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Characterization of Organics in the Feed Streams for the H/F Effluent Treatment Facility

SUMMARY

Analysis of weekly samples from the F- and H-area treblers indicates that tri-n-butylphosphate (TBP) is the major organic species in the feed to the F/H Effluent Treatment Facility (ETF). Concentrations up to 100 mg/L were observed, with an average of 50 mg/L from F-area and 3 mg/L from H-area. Normal paraffinic hydrocarbons (NPH) are present in lesser amounts, ranging up to 4 mg/L. These two species, both foulants of the reverse osmosis (RO) membranes, account for almost all of the dissolved organic carbon present in the samples.

Samples from the sources which feed the treblers (and will feed the ETF) indicate that all eight canyon evaporators

contribute TBP. None of the four tank farm evaporators contribute TBP. If TBP is to be removed at the sources, either the overhead streams from a number of evaporators will have to be piped to one or two central locations for treatment, or up to eight individual treatment points would have to be maintained.

BACKGROUND

A characterization study of ETF feeds performed in 1984 showed total organic carbon (TOC) concentrations up to 500 mg/L.[1] The TOC was not further characterized. For testing purposes simulants were prepared using the average of 39 mg/L TOC, added as a 30 vol% TBP solution in kerosene (NPH).[2] This assumed that the measured TOC had the same ratio of TBP to NPH as the F-area PUREX solvent. Tests using these simulants showed fouling of the RO membrane, which requires unacceptably frequent cleaning of the RO system.[3] More recent testing indicates that TBP alone fouls the membranes.[4]

Characterization of the organic species was initiated in August 1986 to determine if additional testing of the RO in the presence of other organic species was necessary. Determination of the TBP, NPH, and TOC concentrations was used to calculate carbon balances for the samples. Results indicated that TBP was the major organic species. However, due to widely fluctuating organic concentrations, the characterization was extended for almost a year to ensure that the whole range of plant operations was observed.

SAMPLING AND ANALYSES

Samples were collected directly into wide mouth glass bottles with paper lined plastic caps. HP-Environmental Collections sampled the treblers during their usual weekly sampling. Each sample is a composite, collected over a period of up to 7 days, depending on flows through the trebler and the HP collection schedule. Most samples came from the composite samplers, which collect a volume proportional sample based on the measured flows. When samples were unavailable from these collectors, a backup collector was sampled. Backup collectors are not volume proportional, but continuously sample the trebler flow, and collect the water in a large plastic jug through Tygon tubing. These samples showed higher TOC values and contained phthalate plasticizers.

The main limitation of the samples is due to the sample being collected through a tube which extends below the liquid surface. Any floating organic layer will not be sampled. Since very few samples were close to the solubility limit for NPH, it is unlikely that floating NPH layers were missed. Other floating organics may have been missed. The design of the ETF feed tank should eliminate any such floating layers (if present) from being fed to the RO system.

The samples from the evaporators (sources) were also collected directly in glass bottles. Most of these were from a bottom drain valve on the overheads collection tank. In several instances the samples were dip samples, which were characterized by an organic layer floating on the surface. In most cases the two layers were separated using a separatory funnel, and only the aqueous portion was analyzed.

Analysis consisted of concentrating the organics from 50 ml of water onto a C_{18} extraction column, followed by elution of the organics with tetrahydrofuran (THF). The detailed procedure is given in other reports.[5,6] This method concentrates the organics by a factor of 50, and gives a THF extract that is free of radioactivity. Extraction efficiencies were determined for both TBP and NPH, as 100 and 40%, respectively.[5] The THF extracts were quantitatively analyzed on a capillary GC with FID detector, using a 30 m DB-5 column.

TREBLER DATA

The data from the F- and H-area treblers samples are given in Tables 1 and 2. In both areas the predominant organic is TBP. Significantly higher TOC levels were found in the F-area samples. The average TBP concentration in F-area is 50 mg/L with a range from <1 to 100 mg/L. NPH concentrations ranged from <0.1 to 5.7 mg/L with an average concentration of less than 1 mg/L.

The TBP and NPH concentrations accounted for all or most of the TOC, as noted in the carbon balance column of Table 1. The samples which show low carbon balances either contained plasticizers from the backup sampler, or were samples which tended to plug the extraction columns. It is suspected that biological activity in the samples may have lowered the TBP, but not the TOC concentrations, in some of the samples which were stored for several weeks before analysis. Those samples which have carbon balances significantly greater than 1.0 typically contain high concentrations of TBP. Standards analyzed for TOC indicate that the TOC recovery goes down as the TBP concentration increases, due to stripping of the TBP during the total inorganic carbon portion of the analysis.

H-area trebler results show an average TBP concentration of 3 mg/L with a range of <1 to 20 mg/L. NPH concentrations ranged up to 1.8 mg/L. This is consistent with the use of lower TBP concentrations in the solvent used in H-area extractions. The carbon balances are generally poorer in H-area, due to the low levels of TBP in the samples, and the 3-10 mg/L of TOC observed in all of the samples. The carbon balances are also more sensitive to the analytical errors for both TBP and TOC. Some of the excess TOC in the samples may have been contamination, as most of the samples contained plasticizers. If additional organic carbon species are present they could not be identified in this study.

Table 3 gives the results of the feed samples from the H-area pilot RO unit. These are grab samples collected at the treblers for processing. The results are in agreement with the range of values reported for the composite samples from the treblers. Several results are reported for some samples. These represent duplicates, or samples before and after pH adjustment and filtration. Neither of the pretreatment steps seemed to affect the concentration of organic species. Again, carbon balances are often poor. This is believed to be due to long storage times and biological activity causing a loss of TBP.

SOURCE DATA

The major sources of flows to the treblers were analyzed for TBP and NPH. The results are given in Tables 4 and 5. All eight evaporators associated with the canyons (6 in F-area, 2 in H-area) are sources of TBP. The waste tank evaporators do not contribute TBP. The TBP concentrations range up to 150 mg/L, and the NPH concentrations up to 25 mg/L. These highest levels were from samples which contained an organic layer which was not separated prior to analysis. These would not be typical of the material sent to the treblers.

Although there is quite a bit of variability in the TBP results, all eight evaporators release sufficient TBP in the overheads to cause fouling in the RO system. Removal of TBP at the sources would require that either the effluents from all the evaporators be piped to a central location in each area, or that multiple removal systems be installed and maintained.

In general, the carbon balances were fairly good for these samples, indicating that almost all of the organic carbon was accounted for by the TBP and NPH. Three additional organic species were detected in small amounts from the ARU evaporator in F-area. These could not be identified. However, since the flow from the ARU is scheduled to be recycled within the canyon[1], and since the species could not be found in any of the trebler samples, these compounds are not expected to cause any problems.

LIMITATIONS OF DATA

The data in this report represent routine plant operations over a one year period. Already mentioned is a limitation of the samples due to the sampler not collecting floating organics layers. In addition, based on the way that the collectors obtain the volume proportional sample, if a small volume of water with a high concentration of dissolved organic carbon passed through the trebler it might not be sampled. The resulting composite sample would not contain measurable quantities of that organic species. Such an organic species would not be characterized in the present study, but might have an adverse effect on the RO system in the ETF. This can only be controlled by strict limitations on what can be disposed of in a drain system feeding the ETF.

CONCLUSIONS

The predominant organic species which will be present in the feed to the ETF is TBP, with lesser amounts of NPH. These account for almost all of the TOC in the system. Characterization for a one year period failed to identify any other organic species. Carbon balances were sometimes significantly lower than 100%, indicating that decomposition products of TBP or other organics which could not be identified may be present at various times. For this reason, any organic removal scheme which is used for the ETF should be capable of removing organics in general, rather than a specific method for TBP removal.

The TBP comes from all of the canyon evaporators in both areas. The waste tank farm evaporators do not contribute TBP to the ETF feed. F-area is the larger source, both in terms of flow and concentration of TBP.

QUALITY ASSURANCE

All of the data from this study are recorded in DPSTN-4384 in accordance with the SRL procedures manual. Standard solutions were prepared with reagent grade NPH and TBP to calibrate the analytical methods used. The total organic carbon analyses were performed by ADD, using a wet oxidation method.

REFERENCES

1. J. P. Ryan, Effluent Characterization Study for the 200-Area Effluent Treatment Facility, DPST-84-511, May 23, 1984.

2. J. P. Ryan, Separations Area Effluent Treatment: The Preparation of a Simulant for System Development and Testing, DPST-84-287, February 8, 1984.

3. F. L. Poy, Pilot Scale Test Results for the F/H ETF: Effect of Tributylphosphate/Kerosene on Reverse Osmosis Productivity, DPST-86-485, July 22, 1986.

4. F. L. Poy, Fouling Effects of Tri-n-butylphosphate on Reverse Osmosis Performance and Techniques for Performance Recovery, DPST-87-387, July 28, 1987.

5. H. E. Shook, Jr., Analysis of Organic Materials in Feed to Effluent Treatment Facility, DPST-86-616, December 3, 1986.

6. H. E. Shook, Jr., Analysis of Residual Organic Materials in Aqueous Radioactive Streams from the Purex Process, DP-1744, May 1987.

TABLE 1. F-AREA TREBLER DATA

Date	TIC (mg/L)	TOC (mg/L)	NPH (mg/L)	TnBP (mg/L)	Carbon Balance *
22-Aug-86	<0.5	30	- -	--	- -
29-Aug-86	<0.5	34	3.0	19	0.37
12-Sep-86	<0.5	28	1.0	21	0.44
03-Oct-86	1.0	49	0.7	11	0.14
10-Oct-86	1.0	25	0.9	35	0.78
24-Oct-86	1.1	17	0.8	< 1	0.05
31-Oct-86	<1.0	7	1.2	< 1	0.15
12-Dec-86	0.1	31	0.2	8	0.15
19-Dec-86	0.1	34	0.9	80	1.29
26-Dec-86	0.1	39	2.3	100	1.45
02-Jan-87	0.2	30	5.7	86	1.69
09-Jan-87	0.1	35	4.1	93	1.52
16-Jan-87	0.2	45	0.6	86	1.06
23-Jan-87	<0.1	41	0.7	36	0.49
30-Jan-87	<1.0	36	0.1	46	0.69
06-Feb-87	0.1	36	0.1	8	0.12
13-Feb-87	0.2	43	<0.1	54	0.68
20-Feb-87	0.2	41	0.1	17	0.23
27-Feb-87	<0.1	36	0.1	7	0.11
06-Feb-87	0.7	37	0.5	45	0.66
13-Feb-87	0.3	42	1.3	96	1.26
20-Feb-87	0.3	41	0.3	69	0.92
27-Feb-87	0.1	44	0.7	85	1.06
03-Mar-87	<1.0	43	0.5	87	1.11
10-Mar-87	0.6	39	0.6	25	0.36
16-Mar-87	1.4	32	0.7	52	0.90
24-Mar-87	0.4	43	0.2	33	0.42
01-May-87	0.4	38	0.5	65	0.93
08-May-87	0.3	39	1.7	62	0.91
15-May-87	0.5	32	0.3	71	1.20
22-May-87	2.2	20	0.7	45	1.24
29-May-87	0.9	33	0.6	81	1.32
05-Jun-87	<0.1	31	0.8	69	1.22
19-Jun-87	0.4	27	0.4	73	1.48
26-Jun-87	0.3	26	0.1	53	1.10
02-Jul-87	0.5	7	0.3	13	1.01
10-Jul-87	0.1	18	1.0	9	0.32

* Fraction of TOC accounted for by TBP and NPH

TABLE 2. H-AREA TREBLER DATA

Date	TIC (mg/L)	TOC (mg/L)	NPH (mg/L)	TnBP (mg/L)	Carbon Balance *
22-Aug-86	<0.5	6	- -	--	- -
29-Aug-86	<0.5	5	1.8	12	1.47
05-Sep-86	<0.5	7	0.8	18	1.44
12-Sep-86	<0.5	9	1.7	8	0.63
19-Sep-86	1.0	6	1.4	< 1	0.21
03-Oct-86	1.2	5	0.5	1	0.21
10-Oct-86	4.1	2	0.8	< 1	0.50
24-Oct-86	4.5	2	1.2	< 1	0.76
31-Oct-86	32.0	1	1.0	2	1.43
14-Nov-86	12.3	9	<0.1	19	1.16
12-Dec-86	0.5	4	<0.1	2	0.32
19-Dec-86	0.6	2	0.1	< 1	0.20
26-Dec-86	0.3	2	0.1	1	0.49
02-Jan-87	3.5	2	<0.1	< 1	0.04
09-Jan-87	20.6	10	3.2	4	0.51
16-Jan-87	0.4	3	<0.1	< 1	0.07
23-Jan-87	6.8	3	0.1	< 1	0.09
30-Jan-87	3.3	1	0.1	< 1	0.28
06-Feb-87	0.3	3	<0.1	< 1	0.04
13-Feb-87	3.7	3	0.1	< 1	0.13
20-Feb-87	0.3	3	0.1	< 1	0.05
27-Feb-87	0.1	7	0.1	6	0.46
06-Mar-87	0.3	2	<0.1	< 1	0.06
13-Mar-87	0.1	7	<0.1	5	0.40
20-Mar-87	0.2	3	0.4	< 1	0.17
27-Mar-87	2.1	3	0.4	< 1	0.12
03-Apr-87	<1.0	9	1.1	8	0.57
10-Apr-87	7.7	2	0.2	< 1	0.15
16-Apr-87	6.8	3	0.4	< 1	0.19
24-Apr-87	0.4	2	0.3	< 1	0.35
08-May-87	0.3	1	0.9	2	1.90
15-May-87	0.2	3	<0.1	1	0.13
22-May-87	0.2	4	0.3	1	0.24
29-May-87	0.2	4	0.1	2	0.21
19-Jun-87	0.2	1	0.1	1	0.92
02-Jul-87	0.1	10	0.2	1	0.06
10-Jul-87	0.1	8	0.4	< 1	0.10

* Fraction of TOC accounted for by TBP and NPH

TABLE 3. H-AREA PILOT SCALE RO FEED DATA

Date	TIC (mg/L)	TOC (mg/L)	NPH (mg/L)	TnBP (mg/L)	Carbon Balance *
08-Sep-86	1.0	11	<0.1	20	1.01
08-Sep-86	3.5	13	- -	--	- -
08-Sep-86	<0.5	14	1.7	36	1.51
26-Sep-86	1.1	8	0.6	16	1.14
26-Sep-86	2.8	14	0.3	30	1.17
26-Sep-86	3.5	8	- -	--	- -
28-Oct-86	4.0	15	0.5	23	0.88
13-Nov-86	7.1	1	<0.1	< 1	- -
24-Nov-86	30.6	8	<0.1	< 1	- -
24-Nov-86	26.8	10	<0.1	< 1	0.02
24-Nov-86	33.7	21	<0.1	< 1	- -
11-Mar-87	25.0	2	0.3	< 1	0.49
24-Mar-87	9.9	5	0.5	6	0.80
02-Apr-87	8.6	< 1	<0.1	< 1	- -
15-Apr-87	<1.0	4	0.1	< 1	0.10
18-May-87	0.6	2	0.2	< 1	0.11
20-May-87	3.1	2	0.2	< 1	0.17
20-May-87	1.5	9	0.4	< 1	0.05
22-May-87	0.8	2	0.2	< 1	0.21
27-May-87	0.3	3	0.1	< 1	0.06
02-Jun-87	17.2	8	0.1	39	2.71
03-Jun-87	15.0	23	0.1	62	1.46
04-Jun-87	6.4	2	0.4	2	0.93
05-Jun-87	5.5	4	<0.1	< 1	- -
10-Jun-87	8.6	3	0.2	20	3.84

* Fraction of TOC accounted for by TBP and NPH

TABLE 4. F-AREA SOURCES DATA

Date	TIC (mg/L)	TOC (mg/L)	NPH (mg/L)	TnBP (mg/L)	Carbon Balance *
1F Evaporator					
08-Jan-87	2.4	3	2.6	< 1	0.81
04-Mar-87	10.3	6	<0.1	< 1	- - #
2F Evaporator					
08-Jan-87	4.0	7	5.3	< 1	0.70 #
04-Mar-87	1.7	13	0.1	< 1	0.01 #
1CU Evaporator					
13-Jan-87	<0.1	67	0.7	94	0.76
14-Jan-87	0.2	49	2.5	78	0.89
1EU Evaporator					
17-Nov-86	<1.0	84	12.8	152	1.11 &
13-Jan-87	0.2	56	0.9	50	0.50
14-Jan-87	<0.1	51	2.0	92	1.00
ARU Evaporator					
13-Jan-87	<0.1	62	24.8	81	1.05 &
14-Jan-87	0.9	60	4.1	37	0.30
GP Evaporator					
13-Jan-87	1.1	47	3.7	88	1.07
14-Jan-87	1.2	12	2.1	26	1.27
Hydrate Evaporator					
17-Nov-86	0.9	25	<0.1	72	1.56
13-Jan-87	0.3	24	9.7	43	1.34 &
14-Jan-87	<0.1	31	0.4	58	1.01
Lab Waste Evaporator					
10-Dec-86	4.8	68	19.1	145	1.39 &
13-Jan-87	6.0	51	9.2	87	1.07 &
14-Jan-87	5.4	45	6.3	59	0.82

* Fraction of TOC accounted for by TBP and NPH
# Contamination of sample with NPH during analysis
& Two phase sample - Not separated

TABLE 5. H-AREA SOURCES DATA

Date	TIC (mg/L)	TOC (mg/L)	NPH (mg/L)	TnBP (mg/L)	Carbon Balance *
1H Evaporator					
13-Jan-87	3.5	<1	<0.1	< 1	- -
2H Evaporator					
13-Jan-87	3.0	<1	<0.1	< 1	- -
ARU Evaporator					
12-Jan-87	0.2	36	3.6	118	1.85 #
04-Feb-87	<1.0	43	0.3	72	0.91
GP Evaporator					
12-Jan-87	9.0	21	3.3	77	2.15 #
04-Feb-87	4.9	18	<0.1	31	0.96

* Fraction of TOC accounted for by TBP and NPH
# Contamination of sample with NPH during analysis
& Two phase sample - Not separated

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