Coprecipitation of Organic Compounds from Lake Water by Iron Salts

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■ Known amounts of various organic compounds were added to fresh waters in the presence of added $FeCl_3$ and the extent of recovery of the compounds by coprecipitation was measured. In lake water containing high organic matter and high color, the coprecipitation of added phenol in the neutral to slightly alkaline pH range was greater than in lake water with low organic content and low color. The coprecipitation of citric acid by $FeCl_3$ increased with decreasing organic content of the test water. Ferric chloride addition at neutral pH did not remove dextrose, alkyl benzene sulfonate, or formaldehyde from any of the test waters investigated. The use of iron salts as a means of coprecipitation of dissolved organic matter from fresh waters requires that each compound be investigated in each type of water that is under study.

T he use and evaluation of coprecipitation for the concentration and isolation of organic compounds date from the work of Jeffrey and Hood (1958). They found that 79% of the ^{14}C-labeled organic matter of an aged algae culture in seawater was precipitated by raising the pH of the seawater to 10.0 with $Mg(OH)_2$. A concentration factor of 10^4 was achieved by adding $0.1M$ $FeCl_3$ to the seawater and adjusting the pH to between 7.6 and 8.2. Tatsumoto et al. (1961) identified amino acids from the surface seawater using an iron coprecipitation concentration technique. They recovered 53% of ^{14}C-labeled phenylalanine from the seawater by coprecipitation. Williams and Zirino (1964) could recover 36–63% organic matter from seawater with ferric hydroxide between pH 4 and 7. Chapman and Rae (1967) obtained a recovery of 16–90% of various organic compounds from seawater with ferric hydroxide and a recovery of 48–63% with copper hydroxide. This note presents the results of a study on the application of coprecipitation technique for the concentration of selected organic compounds in fresh water. Lake Mendota, a hard-water, eutrophic lake of glacial origin in south-central Wisconsin and Lake Mary, a soft-water, dystrophic lake in northern Wisconsin, were chosen for the study. Lake Mendota water having 10 mg/l. of dissolved organic carbon and color of 5–15 chloroplatinate units was used as representative of low-organic-content water. Lake Mary contains 40 mg/l. of dissolved organic carbon and color of 150 chloroplatinate units. The water from Lake Mary was used as representative of high-organic and highly colored fresh water.

Experimental

Reagents and Apparatus. All reagents used were analytical grade unless otherwise specified. ^{14}C-labeled organic compounds were obtained from the Nuclear-Chicago Corp.

Phipps and Bird multiple stirrer apparatus was used for mixing and flocculating the organic compound with $FeCl_3$. The radioactivity was measured by Nuclear-Chicago Model 186A radioactivity counter.

Sample Collection and Storage. The water samples were collected and stored in polyethylene carboys at 4°C. All experiments were carried out after the water samples were brought to room temperature and filtered through 0.45-μ pore size Millipore filter.

Analytical Procedure. One liter each of water samples containing a known concentration of organic compounds with a known radioactivity was taken in six 1500-ml beakers. To five of the beakers, a known concentration of $FeCl_3$ was added and the pH was adjusted using sodium hydroxide or hydrochloric acid. The sixth beaker did not receive any $FeCl_3$ and was used as a blank. All the samples were mixed for 2 min at maximum speed on the multiple stirrer apparatus, flocculated for 15 min at 40 rpm, and then settled for 1 hr. Four milliliters from each of the supernatants was plated with 1 ml of 1.5% gelatin solution, air-dried, and the ^{14}C radioactivity was measured on the dried sample (Bomstein and Johnson, 1952). The difference in the radioactivity between the blank and the $FeCl_3$-treated water was used to calculate the percent recovery.

Each experiment was repeated twice and three ^{14}C plate countings were made from each of the supernatant samples.

The organic compounds used in the above experiments include phenol, glycine, citric acid, alkyl benzene sulfonate (ABS), formaldehyde, and dextrose.

Results

Recovery of Phenol. Table I shows that in distilled water there was 21% recovery of phenol with $0.005M$ $FeCl_3$ and the recovery increased with the increase in the concentration of $FeCl_3$. In Lake Mendota water, an increasing trend in coprecipitation of phenol with increasing $FeCl_3$ concentrations was noted although the changes in the recovery were not as high as those found in distilled water. Table I also shows that at a pH of 8.5 with $0.01M$ $FeCl_3$, there were significant differences in the coprecipitation of phenol from distilled water, Lake Mendota and Lake Mary waters. There was an increase in the coprecipitation of phenol with an increase in

Table I. Percent Recovery of Phenol by Iron Coprecipitation

FeCl₃, M	% Phenol recovered by coprecipitation[a]		
	Distilled water	Lake Mendota water	Lake Mary water
0.005	21	60	. . .
0.01	29	62	80
0.015	32	66	. . .
0.02	36	68	. . .
0.025	40	70	. . .

[a] Initial phenol concentration $1.06 \times 10^{-7}M$ with a pH of 8.5.

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Table II. Effect of pH on Recovery of Phenol by Iron Coprecipitation

	% Phenol recovered by coprecipitation[a]	
pH	Lake Mendota water	Lake Mary water
7.5	57	87
8.0	56	86
8.5	62	80
9.0	63	82
9.5	...	86
10.0	...	87

[a] Initial concentrations: $1.06 \times 10^{-7} M$ phenol and $1 \times 10^{-2} M$ FeCl$_3$.

Table III. Percent Recovery of Citric Acid by Iron Coprecipitation from Lake Mendota Water

	% Recovery of citric acid by coprecipitation[a]		
FeCl$_3$, M	pH 8	pH 9	pH 10
0.005	48	36	20
0.01	47	38	25
0.015	49	38	...
0.02	49	38	20

[a] Initial citric acid concentration: $6.5 \times 10^{-7} M$.

Table IV. Percent Recovery of Citric Acid by Iron Coprecipitation

	% Citric acid recovered by coprecipitation[a]	
pH	Distilled water	Lake Mendota water
8.0	...	47
8.5	...	44
9.0	70	38
9.5	70	33
10.0	75	25

[a] Initial concentrations: $6.5 \times 10^{-7} M$ of citric acid and $0.01 M$ FeCl$_3$.

Table V. Recovery of Glycine from Lake Mendota and Lake Mary Waters by Iron Coprecipitation

	% Recovery by iron coprecipitation[a]	
pH	Lake Mendota water	Lake Mary water
6.0	20	...
7.0	22	...
8.0	23	25
9.0	29	29
9.5	30	28
10.0	27	10
10.5	11	5

[a] Initial concentrations: $1.1 \times 10^{-7} M$ glycine and $0.02 M$ FeCl$_3$.

the initial dissolved organic carbon content of the test water. However, it cannot be ascertained from these results that dissolved organic carbon alone affected the recovery of phenol by iron coprecipitation, since the inorganic compositions of these waters were also different.

The effect of pH on the coprecipitation of phenol by iron is presented in Table II. In the pH range 7.5–10.0 and with $0.01 M$ FeCl$_3$, the percent phenol coprecipitated did not show a significant change with pH variation. This was found to be true for both Lake Mendota and Lake Mary waters. Since Lake Mary water showed a high percent recovery of phenol, that water was used for further studies on other variables.

It was found that after 2 min of high-speed mixing, increasing the stirring time from 15–30 min or changing the rate of stirring from 40–20 rpm did not vary the percent recovery of the added phenol from the Lake Mary water at pH 8.5. Essentially the same percent recovery was obtained whether the samples were from the supernatant of a settled solution or the filtrate of a 0.45-μ pore size Millipore filtered solution.

Recovery of Citric Acid. Table III shows that in Lake Mendota water there was no change in the percent recovery of citric acid, in the FeCl$_3$ concentration range of 0.005–0.02M. However, the percent recovery of citric acid was affected by the pH variation. The citric acid recovery was 47% at pH 8.0 which decreased with the increase in pH to 9.0 and 10.0. This stepwise decrease in the recovery of citric acid with increase in pH was noted with all the concentrations of FeCl$_3$ used in these experiments.

The recovery of citric acid from distilled water was not affected by the pH changes from 9.0 to 10.0 (Table IV). The Table also presents the variation in the percent recovery of citric acid from Lake Mendota and distilled water. Higher citric acid recovery was observed in distilled water when compared to the recovery from the Lake Mendota water. At lower pH ranges (4.5–6.0), no recovery of citric acid was observed using $0.01 M$ FeCl$_3$. With copper salts as a co-

precipitating agent, Chapman and Rae (1967) found 90% recovery of citric acid at pH 4.5. This result demonstrates the importance of the choice of coprecipitating agent and the optimum pH range for the use of coprecipitation techniques.

Recovery of Glycine. With Lake Mendota water the recovery of glycine by iron coprecipitation was 20% at pH 6.0. An increase in pH from 6.0 to 9.0 showed an increase in the percent recovery of glycine (Table V). No significant changes in the recovery of glycine from Lake Mendota water was observed in the pH range 9.0–9.5, although a decrease in the recovery was observed when the pH was raised to 10.5.

With Lake Mary water, there was a decrease in the recovery of glycine when the pH was increased from 9.5 to 10.0 and from 10.0 to 10.5. Glycine recoveries from low and high organic content waters, as exemplified by Lake Mendota and Lake Mary waters, were similar in the pH range of 8.0 to 9.5.

When the initial concentration of glycine was changed from $5.5 \times 10^{-8} M$ to 1.1×10^{-7} and 2.2×10^{-7}, the recovery of glycine changed from 32 to 29 to 9%, respectively. Thus, a decreasing trend was noted in the % recovery of glycine from Lake Mendota water with increase in glycine concentration.

Recovery of Other Compounds. The recovery of dextrose by iron coprecipitation was investigated using distilled water as the test medium. With the initial concentration of $5 \times 10^{-3} M$ dextrose and $0.01 M$ FeCl$_3$, no significant recovery of dextrose in the precipitate was observed at pH of 7.5, 8.0, 9.0, 10.0, and 11.0.

The recovery of alkyl benzene sulfonate (ABS) by iron coprecipitation from distilled water was studied. The initial and final ABS concentrations in the test solution were measured by the methylene blue method (American Public Health Assoc., 1965). No recovery of ABS was found within the pH range 7.0–10.0 with $0.01 M$ FeCl$_3$.

Similar experiments with $1.3 \times 10^{-5} M$ formaldehyde in distilled water showed no recovery by coprecipitation with $0.01 M$ FeCl$_3$ at pH 8.5.

Removal of Color. A set of experiments was carried out to study the effect of pH change on the color of Lake Mary water. The surface water of Lake Mary had 150 units of color and a pH of 6.0. Water samples from Lake Mary were adjusted to various pH values ranging from 6.5 to 10.5 and the color was read in each sample. No change in color units was observed in the above-mentioned pH range.

In another set of experiments, $0.01M$ $FeCl_3$ was added before adjusting the pH of Lake Mary water. This addition of $0.01M$ $FeCl_3$ resulted in a 100% removal of color when the pH was raised from 6.0 to 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, and 9.5. The color removal was 80% at pH 10.0 and 10.5.

Discussion

The organic compounds used in the study belong to different classes having varied functional groups. The percent recovery of these compounds by coprecipitation by iron varied depending on the nature of the compounds.

The type of water had an effect on the percent recovery of phenol and citric acid. An increase in the dissolved organic content of the water was correlated with an increased percent recovery of phenol, while for citric acid, the opposite trend was found. No significant change in the percent recovery of glycine was observed with the change in the dissolved organic content in water.

Tables I and III present the effect of increase in $FeCl_3$ concentration on phenol and citric acid recovery in the alkaline pH range. The increase in $FeCl_3$ concentration increased the percent recovery of phenol, while for citric acid the changes in the recovery with the variation of $FeCl_3$ concentrations were not significant.

The effects of pH on the percent recovery were different for each of the organic compounds studied. There was a decrease in the percent recovery with an increase in the pH from 8.0 to 10.0 in the case of citric acid. For phenol, there was no pH effect between 7.5 and 10.0 on the percent recovery. In the case of glycine, a decrease in the recovery was observed when the pH was increased from 9.5 to 10.5, while an increase in the recovery was noted when the pH was raised from 6.0 to 9.0.

The positive effect of the presence of organic matter on phenol recovery and the fact that the percent recovery was not affected by the pH, suggests that the mechanism may be more than a simple coprecipitation. The high phenol recovery from water with high organic content indicates a possible chemical interaction between the organic matter of Lake Mary water and phenol. In the case of citric acid and glycine, the percent recovery is probably a combination of the effect of pH and $FeCl_3$.

This investigation and others have shown that iron coprecipitation can be used to effectively concentrate some dilute solutes from natural waters. It is apparent from these results that the percent removal of a specific compound requires an evaluation of the procedure on the waters under investigation since the removal of various organic compounds has been found to be dependent on the type of compound, type of water, concentration of iron and pH.

Literature Cited

Amer. Public Health Assoc., "Standard Methods for the Examination of Water and Wastewater," 12th ed., AWWA, APHA, WPCF, New York, N.Y., 1965.
Bomstein, R. A., Johnson, H. J., *J. Biol. Chem.*, **198,** 143–53 (1952).
Chapman, G., Rae, A. C., *Nature*, **214,** 627–8 (1967).
Jeffrey, L. M., Hood, D. W., *J. Mar. Res.*, **17,** 247–71 (1958).
Tatsumoto, M., Williams, W. T., Prescott, J. M., Hood, D. W., *ibid.*, **19,** 89–95 (1961).
Williams, P. M., Zirino, A., *Nature*, **204,** 462–4 (1964).