,115	145	1,392	95	665	80	560
Ni-Nickel	ND	-	ND	-	ND	-	ND	-
Pb*-Lead	1.32	7.3	2.70	25.9	1.24	8.7	1.15	8.0
Sn-Tin	ND	-	ND	-	ND	-	ND	-
Zn-Zinc	5.3	29.5	4.7	45.1	4.5	31.5	4.5	31.5

*Metals for which Maximum Contaminant Levels (MCL) are established for finished drinking water.

Note: Extracts were acidified and then centrifuged (2700 x g) to remove residual solids prior to analysis.
Initial suspended solids concentrations were: C-07-19 = 179.4 mg/L; C-07-22 = 104.19 g/L;
C-08-01 = 142.9 g/L.

TABLE 3.9. METAL COMPOSITION OF CLARIFIED SLUDGE EXTRACTS COLLECTED BY ACIDIFICATION OF HEMPHILL (H), CANDLER (D) AND QUARLES (Q) SLUDGE SAMPLES

Metal	H-07-22		D-08-01		Q-08-01	
	mg/L	mg/kg SS	mg/L	mg/kg SS	mg/L	mg/kg SS
Al-Aluminum	1,020	117,650	550	50,691	1,800	18,480
Ag*-Silver	0.005	0.58	0.0011	0.1	0.002	0.02
Ba*-Barium	ND	-	ND	-	ND	-
Cd*-Cadmium	0.007	0.81	0.0163	1.5	0.0169	0.17
Cr*-Chromium	0.852	98.3	0.372	34.3	1.152	11.8
Cu-Copper	0.796	91.2	0.525	48.4	3.07	31.5
Fe-Iron	274	31,600	92	8,479	1,151	11,817
Hg*-Mercury	0.0036	0.42	0.0014	0.13	0.0005	0.005
Mn-Manganese	55	6,344	18.5	1,705	79	811
Ni-Nickel	ND	-	ND	-	ND	-
Pb*-Lead	0.778	89.7	0.479	44.1	1.074	11.0
Sn-Tin	ND	-	ND	-	ND	-
Zn-Zinc	1.6	184.5	0.5	46.1	2.9	29.8

*Metals for which Maximum Contaminant Levels (MCL) are established for finished drinking water.

NOTE: Extracts were acidified and then centrifuged (2700 x g) to remove residual solids prior to analysis. Initial suspended solids concentrations of sludges prior to acidification were:
H-07-22 = 8.67 g/L; D-08-01 = 10.85 g/L; Q-08-01 = 97.4 g/L.

TABLE 3.10. METAL COMPOSITION OF LIQUID ALUM SAMPLES OBTAINED
FROM CHATTAHOOCHEE AND CANDLER WATER TREATMENT PLANTS

Metal	Chattahoochee		Candler	
	mg/L	mg/kg Al	mg/L	mg/kg Al
Al - Aluminum	60,300	-	55,050	-
Ag - Silver	0.25	4.15	0.2	3.63
Ba - Barium	ND	-	ND	-
Cd - Cadmium	0.025	0.41	0.3	5.4
Cr - Chromium	77.5	1,285	40	726.6
Cu - Copper	5.5	91.2	2.8	50.9
Fe - Iron	1,845	30,600	2,080	37,780
Hg - Mercury	0.0048	0.08	0.0032	0.06
Mn - Manganese	20	331.7	20	363.3
Ni - Nickel	43.5	723.1	43.5	844.7
Pb - Lead	6.6	298.5	4.06	181.6
Sn - Tin	155	2570.5	155	2815.6
Zn - Zinc	8.5	141.0	8.5	154.4

concentrations. The major contaminant in both products was iron at concentrations of 1845 mg/L and 2080 mg/L, which were less than 4 percent of the concentration of aluminum. Numerous contaminants were contained at concentrations of 1-100 mg/L, including chromium, copper, manganese, nickel, lead and tin. Silver, cadmium and mercury were contained at trace levels of ≤ 0.3 mg/L. The impact of all contaminants on product-water quality is examined in a later section.

Evaluation of Sludge and Extract Metal Composition

Comparison of sludge metal composition in Table 3.6 with metals contained in sludge extracts, as presented in Tables 3.8 and 3.9, provides a means of establishing the extent to which sludge metals were extracted. This comparison is presented in Table 3.11 for four sludges.

The Chattahoochee (C-07-22) and Quarles (Q-08-01) sludges were extracted using acid application rates of 2.2 meq/g SS and 3.5 meq/g SS, respectively. A total of 26 to 35 percent of the total aluminum was extracted. This, however, is not indicative of the fraction of the coagulant-aluminum that was extracted because total-sludge aluminum included both that contained in aluminum-hydroxide precipitates and all other aluminum contained in influent soil, silt and sediment. The extent of extraction of other contaminants ranged from 5 to 91 percent and 3 to 63 percent for the Chattahoochee and Quarles sludges, respectively.

The sludges from the Candler (D-08-01) and Hemphill (H-07-22) plants were extracted at elevated acid doses of 14.5 meq/g-SS and 33.2 meq/g-SS, respectively. As expected, higher levels of sludge metals were extracted. For the Candler sludge, 66 percent of the aluminum was extracted. The copper concentration of the acid extract exceeded that in the initial sludge, resulting in an extraction efficiency of 127 percent. This

TABLE 3.11. PERCENT OF TOTAL METAL EXTRACTED FROM SLUDGES BY ACIDIFICATION
AND CONTAINED IN ALUMINUM EXTRACTS

Metal	C-07-22	Q-08-01	D-08-01	H-07-22
Al	26	35	66	(115)
Ag	5	14	40	(125)
Ba	ND	ND	ND	ND
Cd	91	26	(102)	35
Cr	31	19	74	90
Cu	65	62	(127)	(147)
Fe	29	24	18	56
Hg	35	3	50	(213)
Mn	58	63	47	138
Ni	ND	ND	ND	ND
Pb	44	16	86	55
Sn	ND	ND	ND	ND
Zn	36	31	50	100

ND = Not detected in acid extract.

discrepancy was attributed to the variations due to the heterogeneous nature of the sludge and to analytical variations in the two analyses. The percent extraction for the remaining metals ranged from 18 to 102 percent and were, in general, higher than those experienced for the Chattahoochee and Quarles sludges, which were extracted at much lower acid doses.

The acid application rate for the Hemphill sludge was 33.2 meq/g-SS and was the highest employed throughout the study. The Hemphill study was also the one with the lowest suspended solids concentration. The high acid dose promoted a high level of metal extraction while the low suspended solids concentration was indicative of a low level of metal available for extraction. The extraction level for aluminum was 115 percent, indicating more was extracted than was contained in the sludge suspension. The variation of 15 percent, however, was acceptable due to the analytical issues noted above and the heterogeneous nature of the sludge suspension. Data on the degree of extraction of silver, copper and manganese were 125 percent, 147 percent and 138 percent. Although higher than the value for aluminum, they were deemed acceptable for similar reasons, and indicated complete extraction of those metals. The unrealistically high value (i.e., 213 percent) for mercury was attributable to the trace quantities of the metal in the sludge and the extract and the associated difficulty in obtaining reliable concentrations for this metal. Use of the metal data for the Hemphill extract (as opposed for total sludge metal) would result in an apparent conservative estimate of extract quality when evaluating its impact on product water when recycling the coagulant.

Commercial Alum as a Source of Trace Metals

As indicated by data in Table 3.10, commercial alum in use at the Chattahoochee and Candler plants at the time of the study contained

significant levels of virtually all of the metals investigated. In an effort to determine the relative impact of the metals contained in the coagulant solution added to the raw water on the metal composition of the associated sludge suspensions, the metal contents of the two sludges were expressed in terms of the aluminum content of each sludge. For example, the aluminum and silver concentrations of the Chattahoochee sludge were 4904 mg/L and 24 µg/L, respectively (see Table 3.6). The silver concentration, per unit mass of aluminum, was then 4.89 mg Ag/kg Al. From Table 3.10, the silver composition of commercial alum was 4.15 mg/kg Al. Using these data, for comparison purposes, the hypothesis was that silver added with alum addition was retained in the aluminum-hydroxide-induced floc and that if the ratio of sludge metal to alum metal, on the basis of unit mass of aluminum, was 1.0, then it could be concluded that the commercial alum could be considered to be a primary source of the silver contained in the sludge. This hypothesis therefore was based in part on the assumption that all sludge aluminum was attributed to aluminum hydroxide produced by addition of alum. Continuing with the analysis of silver, the ratio of sludge-Ag to alum-Ag was 1.2 indicating that alum was potentially a major contributor of silver to the sludge. For the Candler sludge, this ratio was 0.9 similarly indicating alum to be a major source of silver.

Analysis of the sludge-metal to alum-metal ratios in Table 3.12 indicated that silver (Ag), chromium (Cr), nickel (Ni) and tin (Sn) had ratios of sludge-metal to alum-metal of 0.7 to 1.2. Given the inherent variations included in such an analysis, it is then reasonable to speculate that a major source of the metal contaminants in the sludge was the commercial alum used at the plant.

TABLE 3.12. COMPARISON OF SLUDGE METAL CONTENT TO THAT FOR LIQUID ALUM PRODUCT USED FOR THE CHATTAHOOCHEE AND CANDLER PLANTS

Metal	Chattahoochee Sludge*		Candler Sludge**	
	$\frac{\text{mg}}{\text{kg Al}}$	Ratio of*** Sludge-Metal to Alum-Metal	$\frac{\text{mg}}{\text{kg Al}}$	Ratio of*** Sludge-Metal to Alum-Metal
Ag	4.89	1.2	3.31	0.9
Ba	5.1	-	-	-
Cd	2.24	5.5	19.25	47.1
Cr	1121.5	0.9	601.7	0.8
Cu	846.2	9.3	99.4	9.8
Fe	847,880	2.8	623,345	16.5
Hg	0.08	10.7	3.37	56.2
Mn	50,775	153.0	46,931	129.2
Ni	530.2	0.7	601.7	0.7
Pb	1243.9	4.2	673.9	3.7
Sn	2039.2	0.8	-	-
Zn	2650.9	18.8	1203.4	7.8

*Sludge sample C-07-22-S; alum sample C-08-01-A

**Sludge sample D-08-01-S; alum sample D-08-01-A

***Ratio of (mg-metal/kg Al in sludge) to (mg-metal/kg Al in liquid alum)

Sludge to alum metal ratios of 2 to 20 would be indicative of 50 percent to 5 percent contribution of metal by alum, respectively. Copper (Cu), iron (Fe), lead (Pb) and zinc (Zn) had ratios of from 2.8 to 18.8 indicating alum as a significant but low contributor of metal to sludge solids. Cadmium had metal ratios of 5.5 and 47 indicating a wide variation in contribution by alum, as did mercury, with ratios of 10.7 and 56.2.

Manganese was the single metal for which virtually all of it was attributable to non-alum sources. The ratios of 153 and 129.2 indicated only 0.7 to 0.8 percent of the metal could be attributable to alum. For metals which are controlled with MCL values, silver and chromium contamination could be attributed to commercial alum in total, while contamination by cadmium (Chattahoochee only) and lead was significantly (i.e., 18-27 percent) affected by alum.

To place the contaminant levels for commercial alum and acid sludge extracts in proper perspective, the metal data were normalized to similar aluminum concentrations. Since the acidic extracts and commercial alum are added to raw waters to promote coagulation on the basis of formation of aluminum hydroxide precipitates, a 1.0 mg/L dose of aluminum in a raw water was chosen. This is reflective of an approximate alum dose of 11.1 mg/L [as $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$] and is within the range of acceptable alum doses used to treat surface waters. The resulting concentration of each contaminant metal in the rapid-mix portion of a treatment plant was determined. It must be stressed that the concentrations calculated do not account for any removal of the metal in the coagulation process and therefore can only be used to reflect the maximum concentration that would be achieved with the solutions added. Furthermore, with the sole exception of iron, all projected metal concentrations were very low and were expressed in units of nano-grams per

liter (ng/L). Finally, the metals were grouped in terms of those metals controlled by MCL values; those for which a secondary MCL was previously established; and those for which no current controls exists.

The projected metal concentrations at an aluminum dose of 1.0 mg/L using commercial alum and acidic extracts are included in Table 3.13. Examination of the projected concentrations for the MCL-metals, indicated that the concentrations of silver (0.9-4.9 ng/L), cadmium (0.4-29.6 ng/L) and mercury (0.06-3.5 ng/L) were less than 0.3 percent of the MCL values. Chromium (640-2225 ng/L) and lead (182-2160 ng/L) concentrations were less than 5 percent of the MCL value. In the case of acidic extracts this indicates that a 20-fold concentration of these metals would have to occur by repeated acidic extraction and recycle before the MCL would be exceeded.

Examination of the contaminant metal concentrations for the commercial alum products (C-Alum and D-Alum in Table 3.13) indicated reasonable agreement between the two products, as was indicated previously in Table 3.10. Comparison of acid extracts from the Chattahoochee plant with the alum for the plant indicates that silver was the only metal that was lower in the extracts than in the commercial alum product. Chromium concentrations for Chattahoochee extracts were slightly higher (a 1.1- to 1.7-fold increase) than that for the commercial alum. Cadmium showed the greatest deviation from the commercial alum, ranging from approximately 3 to 35 times higher than commercial alum. The highest concentration for cadmium was however only 0.14 percent of the MCL of 10 μ g/L. Finally, mercury and lead were at elevated values which were approximately 2 to 14 times higher than the concentrations for commercial alum.

Comparison of the Candler extract with the commercial alum from the Candler plant indicated that silver and chromium in the extract were less

TABLE 3.13. PROJECTED CONCENTRATION OF METALS IN FLOCCULATED WATER ATTRIBUTABLE TO REUSE OF SLUDGE EXTRACT SOLUTION AND COMMERCIAL ALUM PRODUCTS AT AN ALUMINUM DOSE OF 1 mg/L (ALUM DOSE \cong 11.1 mg/L)

Metal	MCL*	Chattahoochee				H-07-22	Candler		Q-08-01
		C-Alum	C-07-19	C-07-22	C-08-01		D-Alum	D-08-01	
Ag, ng/L	50,000	4.2	0.95	0.9	0.9	4.9	3.6	2.0	1.1
Ba, ng/L	1,000,000	-	-	-	-	-	-	-	-
Cd, ng/L	10,000	0.4	1.1	8.0	14.1	6.9	5.4	29.6	9.4
Cr, ng/L	50,000	1,285	1,463	1,368	2,225	835	727	676	1196
Hg, ng/L	2,000	0.08	0.2	1.1	0.2	3.5	0.06	2.5	0.3
Pb, ng/L	50,000	299	695	2,160	1,033	763	182	871	597
Cu, ng/L	1,000,000**	91.2	879	2,160	1,900	780	50.9	955	1706
Fe, mg/L	0.3**	0.03	1.0	1.0	0.4	0.27	0.04	0.17	0.64
Mn, ng/L	50,000**	153	105,260	116,000	79,167	53,922	129	33,636	43,890
Zn, ng/L	5,000,000**	141	2,790	3,760	3,750	1,569	154	909	1,611
Ni, ng/L	-	723.1	-	-	-	-	845	-	-
Sn, ng/L	-	2,570	-	-	-	-	2,816	-	-

*MCL = primary maximum contaminant level MCL for finished drinking water, unless noted otherwise

**Secondary MCL values

NOTE: ng/L = 10^{-3} μ g/L = 10^{-6} mg/L

than the commercial alum; cadmium was higher by a factor of 5.5; and lead and mercury were higher by factors of approximately 5 and 42. The concentrations for metals in the Hemphill and Quarles extracts were generally within the limits established by the other extracts.

Copper and zinc are not regulated in drinking water standards but secondary MCL values for these metals previously employed were 1 mg/L (1,000,000 ng/L) and 5 mg/L (5,000,000 ng/L), respectively. In all instances, the extracts and commercial alum had projected concentrations that were less than 0.2 percent of the secondary MCL values. The projected concentrations for the commercial alums were 91.2 ng/L and 50.9 ng/L for copper and 141 ng/L and 154 ng/L for zinc. The projected concentrations for the extracts ranged from 879 ng/L to 2160 ng/L for copper and from 909 ng/L to 3760 ng/L for zinc and were significantly higher than those for commercial alum.

Iron and manganese were previously regulated for aesthetic reasons at concentrations of 0.3 mg/L (300,000 ng/L) and 0.05 mg/L (50,000 ng/L), respectively. The iron concentration in commercial alum ranged from 0.03 to 0.04 mg/L and was well below the value of 0.3 mg/L. The projected iron concentration for the extracts ranged from 0.17 mg/L to 1.0 mg/L, indicating that iron concentrations approached or equaled the concentration of aluminum added (i.e., 1 mg/L) as a coagulant. Providing that the iron is oxidized to the ferric form upon addition, it would serve to enhance coagulation through production of ferric hydroxide flocs. This could thereby contribute to enhanced coagulation using sludge extracts when doses are based totally on aluminum.

Projected manganese concentrations for commercial alum were 153 ng/L and 129 ng/L and were well below the standard of 50,000 ng/L. The sludge extracts, however, had concentrations which were much higher, ranging from

0.034 mg/L to 0.116 mg/L as compared to the standard of 0.05 mg/L. These concentrations would require additional treatment to assure that manganese was oxidized to an insoluble form and removed by sedimentation or filtration.

Nickel and tin were not detected in sludge extracts. Nickel concentrations in commercial alum were 723 ng/L and 845 ng/L, while tin concentrations were 2750 ng/L and 2816 ng/L. No MCL values have been established for these values, however, the nickel concentrations were all below the lowest MCL value (i.e., mercury MCL = 2000 ng/L), while the tin concentrations were slightly above the lowest MCL value.

Organic Constituents

The organic composition of filtered acid extracts was examined using total organic carbon (TOC) analyses; a humic-substance extraction with an XAD-8 resin; and a GC/MS scan for priority pollutants. Sludge samples were not examined using TOC or the humic-substance extraction, nor were commercial liquid-alum samples.

TOC and Humic-Substance Concentrations

The TOC of acid extracts of sludge suspensions (see Table 3.7) are presented in Table 3.14. The TOC ranged from 353 mg/L to 1,792 mg/L. Comparison with aluminum data in Tables 3.8 and 3.9 indicate that TOC concentrations were equal to 35 percent to 100 percent of aluminum concentration, with an average of 66 percent. This makes soluble organic carbon the second or third most significant component in acidic extracts of sludge, depending on the concentration of iron in the extract.

Passing acidic extracts through XAD-8 resins followed by alkaline elution was used to establish the fraction of the TOC which was composed of humic substances. Humic-substance carbon ranged from 380 mg/L to 1,140 mg/L

TABLE 3.14. TOC CONCENTRATION IN EXTRACTS AND HUMIC SUBSTANCE CONCENTRATION IN EXTRACTS BASED ON ADSORPTION ON XAD-8 RESIN AT pH < 2

Sludge Extract	TOC mg/L	Humic Substance-Carbon	
		percent	mg/L
C-07-19-S	1,186	78	930
C-07-22-S	981	38	380
C-08-01a-S	779	55	425
H-07-22-S	353	46	160
Q-08-01-S	1,792	63	1,140
D-08-01-S	326	52	170

TABLE 3.15. PROJECTED INCREASE IN CONCENTRATION OF ORGANIC CARBON IN FLOCCULATED WATER ATTRIBUTABLE TO USE OF ALUMINUM EXTRACT AT AN ALUMINUM DOSE OF 1 mg/L

Sludge Extract	TOC mg/L	Humic Substance-Carbon	
		mg/L	
C-07-19-S	0.62	0.49	
C-07-22-S	0.78	0.30	
C-08-01a-S	0.62	0.35	
H-07-22-S	0.35	0.16	
Q-08-01-S	1.0	0.63	
D-08-01-S	0.59	0.31	

and accounted for 38 percent to 78 percent of the SOC. Therefore, a major portion of the organic matter was attributable to colored, high-molecular-weight organic matter similar to that commonly found in the natural environment.

With respect to impact on finished water quality, data in Table 3.15 indicate the incremental increase in TOC and humic-acid carbon in flocculated waters at an aluminum dose of 1 mg/L (i.e., alum = 11.1 mg/L). Incremental increases in TOC concentrations in flocculated waters ranged from 0.35 to 1.0 mg/L, while humic-substance carbon concentrations ranged from 0.16 to 0.63 mg/L.

Priority Pollutant Organics

To investigate the potential for contamination of drinking water by recycle of specific organic compounds extracted with aluminum, GC/MS scans were made of numerous sludge and acid extracts as presented in Appendix A. The GC/MS evaluation included analysis for the compounds included in Table 2.1 using surrogates included in Table 2.2. While several sludge and extract samples were scanned using the GC/MS system, only four samples were done following a strict protocol using acid-cleaned and baked glassware with blank (distilled water) samples extracted in identical glassware to assure no false-positive results. These samples were the sludges and sludge extracts for samples C-07-22, H-07-22, D-08-01 and Q-08-01.

A total of six (6) specific purgeable organic compounds were detected in one or more of the sludge samples and three acid/neutral extractables were detected in one sludge, as presented in Table 3.16. Chloroform (CHCl_3) was found in all sludge samples at concentrations of 15.5 $\mu\text{g/L}$ to 518.6 $\mu\text{g/L}$ and was the single most prevalent compound detected in all sludge samples. The concentration of 1,1,1-trichloroethane in D-08-01 was 160.3 $\mu\text{g/L}$ and was

TABLE 3.16. ORGANIC PRIORITY POLLUTANTS CONTAINED IN DETECTABLE AMOUNTS
IN SLUDGES FROM CHATTAHOOCHEE (C), HEMPHILL (H), CANDLER (D)
AND QUARLES (Q) WATER TREATMENT PLANTS

Compound	C-07-22		H-07-22		D-08-01		Q-08-01	
	µg/L	mg/kg SS	µg/L	mg/kg SS	µg/L	mg/kg SS	µg/L	mg/kg SS
PURGEABLES								
Benzene	5.2	0.05	5.5	0.63	-	-	-	-
Toluene	1.3	0.012	-	-	-	-	-	-
Chloro- benzene	-	-	-	-	-	-	1.8	0.018
1,2-Dichlo- roethane	-	-	-	-	-	-	2.2	0.023
1,1,1-Tri- chloroethane	-	-	-	-	160.3	14.8	-	-
Chloroform	15.5	0.15	325.0	37.5	309.9	28.6	518.6	5.32
NEUTRAL EXTRACTABLES								
Anthracene	-	-	-	-	-	-	10.2	0.105
Pyrene	-	-	-	-	-	-	17.7	0.18
ACID EXTRACTABLES								
2,4-Dichloro- phenol	-	-	-	-	-	-	6.1	0.063

NOTE: The base-extractable priority pollutants, 3,3'-Dichlorobenzidine and benzidine, were not examined.

the second most prevalent compound detected in any sludge sample. The remaining compounds detected were (in decreasing order of highest concentration detected) pyrene, anthracene, 1,4-dichlorophenol, benzene, toluene, 1,2-dichloroethane and chlorobenzene. These compounds were detected at concentrations of 1.3 µg/L to 17.7 µg/L. Therefore, the sludges contained few priority pollutants and those detected in concentrations above 20 µg/L were volatile purgeable organic contaminants. Reconstructed ion chromatographs (RIC) for these samples and their blanks are contained in Appendix A.

Examination of two commercial alum samples and the acid extracts for sludges C-07-19, H-07-22, D-08-01 and Q-08-01 indicated that no detectable priority pollutants were contained in these samples. Apparently, the process of acid extraction did not result in their separation from sludge solids; resulted in their discharge to the atmosphere; or resulted in their destruction. Nevertheless, the compounds were not detected in the acid extracts and the recycle of specific toxic organic compounds in coagulant recovery systems does not appear to be a significant issue. Recycle of organic matter, measured as TOC previously, remains an issue.

UTILITY OF RECOVERED COAGULANTS

A series of jar test studies were conducted to determine the effectiveness of the recovered coagulants produced with sludge samples D-08-01, H-07-22, Q-08-01 and C-07-19. These tests were conducted with a sample of raw water (C-09-19-R) from the Chattahoochee plant, aliquots of which had initial turbidity values of 11-16 NTU and initial pH of 7.13.

The results for the studies are presented in Figure 3.14 in which settled (30 min) turbidity is plotted against aluminum dose. All recovered coagulants were effective in reducing turbidity of ≤ 1 NTU at aluminum doses

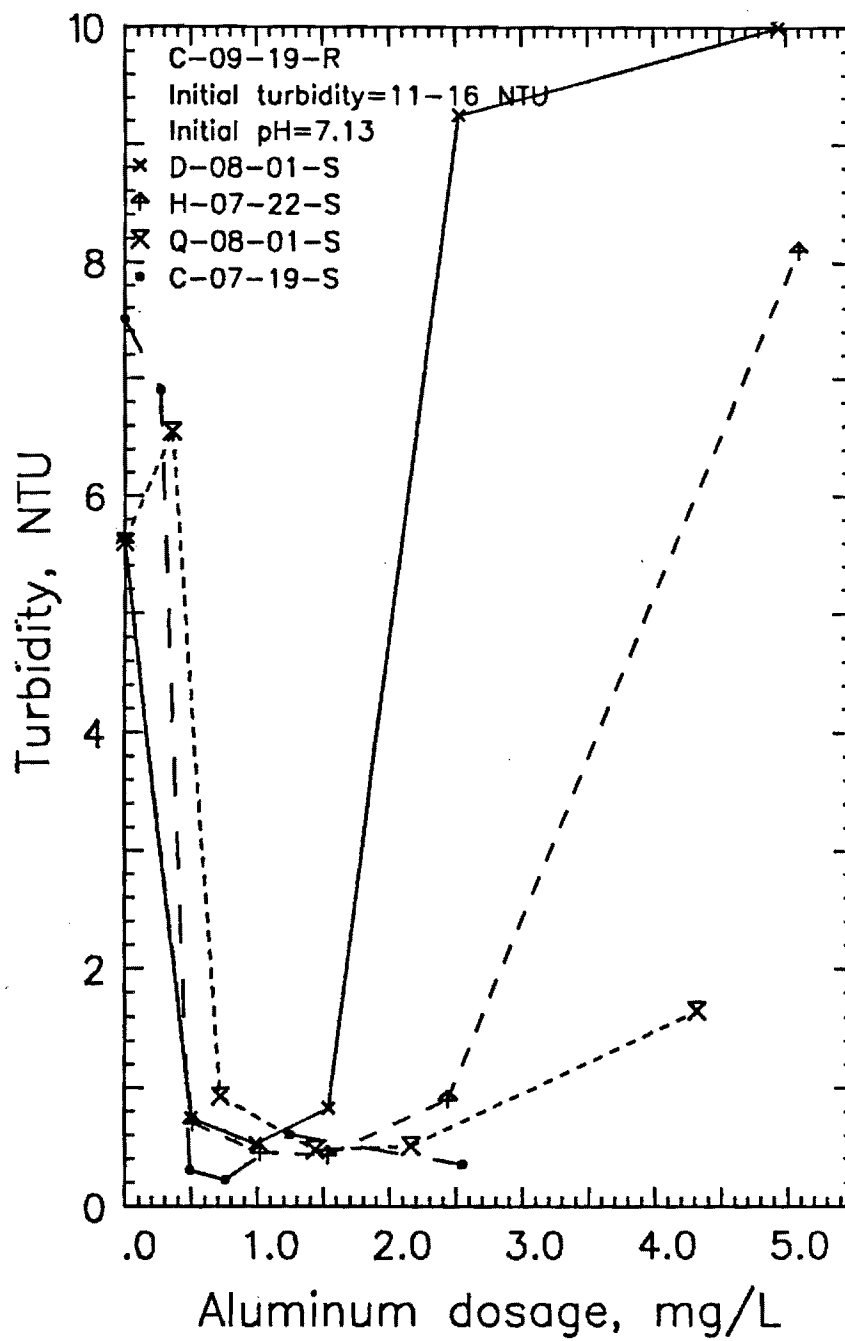


Figure 3.14. Turbidity of Settled Supernatant in Jar-Test Studies Using Four Recovered Coagulants to Treat a Raw Water (C-09-19-R) from the Chattahoochee Plant.

as low as 0.5 to 0.8 mg/L. Using aluminum concentrations alone, this concentration range is comparable to an alum dose of 5.6 to 8.9 mg/L [as $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$], a range typical of that used at the Chattahoochee Water Treatment Plant.

The data in Figure 3.14 indicate an apparent sweep-floc coagulation, in which turbidity particles are destabilized and flocculated for effective removal, followed by restabilization due to pH reduction (i.e., no pH adjustments were made). The data clearly confirm the excellent utility of the recovered coagulants for water treatment.

Sludge Thickening and Dewatering Properties

Preliminary studies were conducted on acidified sludges to establish the extent to which a coagulant solution could be separated from residual solids and subsequently dewatered.

Thickening of Acid Extracts of Sludge

To examine the extent to which acid extracts could be gravity thickened, acidified sludges were conditioned and allowed to settle under quiescent conditions to an ultimate compacted volume. In addition, interfacial settling velocities were recorded for these conditioned slurries.

Representative data for a sludge sample (i.e., H-09-10d) are presented in Table 3.17. The suspended solids concentration of the initial suspension was 23.5 g/L, as indicated in Table 3.1. The interfacial settling velocity for the suspension was 0.19 ft/h and the suspension had an ultimate settled volume of 45.4 percent of the initial suspension volume, i.e., the sludge suspension was concentrated by gravity settling by a factor of 2.2 (i.e., 0.454^{-1}). Conditioning the suspension with sulfuric acid to reach a pH of 2.0 produced similar results in an elapsed time of 2.5 h. A series of polymer conditioning studies were conducted to select a polymer which could

TABLE 3.17. THICKENING OF SLUDGE SUSPENSIONS (H-09-10d-S) FROM HEMPHILL PLANT
FOLLOWING VARIOUS CONDITIONING STEPS

Conditioning	Settled Sludge Volume %*	Interfacial Settling Velocity ft/hr
1. Unconditioned.....	45.4 (2.3 h)	0.19
2. Acid addition (pH=2).....	45.3 (2.5 h)	0.23
3. Acid addition (pH=2); polymer addition (20 ppm).....	29 (12 h)	-
4. Acid addition (pH=2); polymer addition; decant 45% of clarified liquid:		
a. Lime addition (pH=9).....	9.2 (23 h)	0.0045
b. Lime addition (pH=10).....	2.6 (2.5 h)	0.0096
c. Lime addition (pH=11).....	20.3 (2.3 h)	0.14
d. Lime addition (pH=12).....	43.8 (1.0 h) 24.6 (2.0 h)	0.27 0.24

* () = settling time in hours

destabilize the suspension at a pH of 2. An anionic polymer, Nalco 7181, was selected because of its broad range of effectiveness. At a polymer dose of 20 ppm, the sludge was concentrated by a factor of 3.4 (i.e., settled volume = 29%) in 12 h. It was therefore possible to recover approximately 70 percent of the extracted coagulant by polymer conditioning and gravity settling. This option would allow for recovery of the majority of the extracted coagulant; concentration of the remaining solids prior to dewatering; and further conditioning of the resulting slurry for other purposes.

The effect of lime addition on thickening was examined with an acidified suspension which had been gravity thickened and decanted (i.e., 45 percent of the liquid had been removed as a clarified, solids-free solution) to simulate recovery of a coagulant-rich supernatant liquid. Lime was then added to this concentrated material to pH levels of 9, 10, 11 and 12. At a pH of 9, the settled sludge volume was 9.2% of total suspension volume (after 23 h of quiescent settling), which was a 10.8-fold increase in solids concentration. As lime application increased (i.e., pH = 9 to 12), the settling velocity increased dramatically. However, the settled sludge volume also increased due to the addition of lime and the precipitation of the acid-extracted aluminum. Therefore, it was apparent that acidified sludges could be effectively separated by gravity settling using a polymer and that lime addition to a concentrated polymer-conditioned sludge could be used to further concentrate the suspension prior to dewatering.

Pressure Dewatering of Acidic Sludge

A total of eight sludges were investigated with 29 filter press runs, which were made with a 250 μ m x 250 mm JWI filter press operated at a pressure of 585-725 kPa (85-105 psi). Filter run times were frequently

limited by suspension volume but were of sufficient length to indicate relative effects of conditioning procedures employed.

Conditioning procedures, as identified in Table 3.18, included (1) acid addition to a specified pH value; (2) polymer conditioning, at an indicated dose; (3) gravity settling and decanting of clarified supernatant liquid; and (4) lime conditioning. In some instances, none of these conditioning steps were employed (e.g., runs 1, 2, 4, 10, 18, 21), while in others all four conditioning steps were employed (e.g., runs 13-17). In the latter case, coagulant recovery by acidic addition, followed by polymer-aided sedimentation with sludge disposal, preceded by pressure dewatering of the lime-conditioned residue, was simulated.

Filtrate volume data for the 29 runs are included in Figures 3.15 to 3.28. Several conclusions can be drawn from the filtrate volume data. Data in Figures 3.16, 3.19, 3.24 and 3.25 indicate that for four sludges the rate of filtrate production was lower for acidified sludges than for unconditioned sludges at ambient pH values. Acidification therefore produced a sludge suspension that was more difficult to dewater and in need of conditioning prior to dewatering.

Data in Figures 3.17 and 3.18 indicate that polymer applications of 280 to 1160 ppm (i.e., 1.8 to 4.9 g/kg of dry solids) resulted in improvements in rate of filtrate production with two sludges acidified to pH = 2.0 to 2.4. Data in Figures 3.21 and 3.22 are for a Hemphill sludge which was to a pH of 2.0 or 3.3 and then polymer conditioned at 20 ppm or 0.85 mg/g dry solids. The suspension was then decanted by 55 percent and the remaining acidic sludge was lime conditioned to pH of 9 to 12. In Figure 3.21 it is apparent that lime addition to achieve pH values of 11.5 to 11.97 improved the rate of filtrate removal for sludges at an initial pH of 2.0. The lime

TABLE 3.18. CHARACTERISTICS AND CONDITIONING OF SLUDGES PREPARED FOR DEWATERING ON JWI PRESSURE FILTER

TABLE 3.16. CHARACTERISTICS AND CONDITIONING OF SLUDGES PREPARED FOR DEWATERING ON LOW PRESSURE FILTER																
Raw Sludge					Conditioned Sludge						Sludge into Press					
Run	Sample	SS g/L	pH	CST (18mm) sec	Acid Addition		Polymer Conditioning		Decant %	Lime	T °C	pH	CST (18mm) sec	TS g/L	TDS g/L	SS g/L
					Dose meq/L	pH	Dose Polymer ppm	Conditioning Dose g/L								
1	C-08-01b-S	77.6	5.9	139	0	-	-	-	0	0	-	5.88	139	77.6	0.0	77.6
2	C-08-21-S	177.7	6.1	678	0	-	-	-	0	0	-	6.1	678	171.7	0.0	171.7
3	C-08-21-S	171.7	6.1	678	275	2.0	-	-	0	0	-	2.0	-	-	-	-
4	C-08-21-S	171.7	6.1	678	0	-	-	-	0	0	-	6.1	678	171.7	0.0	171.7
5	H-08-29-S	120.3	7.7	59.3	NA	2.4	300	N7769	0	0	-	2.4	-	-	19.9	-
6	H-08-29-S	120.3	7.7	59.3	NA	NA	280	N7181	0	0	-	NA	-	-	-	-
7	H-08-29-S	120.3	7.7	59.3	NA	2.0	219	N7181	0	0	-	2.0	-	-	24.7	-
8	C-08-29-S	235.9	7.3	237	NA	2.25	1160	N7181	0	0	-	2.25	31	-	-	-
9	C-08-29-S	235.9	7.3	237	NA	2.25	1000	N7769	0	0	-	2.25	12.0	-	-	-
10	H-09-10a-S	5.1	7.2	NA	0	-	-	-	0	0	-	7.2	23	-	-	-
11	H-09-10a-S	5.1	7.2	NA	38	1.98	-	-	0	0	-	2.0	-	5.1	0.0	5.1
12	H-09-10d-S	23.5	7.2	23	112	1.85	20	N7181	0	0	-	1.85	-	52.7	9.4	43.3
13	H-09-10d-S	23.5	7.2	23	124	2.0	20	N7181	55	17.1	9.0	11.97	10.4	66.1	4.8	61.3
14	H-09-10d-S	23.5	7.2	23	124	2.0	20	N7181	55	6.0	14	9.0	83.3	54.7	4.0	50.7
15	H-09-10d-S	23.5	7.2	23	124	2.0	20	N7181	55	8.1	16.5	9.75	51.4	56.9	1.7	55.2
16	H-09-10d-S	23.5	7.2	23	112	3.3	20	N7181	55	9.6	24	11.5	44.7	58.7	0.4	58.3

TABLE 3.18 (Continued)

Raw Sludge					Conditioned Sludge						Sludge into Press					
Run	Sample	SS g/L	pH	CST (18mm) sec	Acid Addition		Polymer Conditioning		Decant %	Lime	T °C	pH	CST (18mm) sec	TS g/L	TDS g/L	SS g/L
					Dose meq/L	pH	Dose ppm	Polymer		Conditioning Dose g/L						
17	H-09-10d-S	23.5	7.2	23	124	3.3	20	N7181	55	9.6	12	11.4	92.0	57.8	0.07	57.7
18	H-09-10e-S	37.3	7.2	NA	-	-	-	-	0	-	16	7.2	15.0	37.3	0.0	37.3
19	QW-09-16-S	NA	NA	NA	-	-	-	-	0	-	13	NA	NA	NA	NA	NA
20	QW-09-16-S	NA	NA	NA	255	2.4	-	-	0	-	NA	2.4	NA	NA	NA	NA
21	Q-09-18a-S	103.7	6.8	311	-	-	-	-	0	-	7	6.9	310.8	103.7	0.0	103.7
22	Q-09-18a-S	103.7	6.8	311	420	1.75	-	-	0	-	20	1.75	800	120.1	NA	NA
23	Q-09-18a-S	103.7	6.8	311	450	1.75	263	N7181	0	-	24	1.65	NA	121.3	16.1	105.2
24	Q-09-18a-S	103.7	6.8	311	435	1.65	314	N7181	0	-	24	1.65	50.5	NA	NA	NA
25	Q-09-18a-S	103.7	6.8	311	420	1.68	315	N7181	29.7	-	NA	1.75	126.7	151.8	37.8	114.0
26	Q-09-18a-S	103.7	6.8	311	420	1.85	315	N7181	29.7	28.5	24	10.8	329	154.5	3.7	150.8
27	Q-09-18a-S	103.7	6.8	311	420	1.85	315	N7181	29.7	28.5	24	10.4	359	NA	NA	NA
28	C-09-27-S	50.7	NA	16.8	76	2.2	80	N7181	69.9	-	NA	3.3	17.4	156.6	6.0	150.6
29	C-09-27-S	50.7	NA	16.8	76	2.2	80	N7181	69.9	7.5	NA	10.7	54.9	175.6	2.7	172.9

NA = not available

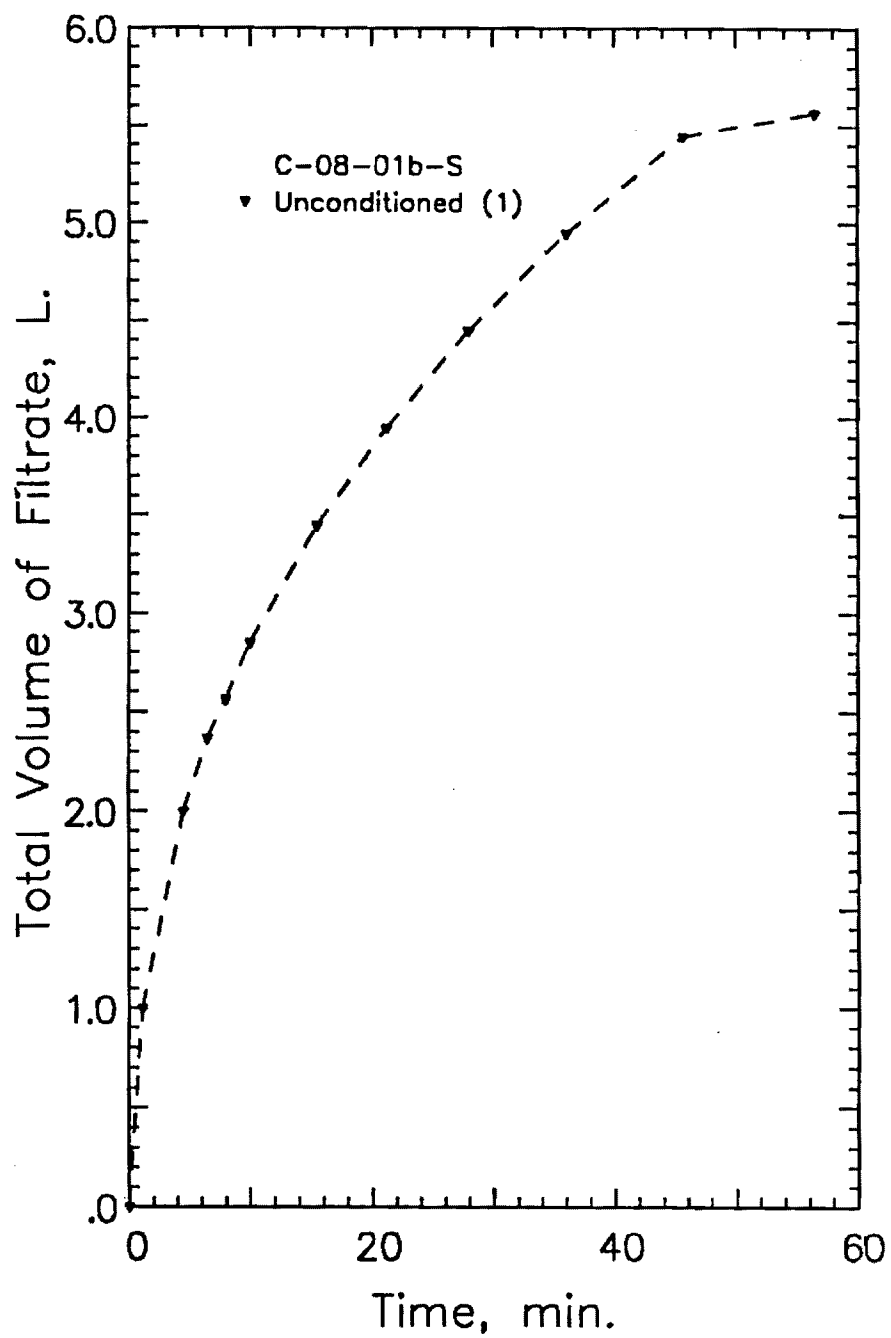


Figure 3.15. Cumulative Filtrate Volume for Unconditioned Sludge C-08-01b-S (Run 1).

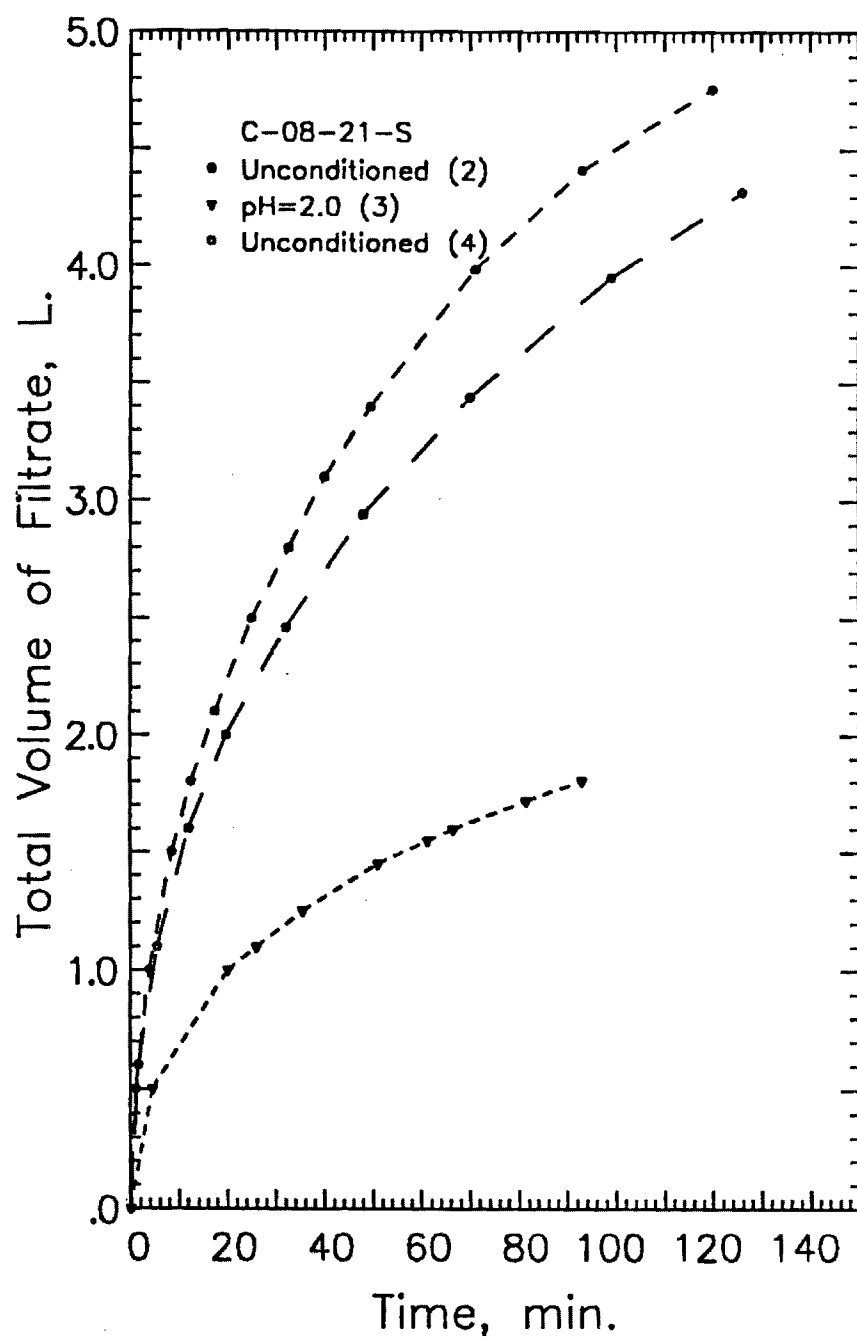


Figure 3.16. Cumulative Filtrate Volume for Unconditioned (Runs 2 and 4) and Acidified (Run 3) Samples of Sludge C-08-21-S.

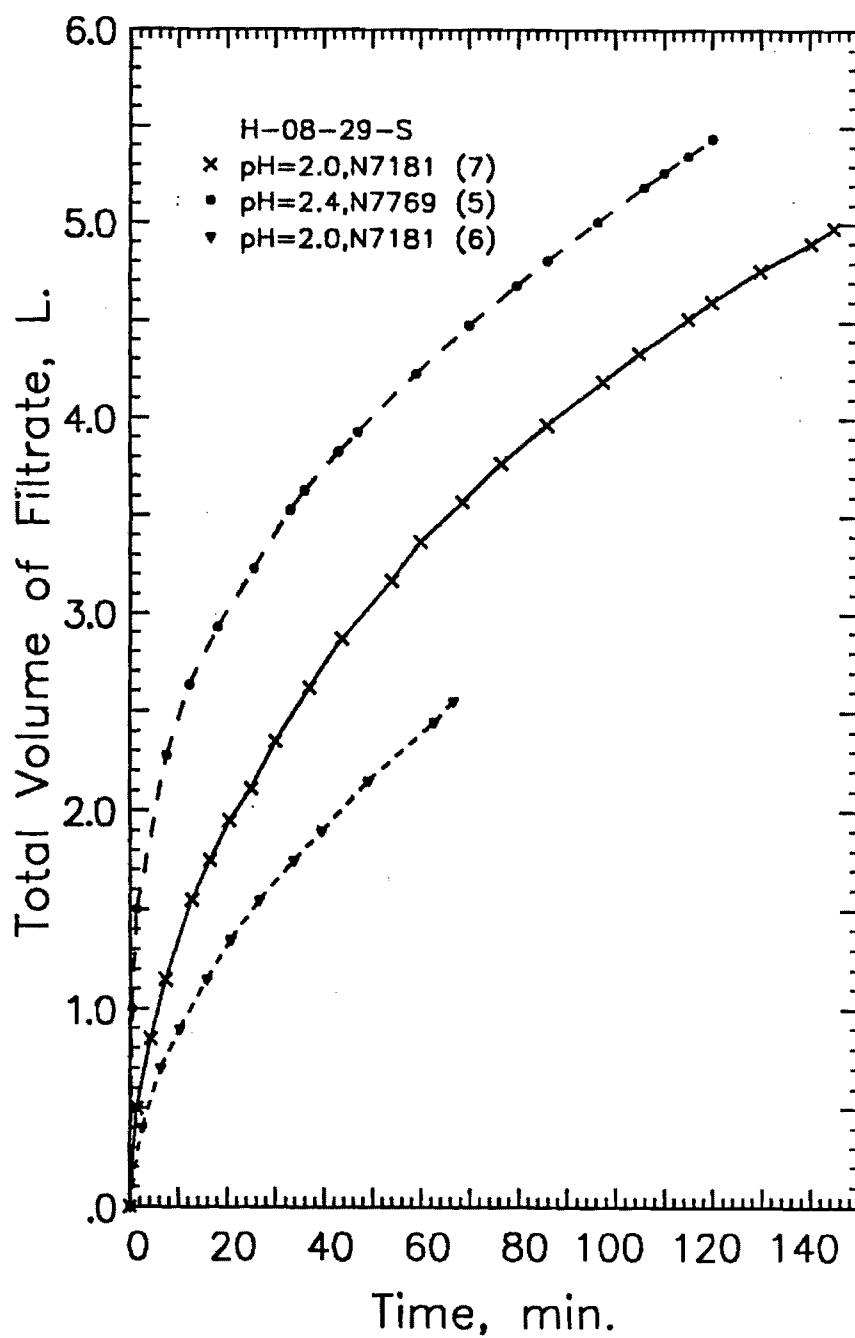


Figure 3.17. Cumulative Filtrate Volume for Polymer-Conditioned Samples of Sludge H-08-29-S (Runs 5-7).

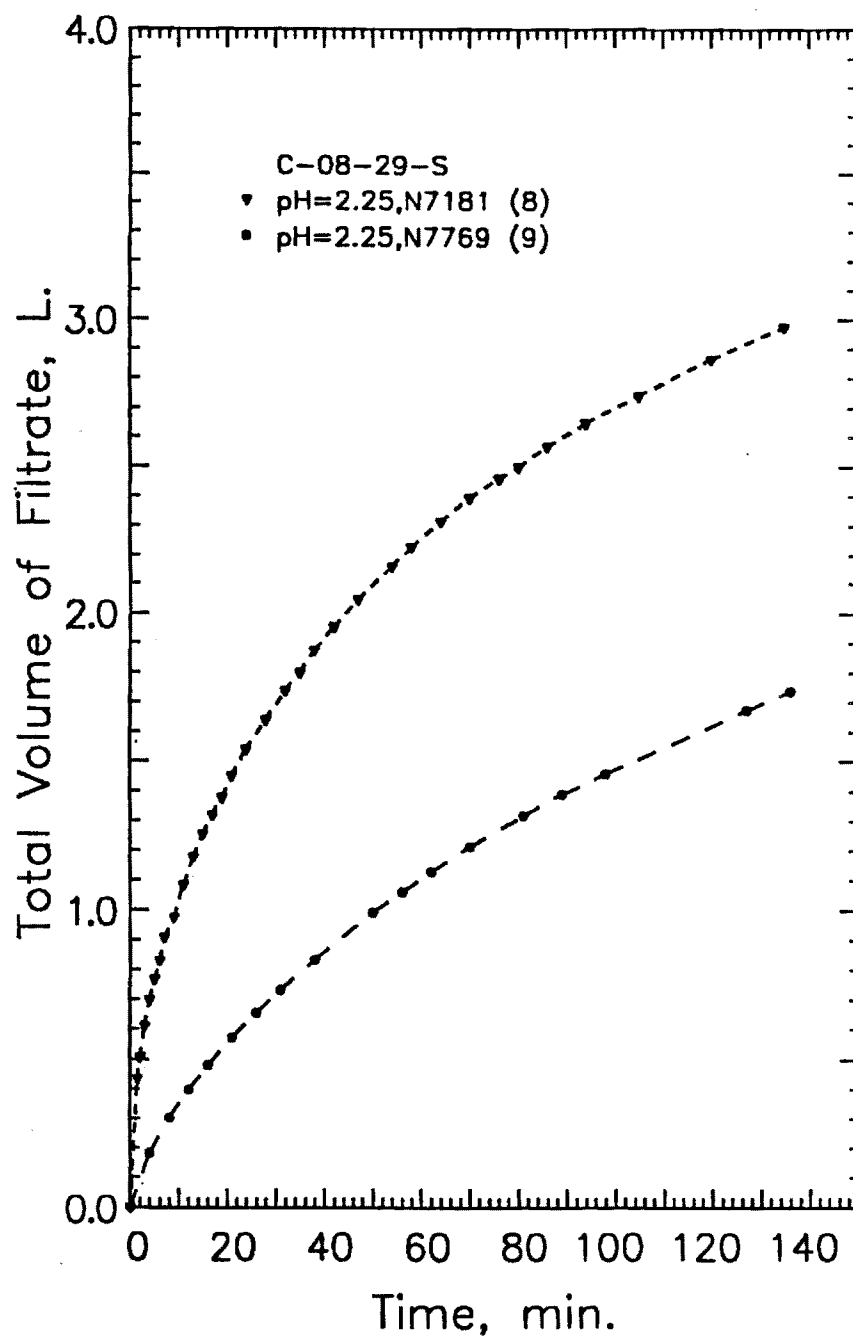


Figure 3.18. Cumulative Filtrate Volume for Polymer-Conditioned Samples of Acidified Sludge C-08-29-S (Runs 8 and 9).

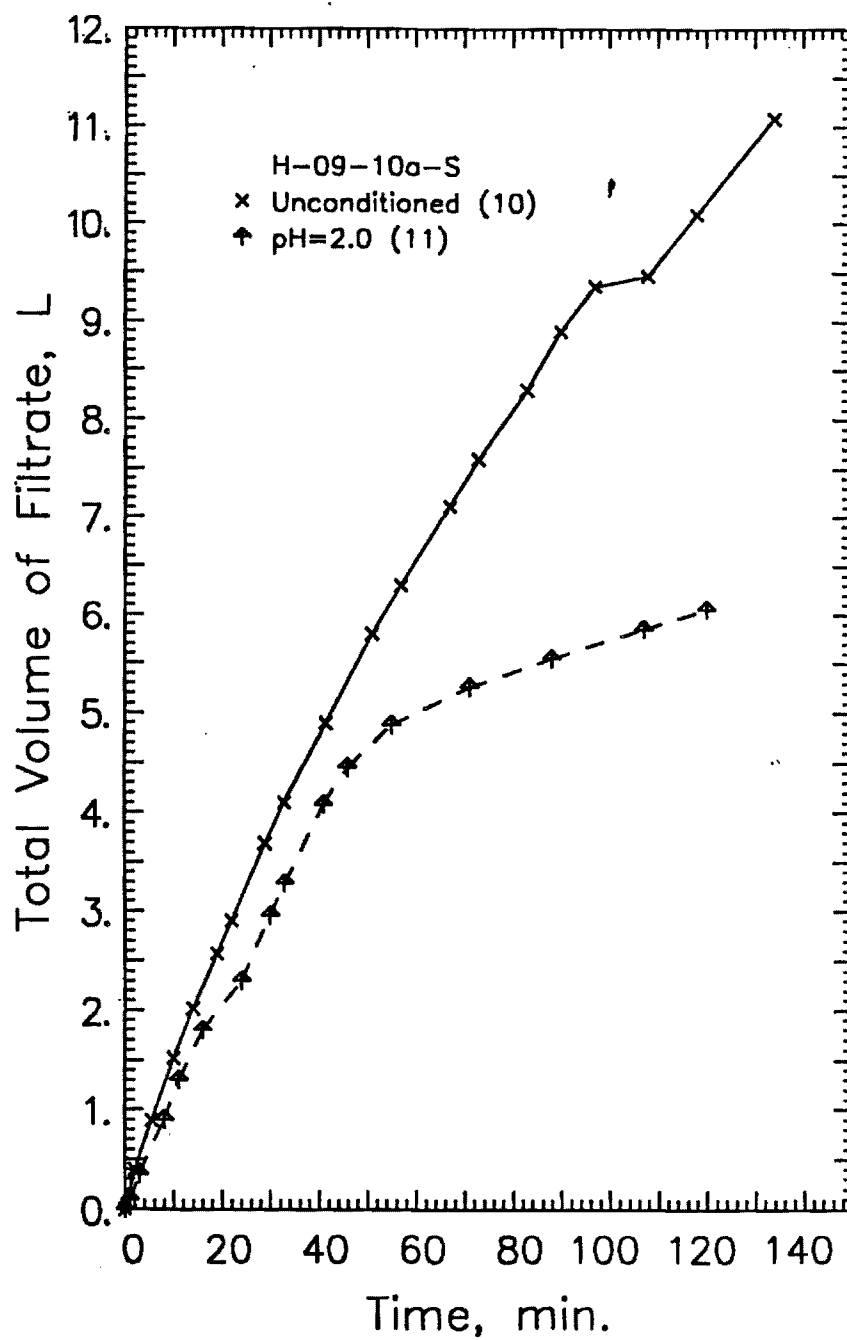


Figure 3.19. Cumulative Filtrate Volume of Unconditioned and Acidified Samples of Sludge H-09-10a-S (Runs 10 and 11).

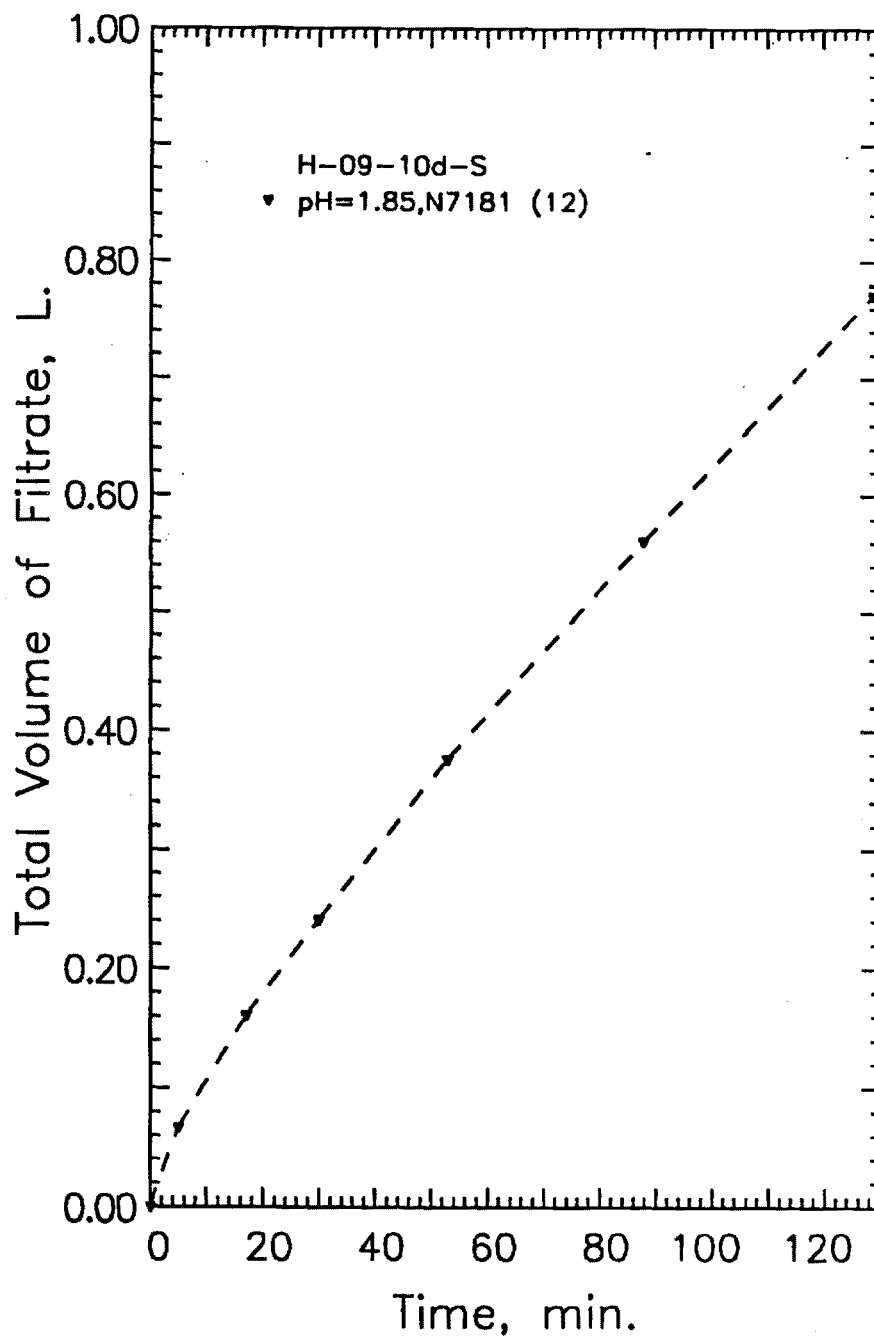


Figure 3.20. Cumulative Filtrate Volume for Acidified Sludge H-09-10d-S (Run 12).

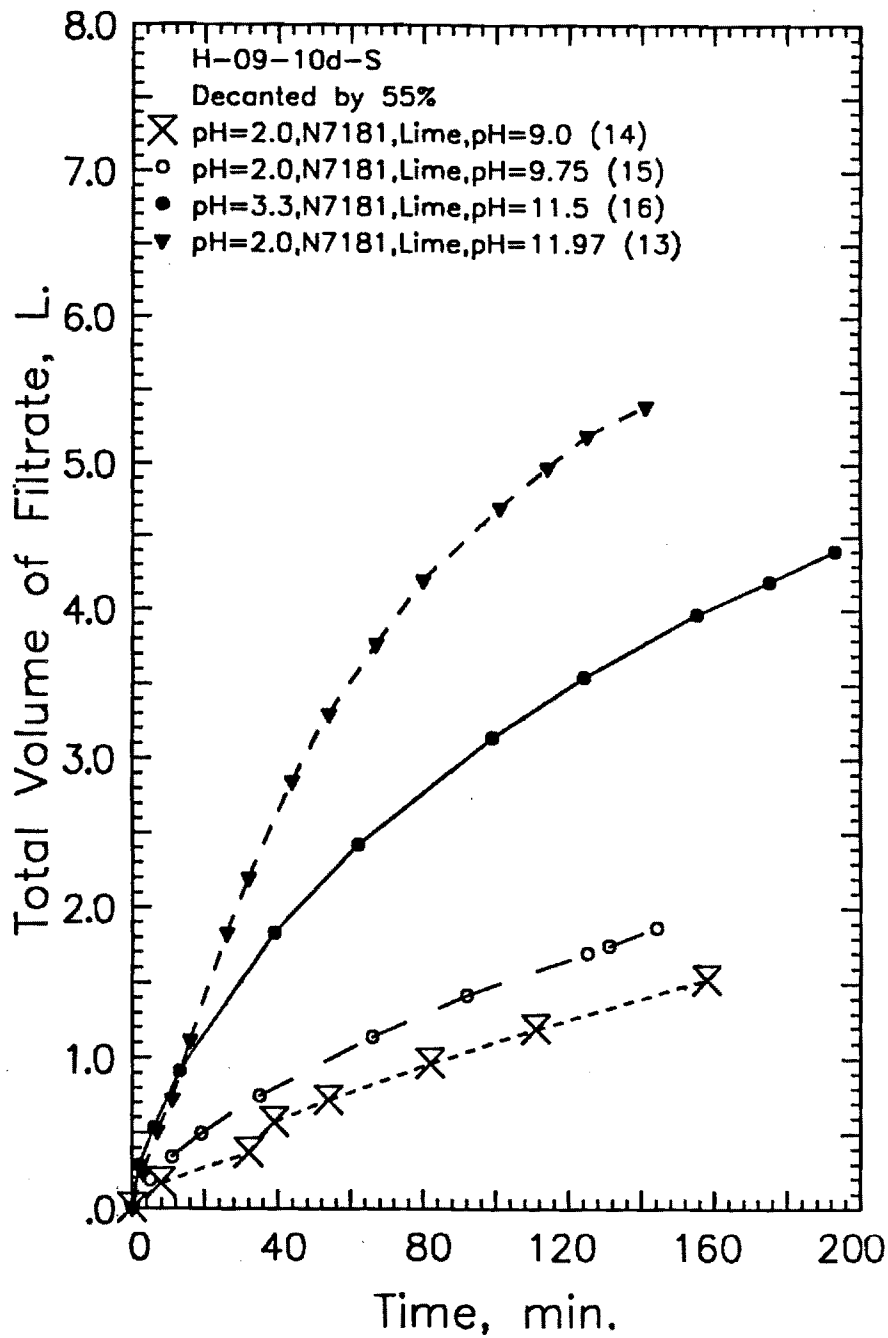


Figure 3.21. Cumulative Filtrate Volume for Sludge Sample H-09-10d-S Following Polymer-Conditioning, Decantation by 55 Percent, and Lime Conditioning to pH Values of 9-12 (Runs 13-16).

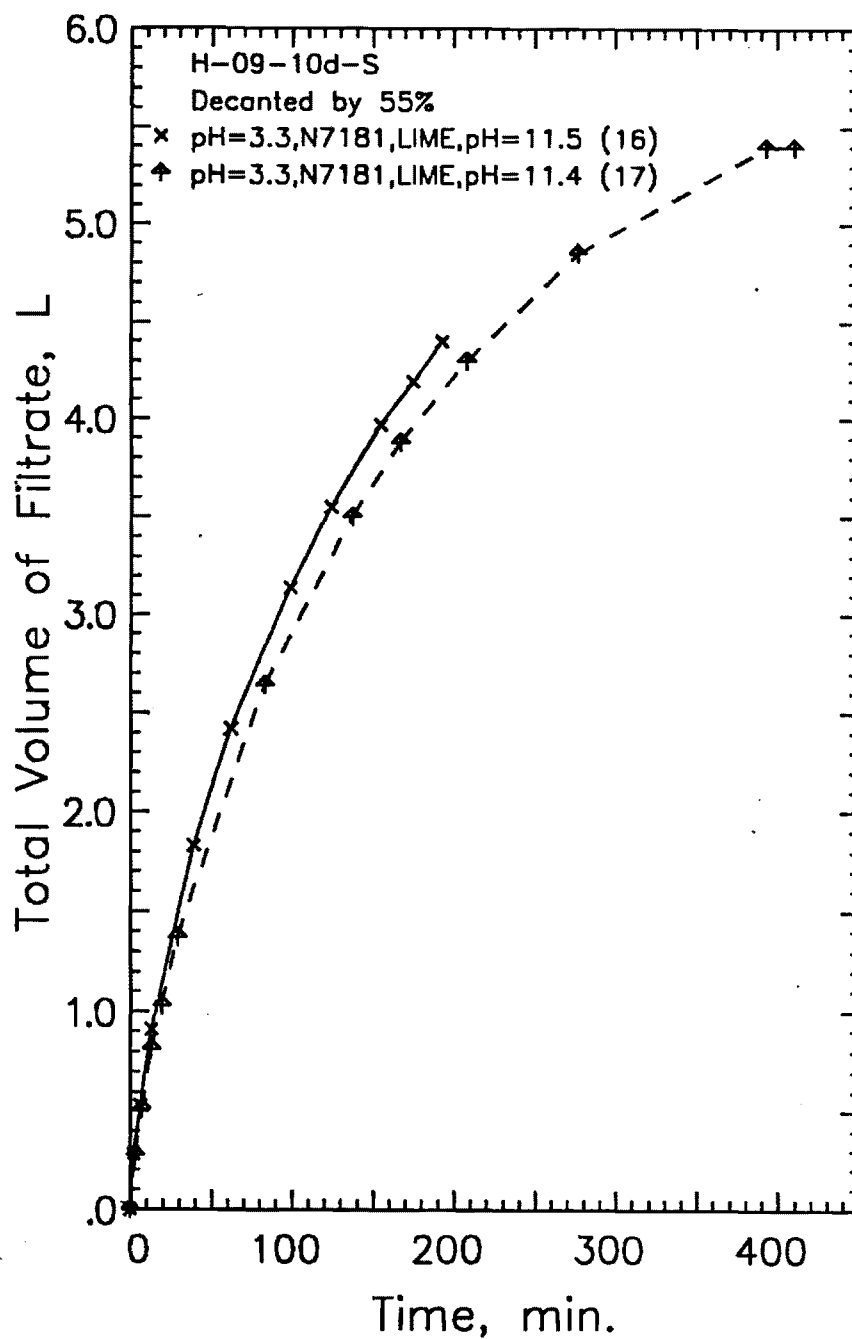


Figure 3.22. Cumulative Filtrate Volume for Sludge Sample H-09-10d-S Following Polymer-Conditioning, Decantation, and Lime Conditioning to pH 11.4-11.5 (Runs 16 and 17).

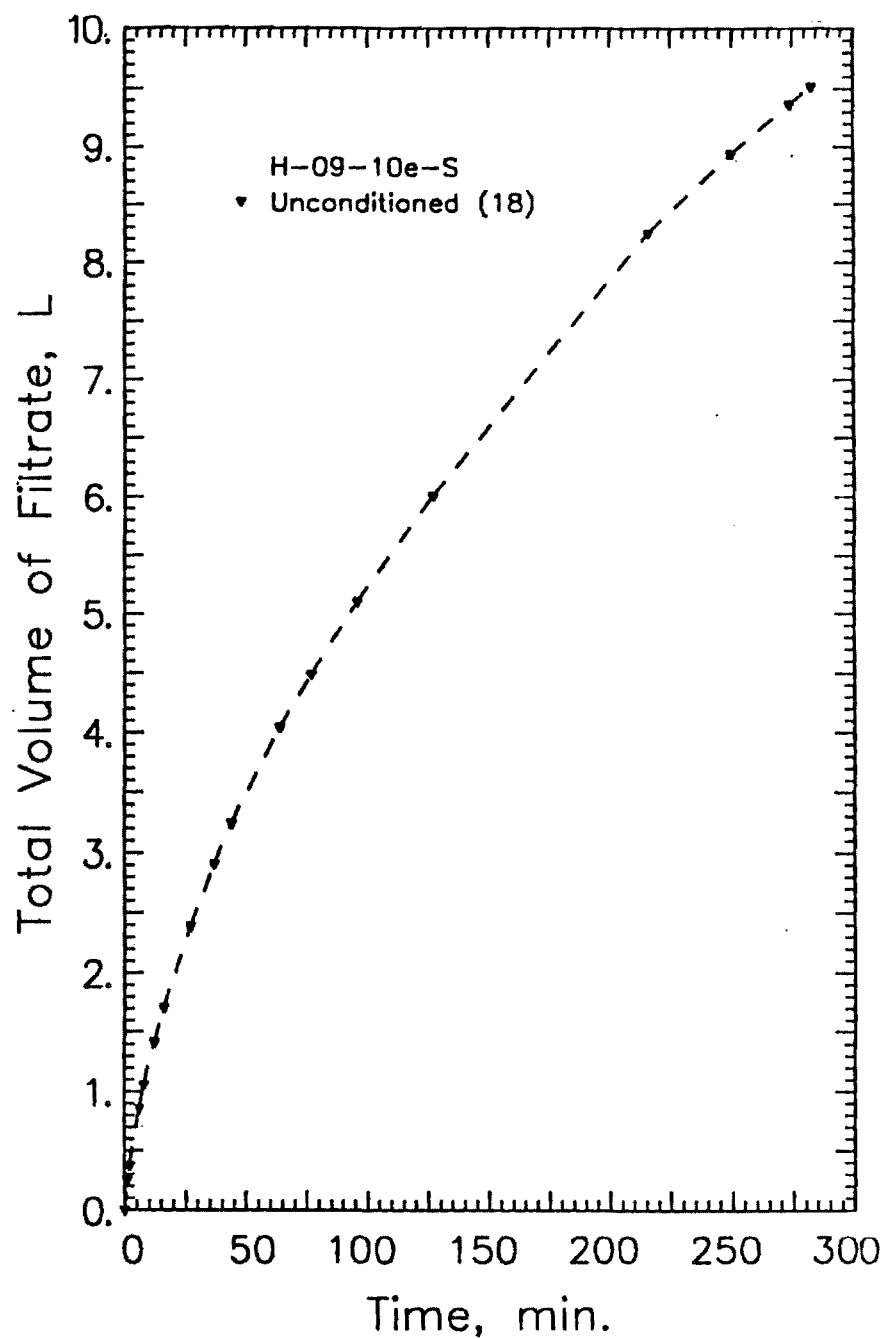


Figure 3.23. Cumulative Filtrate Volume for Unconditioned Sludge Sample H-09-10e-S (Run 18).

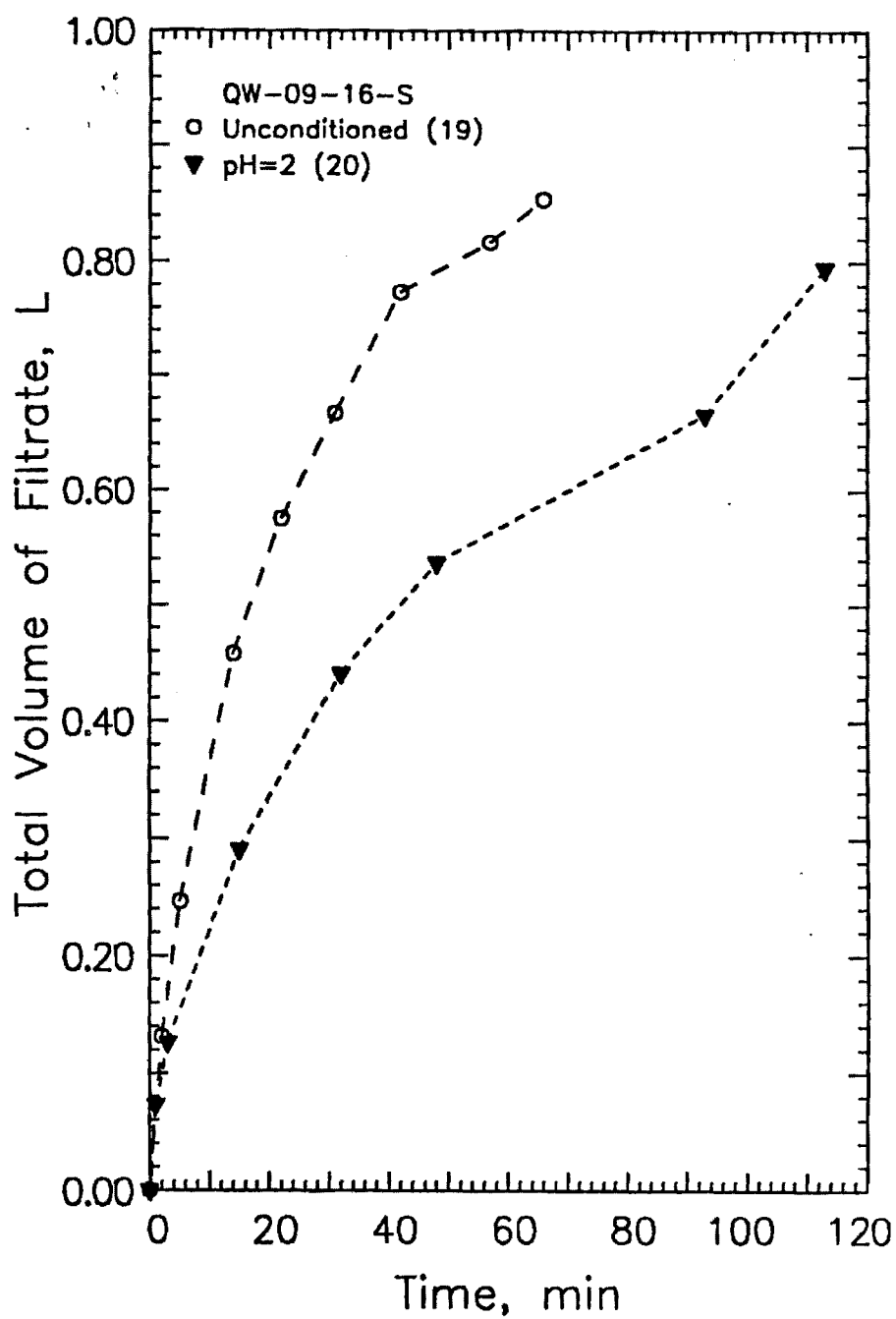


Figure 3.24. Cumulative Filtrate Volume for Unconditioned and Acidified Samples of Sludge QW-09-16-S (Runs 19 and 20).

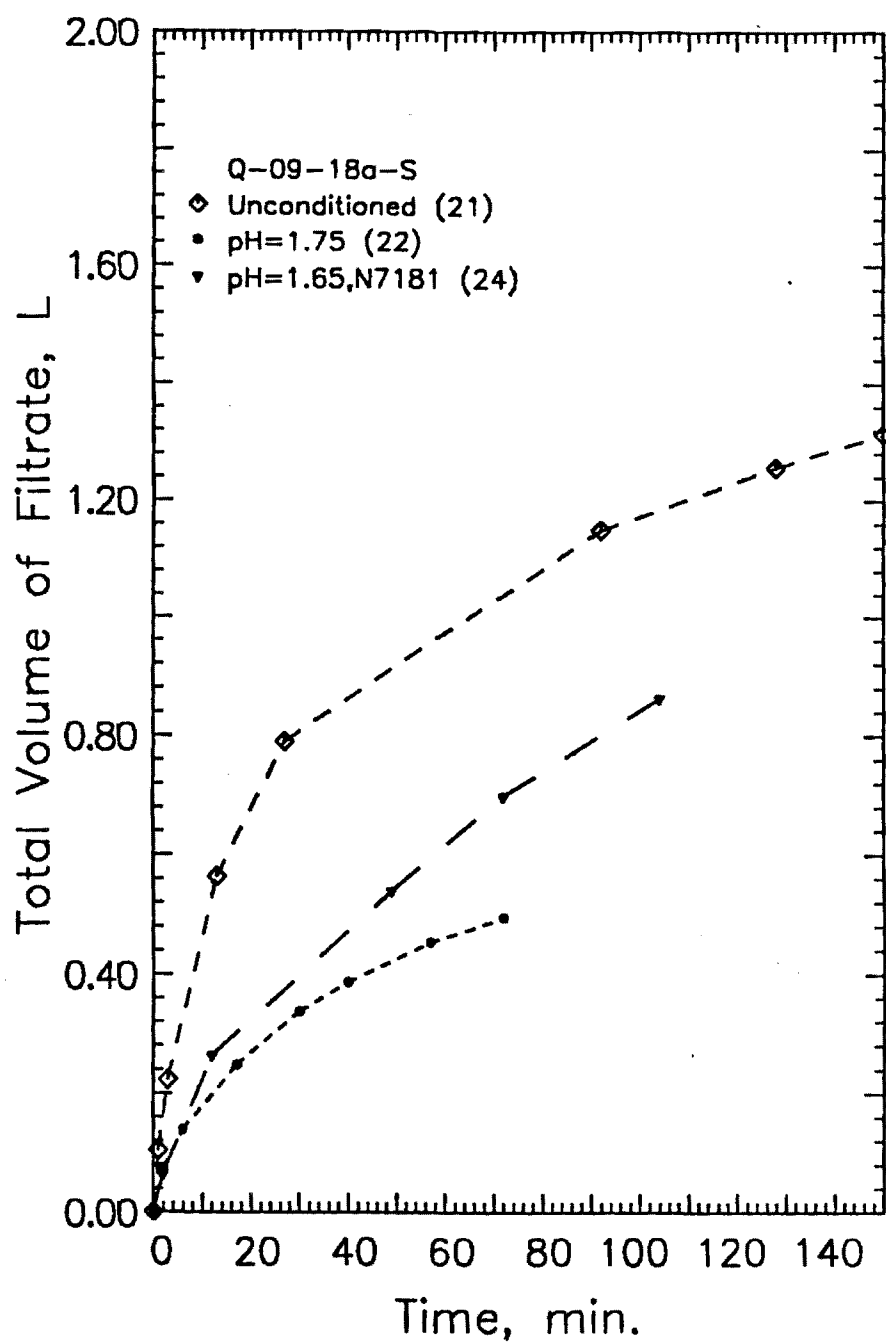


Figure 3.25. Cumulative Filtrate Volume for an Unconditioned and Two Acidified Samples of Sludge Sample Q-09-18a-S (Runs 21, 22 and 24).

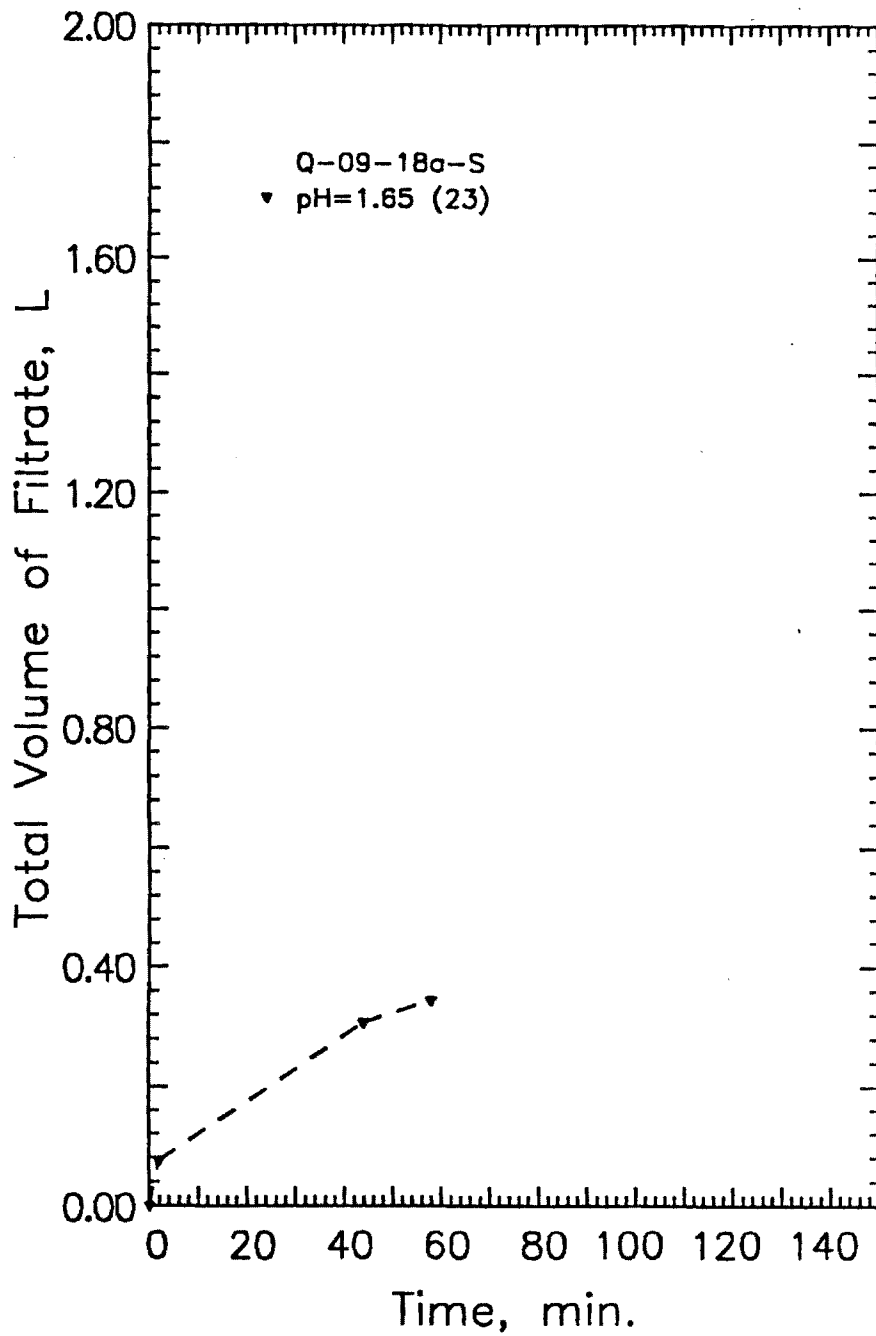


Figure 3.26. Cumulative Filtrate Volume for Acidified Sludge Sample Q-09-18a-S (Run 23).

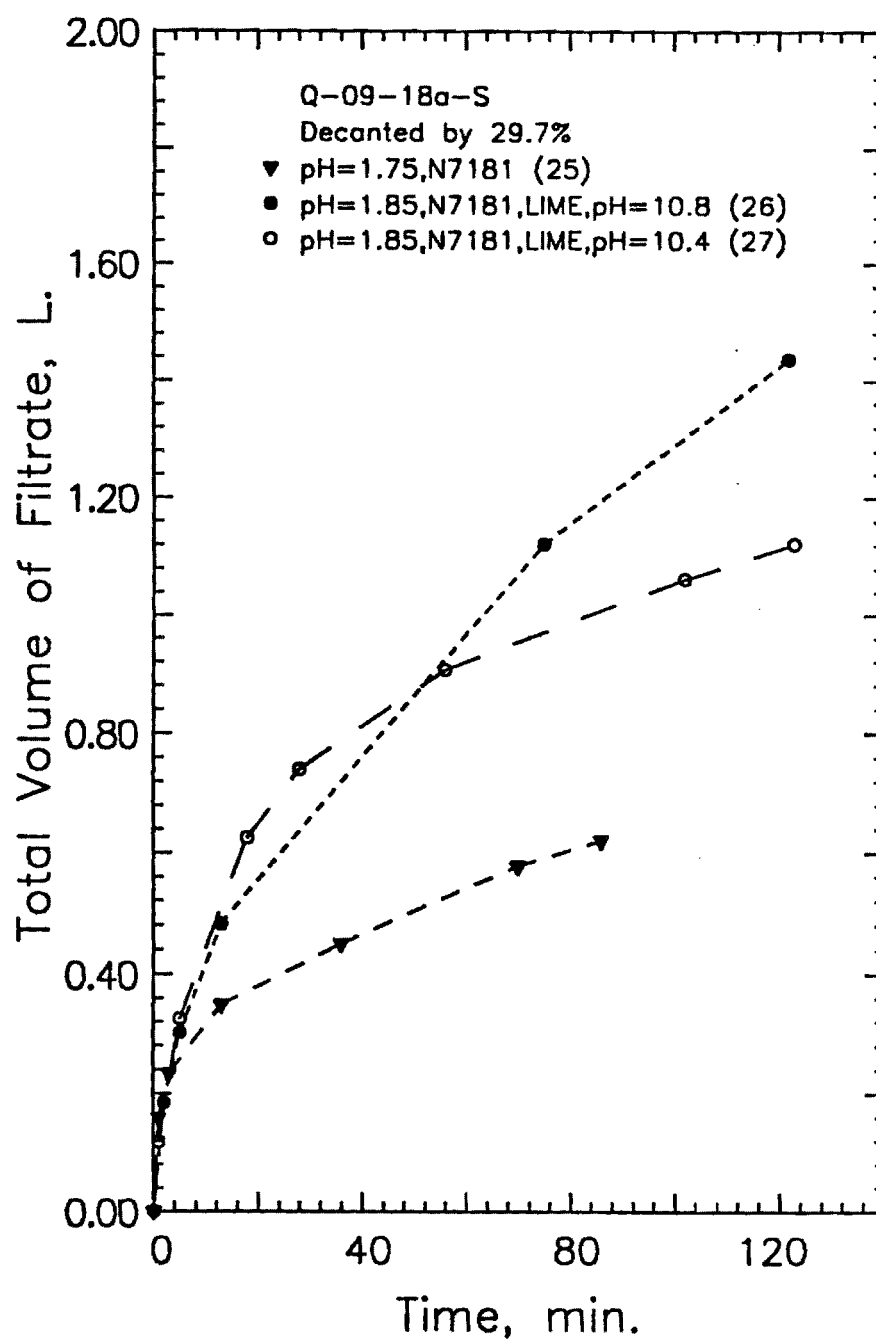


Figure 3.27. Cumulative Filtrate Volume of Acidified, Polymer-Conditioned Decanted Sludge Sample Q-09-18a-S with and without Lime Addition (Runs 25-27).

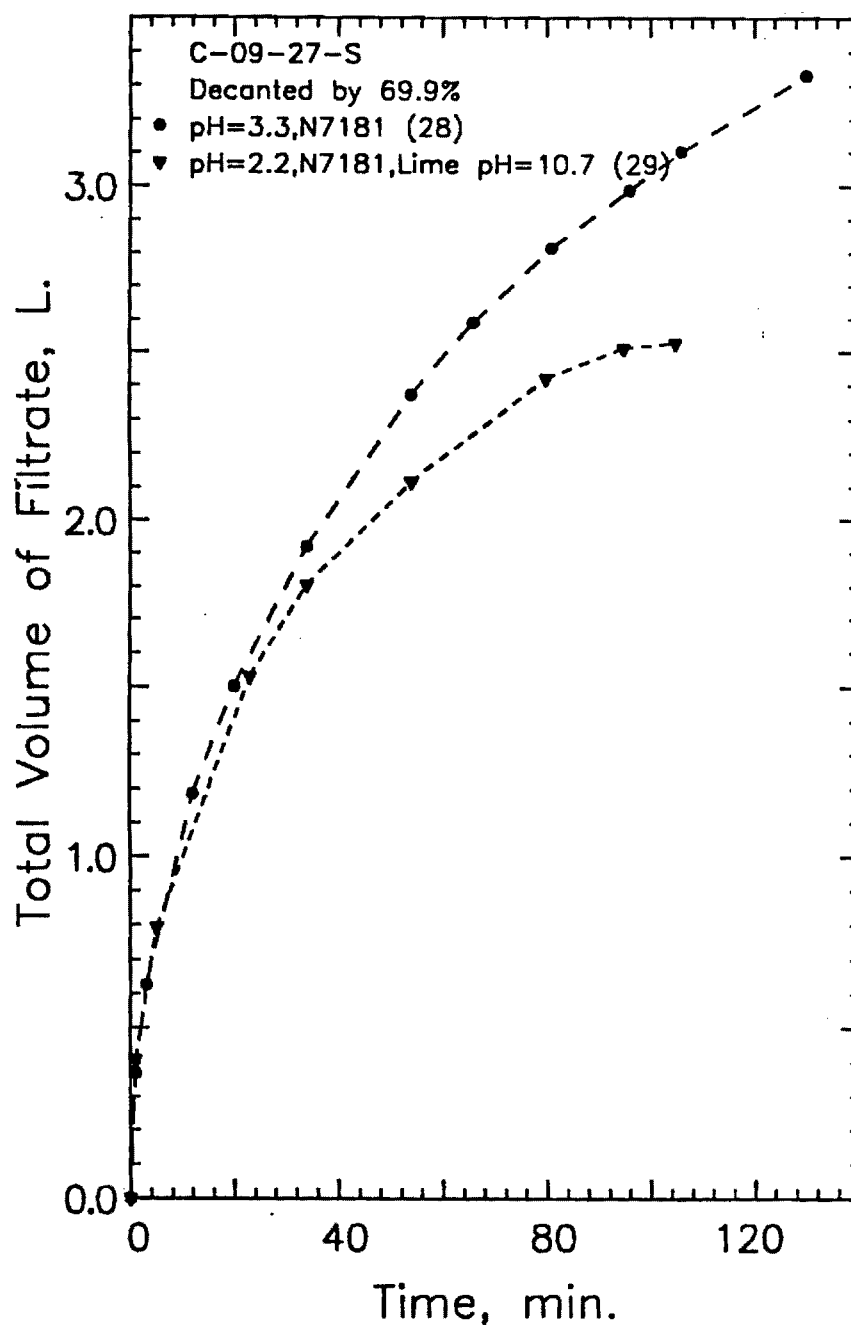


Figure 3.28. Cumulative Filtrate Volume for Acidified Sludge Sample C-09-27-S with and without Lime Conditioning (Runs 28 and 29).

application rate to achieve these pH values were 8.1-9.6 g/L or 0.34-0.41 g lime/g initial dry solids. In Figure 3.22, similar filtrate production rates are indicated for sludges at an initial pH of 3.3. Finally, data in Figure 3.27 indicate similar improvements for a Quarles suspension.

Characteristics of filtrates and dewatered cakes are presented in Table 3.19. Regarding cakes produced with unconditioned sludges at ambient pH values (runs 1, 2, 4 and 18), solids contents of dewatered cakes ranged from 36.3 to 53.3 percent for filtration times of 0.9 to 4.7 h and feed suspended solids concentrations of 37.3 to 177.7 g/L. Two runs (i.e., 10 and 21), however, resulted in cakes that were defined as slurries, due primarily to the fact that filtration times were short and feed solids concentrations were low.

With respect to effects of conditioning procedures, acidified sludges dewatered poorly, as noted previously, and none were filtered for a sufficient time to produce adequate cakes. Polymer conditioning of acidified sludges (i.e., runs 5, 7, 8 and 9) produced cakes with solids contents of 22 to 59.8 percent in filtration times of 2.0 - 2.4 h. Lime conditioning of polymer-conditioned, acidified sludges produced cakes with solids contents of 33 to 56 percent with filtration times of 1.8 to 6.8 n. Therefore, polymer conditioning or lime conditioning would both result in effective dewatering of acidified sludges produced following polymer conditioning and supernatant recovery.

Additional data included in Table 3.19 indicate that the aluminum solubilized by acidification (runs 5, 7, 9, 9, 11, 12, 22-25) could be recovered in the filtrate produced. In addition, it is also apparent that lime conditioning to pH values at and above 9.0 resulted in the retention of solubilized aluminum in the dewatered cake, since filtrate aluminum

TABLE 3.19. CHARACTERISTICS OF DEWATERED CAKE AND FILTRATE SAMPLES COLLECTED USING JWI PRESSURE FILTER

Run	Sample	Time of Filtration h	Dewatered Cake		pH	Filtrate				Solids Capture*** %
			% Solids	Description		Al ³⁺ mg/L	TOC mg/L	TDS g/L	SS mg/L	
1*	C-08-016-S	0.9	#1 39.1 #2 36.3	SOFT SOFT	5.88	-	-	-	-	-
2	C-08-21-S	2.0	#1 52.2 #2 53.3	FIRM FIRM	6.1	-	-	-	-	-
3	C-08-21-S	1.6	#1 (50.6)** #2 (48.4)**	SLURRY SLURRY	2.0	-	-	-	-	-
4	C-08-21-S	2.4	#1 46.4 #2 46.0	FIRM FIRM	6.1	-	-	-	-	-
5	H-08-29-S	2.0	#1 26.5 #2 42.7	SOFT SOFT	2.4	1838	895	19.9	100	99.9
6	H-08-29-S	1.2	#1+ #2+	SLURRY SLURRY	-	-	-	-	-	-
7	H-08-29-S	2.4	#1 22.0 #2 39.5	SLURRY SOFT	2.0	2483	930	24.7	100	99.9
8	C-08-29-S	2.3	#1 35.8	SOFT	2.25	1961	3	-	10	99.9
9*	C-08-29-S	2.3	#1 35.0 #2 36.0	SLURRY	2.25	2303	590	-	3	-
10	H-09-10a-S	2.0	+	SLURRY	-	-	-	-	-	-
11	H-09-10a-S	2.0	+	SLURRY	2.0	225	135	-	500	-
12	H-09-10d-S	2.2	+	SLURRY	1.91	276	285	7.9	3	99.9

Table 3.19 (Continued)

Run	Sample	Time of Filtration h	Dewatered Cake		pH	Filtrate				Solids Capture*** %
			% Solids	Description		Al ³⁺ mg/L	TOC mg/L	TDS g/L	SS mg/L	
13	H-09-10d-S	2.5	33.0	FIRM	11.97	18	50	4.7	25	99.9
14	H-09-10d-S	2.6	+	SLURRY	9.0	18	185	4.0	38	99.9
15	H-09-10d-S	2.4	37.8	FIRM	10.0	10	240	1.7	3	99.9
16	H-09-10d-S	3.2	33.5	FIRM	11.45	33	150	0.4	3	99.9
17	H-09-10d-S	6.8	38.0	FIRM	11.4	35	140	0.1	3	99.9
18	H-09-10e-S	4.7	39.0	FIRM	7.2	-	-	-	-	-
19	QW-09-16-S	1.1	+	SLURRY	-	-	-	-	-	-
20	QW-09-16-S	1.9	*	SLURRY	2.0	-	-	-	-	-
21	Q-09-18a-S	2.5	+	SLURRY	6.9	616	224	-	-	-
22	Q-09-18a-S	1.2	+	SLURRY	1.75	1138	415	-	-	-
13	Q-09-18a-S	1.0	+	SLURRY	1.75	1904	513	-	-	-
24	Q-09-18a-S	1.7	+	SLURRY	1.65	1962	505	-	-	-
25	Q-09-18a-S	1.4	+	SLURRY	1.85	2920	1330	-	-	-
26	Q-09-18a-S	2.0	+	SOFT	10.8	11	538	-	-	-
27	Q-09-18a-S	2.1	+	SLURRY	10.4	-	-	-	-	-

Table 3.19 (Continued)

Run	Sample	Time of Filtration h	Dewatered Cake		pH	Filtrate				Solids Capture*** %
			% Solids	Description		Al ³⁺ mg/L	TOC mg/L	TDS g/L	SS mg/L	
28	C-09-27-S	2.2	59.8	FIRM	3.3	-	-	-	-	-
29	C-09-27-S	1.8	56.0	FIRM	10.7	-	-	-	-	-

*Runs 1-9 were conducted with two chambers while runs 10-29 were conducted with one chamber.

**Solids analysis performed on thin cake-layer at wall of chamber and not indicative of solids content of total cake.

***Calculation based on SS concentration of unconditioned sludge.

[†]In general, those cakes described as "slurry" or "soft" were not handleable as a solid material and were not evaluated for solids content.

concentrations were 11-35 mg/L (see runs 13-17, and 26), as compared to 225 - 2,920 mg/L of aluminum for acidic filtrates (runs 5, 7, 8, 9, 11, 12, 22-25). Another significant result of acidification is an increase in total dissolved solids (TDS) of the filtrate. In runs 5, 7, and 12, the TDS of acidic filtrates ranged from 7.9 to 24.7 g/L, as compared to TDS of <100 mg/L for unacidified filtrates. This is the result of addition of acid which remains in solution and the solubilization of inorganic and organic constituents at a low pH. The impact would appear to be of no major significance relative to reuse of the recovered coagulant and have no major impact on the dewatering process. Finally, the addition of lime to acidified sludges resulted in reduction of filtrate TDS. For example, data for runs 12-17 indicate that without lime addition TDS was 9.4 g/L and that with lime addition to a pH range of 9-12, TDS decreased to values of 0.07-4.8 g/L in the feed and 0.1-4.7 g/L in the filtrate. Data for runs 25 and 26 in Table 3.20 indicate that a 90 percent reduction in TDS was achieved when pH was adjusted for 1.75 to 10.8 using a lime dose of 28.5 g/L.

In summary, the data in Figures 3.15 to 3.28 and Tables 3.18 and 3.19 indicate that acidified sludges can be effectively conditioned for mechanical dewatering systems with polymers and with lime, making sludge disposal following acidification an easily achieved task. With polymer conditioning, in addition, aluminum recovery in the filtrate is possible and the volume of sludge produced is minimized.

4. PROCESS DESIGN CONSIDERATIONS FOR ALUMINUM RECOVERY AT THE NORTH AREA PLANT

The North Area water treatment plant for the City of Atlanta and Fulton County was to include an assessment of aluminum recovery in the preliminary design procedures. The experimental data presented herein were focused on key issues of contaminant levels in recovered coagulants and the feasibility of coagulant recovery. The analysis presented below for coagulant recovery was based on design data developed for the design of a conventional, run-of-the-river, water treatment plant by Williams-Russell-Johnson, Inc. and Jordon, Jones and Goulding, Inc.: A Joint Venture and referred to herein as the design engineers.

Three cases were used in the assesement of sludge handling and treatment options, including low-, medium- and high-turbidity conditions, or cases I, II and III, respectively, for raw waters to be supplied from the Chattahoochee River.

Design of the aluminum recovery portion of the North Area plant is to be based on a flow of $1.3 \text{ m}^3/\text{s}$, or 30 mgd, with a maximum flow of $2.0 \text{ m}^3/\text{s}$, or 45 mgd over a 24-hour period. The dry-solids loading specified for use is based on medium-turbidity conditions of 20 mg/L or $166 \text{ lb}/10^6 \text{ gal}$. This estimate was based on an influent suspended solids concentration of 13 mg/L and an aluminum hydroxide concentration of 7 mg/L, resulting in a sludge with an estimated aluminum content of 12.1 percent, based on coagulant aluminum only. For low- and high-turbidity conditions, the estimated aluminum contents of sludges are 19.8 and 4.5 percent, respectively.

Experimental data collected for four sludge samples, ranging in suspended solids concentration from 8.67 to 104.19 g/L and presented in Table 4.1, indicated that aluminum content varied from 4.7 to 10.2 percent.

TABLE 4.1. TOTAL ALUMINUM CONTENT OF ALUM SLUDGES FROM CHATTAHOOCHEE RIVER PLANTS AND BASED ON STRONG ACID DIGESTION OF SLUDGE SOLIDS

Sludge Sample	Suspended Solids Concentration g/L	Percent Aluminum %
<u>Low Solids Concentration</u>		
H-07-22-S.....	8.67	10.2
D-08-01-S.....	10.85	7.7
<u>High Solids Concentration</u>		
Q-08-01-S.....	97.4	5.3
C-07-22-S.....	104.19	4.7

In general, low aluminum content values were associated with high suspended solids concentrations and vice-versa. This is in keeping with a lower coagulant dose, relative to suspended solids concentration, for a high turbidity load on a plant, resulting in a lower percentage of aluminum in the sludge. Therefore, the design value for aluminum content of 12.1 percent was a reasonable value.

The concentration of the thickened sludge to be pumped to the sludge treatment facility was estimated by the design engineers to vary from 4 to 8 percent. These values are for sludges obtained from a thickener underlying Lamella settling units following the coagulation-flocculation basins. In examination of suspended solids data for thickened sludge samples in the aluminum recovery research project, the concentrations of thickened sludges ranged from 5.1 to 23.6 percent and averaged in excess of 12 percent, as presented in Table 4.2. The data for unthickened sludges in Table 4.2 are for dilute sludges collected from sedimentation basins operated with no specific intent to thicken sludge and had concentrations of 0.9 to 2.4 percent. From comparison of the design values of 4 to 8 percent solids to the data in Table 4.2, it is apparent that the design values may be conservative, but are reasonable because of the projected impact of the extended detention-time period in the presedimentation basin and the resulting reduction in influent turbidity and increased solids detention in the sedimentation basin.

The mass and volume of thickened sludge to be treated at the medium-turbidity design condition are presented in Table 4.3. These values represent the quantities of sludge to be pumped from Lamella settlers to a separate sludge treatment facility on a 5 day/week basis. These values are to be used in the evaluation of an aluminum recovery system for the North Area plant.

TABLE 4.2. SUSPENDED SOLIDS CONCENTRATION OF SLUDGE SAMPLES
FROM FOUR ATLANTA-AREA WATER TREATMENT PLANTS

Sample	Suspended Solids Concentration Percent
<u>THICKENED SLUDGES</u>	
<u>CHATTAHOOCHEE</u>	
C-07-19-S.....	17.9
C-07-22-S.....	10.4
C-08-01a-S.....	14.3
C-08-01b-S.....	7.8
C-08-21-S.....	17.2
C-08-29-S.....	23.6
C-09-27-S.....	5.1
<u>QUARLES</u>	
Q-08-01-S.....	9.7
Q-09-18-S.....	10.4
<u>HEMPHILL</u>	
H-08-29-S.....	12.3
<u>UNTHICKENED SLUDGES</u>	
<u>CANDLER</u>	
D-08-01-S.....	1.1
<u>HEMPHILL</u>	
H-07-22-S.....	0.9
H-09-10d-S.....	2.4

TABLE 4.3. PROJECTED SLUDGE MASS AND VOLUME LOADING
FOR DESIGN CONDITION BASED ON A 5-DAY/WEEK
OPERATIONAL CYCLE

Flow	Sludge Mass <u>lb/d</u>	Sludge Volumetric Flow gpd	
		<u>4% solids</u>	<u>8% solids</u>
Average Flow - 30 mgd.....	7,000	21,000	10,500
Maximum 24-h Flow - 45 mgd...	10,460	31,360	15,680

Note: 1 mgd = 0.0438 m³/s; 1 lb/d = 0.454 kg/d; 10,000 gpd = 37.85 m³/d

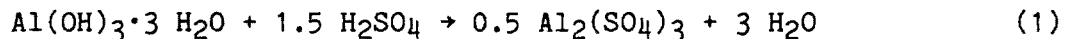
ALUMINUM RECOVERY

Recovery of aluminum contained in the aluminum-hydroxide portion of alum sludge is to be accomplished by sludge acidification with sulfuric acid to solubilize aluminum; polymer-aided, gravity sedimentation to separate an aluminum-rich supernatant liquid from residual sludge solids; reuse of supernatant as a coagulant; and dewatering of residual sludge solids. Each of these steps are presented below under the topics of acidification, sedimentation and dewatering.

Acidification

Sulfuric Acid Requirement

The quantity of sulfuric acid required to extract aluminum from sludge solids is dependant on the amount of aluminum-hydroxide and other reactive solids in the suspension and the characteristics of the solution in which the solids are suspended. In consideration of the aluminum-hydroxide solids alone, the extraction reaction can be represented as:



Based on this equation, the stoichiometric acid requirement is 5.44 lb H_2SO_4 /lb Al.

Data from a comprehensive examination of four sludge samples indicated that acid requirements ranged from 2.27 to 15.95 lb H_2SO_4 /lb Al and that the portion of total aluminum extracted from the four sludges in a 40-min. period ranged from 18 to 64 percent. These efficiency values were relatively low since they were based on total aluminum in the sludge solids, not just that contained in aluminum-hydroxide solids, and since the extraction was carried out over a short time period.

To estimate the acid requirement based on sludge-aluminum content, the stoichiometric and experimental values were used in conjunction with the

estimated aluminum mass flow associated with the sludge, i.e., 847 lb Al/d, or a suspended solids loading of 7000 lb/d at 12.1 percent aluminum. These, and all subsequent, acid requirements, are expressed in terms of 66°Be sulfuric acid, which is 93.2 percent H_2SO_4 with a specific gravity of 1.84 (15.3 lb/gal). The estimated volumes of acid required are presented in Table 4.4 and are 325 gal/d and 135-947 gal/d for the stoichiometric and experimental values, respectively.

Additional data relative to acid requirements were collected during experimental studies of aluminum recovery. These data were for studies in which sludge pH was lowered with sulfuric acid to values between 1.0 and 2.2 and aluminum was recovered by sedimentation or filtration. During these studies, total sludge aluminum was not determined and therefore acid doses were based on a unit solids loading. In that the sludges examined apparently had less than 12.1 percent aluminum, as presented in Table 4.1, experimentally-determined acid requirements based on dry solids will tend to be lower than those based on aluminum content. In addition, acid addition to sludges results in an immediate pH depression followed by a dynamic period in which pH values increase due to the dissolution of aluminum and the resulting neutralization of acid. The acid-addition results from the experimental studies have been summarized in terms of the extent to which sludge pH was decreased, i.e., $\text{pH} \approx 1$ and $\text{pH} \approx 2$, at the end of the initial 5-minute period following acidification and are presented in Table 4.5. It is apparent that there was considerable variation between the three sludges, with a three-fold difference between the extremes in each case. This could, in part, be attributed to differences in aluminum content between the various sludges and variations in other acid-consuming components. In addition, initial depression of pH to a value of

TABLE 4.4. ESTIMATED SULFURIC ACID (66°Be) REQUIREMENT BASED
ON SLUDGE ALUMINUM CONTENT FOR 7000 lb/d (5 d/week)
OF DRY SLUDGE SOLIDS

Description	Sulfuric Acid - 66°Be	
	lb/d	gal/d
Stoichiometric.....	4,945	325
Experimental		
2.27 lb H ₂ SO ₄ /lb Al.....	2,063	135
15.95 lb H ₂ SO ₄ /lb Al.....	14,500	947

TABLE 4.5. AVERAGE SULFURIC ACID DOSES FOR EXPERIMENTAL EXTRACTION
OF CHATTAHOOCHEE RIVER SLUDGES

Sludge Source	Sulfuric Acid	
	lb H ₂ SO ₄ /lb dry solids	
	pH \approx 2	pH \approx 1
Chattahoochee.....	0.08	0.19
Hemphill.....	0.24	0.65
Quarles.....	0.21	0.3

approximately 1 required from 0.5 to 2.7 times more acid than for pH of approximately 2. In examination of the acid requirements which ranged from 0.08 to 0.65 lb H_2SO_4 /lb dry solids, Westerhoff and Daly (1974) presented a value of 0.39 lb H_2SO_4 /lb dry solids for a Fulton-process design for aluminum recovery. Westerhoff and Cornwell (1978) presented values of 0.6 to 0.7 lb H_2SO_4 /lb dry solids to reduce sludge pH to approximately 2 for an alternative aluminum recovery system. Therefore, data presented in Table 4.5 for pH \approx 1 appear to be reasonable for use in a conservative approach to design. Based on data for pH \approx 1 in Table 4.5, sulfuric acid volume requirements presented in Table 4.6 ranged from 93 to 320 gal/d, which were essentially equal to or less than that presented earlier in Table 4.4 based on a stoichiometric basis.

In summary, the volumes of sulfuric acid required to acidify 7000 lb/d of sludge containing 12.1 percent aluminum were estimated. On the basis of aluminum content, the daily volumes required were 325 gal/d (stoichiometric) and 135-947 gal/d (experimental: minimum-maximum). Based on solids content, the daily volumes were estimated to be 93, 148 and 320 gal/d. Due to the uncertain nature of the estimates for sludge aluminum content and total sludge quantity and since all but one experimental estimate were equal to or less than the stoichiometric estimate, the acid requirement is to be based on the stoichiometric value, i.e., 325 gal/d. The annual chemical cost for 66°Be sulfuric acid is estimated to be \$46,500 (\$72/ton). In addition, based on a need for a 45-day supply of acid, a storage tank with a volume of 10,000 gal is recommended. The tank is to be constructed of carbon steel with schedule 80 steel piping. Since the freezing point for 66°Be sulfuric acid is -26°F, the storage tank can be located external to the sludge treatment building.

TABLE 4.6. ESTIMATED SULFURIC ACID (66°Be) REQUIRED FOR RECOVERY
OF ALUMINUM FOR 7000 lb/d OF DRY SLUDGE SOLIDS

<u>Experimental Design Basis</u>	<u>Sulfuric Acid - 66°Be</u>	
	<u>lb/d</u>	<u>gal/d</u>
Chattahoochee.....	1,430	93
Hemphill.....	4,880	320
Quarles.....	2,253	148

Acidification-Reactor System

The system for aluminum recovery must be compatible with the proposed design for a traditional lime-treatment scheme. This system includes two 15,000-gal conditioning tanks for lime conditioning of thickened sludge, followed by a high-pressure filtration system for dewatering. The aluminum recovery system must be integrated into the proposed system to the maximum extent possible.

In the current scheme, thickened sludge is to be pumped once daily on a five-day schedule to the sludge treatment facility. Therefore, the average daily flow of sludge will contain 7000 lb/d of dry solids in volumes of 21,000 gal and 10,500 gal for 4 percent and 8 percent solids, respectively. At 4 percent solids, both 15,000-gal conditioning tanks will be required to treat the total sludge volume. To alleviate this problem the tank volumes must be increased to 25,000 gal/each or a minimum sludge solids concentration of 5.6 percent solids must be required. For purpose of this analysis it will be assumed that the two tanks will be provided with sufficient total volume to accommodate the flow for a two-day period, i.e., one tank will hold the total sludge volume from any one day. For acidification of the sludge, acid is to be added to the sludge contained in one of the conditioned tanks. Intensive mixing energy should be provided to meet a G value of approximately 300 s^{-1} or higher. This requirement should be met with an applied power input of $5 \text{ HP}/10^3 \text{ ft}^3$, or 75 HP for a 15,000-gal tank. The mixer should be a variable-speed system to allow for downward adjustment in the event foaming or frothing problems are created. The time-period for the extraction reaction should be a minimum of 2 hours during which time the acidified suspension is to be mixed. At the end of the 2-hour period, and presumably prior to the end of an 8-hour shift, the sludge suspension is to be polymer conditioned for gravity clarification.

Sedimentation

Separation of the unreacted sludge solids and the aluminum-rich extract will be performed on a batch basis in one of the two conditioning tanks following polymer conditioning. Polymer conditioning will be performed using a non-ionic polymer, in combination with a cationic polymer, both to be applied in liquid form. Polymer conditioning studies indicate that application rates of approximately 0.2 to 1.2 gal/ton of dry solids are required. At a solids loading of 7000 lb/d, the polymer requirement is estimated to be 0.7 to 4.2 gal/d. Two polymer blending and aging systems are recommended for application of two polymers. These systems should contain tanks with volumes of 400 gal/each to allow for daily dilution and aging of the polymers. Two polymer metering pumps with flow indicators should be included in the polymer application system. Alternatively, two compact polymer blending systems should be installed to minimize space requirements and manual preparation of polymer solutions.

Following polymer conditioning of the sludge, a minimum period of 2-h is to be provided to allow for clarification of the aluminum extract solution and thickening of the residual sludge solids. Through the use of two conditioning tanks, however, the batch sedimentation process could be allowed to proceed overnight to assume maximum clarification and thickening.

Following gravity sedimentation, the clarified aluminum extract must be decanted to a storage tank for use in the coagulation process and the sludge must be withdrawn from the first conditioning tank into the second conditioning tank, if it was not previously discharged therein. The quantities of sludge and extract are to be estimated based on the use of 7000 lb/d of dry sludge solids, containing 847 lb/d of aluminum. It is assumed that 90 percent of the aluminum in aluminum-hydroxide precipitates

is solubilized upon acidification and that 70 percent of the acidified suspension can be withdrawn as a clarified solution for reuse. Therefore, on a mass basis, the residual sludge will contain 4795 lb/d of dry sludge solids and 229 lb/d of soluble aluminum and the recovered coagulant will contain 534 lb/d of soluble aluminum. The percent recovery of aluminum is then 63 percent ($534/847$) which can be increased to near 90 percent if the soluble aluminum in the residual sludge can be recovered.

Assuming the initial solids concentration of the thickened sludge prior to acidification is 8 percent, and that sludge volume does not change upon acidification, the residual sludge after conditioning and thickening is contained in a volume of 3150 gal/d at a concentration of approximately 18.3 percent. The volume of the recovered coagulant is 7350 gal with an aluminum concentration of 8.7 g/L. For an initial sludge concentration of 4 percent, the following data apply: residual sludge = 6300 gal/d at 9.1 percent; recovered coagulant = 14,700 gal/d at 4.4 g Al/L.

To facilitate the management of the recovered coagulant solution, a multiple-level decant system and pump must be added to the conditioning tanks to recover and transport the recovered coagulant. Based on a projected need to maintain at least a minimum of a 3-day supply (i.e., $605 \text{ lb/d} \times 3 \text{ d} = 1815 \text{ lb Al}$) of coagulant for use in the coagulation process, tank volumes of 25,000 gal and 50,200 gal are required, respectively, for initial sludge concentrations of 8 and 4 percent. These tank volumes are equivalent to a 3.4-day supply of recovered coagulant from the sludge treatment facility. In addition, since the recovered coagulant is much more dilute than commercial-strength alum, the coagulant feed system must be capable of administering a higher volumetric flow rate of product, i.e., approximately 6-12 gal/min.

Dewatering

The estimated quantity of sludge remaining after decanting the recovered coagulant solution is 3150-4500 gal/d (5 d/week) with a dry solids loading of 4795 lb/d (5 d/week). The daily volume of sludge is 30 percent of the base design condition (i.e., 10,500 - 21,000 gal/d) and the dry solids loading is 68.5 percent of the base design condition (i.e., 7,000 lb/d). Treatment of the residual sludge is to be accomplished using lime conditioning.

Application of lime to the acidified sludge will result in improved dewatering characteristics through precipitation of residual soluble aluminum and added sulfuric acid as a complex calcium-alumino-sulfate precipitate. The lime dose, expressed as commercial lime currently used at the Chattahoochee Settled Solids Facility, was experimentally estimated to be 0.3 lb lime/lb dry sludge solids. In estimating the quantity of sludge solids produced, it was assumed that the sludge would be composed of the sum of the mass of the dry sludge solids, sulfuric acid added, lime added and residual soluble aluminum. Therefore, for an acidified sludge with a mass flow of 4795 lb/d of dry sludge solids, the quantity of dry sludge solids to be dewatered for disposal would be 7850 lb/d (5 day/week). This mass would be contained in volumes of 3150 - 6300 gal/d at dry-sludge-solids concentrations of 30 and 15 percent solids.

The estimated solids content of a dewatered cake is 40 percent and the estimated density of the dewatered cake is 78 lb/ft³. The resulting volume of sludge produced 5 days/week is then 252 ft³/d. Using a 60-chamber press with a capacity of 1.14 ft³/chamber, a total of 3.7 cycles would be required on a daily basis. Given the highly concentrated nature of the feed sludge, it is anticipated that the total cycle time for a filter now would be 1.5 h,

thereby allowing sufficient time to complete the dewatering operation during a single 8-hour shift.

An alternative procedure for dewatering and for enhanced recovery of residual aluminum is to dewater the sludge without lime conditioning. Polymer conditioning would be required to improve dewatering properties but virtually all residual aluminum and soluble acid would be recovered for reuse or recycle. Using this alternative procedure, the quantity of dry sludge solids produced from an acidified sludge would be 4795 lb/d (5 d/week) and would be contained in volumes of 3150 - 6300 gal/d. At an estimated solids content for a dewatered cake of 35 percent and a cake density of 74 lb/ft³, the sludge volume produced 5 days/week would be 162 ft³/d. Using a 60-chamber press with a capacity of 1.14 ft³/chamber, a total of 2.4 cycles would be required daily. In addition, the volume of additional coagulant recovered in the filtrate would be 2030 gal/d and 5180 gal/d, increasing the total volume of the recovered coagulant to 9380 gal/d and 19,880 gal/d, respectively, for 8 and 4 percent solids concentration of the initial thickened sludge. Overall aluminum recovery would be increased to 80 and 86 percent, respectively. Therefore, direct dewatering of the residual acidified sludge would further reduce sludge disposal requirements and improve coagulant recovery efficiency.

SUMMARY

The system design for implementation of aluminum recovery at the North Area plant is summarized in Tables 4.7 and 4.8. The proposed design changes are compatible with the current system design for land disposal of sludge solids following pressure filtration of lime-conditioned sludge.

TABLE 4.7. DESIGN SUMMARY OF MATERIAL FLOW FOR ALUMINUM RECOVERY
AT PROPOSED NORTH AREA PLANT

PLANT DESIGN FLOW.....	30 mgd
INFLUENT THICKENER SLUDGE	
Mass, dry solids.....	7,000 lb/d
Volume	
4%.....	15,000 gal/d
8%.....	10,500 gal/d
Aluminum.....	847 lb/d
ACID REQUIREMENT (66°Be)	
Volume.....	325 gal/d
Mass.....	4,945 lb/d
POLYMER REQUIREMENT	
Anionic & non-ionic polymer.....	4.2 gal/d (max)
COAGULANT RECOVERY	
Material balance on Al	
Influent sludge.....	847 lb/d
Recovered coagulant.....	534 lb/d
Residual sludge	
Soluble.....	84.7 lb/d
Insoluble.....	228.3 lb/d
TOTAL.....	313 lb/d
Volume balance - 4% influent solids	
Influent sludge.....	21,000 gal/d
Recovered coagulant.....	14,700 gal/d
Residual sludge.....	6,300 gal/d
Volume balance - 8% influent solids	
Influent sludge.....	10,500 gal/d
Recovered coagulant.....	7,350 gal/d
Residual sludge.....	3,150 gal/d

Lime conditioning	
Lime required.....	2,100 lb/d
Sludge produced	
Mass, dry solids.....	7,850 lb/d
Volume.....	252 ft ³ /d
Polymer conditioning	
Polymer required.....	4.2 lb/d
Sludge produced	
Mass, dry solids.....	4,795 lb/d
Volume.....	162 ft ³ /d
Recovered coagulant	
4% solids.....	5,180 gal/d
8% solids.....	2,030 gal/d

TABLE 4.8. DESIGN SUMMARY OF ADDITIONAL EQUIPMENT REQUIREMENTS
FOR ALUMINUM RECOVERY AT PROPOSED NORTH AREA PLANT

Description	Equipment Specification
<u>SLUDGE TRANSFER</u>	
Lamella thickener to sludge treatment (10,500 to 15,000 gpd).....	Existing equipment
<u>ACIDIFICATION</u>	
Acid storage and application system.....	Storage tank with volume of 10,000 gal (external or internal facility) Application pump/metering system
pH monitor.....	pH probe and continuous digital, or equivalent, display located at acid- control system
<u>ACIDIFICATION REACTOR SYSTEM</u>	
Sludge conditioning tank.....	Existing system (volume may need to be increased for <u>one</u> tank to 25,000 gal)
Tank additions Mixer.....	Mixer (5 HP/10 ³ ft ³) with variable (3-speed) control to allow for use in mixing acidified sludge; blending polymer with sludge; and flocculating polymer- conditioned sludge
Baffling.....	± 1 -foot vertical baffles mounted at quarter points in tank to improve mixing efficiency
Coagulant decant.....	Multiple-port, draw-off system located along vertical wall of both tanks at 30, 50 and 70 percent points

TABLE 4.8 (Continued)

Decant pump.....	Pump to transport acidic coagulant (7,000 to 15,000 gal/d) to storage tank at rate of 250-500 gpm
Sludge transfer pump.....	Pump to remove residual acidic sludge from conditioning tank and transport back into same or second conditioning tank following polymer addition in suction side of pump or in-line static mixer
<u>POLYMER CONDITIONING</u>	Two polymer blending systems for application of polymer to acidified sludge
<u>RECOVERED COAGULANT STORAGE</u>	A 50,000-gal tank for storage of recovered coagulant and a coagulant application system with nominal application rate of 6-12 gal/min

5. REFERENCES

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APPENDIX

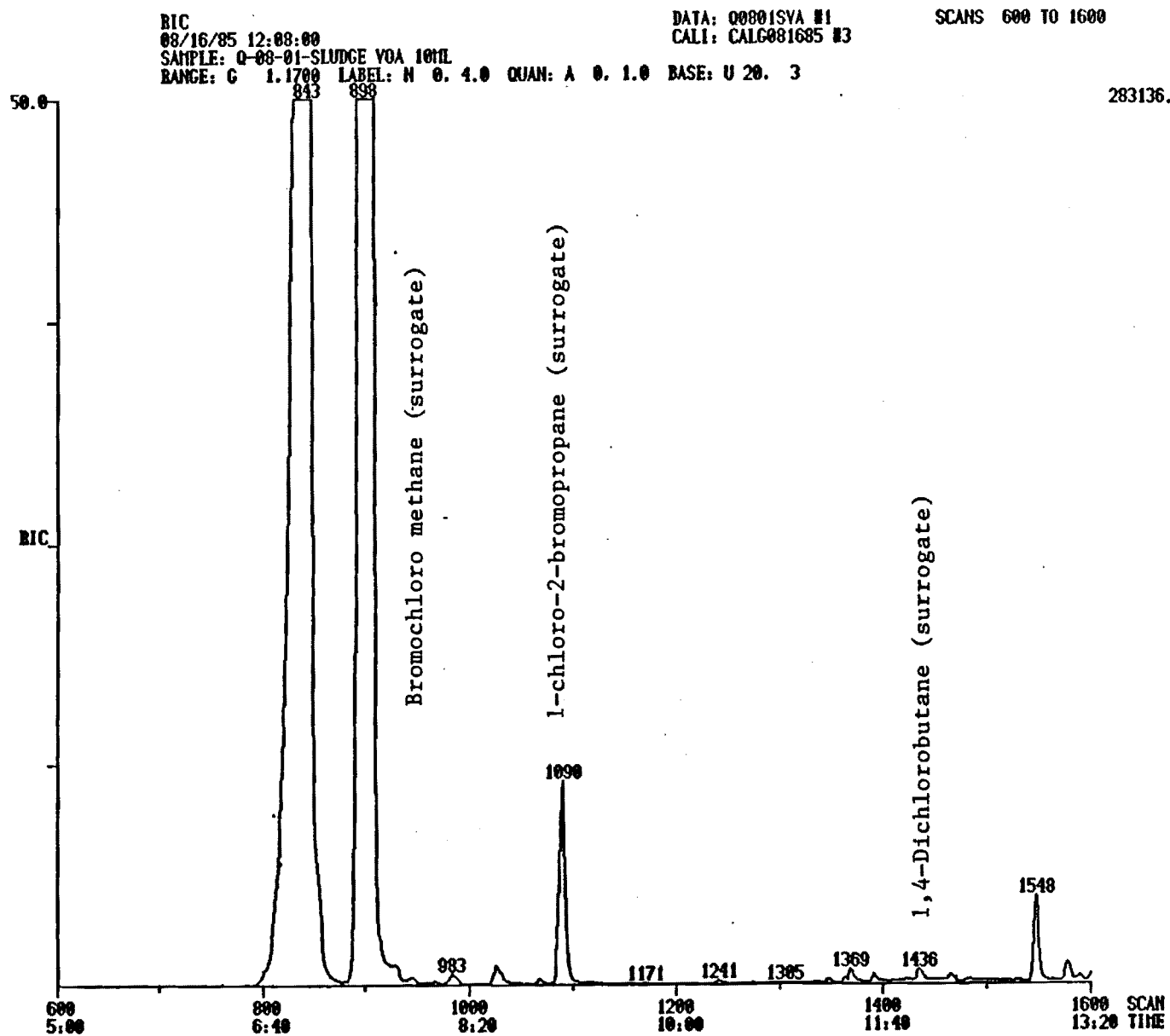


Figure A1. GC-MS Trace of Purgeable Fraction for Quarles Sludge Sample (Q-08-01).

BIC
08/09/85 14:26:00
SAMPLE: Q-08-01-SLUDGE+IS 20PPM
RANGE: C 1.2100 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 00001S #1
CALI: CAL0000885 #15

SCANS 1 TO 2100

61440.

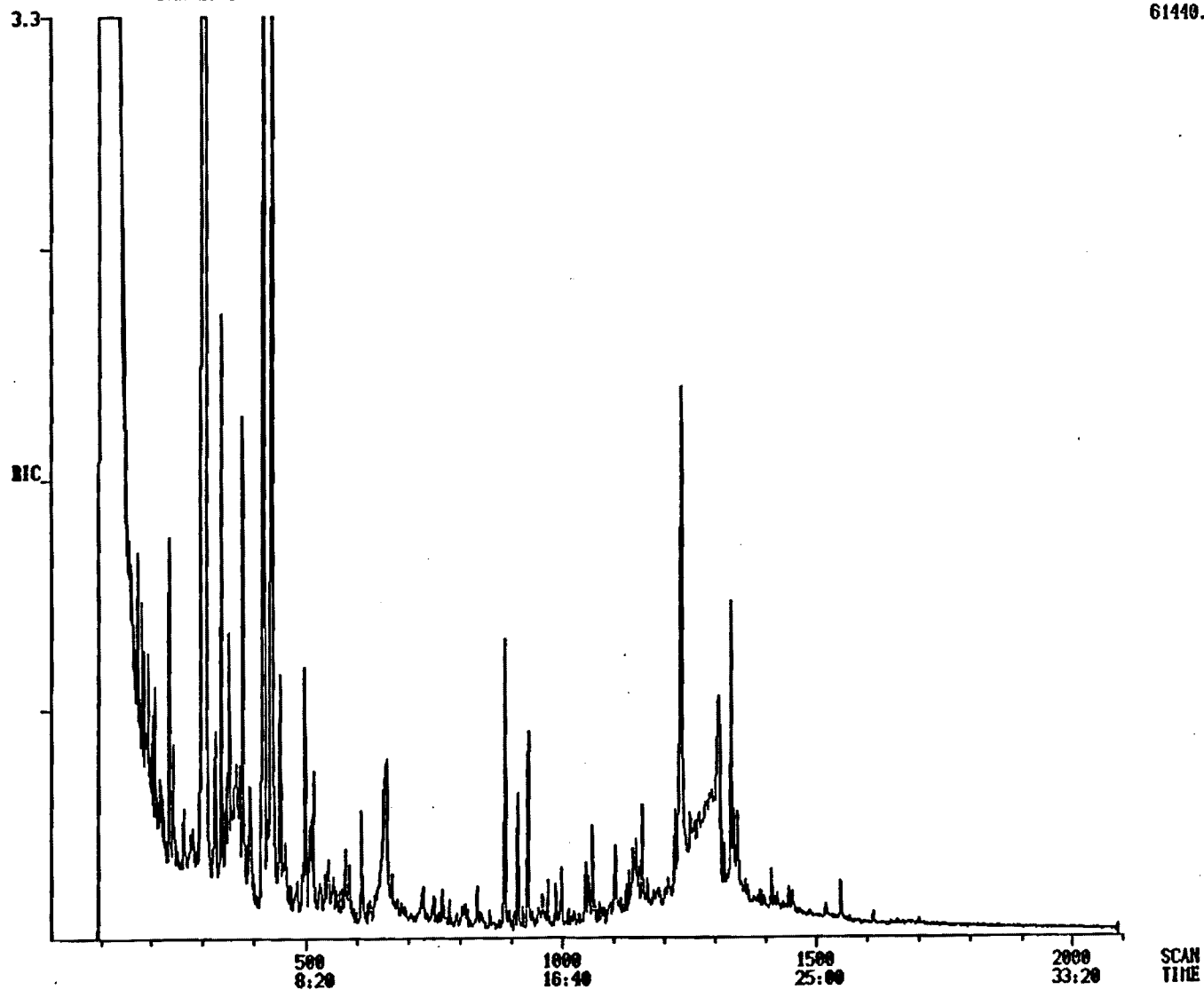


Figure A2. GC-MS Trace of Acid/Neutral Fraction for Quarles Sludge Sample (Q-08-01).

RIC
08/16/85 11:24:00
SAMPLE: D-08-01-SLUDGE VOA 10ML +IS
RANGE: G 1.1700 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: D0801SYA #1594
CALI: CALG080885 #15

SCANS 600 TO 1600

337920.

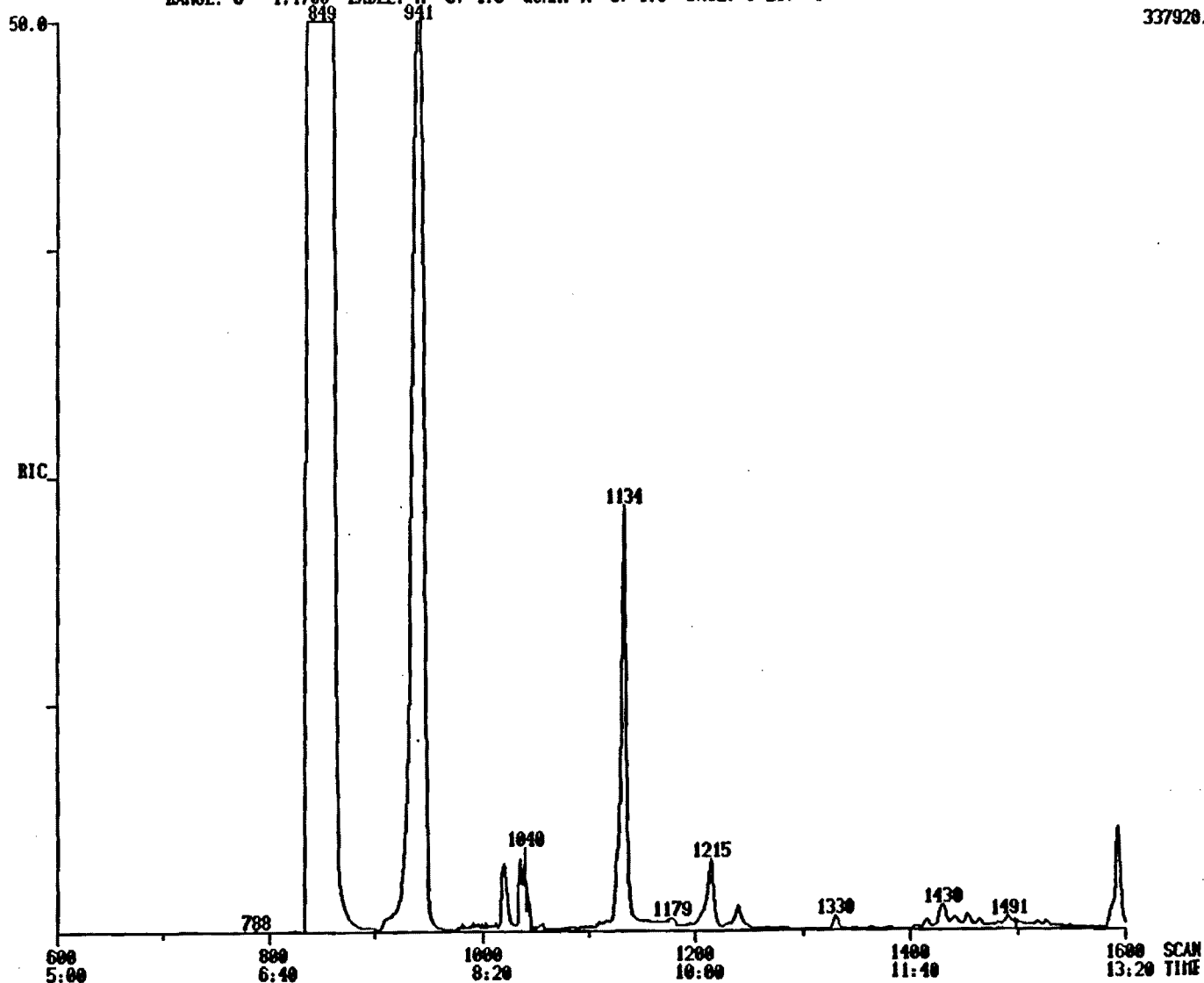


Figure A3. GC-MS Trace of Purgeable Fraction for Candler Sludge Sample (D-08-01).

RIC
08/09/85 15:14:00
SAMPLE: D-08-01-SLUDGE
RANGE: G 1.2100 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: D0801S #1
CALI: CALG080805 #15

SCANS 1 TO 2100

61781.

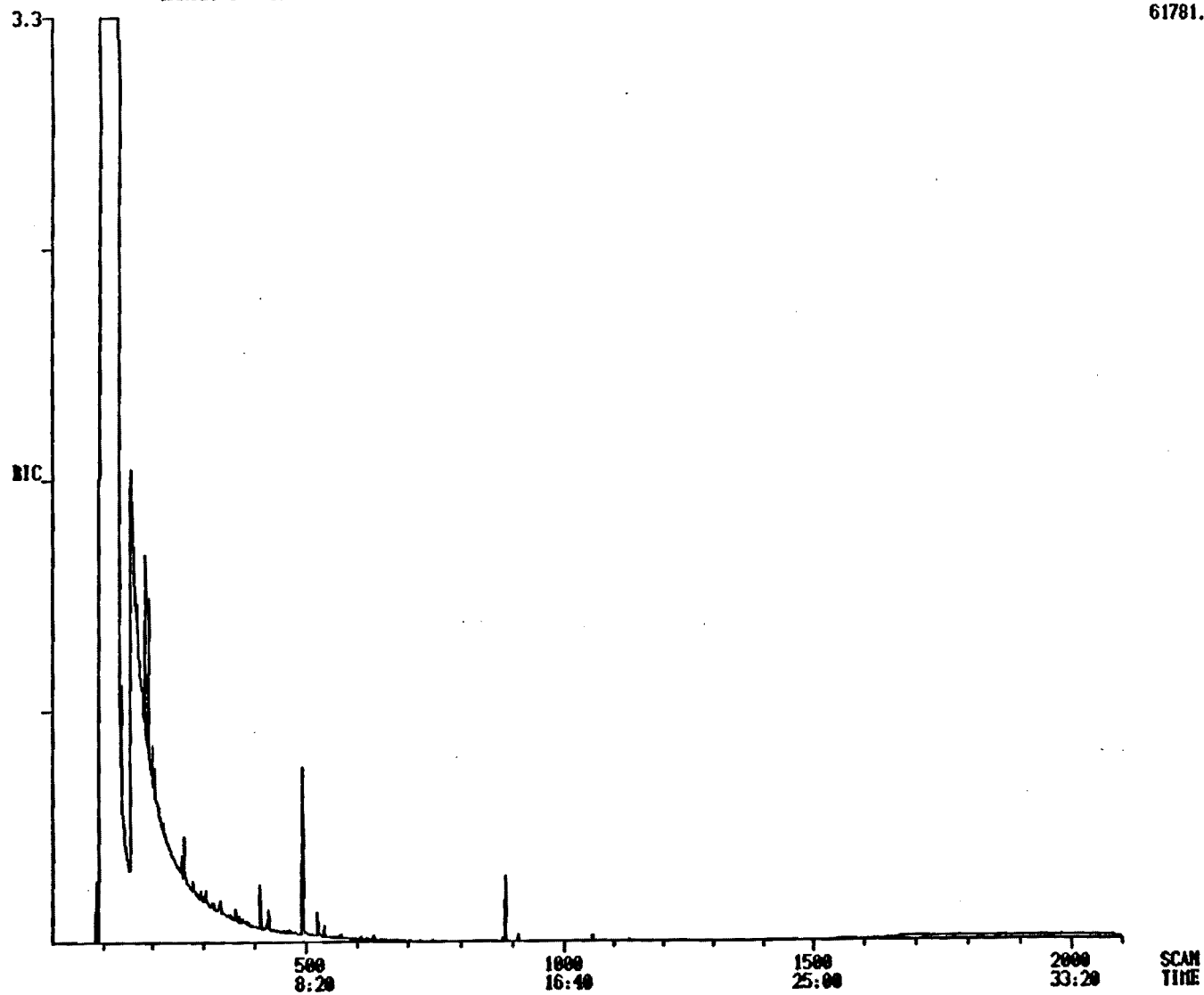


Figure A4. GC-MS Trace of Acid/Neutral Fraction for Candler Sludge Sample (D-08-01).

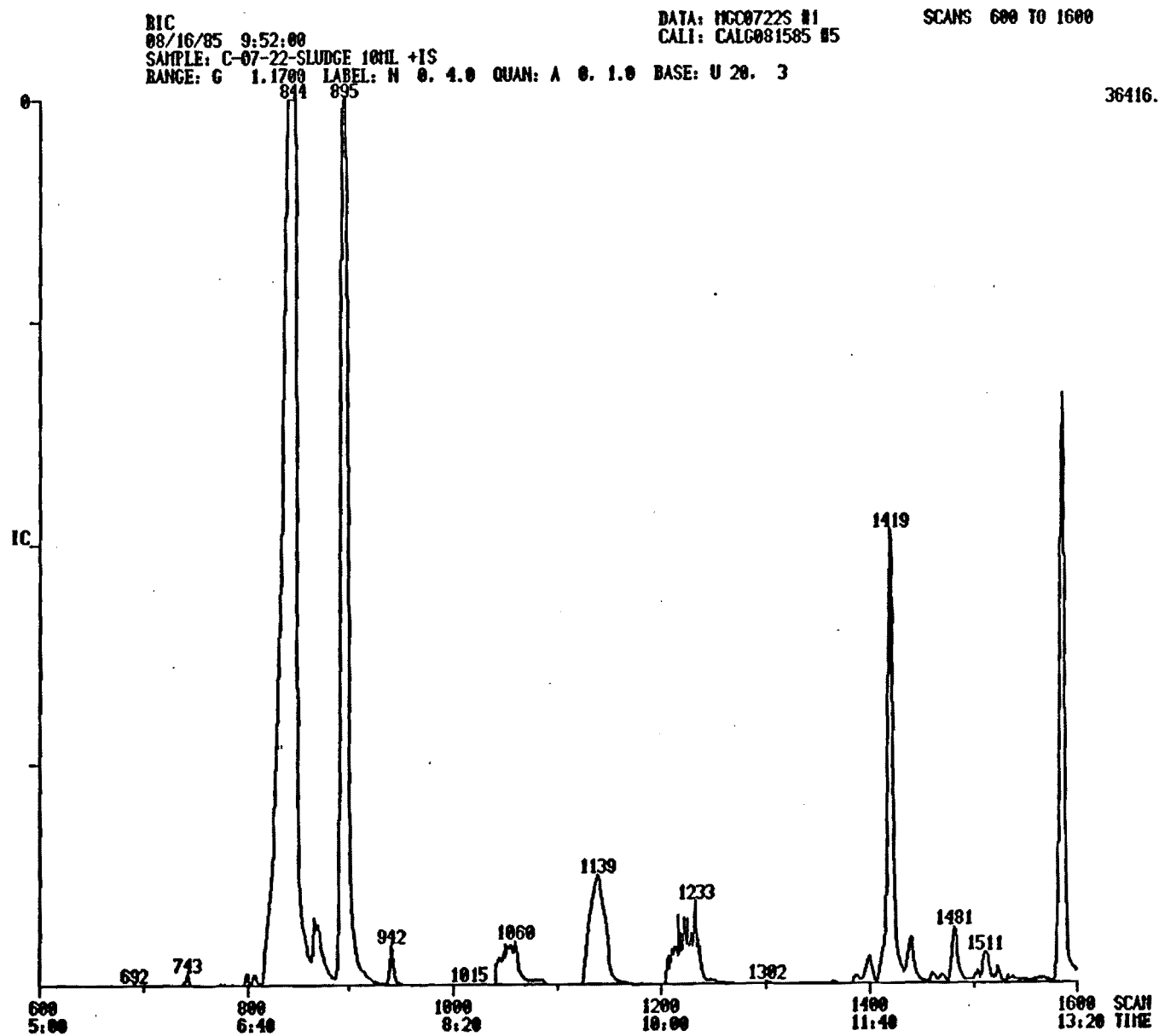


Figure A5. GC-MS Trace of Purgeable Fraction for Chattahoochee Sludge Sample(C-07-22).

RIC
08/08/85 17:26:00
SAMPLE: C-07-22-SLUDGE+IS 20PPM
RANGE: G 1.2100 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: C0722S #1
CALI: CALG000885 #15

SCANS 1 TO 2100

63966.

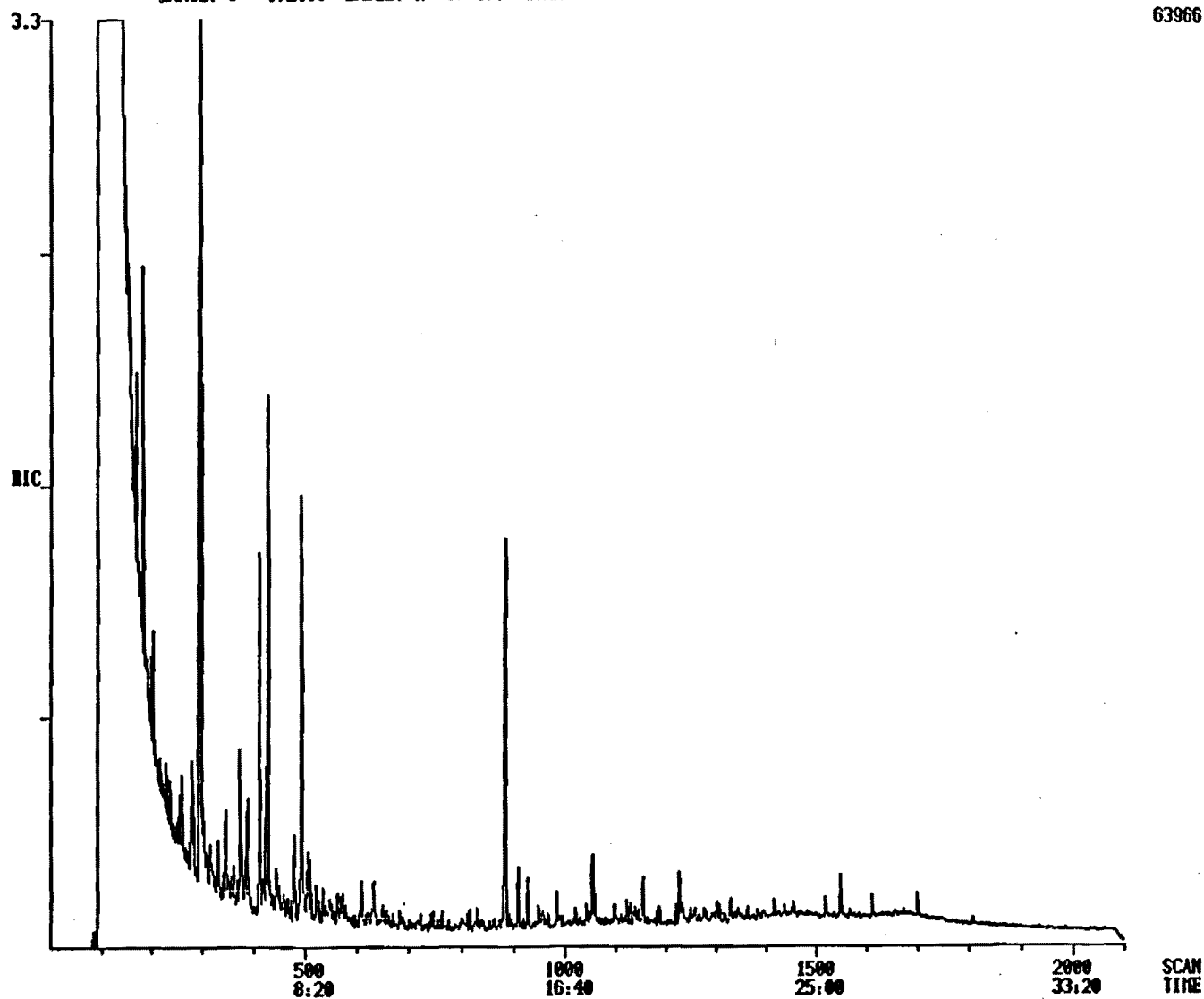


Figure A6. GC-MS Trace of Acid/Neutral Fraction for Chattahoochee Sludge Sample (C-07-22).

RIC
08/16/85 9:12:00
SAMPLE: H 07 22-SLUDGE
RANGE: G 1.1700 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

SCANS 600 TO 1600

149248.

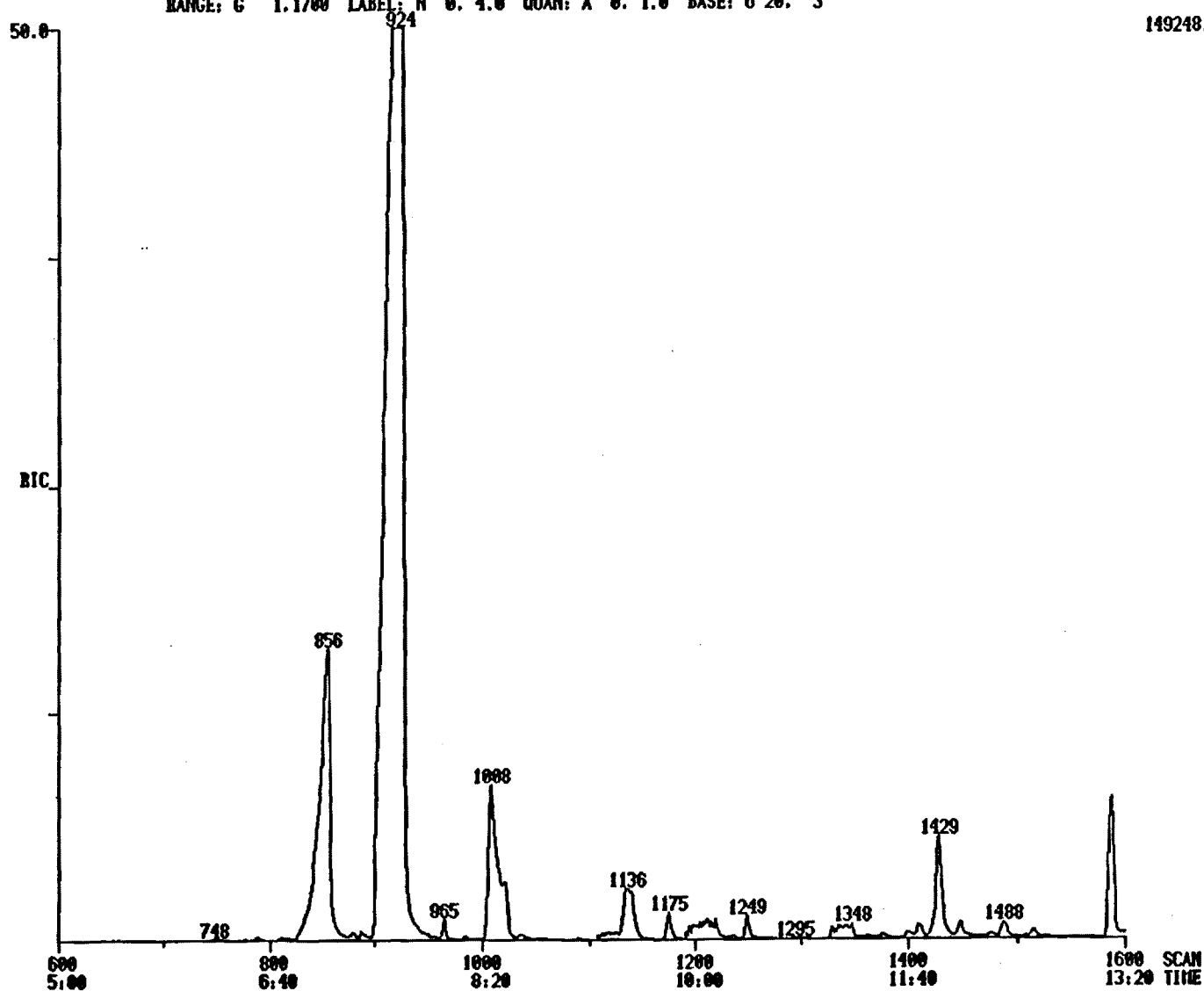


Figure A7. GC-MS Trace of Purgeable Fraction for Hemphill Sludge Sample (H-07-22).

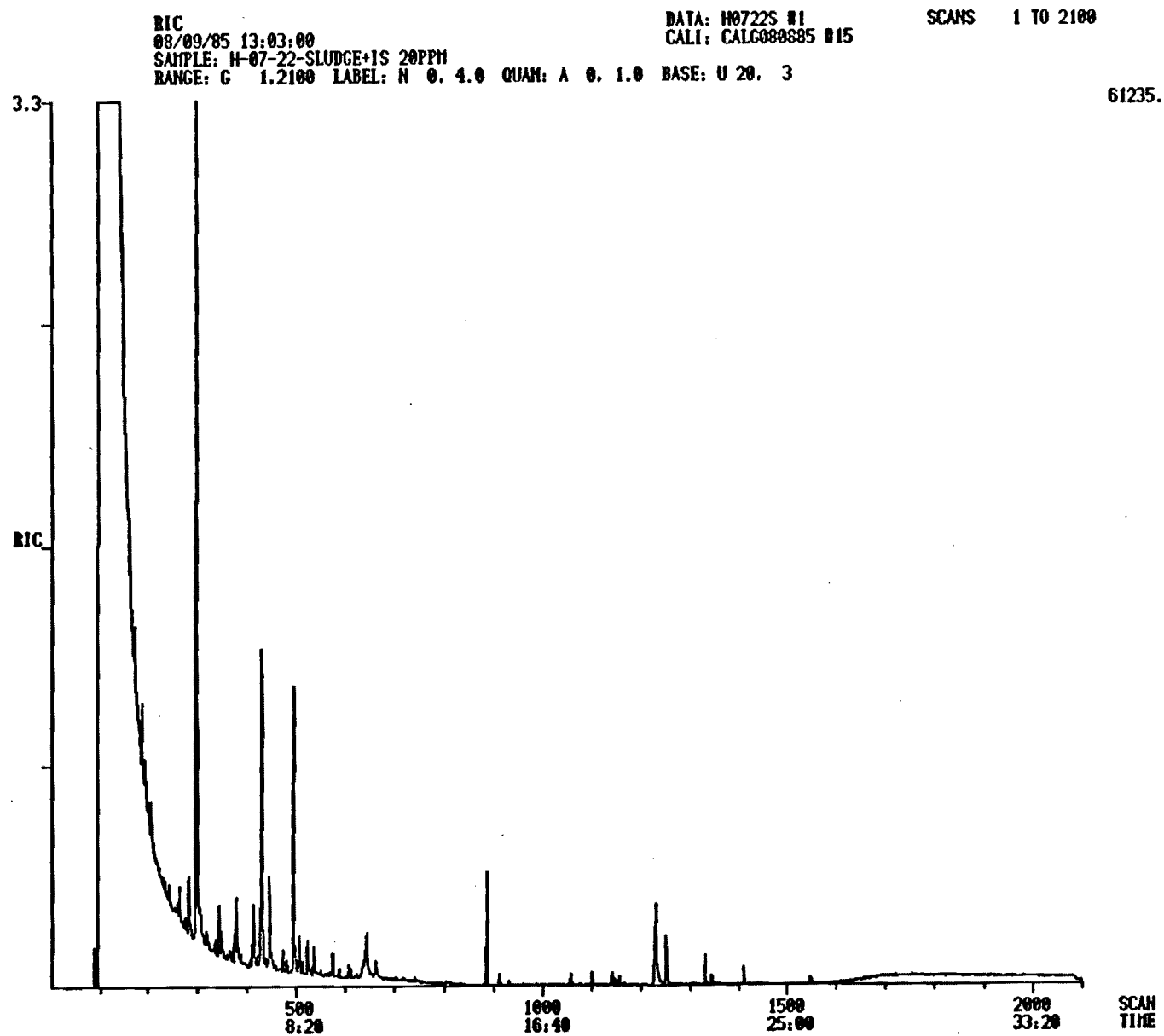


Figure A8. GC-MS Trace of Acid/Neutral Fraction for Hemphill Sludge Sample (H-07-22).

RIC
08/16/85 16:12:00
SAMPLE: AA C-08-01-A VOA 5ML +IS
RANGE: G 1.1700 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: C0801AY0A W1
CALI: CALG081685 #3

SCANS 600 TO 1700

757760.

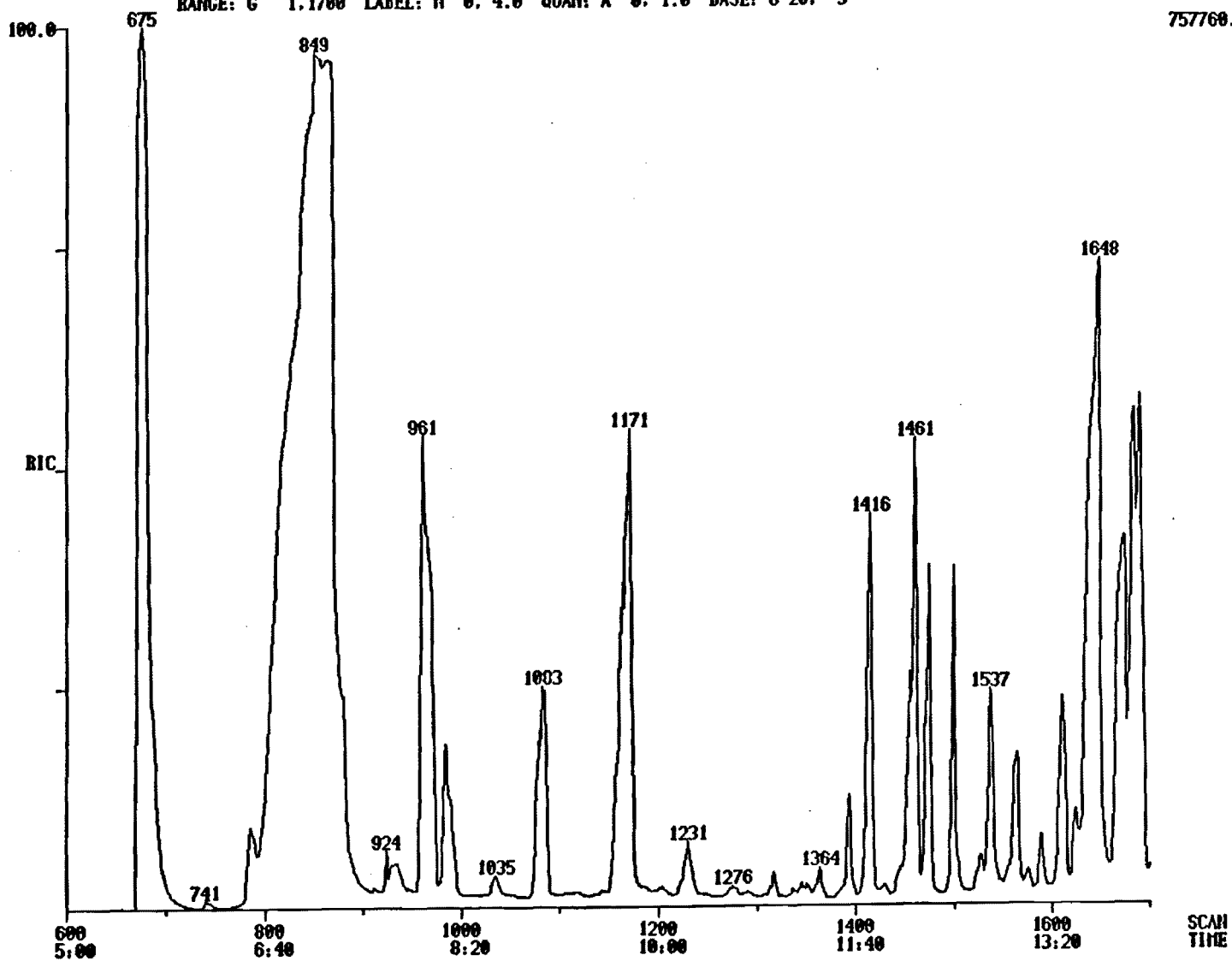


Figure A9. GC-MS Trace of Purgeable Fraction for Chattahoochee Sludge Sample (C-08-01a).

RIC
09/06/85 14:11:00
SAMPLE: Q-08-01-SLUDGE 8/23 2ML + IS
RANGE: G 1.1500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: Q0801SYA #1
CALI: CALG090685 #20

SCANS 600 TO 1500

16208.

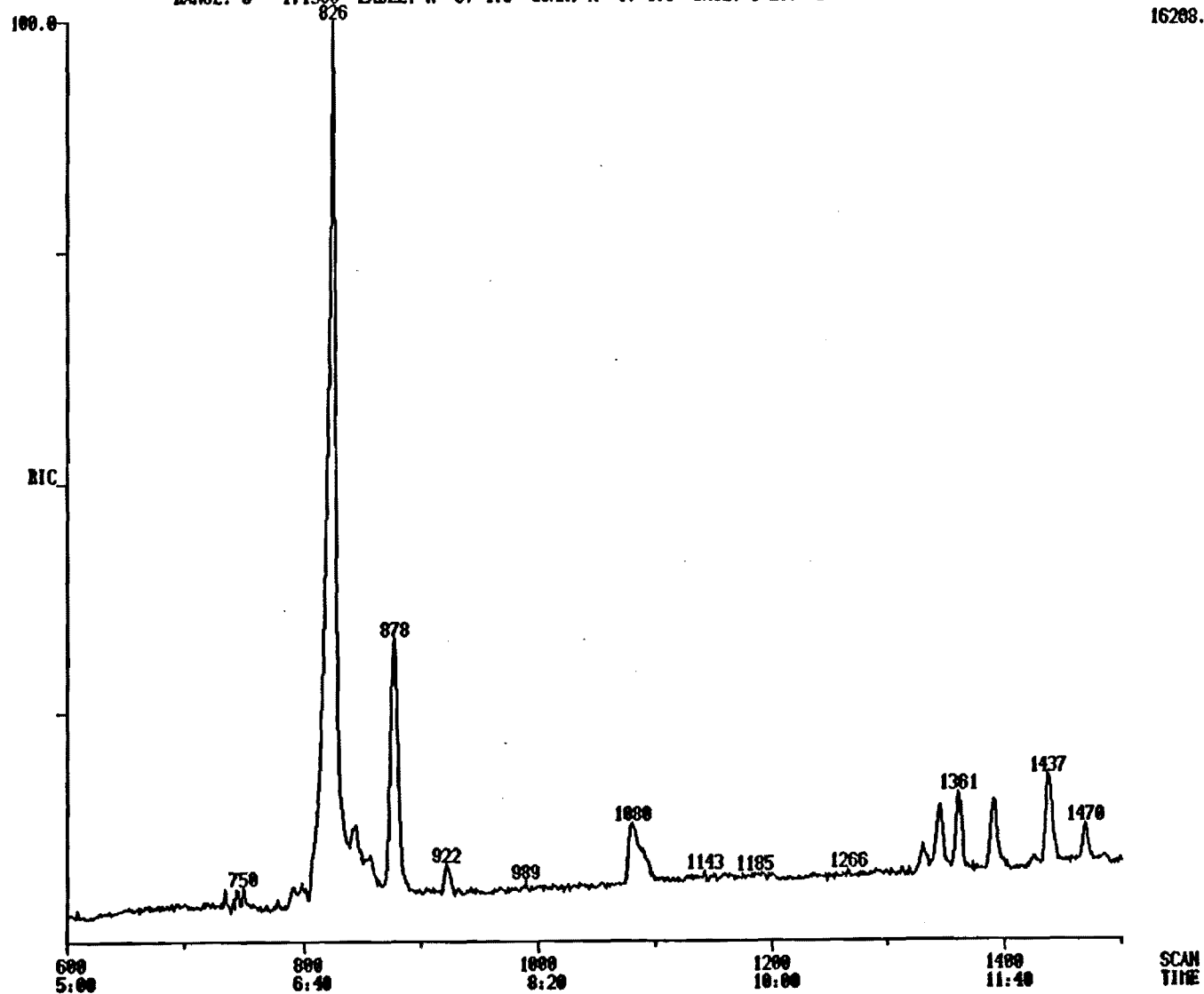


Figure A10. GC-MS Trace of Purgeable Fraction for Sulfuric Acid Extracts of Quarles Sludge Sample (Q-08-01).

RIC
09/14/85 11:11:00
SAMPLE: DRINKING WATER PLANT SLUDGE EXTR. A/B FRAC. + IS
RANGE: C 1.1500 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3

DATA: 00001S #1
CALI: CALG091485 #5

SCANS 1 TO 1450

14048.

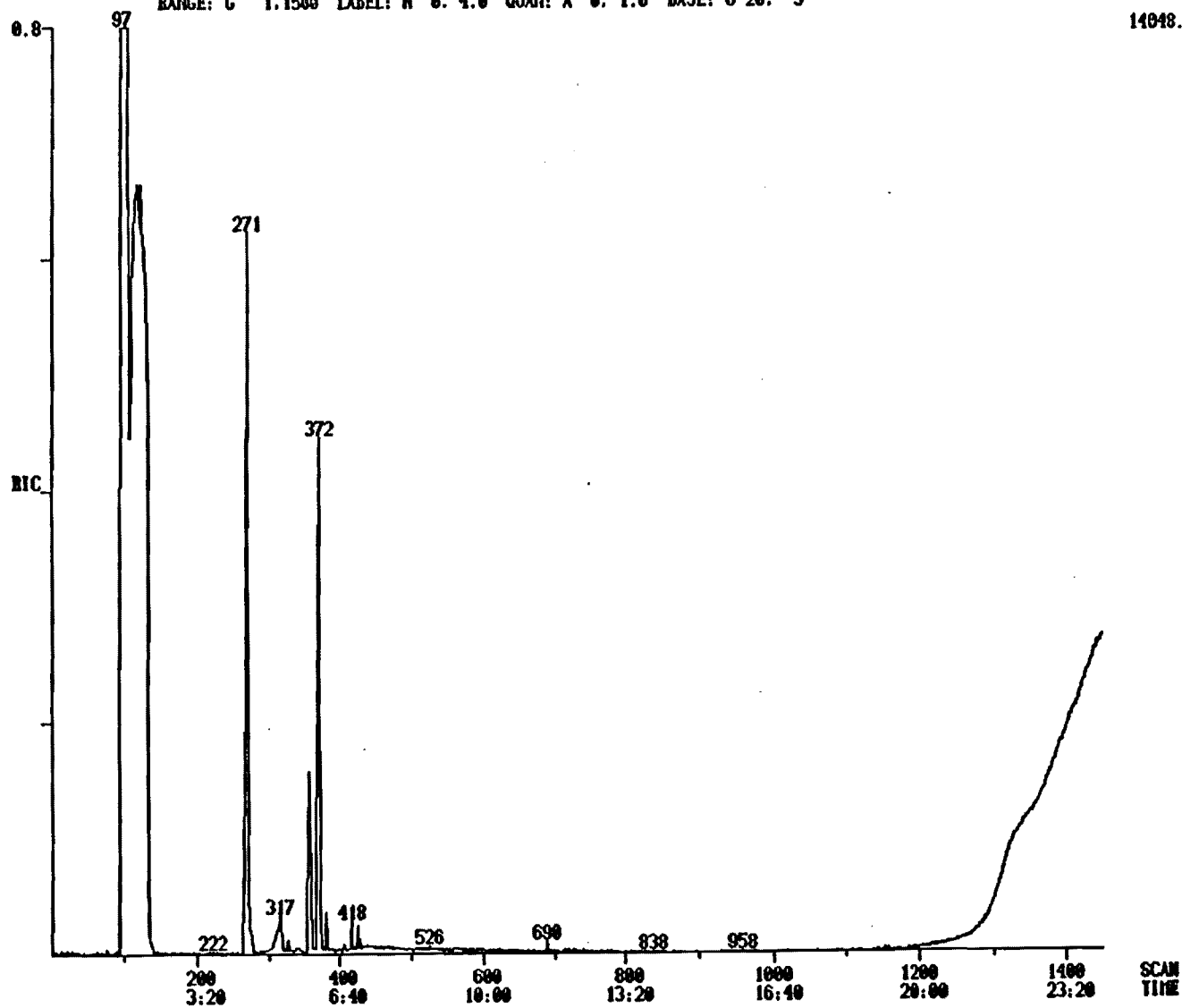


Figure All. GC-MS Trace of Acid/Neutral Fraction for Sulfuric Acid Extracts of Quarles Sludge Sample (Q-08-01).

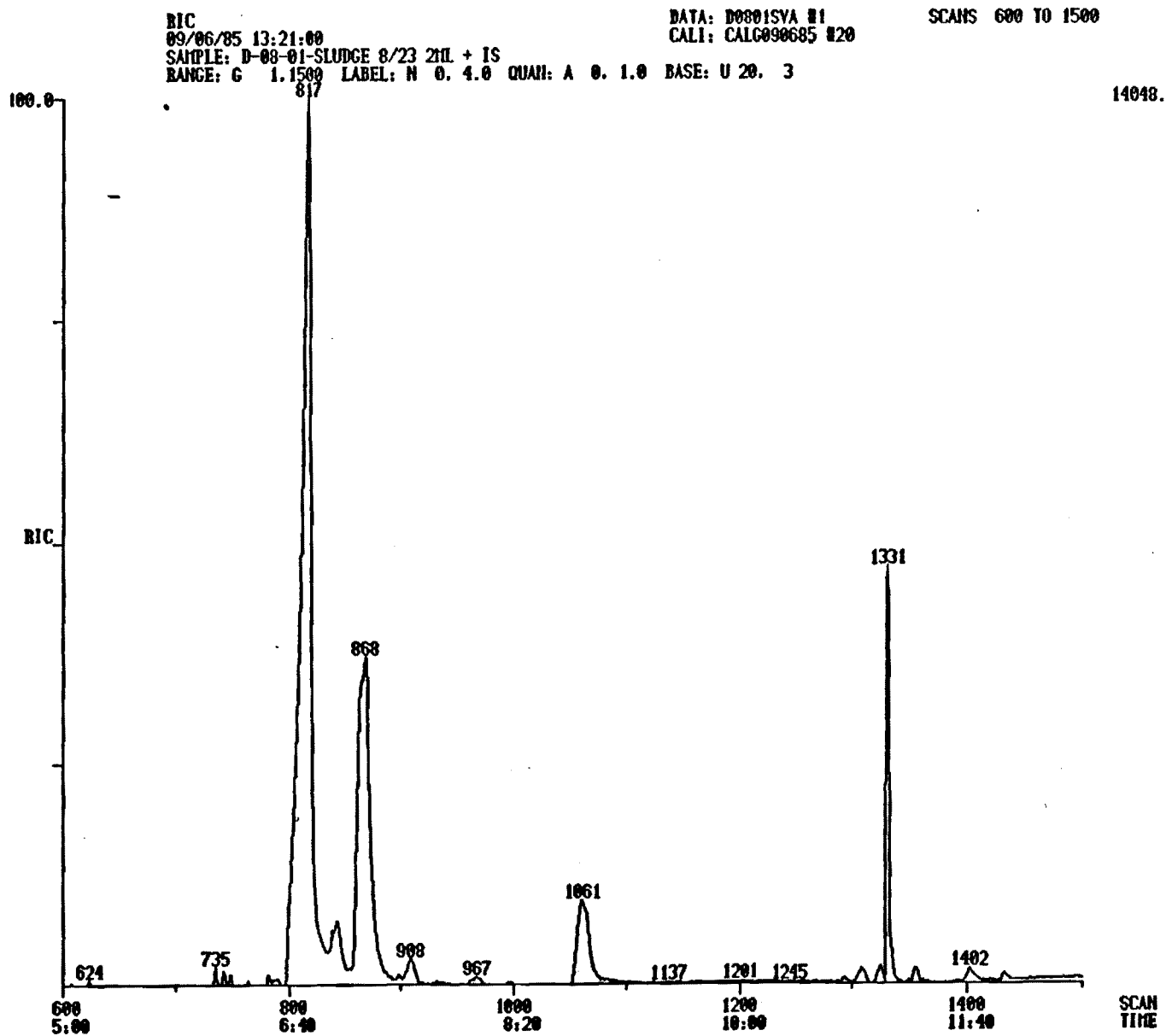


Figure A12. GC-MS Trace of Purgeable Fraction for Sulfuric Acid Extracts of Candler Sludge Sample (D-08-01).

RIC
09/13/85 15:44:00
SAMPLE: D-08-01-SLUDGE 082385
RANGE: 6 1.1471 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: D0801S #1
CALI: CALG091385 #5

SCANS 1 TO 1471

28832.

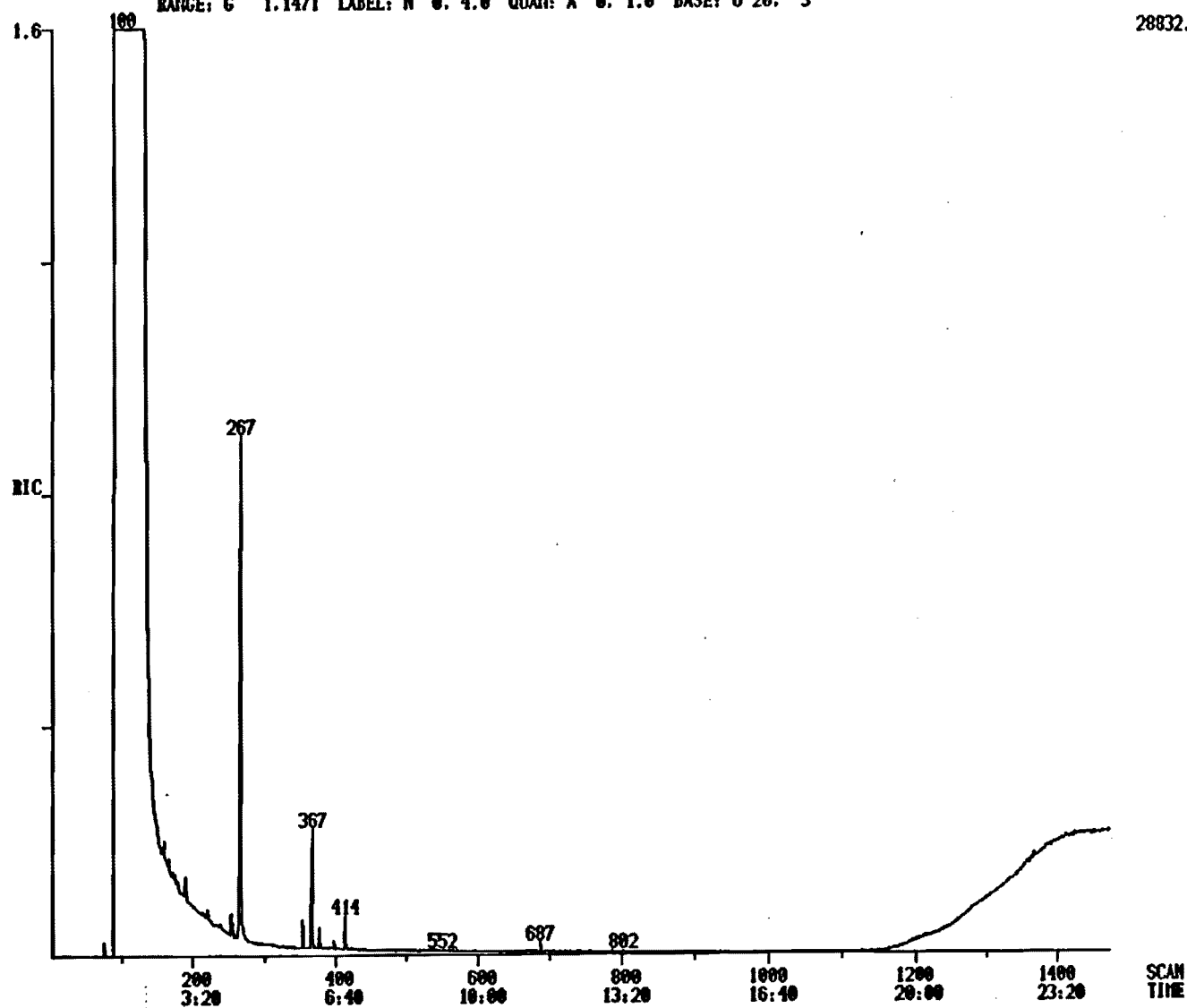


Figure A13. GC-MS Trace of Acid/Neutral Fraction for Sulfuric Acid Extracts of Candler Sludge Sample (D-08-01).

RIC
09/06/85 14:58:00
SAMPLE: H-07-22-S-211
RANGE: G 1.1500 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

SCANS 600 TO 1500

7848.

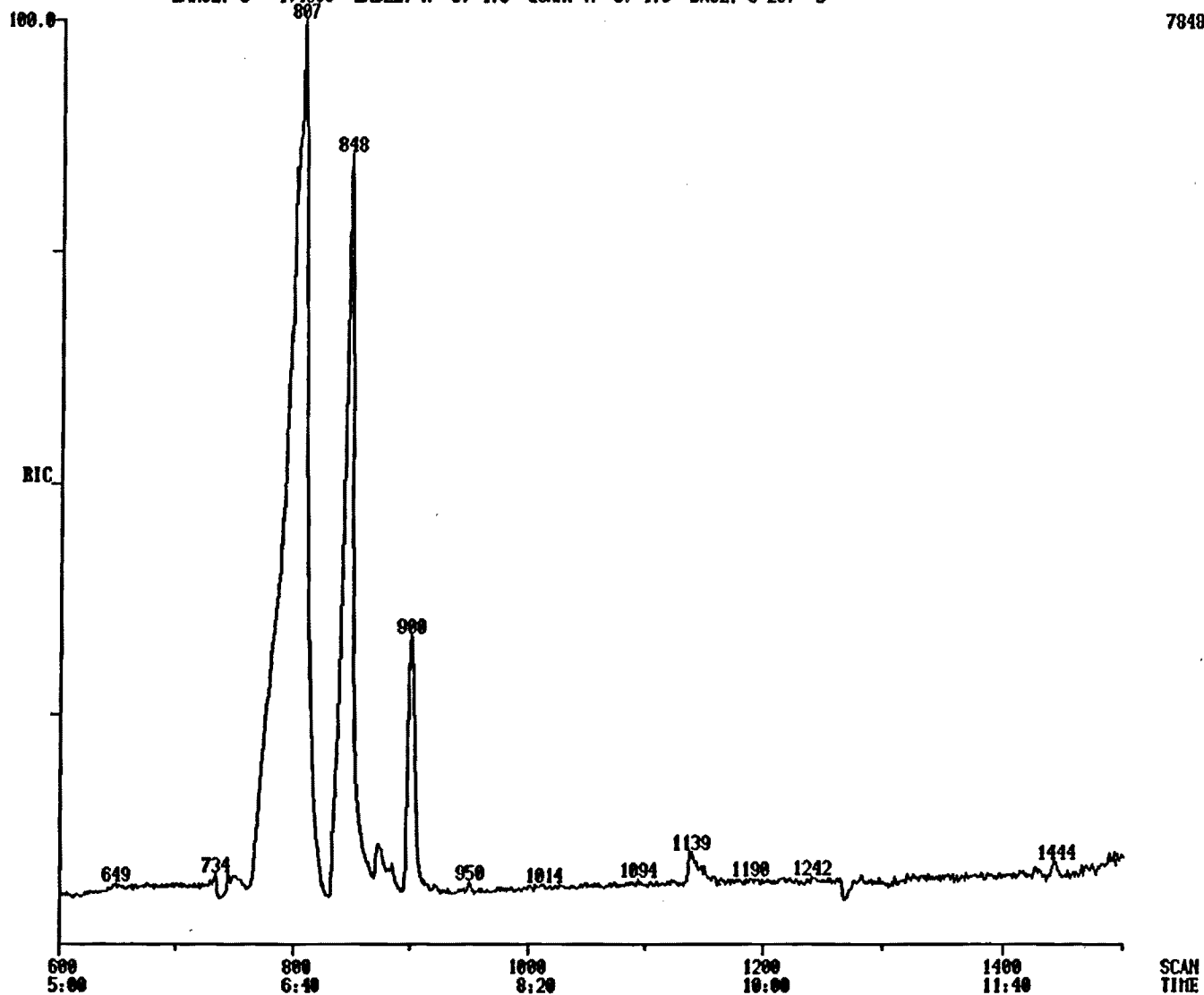


Figure A14. GC-MS Trace of Purgeable Fraction for Sulfuric Acid Extracts of Hemphill Sludge Sample (H-07-22).

RIC
09/13/85 18:01:00
SAMPLE: DRINK WATER SLUDGE H0722S + IS
RANGE: G 1.1500 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

SCANS 1 TO 1450

DATA: H0722S #1
CALI: CALG091385 #5

29440.

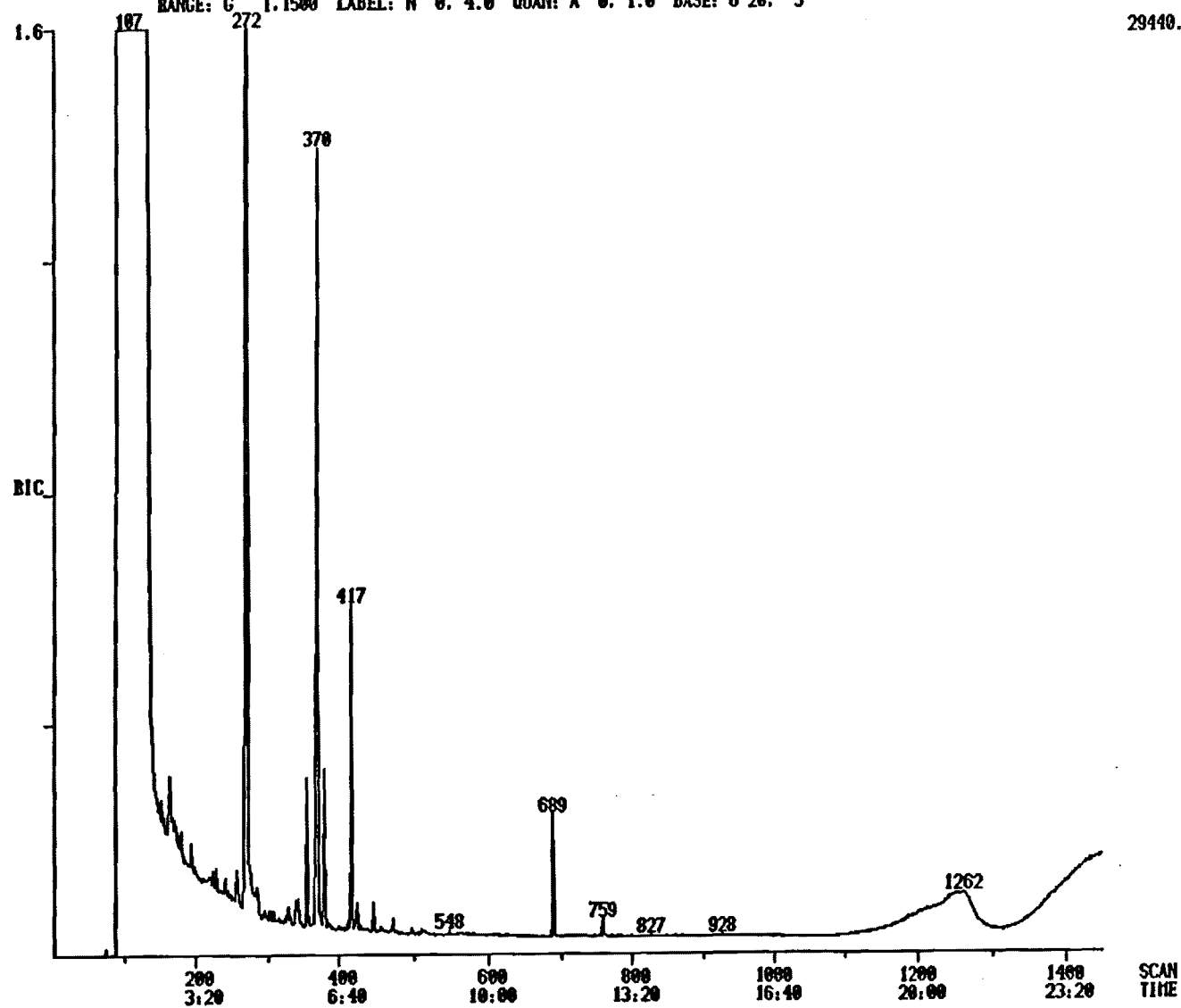


Figure A15. GC-MS Trace of Acid/Neutral Fraction for Sulfuric Acid Extracts of Hemphill Sludge Sample (H-07-22).

RIC
09/04/85 12:44:00
SAMPLE: C-07-19-SLUDGE UNFILTRED+IS 20PPM
RANGE: G 1.1911 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: C0719S #1
CALI: CALC090485 #8

SCANS 1 TO 1911

259277.

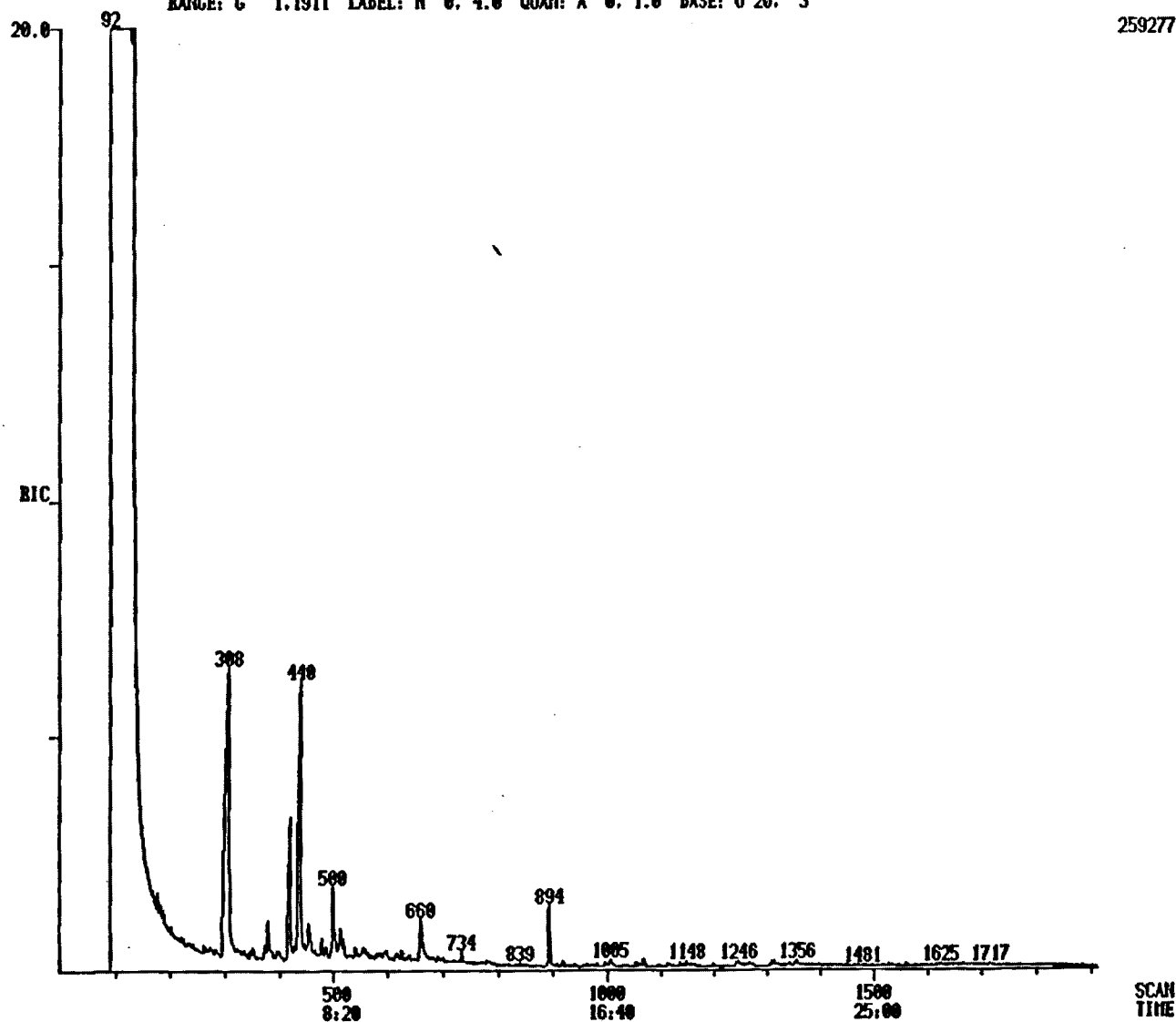


Figure A16. GC-MS Trace of Acid/Neutral Fraction for Sulfuric Acid Extracts of Chattahoochee Sludge Sample (C-07-19).

RIC
08/19/85 4:36:00
SAMPLE: D0801A VOA 5ML + IS
RANGE: G 1.1700 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: D0801AVOA #1
CALI: CALG080885 #15

SCANS 600 TO 1700

432640.

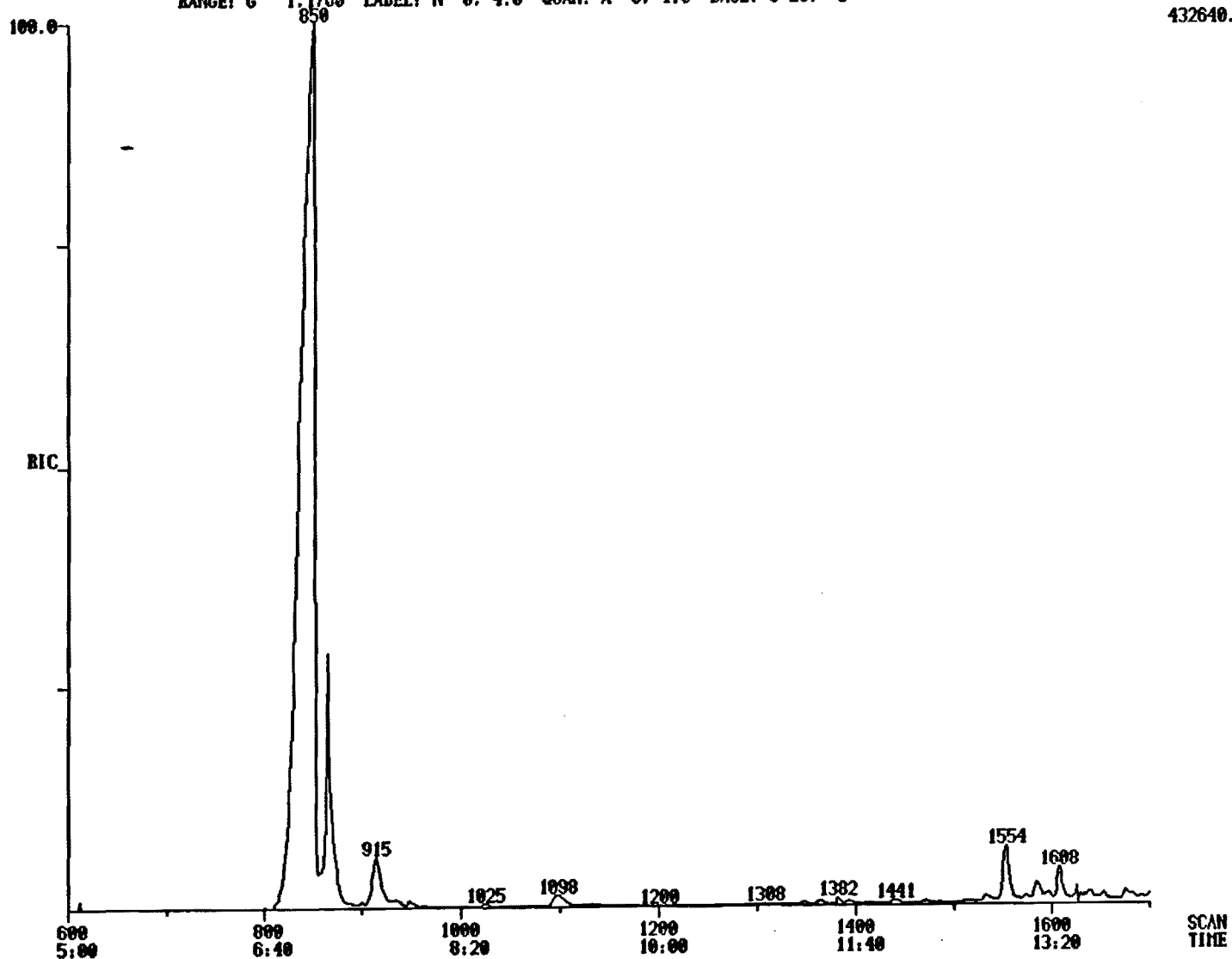


Figure A17. GC-MS Trace of Purgeable Fraction for Sulfuric Acid Extracts of Candler Sludge Sample (D-08-01a).

BIC
09/25/85 11:28:00
SAMPLE: C 07-22-SLUDGE UNFILTRED
RANGE: G 1.2100 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: C0722SUNFIL #1
CALI: CALG092585 #5

SCANS 1 TO 2100

163226.

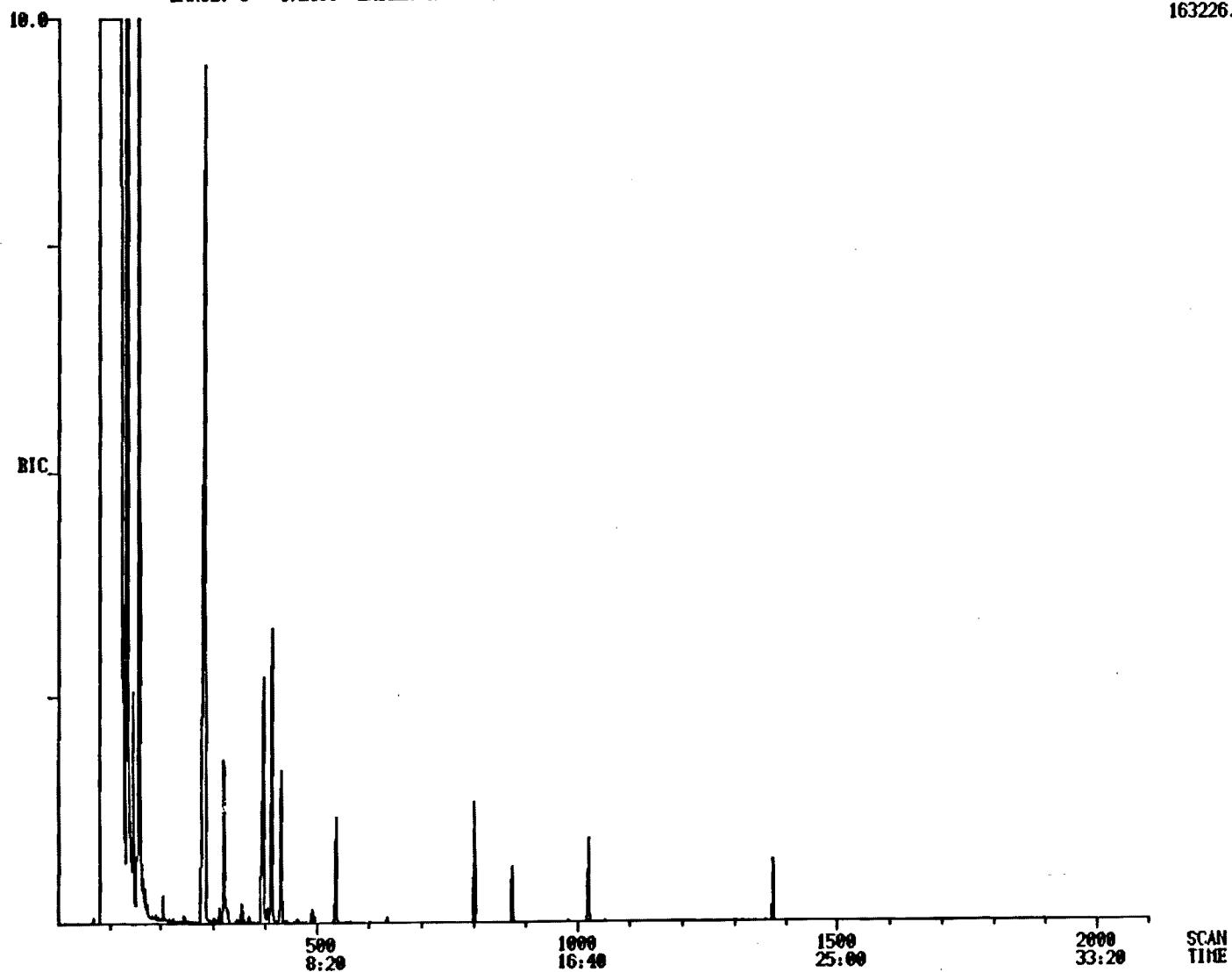


Figure A18. GC-MS Trace of Acid/Neutral Fraction for Sulfuric Acid Extracts of Chattahoochee Sludge Sample (C-07-22).

RIC
09/25/85 12:24:00
SAMPLE: C 08-01A SLUDGE 0820 UNFILTRED
RANGE: G 1.2100 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: C0801AS #1
CALI: CALG090685 #20

SCANS 1 TO 2100

110665.

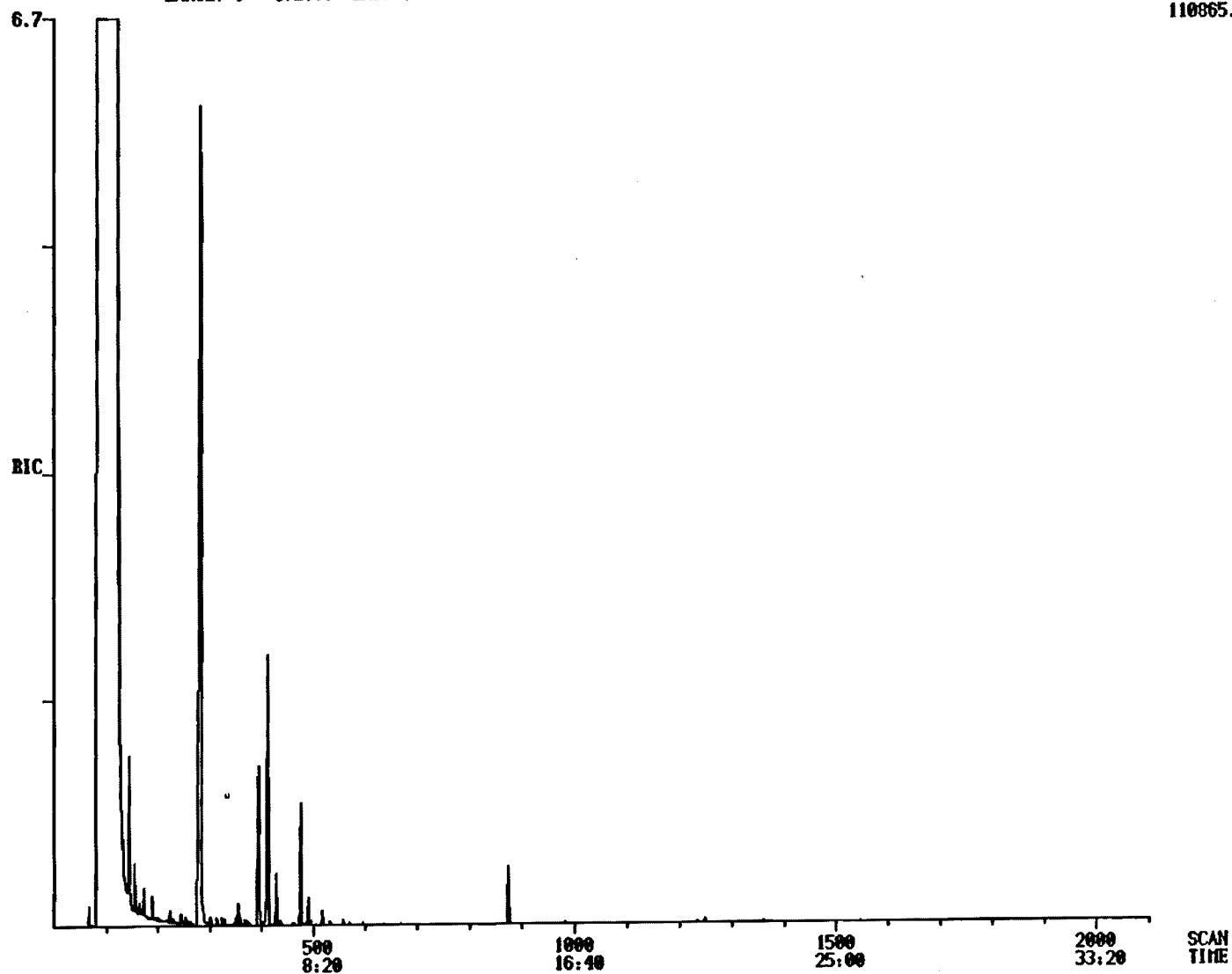


Figure A19. GC-MS Trace of Acid/Neutral Fraction for Sulfuric Acid Extracts of Chattahoochee Sludge Sample (C-08-01a).

RIC
09/06/85 10:19:00
SAMPLE: BLANK 0820 57L + IS
RANGE: 6 1.1500 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: BLK0820VA #1
CALI: CALG090685 #20

SCANS 600 TO 1500

69248.

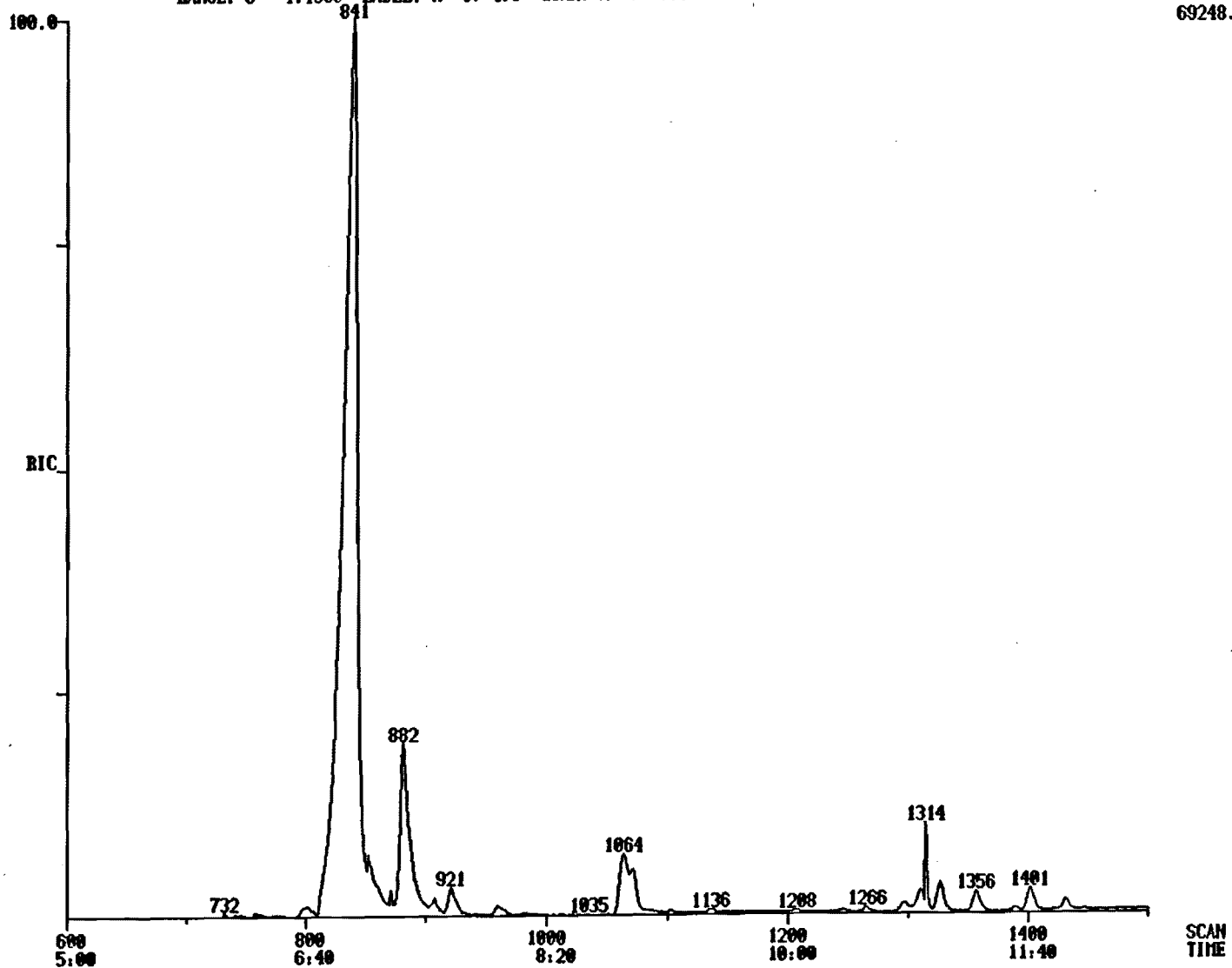


Figure A20. GC-MS Trace of Purgeable Fraction for Distilled Water Blank of 8/20.

BIC
09/05/85 16:03:00
SAMPLE: BLANK 0821 5ML +IS
RANGE: G 1 1500 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: BLK0821VA #1
CALI: CALG090505 #14

SCANS 600 TO 1500

82304.

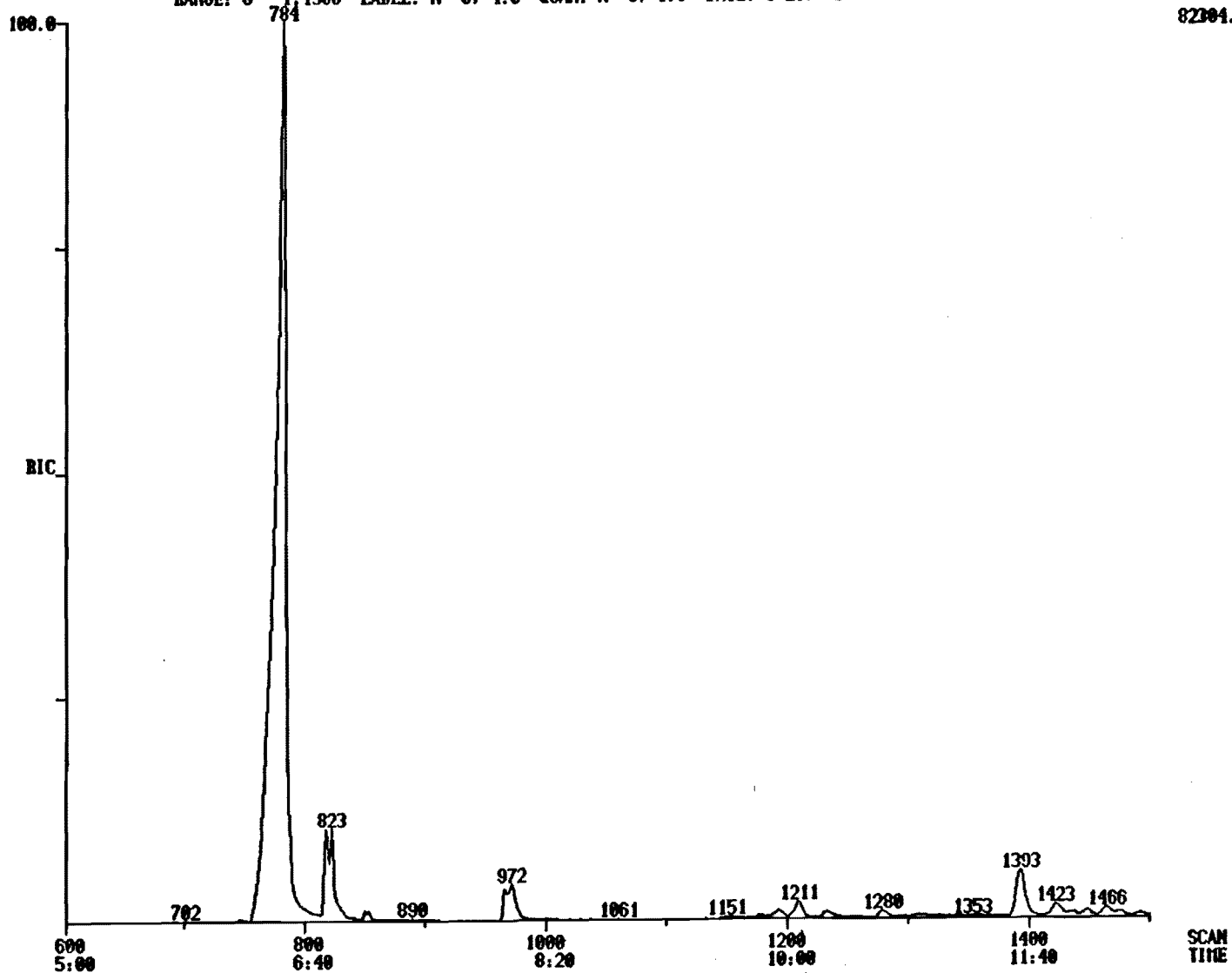


Figure A21. GC-MS Trace of Purgeable Fraction for Distilled Water Blank of 8/21.

RIC
09/06/85 11:46:00
SAMPLE: BLANK 0823 5ML + IS
RANGE: G 1.1500 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20, 3

DATA: BLK0823VA #1
CALI: CALG090685 #20

SCANS 600 TO 1500

23296.

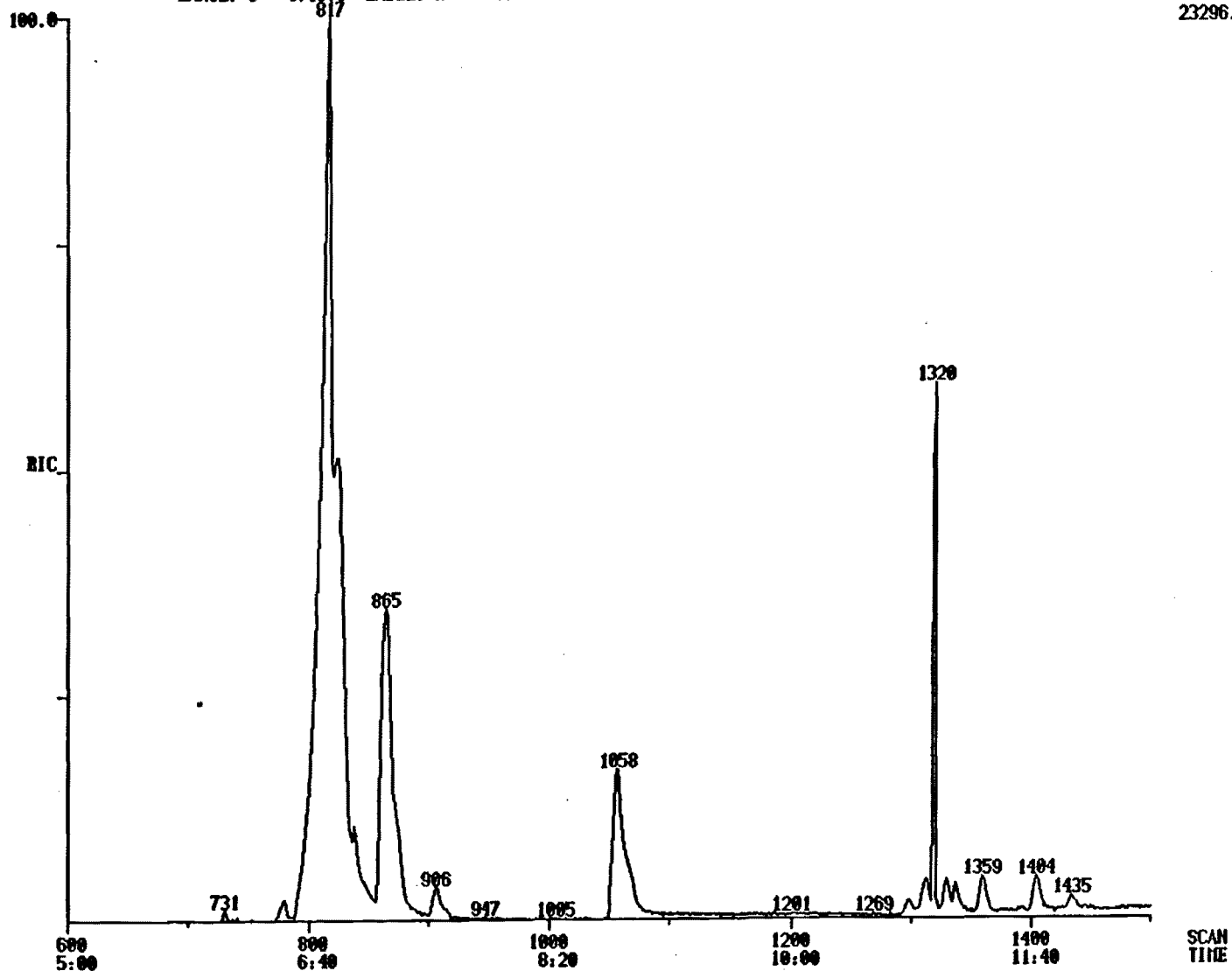


Figure A22. GC-MS Trace of Purgeable Fraction for Distilled Water Blank of 8/23.

RIC
09/25/85 13:12:00
SAMPLE: D 08-01-ALUM
RANGE: G 1.1847 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: D0001ALUM09 #1
CALI: CALG090605 #20

SCANS 1 TO 1847

165478.

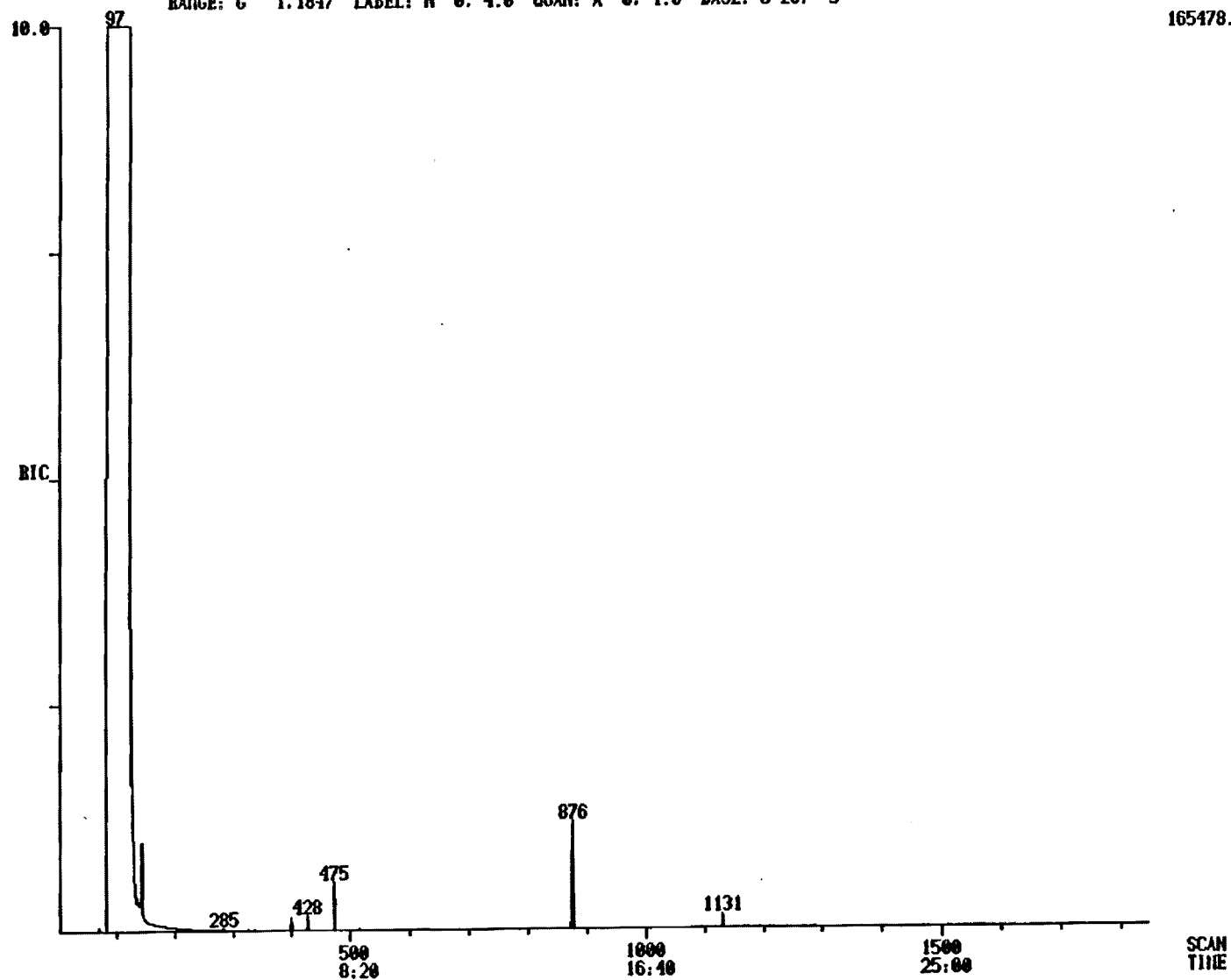


Figure A23. GC-MS Trace of Acid/Neutral Fraction for Commercial Alum Used at Candler Water Treatment Plant.

RIC
08/26/85 15:12:00
SAMPLE: C 08/01 ALUM EXT +IS 20 PPM
RANGE: G 1.2100 LABEL: N 0.4.0 QUAN: A 0.1.0 BASE: U 20. 3
DATA: C0801ALUM 01153
CALI: CAL0802085 013
SCANS 300 TO 2100

54520.

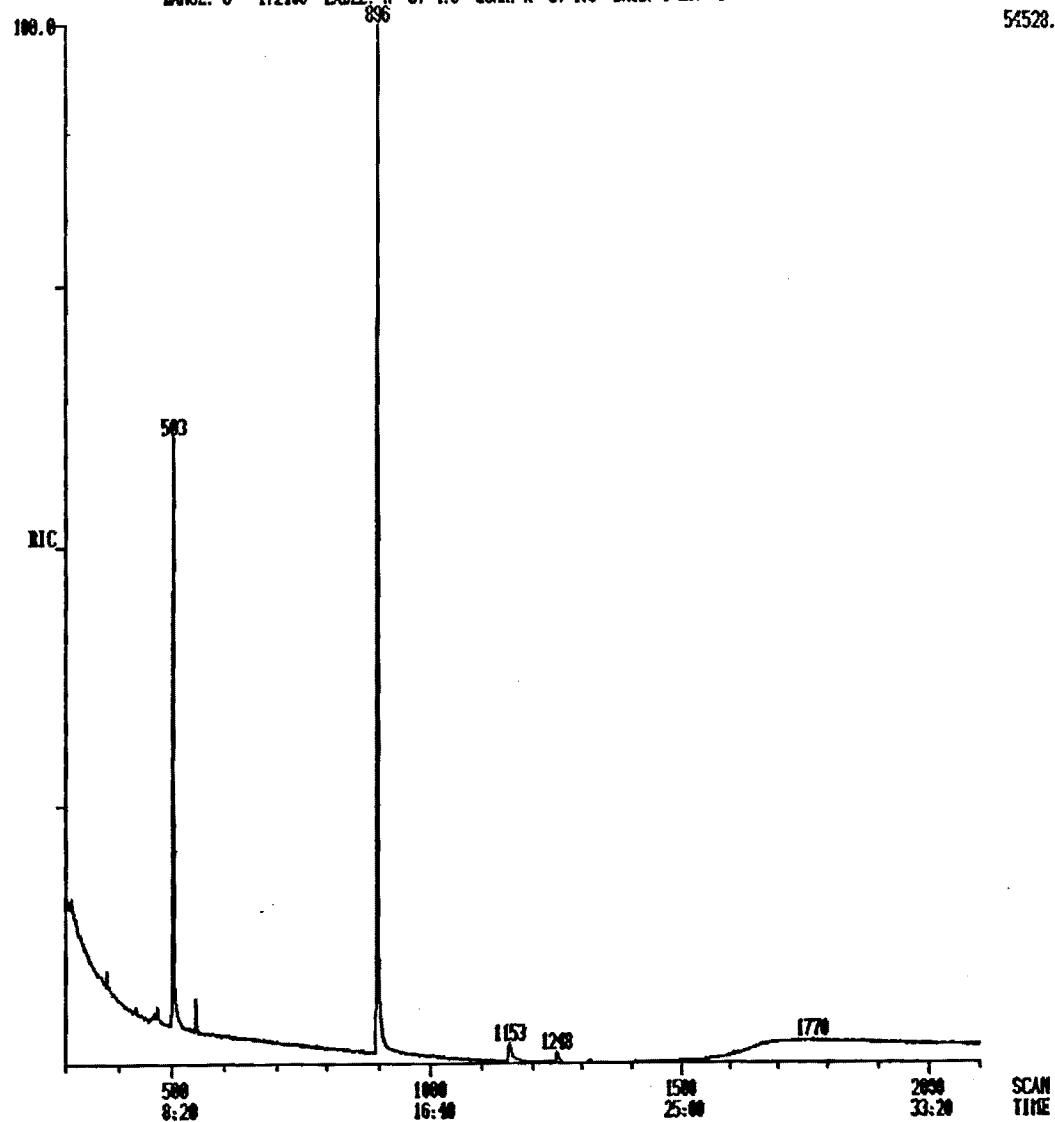


Figure A24. GC-MS Trace of Acid/Neutral Fraction for Commercial Alum Used at Chattahoochee Water Treatment Plant.