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Identification and Separation of the Organic Compounds in Condensate Waters from a Coal-Gasification Process

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ABSTRACT

Solvent extraction, GC-MS, and HPLC techniques were used to characterize the principal organic solutes in a coal-gasification condensate water. Results of previous studies showed that a significant fraction of the Chemical Oxygen Demand (COD) in many condensate waters does not respond to standard GC-MS analysis. Many of these uncharacterized compounds are difficult to treat by biological oxidation or solvent extraction. Solvent-extraction results indicated that a significant fraction of the COD is more polar than dihydroxy benzenes. A sample-preparation technique involving a distillative change of solvent from water to isopropanol allowed qualitative analysis of very hydrophilic compounds of low volatility by GC-MS. A reversed-phase HPLC technique was used to characterize 69-84% of the COD in four condensate water samples. Dimethyl hydantoin and related compounds, previously unreported in condensate waters, were shown to represent 1-6% of the COD in these samples. Some chemical changes were observed during storage of condensate-water samples.

INTRODUCTION

In the gasification process coal reacts with steam and air or oxygen. When the product gases are quenched, a condensate water is formed. The condensate waters from high-temperature processes, such as the Texaco and Koppers-Totzek processes, are comparatively clean. However, the condensate water from a lower-temperature process is contaminated with high concentrations of phenols and other organic compounds. It is typically buffered at a pH between 8 and 9 by large concentrations of ammonia and acid gases (CO_2 and H_2S). It has been estimated that a commercial-scale plant with a Lurgi gasifier will generate a large flow, about 0.45×10^6 kg/h, of condensate water (1). The net water requirement of the process can be reduced substantially if the condensate water can be recycled. The general aspects of condensate-water management and treatment have been discussed previously (1, 2, 3). One promising alternative is to recycle adequately purified condensate water to the cooling tower (4, 5).

Previous Analyses of Condensate Waters

It is difficult to design wastewater treatment systems or to interpret experimental studies of treatment processes without detailed knowledge of the composition of condensate waters. Generic analyses such as the chemical oxygen demand (COD) or the total organic carbon (TOC) provide a measure of the total concentration of organic compounds in a mixture. The COD or TOC can be compared, in consistent units, to the sum of the individual compounds identified by other techniques (6). This is a useful way of assessing how complete the analysis is. Mohr and King (7) summarize thirteen analyses of coal-gasification condensate waters. In eight of these analyses, either the COD or TOC was available for comparison. These analyses accounted for 34 to

92% of the COD with a median value of 49%, and they accounted for 20 to 77% of the TOC with a median value of 51%. It should also be noted that the COD or TOC analyses do not necessarily measure all organic compounds in a water stream.

The most common analytical technique employed in these previous studies used methylene chloride extraction followed by combined gas chromatography and mass spectrometry (GC-MS). Stamoudis and Luthy (8) report recoveries of 82% for phenol and 65% for C_2-phenols with this technique. The results of solvent extraction experiments, discussed subsequently, show that in condensate waters there is a sizeable concentration of organic compounds which are more polar than phenol. These polar compounds probably have even lower recoveries in the methylene chloride/GC-MS technique, due to incomplete extraction.

Condensate-Water Treatment Processes

Solvent extraction processes can recover organic compounds either for sale or for fuel value. The phase equilibrium is characterized by the equilibrium distribution coefficient (K_D), defined as the weight fraction of the solute in the organic phase divided by the weight fraction in the aqueous phase at equilibrium. In a countercurrent extraction process $K_D S/W$ (S and W are the mass flow of solvent and water) must be greater than unity if the solute is to be removed effectively. The cost of the process is determined primarily by S/W and the number of stages; hence large values of K_D are desirable.

Table 1 summarizes the results of experimental tests of condensate-water treatment processes. These results are discussed in greater detail elsewhere (7). Lines 1 through 4 of the table show that extraction with these solvents removed nearly all of the phenols, but the COD removal ranged from 46 to 88%. This indicates that organic compounds present at substantial concentrations in these condensate waters are more polar and hydrophilic than phenol.

Lines 5 through 8 of Table 1 show that activated sludge treatment also removed nearly all of the phenols, but failed to remove 7 to 13% of the COD. Many of these activated sludge treatment methods require pH adjustment or other forms of pretreatment which could be expensive on an industrial scale. Lines 9 through 12 of the table show that solvent extraction followed by biological oxidation removed 95 to 96% of the COD or TOC. This combination incorporates the advantages of both processes. The extraction process recovers organics from a concentrated stream, and the biological process receives a dilute feed at nearly constant composition. In Line 13 of Table 1 98% of the COD was removed from one condensate water by solvent extraction followed by activated sludge treatment with powdered activated carbon added to the reactor (PAC/AS). The effluent from this process still had a COD of 640 mg/l (11).

A substantial fraction of the organic compounds in condensate waters are difficult to remove by solvent extraction or biological oxidation. Many of these compounds cannot be removed by either process. Furthermore, nearly all of the compounds which are not removed by these processes are also not identified with commonly employed analytical techniques (7). Methylene chloride/GC-MS analysis identified less than 1% of the organic solutes in the effluents from several treatment processes (Lines 4, 5, 6, 9 and 13 of Table 1; 8, 11). The unidentified solutes which are difficult to remove pose an important wastewater treatment problem.

One purpose of this work was to develop analytical techniques which can account for a larger fraction of the COD. A second purpose was to study the phase equilibria of condensate-water solutes with several solvents. These studies provide information about the physical properties of the solutes and the capabilities of solvent extraction processes.

EXPERIMENTAL PROCEDURE

Samples of condensate water were obtained from a slagging fixed-bed gasifier at the Grand Forks Energy Technology Center (GFETC) of the U. S. Deptartment of Energy. All handling and analyses of the samples were performed under nitrogen. After even a brief exposure to air the solution darkens and precipitates form. A portion of each sample was adjusted to pH 2 with H_2SO_4 at the time of collection. The samples were stored in the dark at 4°C.

The condensate waters were analyzed by reversed-phase high-performance liquid chromatography (HPLC). This technique has advantages for the polar compounds of interest in this study, because aqueous samples can be injected directly into the mobile phase and a preliminary solvent extraction is not required. Details of the HPLC apparatus and all of the procedures used in this study are described elsewhere (7).

Each condensate-water sample was analyzed by gradient-elution HPLC with UV absorbance detection at 280 nm. The HPLC conditions and a chromatogram for one condensate water are shown in Figure 1. Inspection of the chromatogram shows that no major components were detected in the beginning of the chromatogram where the most polar compounds would be expected to elute. Therefore, the samples were eluted a second time with 100% pH-3 water. This solvent maximized the resolution of very polar compounds. Also, water is sufficiently transparent in the far UV that the detector could be operated at 192 nm where many more compounds absorb. Figure 2 shows that several additional compounds were detected with these conditions.

Once the solutes were resolved with the HPLC, it was necessary to obtain qualitative identifications. In the first procedure, co-chromatography, a known compound was added to the condensate water, and the liquid chromatography was repeated. If there was no resolution between the known compound and the peak of interest, then the identification was tentatively confirmed.

The second procedure employed a novel sample preparation technique which allowed GC-MS identification of HPLC fractions. Individual fractions were collected in dilute aqueous solution as they eluted from the HPLC. In many cases the concentration of the solute in this solution was below the detection limit of the GC-MS. Also, water is not compatible with many GC stationary phases, and removing this water in a rotary evaporator is difficult. Therefore, the samples were concentrated by repeated distillation with added isopropanol. The aqueous solution (typically 5 ml) containing the solute was mixed with about 50 ml of isopropanol (HPLC grade, Burdick & Jackson Co.) and was evaporated to about 1 ml in a rotary evaporator. More isopropanol (10 ml) was added, and the mixture was evaporated to a final volume of about 0.1 ml. The resulting solution contained almost no water.

With the conditions stated above and assuming 100% recovery, the concentration of the solute is increased by a factor of 50. The solute must have a relative volatility substantially less than one. However, moderately volatile compounds can be concentrated to the GC-MS detection limit even though the total solute recovery may be quite low. The measured recoveries for several solutes were: dimethyl hydantoin--63%, phenol--86%, and catechol--89%. The solute must be soluble and inert in isopropanol, and the isopropanol must be free of non-volatile impurities which would concentrate during evaporation.

The principal advantage of this distillative solvent-change procedure is that the solute, which may be very hydrophilic, does not have to distribute between an aqueous phase and an organic phase. This technique was intended for qualitative identification only.

Quantitative measurements were obtained by integrating the peaks from the UV absorbance detector. The detector was calibrated by eluting mixtures of known composition with identical chromatographic conditions. The precision of the quantitative analyses is approximately ±5%. Further details of the analytical technique are presented elsewhere (7).

Liquid-liquid phase equilibria were measured by contacting the condensate water with several solvents in simple batch equilibrations. The solvent-to-water ratio was 1:1 by volume. Details of the extraction procedures are discussed elsewhere (7).

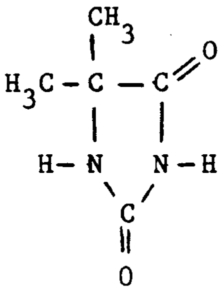
To measure the COD of a raffinate, it was necessary first to remove the residual dissolved solvent. MIBK was removed by stripping with 1.5 moles of water-saturated nitrogen per mole of water. Several commercial sources of MIBK contained an acidic impurity which would affect the COD measurements of stripped raffinates. This impurity was removed by extracting the MIBK repeatedly with NaOH solution before contacting the solvent with the condensate water (7). The COD and organic nitrogen were measured according to standard procedures (15). Organic nitrogen is defined as the difference between Kjeldahl nitrogen and ammonia nitrogen. To increase the precision of this measurement, most of the ammonia was first removed from condensate-water samples by stripping with 4 moles N_2/mole H_2O at 25°C and pH 12. Tests with synthetic solutions showed that thiocyanate responds to the organic nitrogen test (0.24 g N/g SCN^-). The organic nitrogen measurements were corrected for thiocyanate (7).

RESULTS AND DISCUSSION

HPLC and GC-MS Analyses

Table 2 shows the analyses of four condensate waters from the GFETC slagging fixed-bed gasifier. The compounds are arranged in four groups: phenols; dihydroxy benzenes; hydantoins; and methanol, acetonitrile, and acetone. The qualitative identifications of the first three groups were confirmed by HPLC co-chromatography. Compounds in the fourth group were measured by Senetar (16) with a GC technique. As indicated in Table 2, some of the compounds were identified by the isopropanol/GC-MS technique.

An earlier report from this work was the first indication of the presence of dimethyl hydantoin



and related compounds in a condensate water (17). Therefore, the identification of this compound will be discussed in greater detail. Figure 3 is the electron-ionization (EI) mass spectrum of a solute isolated from a condensate water with the isopropanol/GC-MS technique, compared with the spectrum of dimethyl hydantoin as measured in this work and by Rucker, et al. (18). Figure 4 is a similar comparison of the chemical-ionization (CI) mass spectra. On the basis of the EI, CI, and HPLC retention data, 5,5-dimethyl hydantoin is a "confirmed structural assignment" for this condensate-water solute.

As discussed elsewhere (7), methyl hydantoin and methyl hydantoic acid were identified only by co-chromatography, and there was some doubt about the purity of the standard employed. Therefore, these compounds are considered to be identified with a lower level of confidence.

After the initial report, Olson, et al. (19) confirmed the presence of hydantoins in a condensate water from the same gasifier. They adsorbed the compounds on activated carbon, washed the carbon with ethanol, and used GC-MS to measure EI, CI and retention data for the hydantoins. They also obtained EI data for dimethyl derivatives of the hydantoins.

The quantitative analyses in Table 2 show that phenols accounted for 59 to 76% of the COD. Dihydroxy benzenes accounted for 0.02 to 9.5% of the COD. Dihydroxy benzenes are much more polar than phenol and have lower K_D values into diisopropyl ether (DIPE) and methyl isobutyl ketone (MIBK), as shown in Table 3. If, for example, a solvent extraction process was designed to remove 99% of the phenol, then a much lower fraction of the dihydoxy benzenes would be removed. MIBK has much higher K_D values for these compounds than does DIPE, meaning that lower S/W values are possible.

Hydantoins represented 1 to 6% of the COD. The concentration of dimethyl hydantoin varied with time, as discussed elsewhere (7). The value in parentheses in Table 2 is that at the time the sample was taken. This concentration remained constant in the portion of the sample that was immediately acidified to pH 2. In the unaltered portion of the sample, the concentration increased to the value shown without parentheses in Table 2 over a period of about one month. In the sample from run No. RA-106 the molar increase in dimethyl hydantoin nearly equals the molar decrease in acetone concentration. This suggests that dimethyl hydantoin may form in condensate water by the Bucherer-Bergs reaction described by Ware (22).

$$\underset{\text{acetone}}{C_3H_6O} + NH_3 + CO_2 + HCN \longrightarrow \underset{\text{dimethyl hydantoin}}{C_5H_8N_2O_2} + H_2O \qquad (1)$$

Dimethyl hydantoin is much more polar than dihydroxy benzenes. Table 4 shows the K_D values of this compound into several solvents. The first two solvents are Lewis acids. Methylene chloride gives a very low K_D for this compound; therefore, the recovery in the standard GC-MS technique is probably very low. The remaining solvents are listed in order of increasing Lewis basicity. Tributyl phosphate (TBP) exhibits the highest K_D (2.6).

Dimethyl hydantoin is also difficult to remove by biological oxidation. Willson, et al. (5) found that dimethyl hydantoin was not degraded in a biologically active cooling tower. Little is known about the toxicity of dimethyl hydantoin (24), but diphenyl hydantoin is a suspected carcinogen (25).

The analyses in Table 2 account for 69 to 84% of the COD, which is an improvement over most previous analyses. However, an important fraction of the COD remains unidentified. A goal of this work was to provide further chemical evidence about the remaining COD.

Table 5 shows the results of solvent extraction experiments with the condensate water from Run No. RA-120. At a sample age of 0.7 days, one extraction with MIBK removed 89% of the COD. However, a second extraction increased the cumulative removal to only 92.7%. This indicates that the remaining organic constituents have low values of K_D into MIBK. The data at longer sample age show that a chemical reaction occurred which produced solutes that were more difficult to extract. These reactions occurred despite the fact that the sample was stored at low temperature in an inert atmosphere. It is important to be aware of these reactions because many analyses and experimental studies of treatment processes are done with aged samples.

MIBK extraction removed nearly all of the phenols and dihydroxy benzenes. Hydantoin represented only 1% of the COD in this sample. Acetonitrile and acetone are sufficiently volatile that they would be completely removed by the nitrogen stripping procedure employed to remove residual dissolved MIBK from the raffinates. Only about 25% of the methanol would be removed in the nitrogen stripping procedure, and methanol may have a low K_D into MIBK. The concentration of methanol was not measured in this sample, but methanol may account for some of the raffinate COD.

This condensate water contained 210 mg/l of organic nitrogen. Lines 1 through 5 of Table 5 show that the organic nitrogen had a low K_D into MIBK. Also lines 4 and 5 of the table show that the remaining 10% of the COD had a K_D of nearly zero into MIBK.

The extractions in lines 6 and 7 of Table 5 were designed to test for basic functional groups on the poorly extracted solutes. Many compounds with weakly basic functional groups would be ionized, and therefore difficult to extract, at the condensate-water pH of 8.5. Comparison of lines 6 and 7 with line 2 of the table shows that suppression of the ionization of basic functional groups did not improve the extractability of the solutes. Therefore, basic functional groups are not the only reason for the low K_D values of these compounds with MIBK. Similarly, line 8 shows that acidic functional groups are not the only reason for the low K_D values.

The second solvent studied was TBP. This solvent removed more of the COD than MIBK; however, some of the solutions had a low K_D into this solvent also.

The third solvent studied was a mixture of 25% w/w trioctyl phosphine oxide (TOPO) in MIBK. TOPO is a strong hydrogen-acceptor extractant. This solvent removed essentially the same fraction of the COD as did MIBK for this sample, although it did remove a greater fraction than MIBK from another condensate-water sample (7). Solvents containing TOPO have much higher K_D values for phenol and dihydroxy benzene than does MIBK (Table 3). This suggests that TOPO may be able to remove the same fraction of the COD as MIBK at a lower solvent-to-water ratio (S/W). However, Table 2 shows that the K_D decreases as the concentration of phenols increases in the organic phase and the stoichiometric ratio of phenols to TOPO increases. The value of S/W is determined by the K_D corresponding to equilibrium with the aqueous feed to a countercurrent extraction process.

Also, TBP and TOPO may be difficult to regenerate fully because both of these solvents have low volatility. Some solutes could have such low volatilities that they would accumulate in the solvent. It may be possible to recover acidic solutes from TOPO or TBP by back extraction into an aqueous solution at high pH. In the case of 25% TOPO in MIBK, a high ionic strength is necessary to prevent emulsification at high pH (7). Some of the condensate-water solutes are probably not acidic, and these solutes could accumulate in the solvent.

Table 6 shows the results of a one-stage batch distillation of a condensate water after MIBK extraction. Nearly half of the remaining COD was volatile with respect to water. Essentially all the nitrogen compounds were non-volatile, and these compounds did not become volatile when the distillation was carried out at high pH.

Ultrafiltration of an MIBK raffinate with a 1000 MW cut-off membrane did not retain any appreciable fraction of the COD (7).

SUMMARY

Some compounds in condensate waters are not identified and are difficult to remove by solvent extraction or biological oxidation. Dimethyl hydantoin has been identified in condensate waters with an analytical technique employing distillative solvent change, followed by GC/MS. In four condensate waters, compounds accounting for 69 to 84% of the COD were identified. Solvent extraction of these waters with MIBK has advantages over DIPE, particularly for removal of dihydroxy benzenes. MIBK can probably remove about 90% of the COD at an economically reasonable solvent-to-water ratio, but the remaining compounds have very low K_D values. Some of these are volatile; some are not. There are significant concentrations of compounds which are difficult to extract, have low volatility and contain organic nitrogen.

Acknowledgement

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Table 1. Experimental Tests of Condensate-Water Treatment Processes - A Summary of the Literature.

Coal-Gasification Process	Reference	Treatment Process[a]	Fractional Removal of[b]: COD	TOC	Phenols
1. Chapman[c]	9	BA	0.670	0.680	0.996
2. Chapman[c]	10	DIPE	0.456	0.651	0.999
3. Lurgi[d]	10	DIPE	0.755	0.690	0.997
4. GFETC[e] Run No. RA-52	11	MIBK	0.880	0.820	0.999
5. GFETC[e] Run No. RA-52	8	AS	0.851	NR	0.999
6. HYGAS[f] Run No. 64	8	AS	0.825	NR	0.999
7. HYGAS[f] Run No. 79	12	AS	0.931	NR	0.999
8. METC[g] Run No. 95	13	AS	0.874	0.920	0.999
9. GFETC[e] Run No. RA-52	11	MIBK, AS	0.958	0.948	0.999
10. GFETC[e]	14	MIBK, AS	NR	0.947	0.998
11. GFETC[e]	14	DIPE, AS	NR	0.959	0.998
12. HYGAS[f] Run No. 72	12	NBA, AS	0.945	NR	NR
13. GFETC[e] Run No. RA-52	11	MIBK, PAC/AS	0.980	0.965	0.999

Footnotes for Table 1:

a. AS -- activated-sludge treatment
MIBK -- solvent extraction with methyl isobutyl ketone
DIPE -- solvent extraction with diisopropyl ether
NBA -- solvent extraction with n-butyl acetate
PAC/AS -- activated-sludge treatment with powdered activated carbon added to the reactor

b. NR — not reported.

c. Chapman fixed-bed gasifier, Kingsport, TN.

d. Lurgi fixed-bed gasifier, Kosovo, Yugoslavia.

e. GFETC slagging fixed-bed gasifier, Grand Forks, ND.

f. HYGAS fluidized-bed gasifier, Chicago, IL.

g. METC fixed-bed gasifier, Morgantown, WV.

Table 2. Quantitative Analyses of GFETC Condensate Waters[a]

GFETC Run No.:	Qualitative Identification[c]	RA-78	RA-97	RA-106	RA-120
Date of sample:		6/80	6/81	9/81	4/82
Sample age interval (days)[b]:		150-500	40-150	1.7-38	0.7-110
Compound					
1. phenol		4,750	7.250	3,450	4,300
2. C_1-phenols		2,850	3,750	2,140	2,350
3. C_2-phenols	GC-MS	450	470	430	410
4. o-methoxy phenol	GC-MS	260	450	165	260
5. p-hydroxy acetophenone	GC-MS	50	35	5	ND
6. catechol		990	860	40	2
7. 4-methyl catechol	GC-MS	610	500	20	ND
8. resorcinol		60	28	2	ND
9. hydroquinone		35	24	1	ND
10. 5,5-dimethyl hydantoin[d]	GC-MS	1,720 (660)	300 (150)	460 (230)	165 (40)
11. 5-methyl hydantoic acid		95	130	ND	10
12. 5-methyl hydantoin		135	40	ND	35
13. methanol[e]		NA	NA	1,050	NA
14. acetonitrile[e]		NA	NA	365	NA
15. acetone[d,e]		NA	NA	505 (620)	NA
COD (mg/l)		34,900	46,700	22,900	23,400
Fraction of COD due to:					
hydroxy benzenes:		0.586	0.624	0.663	0.7640
dihydroxy benzenes:		0.095	0.059	0.006	0.0002
hydantoins:		0.061	0.010	0.023	0.0100
methanol, acetonitrile, acetone		-	-	0.151	-
Total Fraction Identified:		0.742	0.693	0.843	0.774

Footnotes for Table 2

a. Concentrations in mg/l. Estimated precision: ±5%. ND -- none detected. NA -- not analyzed.

b. With the exception of dimethyl hydantoin and acetone, the concentrations did not change with time and were the same in the portions of each sample that were stored at pH 8.5 and pH 2.

c. The qualitative identifications of the indicated compounds were confirmed by the isopropanol/GC-MS technique. All of the solutes were identified by HPLC co-chromatography.

d. This is the concentration at long sample ages. The value in parentheses is for the portion of the sample stored at pH2 and is also the estimated concentration when the sample was removed from the gasifier. The time dependence of the dimethyl hydantoin concentration is discussed in the text.

e. Data from Senetar (16). Sample age: 600 days.

Table 3. Equilibrium Distribution Coefficients of Phenol and Dihydroxy Benzenes into DIPE, MIBK, and 25% w/w TOPO in DIBK[a]

	DIPE[b]	MIBK[b]	25% w/w TOPO in DIBK[c]					
Stoichiometric Ratio[d]:			10.0	5.0	2.5	1.2	0.6	0.4
phenol	36.5	100.	810	650	460	255	110	76
catechol	4.86	18.7	-	270	200	92	-	-
resorcinol	2.06	17.9	-	-	98	-	-	-
hydroquinone	1.03	9.92	-	-	35	-	-	-

Footnotes for Table 3

a. Solvents: DIPE -- diisopropyl ether, MIBK — methyl isobutyl ketone, TOPO -- trioctyl phosphine oxide, DIBK — diisobutyl ketone.

b. Data from Greminger and King (20).

c. Data from Mac Glashan and King (21).

d. The stoichiometric ratio is the moles of TOPO per mole of phenol in the organic phase at equilibrium.

Table 4. Equilibrium Distribution Coefficients for Dimethyl Hyantoin[a]

Solvent	K_D[b]
Methylene chloride	< 0.05
25% w/w di(2-ethyl hexyl) phosphoric acid in kerosene	< 0.05
Methyl isobutyl ketone (MIBK)	0.25
Tricresyl phosphate (TCP)	0.11
Tributyl phosphate (TBP)	2.6
25% w/w trioctyl phosphine oxide in MIBK	1.2
25% w/w Adogen 363 (R_3N, Sherex Chemical Co.) in kerosene	< 0.05

Footnotes for Table 4:

a. Data from Schonberg (23).

b. Experimental uncertainty: ± 20%.

Table 5. Fraction of COD Removed by Solvent Extraction from GFETC Run No. RA-120 Condensate Water

		Fraction of COD Removed vs. Sample Age[d,f,g,h]			
Solvent[a,b]	No. of Batch Extractions[c]	0.7 Days	15 Days	190 Days	Fraction of Organic N Removed at 190 Days[i,j]
1. MIBK	1	$0.890^{(6)}$	$0.883^{(2)}$	$0.856^{(3)}$	0.30
2. MIBK	2	$0.927^{(2)}$	$0.911^{(2)}$	$0.878^{(2)}$	0.30
3. MIBK	3	-	-	$0.890^{(1)}$	0.37
4. MIBK	4	-	-	$0.900^{(1)}$	0.37
5. MIBK	5	-	-	$0.902^{(1)}$	0.43
6. MIBK	1 and 1 @ pH 12	-	-	$0.878^{(1)}$	0.25
7. MIBK MC	1 1 @ pH 12	-	-	$0.880^{(1)}$	0.11
8. MIBK	1 and 1 @ pH 3	$0.923^{(1)}$	$0.913^{(1)}$	-	
9. TBP	1	-	$0.915^{(1)}$	-	
10. TBP	2	-	$0.938^{(1)}$	-	
11. TBP	1 and 1 @ pH 3	-	$0.945^{(1)}$	-	
12. 25% w/w TOPO/MIBK	1	-	$0.88^{e(2)}$	-	
13. 25% w/w TOPO/MIBK	1 and 1 @ pH 3	-	$0.92^{e(2)}$	-	

Footnotes for Table 5:

a. Solvents: MIBK--methyl isobutyl ketone, MC — methylene chloride, TBP — tributyl phosphate, TOPO/MIBK — 25% w/w trioctyl phosphine oxide in MIBK.

b. 1:1 volume phase ratio in all extractions.

c. Extractions performed at the condensate water pH of about 8.5 unless indicated differently.

d. Experimental uncertainty: ±0.005.

e. Experimental uncertainty: ±0.02

f. The number of replicates is shown in parentheses. The ratio of standard deviation to mean for each extraction was about 0.004.

g. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before COD measurement.

h. Condensate water COD: 23,400 mg/L.

i. Condensate water organic nitrogen: 210 mg/L.

j. Experimental uncertainty: ± 0.10.

Table 6. Batch Distillation of the COD and Organic-Nitrogen Compounds which Remain after MIBK Extraction[a,b,c]

	% Water From Feed	% COD From Feed	% Organic Nitrogen from Feed
Distillate 1	43	38	0
Distillate 2	46	4	3
Bottoms	11	44	90
Total	100	86[d]	93[d]
Feed Conc. (mg/l)	—	3,220	175

Footnotes for Table 6:

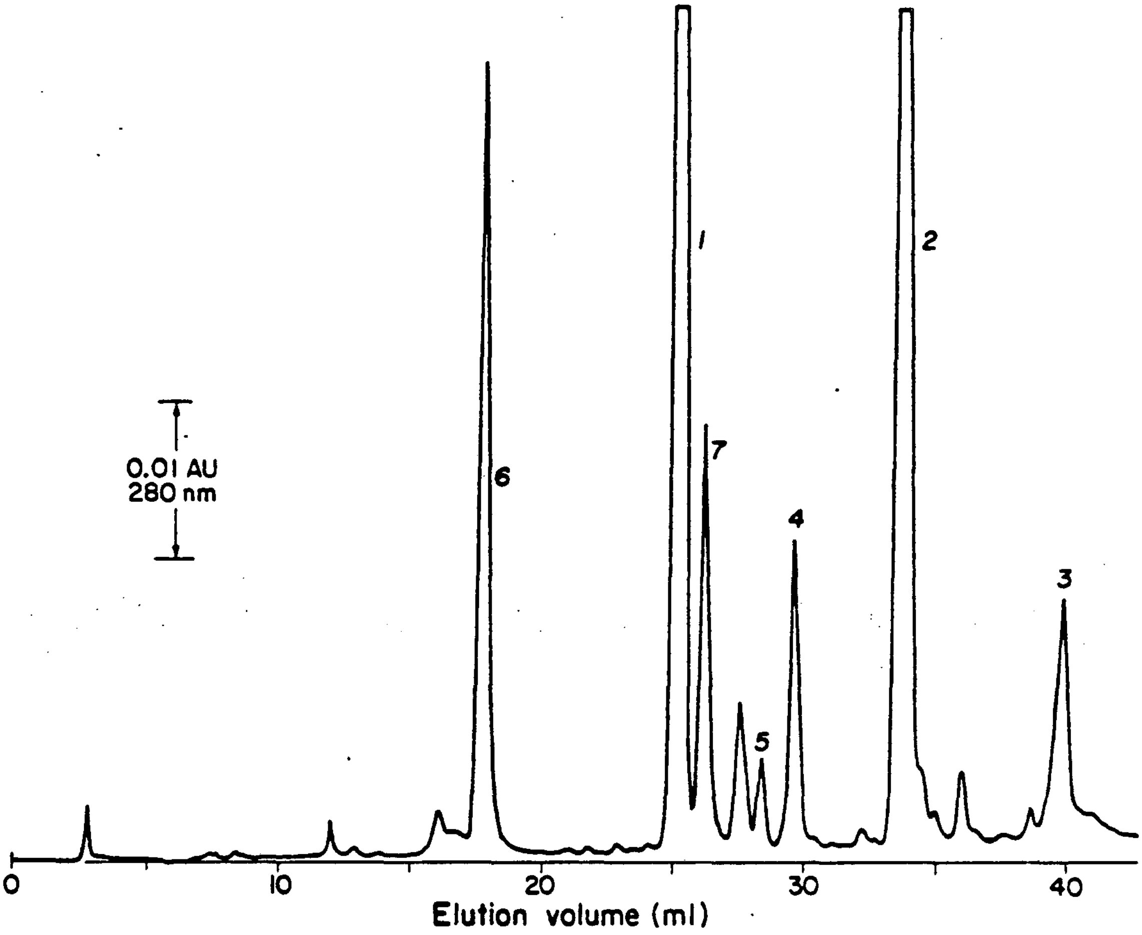
a. Experimental uncertainty: ± 5% of COD or organic nitrogen in feed.

b. The feed to the distillation was the GFETC Run No. RA-120 sample after extraction with MIBK. The feed was adjusted to pH 2 with H_2SO_4 before distillation.

c. Residual dissolved solvent was removed from the raffinate by nitrogen stripping before distillation.

d. Mass balance did not close because a solid precipitate formed in the bottom product during the distillation.

Figure 1: HPLC Chromatogram of GFETC Run No. RA-97 Condensate-Water; Gradient Elution



XBL 8112-1665

Footnotes for Figure 1:

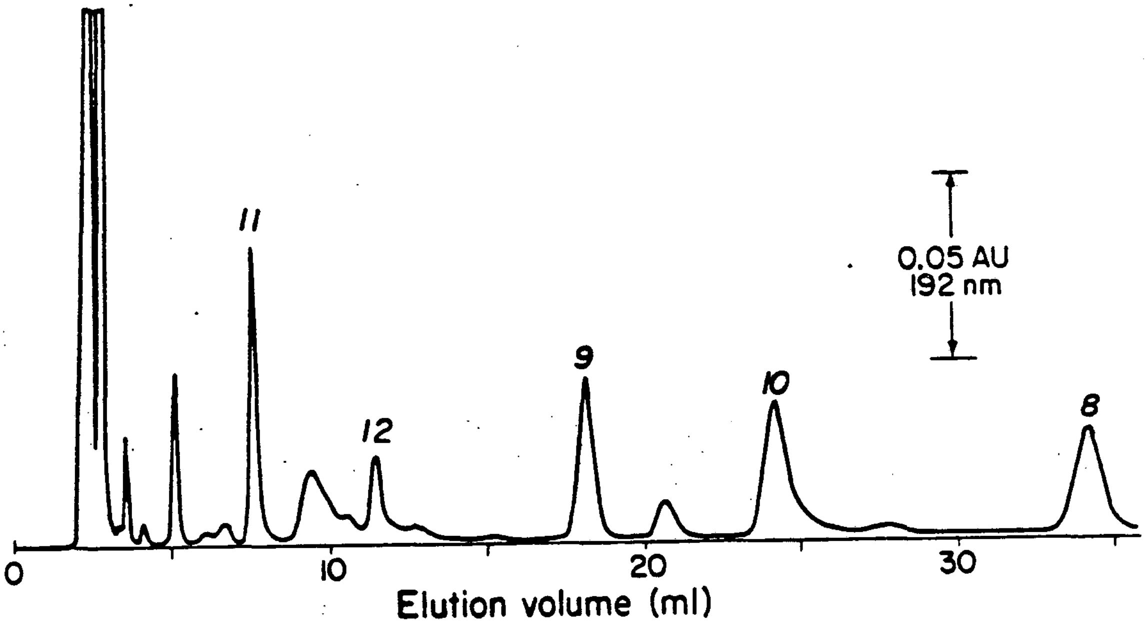
a. Mobile phase: linear gradient from 100% pH-3 H_2O at injection to 30% pH-3 H_2O and 70% methanol at 42 ml elution volume. Flow rate: 1 ml/min.

b. Stationary phase: Waters Associates Radial Pak A C_{18}.

c. UV absorbance detection at 280 nm.

d. Peak Nos. identified in Table 2.

Figure 2: HPLC Chromatogram of GFETC Run No. RA-97 Condensate Water; Isocratic Elution in Water



XBL 8112-1666A

Footnotes for Figure 2:

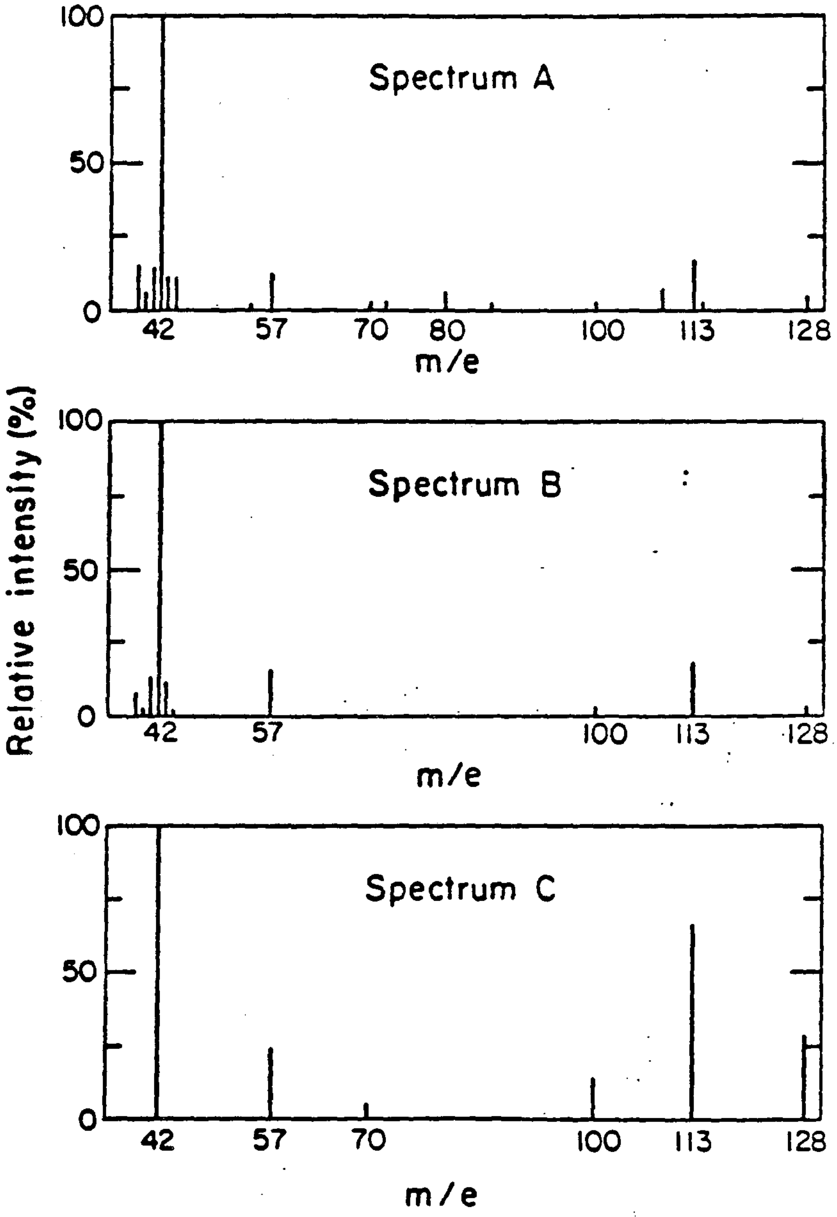
a. Mobile phase: 100% pH-3 H_2O. Flow rate: 1 ml/min.

b. Stationary phase: Waters Associates Radial Pak A C_{18}.

c. UV absorbance detection at 192 nm.

d. Peak Nos. identified in Table.

Figure 3: Comparison of the 70 eV Electron-Ionization Mass Spectra of a Condensate-Water Solute and Dimethyl Hydantoin.



XBL837-973

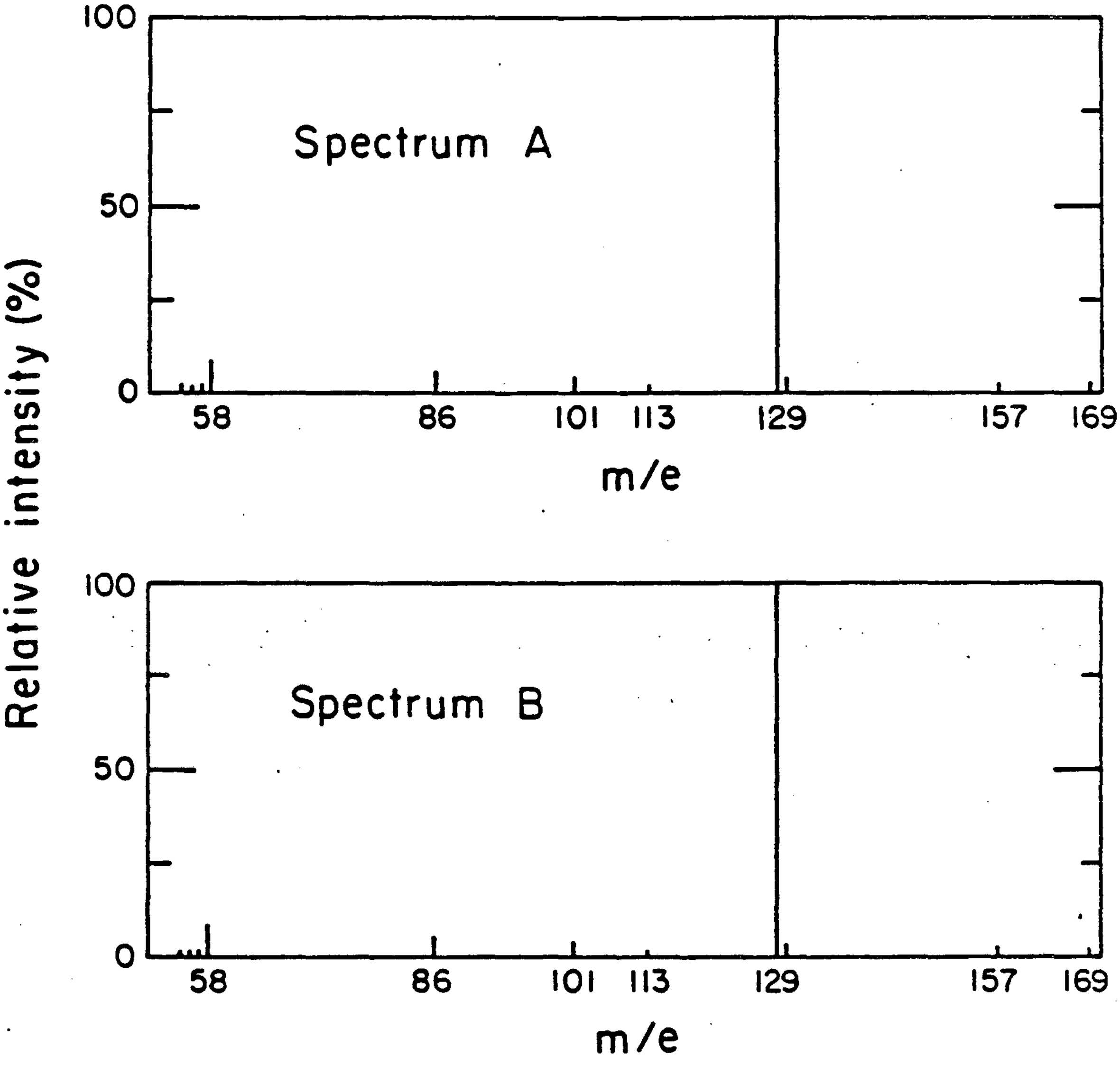
Footnotes for Figure 3:

Spectrum A: Solute isolated from GFETC run No. RA-78 condensate water with the isopropanol/GC-MS technique.

Spectrum B: 5,5-dimethyl hydantoin standard.

Spectrum C: 5,5-dimethyl hydantoin from Rucker, et al. (18).

Figure 4: Comparison of the Chemical Ionization Mass Spectra of a Condensate-Water Solute and Dimethyl Hydantoin



XBL837-810

Footnotes for Figure 4:

Spectrum A: Solute isolated from GFETC run No. RA-78 condensate-water with the isopropanol/GC-MS technique.

Spectrum B: 5,5-dimethyl hydantoin standard. Chemical ionization reagent -- methane

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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