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Efficiencies of Liquid-Liquid Extraction and XAD-4 and XAD-7 Resins in Collecting Organic Compounds from a Coke Plant's Effluent

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The Illinois Environmental Protection Agency is attempting to characterize as fully as possible the anthropogenically derived organic compounds being discharged to and present in the State's waters. This effort has emphasized the quality control problems associated with the identification of low levels ($\geq$ parts/billion, ppb) of organic compounds in the environment. Thus, we have examined the theoretical requirements of composite sampling (SCHAEFFER and JANARDAN 1978), the propagation of errors which occur from sampling through identification (JANARDAN and SCHAEFFER 1979), and the efficiency of sampling methods using capture-recapture methods (JANARDAN et al. 1980). Estimates of the total number of compounds which might be identifiable by gas chromotagraphy/mass spectrometry, gc/ms (SCHAEFFER and JANARDAN 1980) have been made. The theoretical findings have been translated into practice by the development of a multichannel sampler (TIGWELL and SCHAEFFER 1980) which permits the simultaneous collection of a sample by up to four methods. The present paper will describe how these elements interplayed in a study of a coke plant's waste water.

MATERIALS AND METHODS

Sampling and Analysis

The waste stream was located at the bottom of an API skimmer approximately 3m below ground level. A submersible pump was suspended by a rope so that the intake screen was held off the bottom by several inches. This prevented ingestion of the tarry material covering the bottom of the tank to a depth of several cm. A new garden hose was connected to the pump, and the other end was clamped into a 2 L glass beaker. The system was flushed for about 1 hour before sampling began.

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Composite samples were collected using a device described by TIGWELL and SCHAEFFER (1980). One end of a teflon intake line was submerged in the beaker and the other was connected to a tee fitting. The stem of the tee was connected by a teflon line to a 500 mL graduated cylinder which had a short length of glass tubing blown into the bottom. A solution (200 mL) of perdeuteroanthracene (3 mg) and 2-ethylhexanoic acid (3 mg) in aqueous ethanol (1:1 V/V) was metered into the intake line by adjusting the liquid level in the graduated cylinder with the level in the overflowing 2 L beaker. The other end of the tee was connected to the sampler.

The sampler consists of three 50 mL syringe "pumps" held in precision machined mounts. A teflon line connects each pump to a separate channel of an all teflon and glass valve. The single teflon line coming from the tee enters the valve, and the flow is split uniformly.

Here, one outlet port was connected to a glass column (180 x 18 mm, I.D.) containing 20 mL of slurry packed, cleaned XAD-4 resin. The second port was connected to a similar column of XAD-7 resin. The flow from the third port was channeled to a 4.5 L glass bottle. The outlets from the XAD columns were channeled to separate 4.5 L glass bottles. The bottles were capped with teflon-lined caps when they filled. The sampler's timer cycled at 15.6 second intervals at a rate of 10 mL per channel for 20 hours (~46 L/channel).

Chemical Analysis

The adsorbants and aqueous samples were extracted and the extracts cleaned and concentrated. Compounds were identified using a gc/ms/ds (SOMANI et al. 1980). Calibration curves were developed for about 30 major constituents.

Statistical Methods

JANARDAN et al. (1980) described a capture-recapture method which is used here for analyzing the data in Table 1. However, since their Eq. 1 does not always converge if programmed directly, we provide a BASIC program which iterates on the log-transformed equation. The reader should consult the original reference for details.

```
20   DIM N(175), P(175)
30   INPUT "NUMBER OF METHODS=", K
40   PRINT "NO. CMDS BY METHOD, SEPARATED BY COMMAS"
50   INPUT (FOR I=1 TO K, N(I))
60   INPUT "NO. OF DISTINCT COMPOUNDS FROM ALL THE METHODS=", N1
70   FOR N=N1+2 TO 5000
80      R=0
90      FOR J=1 TO K
100       R=R+LOG(N-N(J))
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110      NEXT J
120      R=R-(K-1)*LOG(N+1)
130      L=LOG(N-N1)
140      D=R/L
150      IF D<=1.00001 THEN 190
160   NEXT N
170   PRINT "NO SOLUTION FOUND"
180   STOP
190   PRINT "ESTIMATE OF TOTAL NUMBER OF COMPOUNDS=";N
200   REM STANDARD DEV. OF THE ESTIMATE OF TOTAL COMPOUNDS
210   S1=0
220   FOR I=1 TO K
230      P(I)=N(I)/N
240      S1=S1+(1/(1-P(I)))
250   NEXT I
260   P=N1/N
270   V=N/((1/(1-P))+(K-1)-S1)
280   S=V**.5
290   S=INT(S+.5)
300   PRINT "STANDARD DEV. OF ESTIMATE OF TOTAL COMPOUNDS=";S
```

As an illustration for the data in Table I - "Total" - the user inputs: (K=)4; (NO. COMPOUNDS BY METHOD) 70, 41, 40, 90 (TOTAL NO. COMPOUNDS) 136.

RESULTS AND DISCUSSION

From the data in Table 1 columns (1) and (2), we estimate that the grab sample actually contained about 100 distinct identifiable compounds (Table 2, row a). One hundred and thirty-two compounds were identified in the composite samples (Table 1, Table 2, row K). Table 2 gives the total number of compounds estimated to have actually been present in the source. For example, coke plant wastes, like those from coal conversion, contain hundreds of compounds, many of which are strong mutagens (RUBIN et al. 1976). Analysis of such samples presents severe technical challenges which provide a good test of the statistical methods. Thus, in order to maximize the information which could be obtained from a composite sample, a grab pre-sample was collected and analyzed with the results shown in Table 1.

TABLE 1

NUMBER OF COMPOUNDS IDENTIFIED BY EACH METHOD

	GRAB (I)				COMPOSITE			
			XAD-4 (II)		XAD-7 (III)		L/L (IV)	
	U(1)*	D(2)	U(3)	D(4)	U(5)	D(6)	U(7)	D(8)
Method	53	34	28	25	27	28	70	40
Total	70		41		40		90	

*Total Acid fraction underivatized (U) or derivatized (D) with Meth-Prep II.

Sixty-six of the compounds identified in grab sample (I) were also identified in composite IV. Ninety-four compounds were identified in all, from which the estimated total number of compounds is 96 + 2. This suggests that the chemical composition of the effluent did not change extensively between the times these were collected.

Rows (b)-(e) of Table 2 give the recoveries for XAD-4, XAD-7 and liquid-liquid extraction. XAD-4 and XAD-7 recovered about the same number of compounds (40) with similar efficiencies (75%). Combining the data from the two resins, (row e) the number of compounds identified increases to 63, although the overall identification rate (80%) remains about the same. However, the individual resins only recovered about 50%, and the combined resin data 70%, of the compounds identified in the liquid-liquid extracts (row d). Thus, while liquid-liquid extraction recovered a higher absolute number of compounds, it had a lower recovery efficiency (65% versus 75-80%), as can be seen by comparing rows (a) or (d) with (b), (c) or (e). These results contrast with those reported previously (JANARDAN et al. 1980) where XAD-4 and liquid-liquid extraction captured about the same number of compounds with comparable efficiency (30%). We think that the low recoveries on the resin in the present case resulted from break through which permitted "flushing" of trace compounds by those present at higher levels. (The effluent streams from passage through the resin, which had been collected to monitor break through, have not been analyzed.)

Rows (f) and (g) and (h) and (i) of Table 2 show that the combination of either resin with liquid-liquid extraction was equally effective. However, the estimates obtained by considering "method" without regard to derivation status (rows (h) and (i)) are somewhat higher than those obtained than if this is considered (rows (f) and (g)). This pattern is repeated in rows (j) and (k) where the estimates obtained without regard to derivatization status (row (k)) are higher than those which include this information (row (j)).

Row (l) of Table 2 compares the results from the pre-sample (I) with those from the composites (II, III, IV). Comparing row (m), which is the total number of compounds observed regardless of method, with rows (j) or (k) for the total composite, shows that only four compounds were identified in the grab presample (I) which were not subsequently identified in the composite. Thus, the total number of compounds observed in the composite (132) is about the same as the 140 compounds estimated from the pooled data in row (l). These results are only slightly lower than the total number of compounds (148 + 4 to 156 ± 6) estimated from the separate lists in rows (m) and (n).

TABLE 2

PREDICTED TOTAL NUMBER OF COMPOUNDS IN SAMPLE

Data Used	Number of Distinct Compounds Observed	Estimated	Recovery, %
a. (1), (2)	70	104 ± 14(S.D.)	67.3
b. (3), (4)	41	57 ± 8	71.9
c. (5), (6)	40	50 ± 6	80.0
d. (7), (8)	90	138 ± 18	65.2
e. (3)-(6)	63	76 ± 5	82.9
f. (3),(4),(7),(8)	112	154 ± 12	72.7
g. (5)-(8)	109	142 ± 10	76.8
h. II, IV	112	191 ± 27	58.6
i. III, IV	109	169 ± 21	64.5
j. (3)-(8)	132	168 ± 9	78.6
k. II-IV	132	207 ± 20	63.8
l. I, II & IV	136	140 ± 3	97.1
m. (1)-(8)	136	148 ± 4	91.9
n. I-IV	136	156 ± 6	87.2

CONCLUSION

These results, taken together with our earlier study (JANARDAN et al. 1980), suggest that the chemical characterization of a complex wastes requires the simultaneous collection of samples by several methods.

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