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INTRODUCTION

Xanthates are dithiocarbonates which are used in the flotation processes for most sulfide minerals, the metallic elements such as copper, nickel, lead, zinc, silver and gold, and a number of oxidized minerals of lead and copper. Flotation is a physiochemical method of concentrating finely ground ores. The process involves chemical treatment of an ore pulp to create conditions favorable for the attachment of certain mineral particles to air bubbles. The air bubbles carry the selected minerals to the surface of the pulp and form a stabilized froth which is skimmed off while the other minerals remain submerged in the pulp. Xanthates fit into this process by functioning as "collectors." Collectors aid in the attachment of a mineral particle to an air bubble. Sodium isopropylxanthate is one of the most commonly used xanthates (Dow Chemical Co., 1976).

Since xanthates may get into nearby water systems through effluents from tailing ponds, toxicity information is important. Acute toxicity values found in the literature are summarized in Table 1.

Hawley (1972) and Hardie, *et al.* (1974) do not give test conditions so their values are hard to compare with other values. Webb, *et al.* (1975) obtained their data from static tests in water with hardness of 118-125 mg/l. They also ran an eight-day, flow-through test in which 100% mortality occurred at a concentration of 0.3 mg/l sodium isopropylxanthate. Fuerstenau (1974), doing static tests with rainbow trout in water of 348 ppm

hardness found a lethal threshold concentration of 18-20 mg/l.

TABLE 1. Ninety-six Hour LC50 Values for Sodium Isopropylxanthate

| <u>Species</u> | <u>96-hr LC50 (mg/l)</u> | <u>Reference</u> |
|------------------------------|------------------------------|------------------------------|
| <i>Daphnia magna</i> | 0.1-1.0 | Hawley (1972) |
| <i>Notropis anterinoides</i> | 0.01-0.1 | Hawley (1972) |
| <i>Pimephales promelas</i> | 0.32-5.6 | Hawley (1972) |
| Catfish | >10 | Hardie, <i>et al.</i> (1974) |
| Snails | 10-100 | Hardie, <i>et al.</i> (1974) |
| Tadpoles | 10-100 | Hardie, <i>et al.</i> (1974) |
| <i>Salmo gairdneri</i> | 100-180 | Webb, <i>et al.</i> (1975) |

Chemical degradation is also of concern in xanthate toxicity.

Xanthate solutions are not stable in acid medium (Dyer and Phifer, 1969). However, literature reports indicate that alkaline solutions of xanthate are somewhat stable. Harris (1970), quoting other papers, reports that over an eight-day period a study showed that 75% decomposition took place at pH 6.5 but only 25% at pH 10.8. Other studies showed that a minimum of decomposition took place at pH 10-13. Fuerstenau (1974) working with ethylxanthate and amylxanthate at 12°C and pH 8.6 at concentration of about 52 ppm found no significant decomposition. Trofimovich, *et al.* (1976) reports that solutions of ethyl, isopropyl, isobutyl and isoamyl potassium xanthates are stable in water at neutral pH, at a temperature of 20°C and a concentration of 10 mg/l.

Joedodibroto (1963) showed that the decomposition rate decreased with increased molecular weight of the xanthate and in going from a primary to

a secondary alkyl xanthate.

The purpose of the present study was to obtain values of acute toxicity of sodium isopropylxanthate and to determine if xanthate solutions change over time with regard to toxicity.

MATERIALS AND METHODS

Acute Toxicity

Acute toxicity was evaluated by 48-hr static bioassays set up according to methods recommended by the American Public Health Association (1975). Dilution water was supplied from two sources: a well located on the University of Minnesota St. Paul Campus and the South Kawishiwi River near Ely, Minnesota. Analyses of these waters are given in Table 2.

The fish used in all tests were four-week-old, laboratory-reared fathead minnows, *Pimephales promelas*. The fish were placed in testing chambers 24 hours prior to the addition of the toxicant. The fish were not fed during the experiments.

Twenty-liter, glass test chambers (50 cm x 25 cm x 16 cm high) were used at the University of Minnesota, and 6-l, cylindrical linear polyethylene chambers were used at the Kawishiwi River. Ten fish were placed in each chamber.

Sodium isopropylxanthate (supplied by the Dow Chemical Co. and manufactured under the Z-11 trademark) was introduced by siphoning approximately 75% of the water out of the test chamber into a glass jar. Toxicant concentrations were obtained by pipetting the proper amount of xanthate stock solution into the jar and siphoning its contents back into the test chamber. Xanthate levels were checked by ultraviolet spectrophotometry (Dyer and

TABLE 2. Chemical Characteristics of Dilution Water

| <u>Item</u> | <u>Concentration (mg/l)</u> | |
|-------------------------------------|-----------------------------|--------------------|
| | <u>Well Water</u> | <u>River Water</u> |
| Total Hardness as CaCO ₃ | 220 | 22 |
| Calcium as CaCO ₃ | 140 | 11 |
| Iron | 2 | 0.6 |
| Chloride | <1 | 2.0 |
| Sulfate | <5 | 1.7 |
| Sulfide | 0.0 | |
| Fluoride | 0.22 | <0.1 |
| Total Phosphates | 0.03 | |
| Sodium | 6 | 1.1 |
| Potassium | 2 | 0.40 |
| Copper | 0.0004 | 0.0019 |
| Manganese | 0.0287 | 0.041 |
| Zinc | 0.0044 | <0.0015 |
| Cobalt, Nickel | <0.0005 | <0.0021 |
| Cadmium, Mercury | <0.0001 | 0.00026 |
| Ammonia Nitrogen | 0.20 | |
| Organic Nitrogen | 0.20 | |
| Color | | 360 |
| Turbidity | | 1.9 |
| Suspended Solids | | 1.6 |

Phifer, 1969).

Temperature, pH and dissolved oxygen concentration in each chamber were recorded each day. Total alkalinity in control chambers was recorded at the termination of the experiment. These data are in Table 3.

TABLE 3. Test Conditions

| | pH | | Temperature °C | | O ₂ (mg/l) | | Total Alkalinity |
|-------------|------|-----------|----------------|-----------|-----------------------|---------|------------------|
| | Mean | Range | Mean | Range | Mean | Range | Range |
| Well water | 8.45 | 8.35-8.51 | 24.6 | 23.9-25.6 | 6.9 | 6.8-7.1 | 225-230 |
| River water | 7.09 | 7.04-7.14 | 24.0 | 23.4-24.5 | 6.9 | 6.8-7.1 | 17 |

The trimmed Spearman-Kärber method described by Hamilton, *et al.* (1977) was used to estimate the 48-hr LC50.

Degradation Tests

Solutions of sodium isopropylxanthate were prepared and aged 96 hours in glass Erlenmeyer flasks. The solutions were stored at room temperature in unstoppered flasks under a ventilation hood. A Beckman DB-GT spectrophotometer and a recorder were used to scan the absorbance of solutions from 360 to 200 nm every 24 hours. All solutions were diluted to a concentration of approximately 10 mg/l so they could be read on the absorbance scale. Maximum absorbance occurred at 302 nm.

The first series of solutions was prepared with well water at xanthate concentrations of 10 mg/l and 50 mg/l, which are representative of levels used in acute toxicity tests.

The second series of solutions was prepared with deionized water at a xanthate concentration of 5 g/l which is representative of a stock solution.

Bioassays were also conducted to determine if a stock solution of xanthate degrades over time with respect to toxicity. One liter of stock solution with a concentration of 20 g xanthate per liter of solution was mixed in a volumetric flask. The flask was covered with a stopper and stored in the testing room during the course of the experiment. The first 48-hr static bioassay in this series was conducted using the fresh stock solution. The second bioassay used 24-hr-old stock, the third used 48-hr-old stock, and the fourth used 9-day-old stock. The bioassays were conducted in a manner similar to that described in the previous section.

RESULTS

Spearman-Kärber estimates of the 48-hr LC50's derived from all acute bioassays including the degradation tests are given in Table 4. Data from the absorbance degradation experiment are given in Table 5.

DISCUSSION

The overall mean of the ten 48-hr LC50's presented in Table 4 is 35.2 mg/l. This value is higher than most of those reported in the literature.

The course of toxic action of sodium isopropylxanthate appears to be inconsistent. Mortality would occur either in the first 24-hour period or after the second day. In some of the high treatments, the solution would turn cloudy overnight and all the fish would die. This cloudiness is thought to be due to bacteria. If the high treatment did not turn

TABLE 4. Spearman-Kärber Estimates of the 48-hr LC50 for Acute Bioassays with Sodium Isopropylxanthate

| <u>Test</u> | <u>48-hr LC50 (mg/l)</u> | <u>95% Confidence Interval</u> |
|--------------------------|----------------------------------|------------------------------------|
| <u>Acute Tests</u> | | |
| Well water | 31.11 | 26.24-36.89 |
| Well water | 38.52 | -- |
| River water | 32.52 | 27.32-38.72 |
| River water | 35.65 | 29.63-42.90 |
| River water | 46.45 | 41.77-50.56 |
| River water | 47.41 | -- |
| <u>Degradation Tests</u> | | |
| Fresh stock | 24.86 | 21.74-28.44 |
| 1-day-old stock | 39.81 | 35.25-44.95 |
| 2-day-old stock | 25.14 | 20.00-31.60 |
| 9-day-old stock | 30.49 | 27.33-34.02 |

cloudy the fish would still die although at a slower rate. Toxicity was indicated by erratic swimming and loss of orientation followed by lethargy, "gasping" on the bottom of the tank, and finally death. Forty-eight hour LC50's do not appear to be significantly different between the bioassays run in well water and bioassays run in river water.

The degradation experiments (Table 5) show that lower concentrations of xanthates degrade to some extent in a static situation. However, stock solutions at higher concentrations do not degrade in 96 hours. This is supported by the degradation bioassays. The 48-hr LC50 values are not significantly different (with the exception of the one-day-old stock) which indicates that stock solution did not break down. It is not known whether the stability of the stock solutions is due to the high xanthate concentration or to the high pH.

La Prensa

TABLE 5. Absorbance of Sodium Isopropyl-xanthate Solutions Over 96 Hours

| <u>Age of Stock (hr)</u> | <u>Abs. (302 nm)</u> | <u>% of Fresh Stock</u> |
|---|----------------------|-------------------------|
| <u>Well Water 50 mg/l (pH 8.60)</u> | | |
| Fresh | 1.040 | -- |
| 24 | 0.920 | 88.5 |
| 48 | 0.905 | 89.0 |
| 72 | 0.870 | 83.7 |
| 96 | 0.855 | 82.2 |
| <u>Well Water 10 mg/l (pH 8.62)</u> | | |
| Fresh | 0.970 | -- |
| 24 | 0.920 | 94.8 |
| 48 | 0.880 | 90.7 |
| 72 | 0.820 | 84.5 |
| 96 | 0.780 | 80.4 |
| <u>Deionized Water 5 g/l (pH 10.22)</u> | | |
| Fresh | 1.000 | -- |
| 24 | 1.020 | 102.0 |
| 48 | 0.985 | 98.5 |
| 72 | 1.005 | 100.5 |
| 96 | 0.990 | 99.0 |

REFERENCES

- American Public Health Association. 1975. Standard Methods for the Examination of Water and Wastewater. 14th ed.
- Dow Chemical Co. 1976. Flotation Fundamentals and Mining Chemicals. 78 p.
- Dyer, J. and L.H. Phifer. 1969. Cellulose Xanthic Acid. I. Studies of Model Systems. *Macromolecules* 2:111-117.
- Fuerstenau, M.C. 1974. The Toxicity of Selected Sulfhydryl Collectors to Rainbow Trout. Bureau of Mines Open File Report 11-75. 28 p.
- Hamilton, M.A., R.C. Russo, and R.V. Thurston. 1977. Trimmed Spearman-Kärber Method for Estimating Median Lethal Concentrations in Toxicity Bioassays. *Environ. Sci. Technol.* 11:714-719.
- Harris, G.H. 1970. Xanthates. Pages 419-429 in *Encyclopedia of Chemical Technology*, Vol. 22, 2nd ed. John Wiley and Sons Inc.
- Hawley, J.R. 1972. The Use, Characteristics and Toxicity of Mine-mill Reagents in the Province of Ontario. Ministry of the Environment, Ontario. 244 p.
- Joedodibroto, R. 1963. The Mechanism of the Decomposition of Xanthates of Model Compounds. Ph.D. Thesis, Syracuse University, New York.
- Trofimovich, E.M., S.M. Rykova, M.A. Molchanova, and L.B. Aleksandrovskaya. 1976. Materialy po Gigienicheskomu Normalirovaniyu Ksantogenator Kaliya C₂-C₅ v Vode Vodoemor. *Gigienina i Sanitariya* 6:95-97. Translated by Ralph McElroy Co., Custom Division, Texas.
- Webb, M., H. Ruber, and G. Leduc. 1976. The Toxicity of Various Mining Flotation Reagents to Rainbow Trout (*Salmo gairdneri*). *Water Res.* 10:303-306.

Wixson, B., and N. Gale. 1974. Pages 109-122 *in* Water Resources
Problems Related to Mining. Proc. No. 18. American Water Resources
Association.

