Institute for Fisheries Research

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ANALYSIS OF HATCHERY WATER SUPPLY SAMPLES

by

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In 1958 the Hatchery Section of the Fish Division requested that the Institute for Fisheries Research undertake chemical analyses of the water supplies at hatchery facilities within the State. It was felt that such analyses might assist fish culturists in production problems. This report summarizes results of these analyses.

Analyses of 22 elements were requested by the Hatchery Section. We have succeeded in obtaining meaningful results for only 17 elements; the remaining elements were present in such low concentrations that we were unable to find a suitable technique for measurement. In the case of three elements (fluoride, strontium, and aluminum) small quantities were detected but the amount present was so near the limit of sensitivity of the method that the only result which can-be given is that the concentration was **below a given value.** Concentrating water samples by evaporation in some **instances assisted** by providing a measurable concentration. However, **evaporation also** concentrated interfering ions which often made analysis difficult or impractical,

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The only method which might be practical for analysis of the trace elements which were not determined would be to pass large quantities of **Ylater** (several hundred gallons). through exchange resins and then attempt to separate various fractions by chromatographic techniques. Such **a** procedure would require temporary installation of a pumping device and ' a resin column at each water source. Bioassay techniques might also be used to advantage for certain ions, e. g. , cobalt, but this was not feasible with the facilities which were available.

All water samples for analyses (see Table 1)' were collected by Dr. Leonard N. Allison. We are grateful for Dr. Allison's assistance and cooperation in collecting extra samples where needed and for performing the field analyses given in Table 2. The Bureau of Commercial Fisheries at Ann Arbor made available a Beckman DU spectrophotometer with flame attachment for this work. Ors. Stanford H. Smith -and Alfred M. Beeton of the U. S. Fish and Wildlife Service gave many suggestions and loaned several pieces of apparatus.

Methods

Two water **samples** were collected at each station. A one-half liter polyethylene bottle was used for one sample and a one liter glass. bottle was used for the other. Containers were washed with acid before they were used. Samples were preserved with 5 ml. of chloroform and 5 ml. of concentrated hydrochloric acid. Water from polyethylene bottles was used in the determination of aluminum, iron, magnesium, total and

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soluble phosphorus, potassium, silica, sodium, sulfate, strontium, and calcium. Samples from the glass containers were used for the determination of nitrogen.

A second series of water collections was made using polyethylene bags. The bags had a capacity of approximately 5 gallons. These samples were used for analysis of manganese and halogens. No preservatives, acids, or organic solvents were added to these samples since these chemicals often contain halogens as impurities.

The aluminum determination required a photometric comparison at 525 m μ of unknowns and a reference standard series. Standards were an aluminum solution in an acetate buffer which had been treated in the same manner as the unknowns. This procedure was essentially the same as that given in Standard Methods for the Examination of Water, Sewage, and Industrial Wastes 10th edition, 1955, pp. $38-40$.

Soluble chloride ion was determined in two ways, The first was the "tentative titrametric procedure" given in Standard Methods pp. 61-62. It utilized mercuric nitrate and a mixed indicator consisting of diphenylcarbazone and bromophenol blue. When results using this procedure were compared with results of analysis of soluble fluoride, bromide and iodide, . in the same range concentration as the chloride, it was found that the test was nonspecific and gave the total concentration of soluble halogen ions. It was necessary to employ mercuric chloranilate for specific determination of soluble chloride ions. References to this procedure are given in a Fisher Scientific Company technical data brochure and may be found in Analytical Chemistry, 29: pp, 1187 (August 1957) and 30: pp. 202 (February 1958).

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The ion-specific measurements of soluble fluoride were made with thorium chloranilate. References to this colorimetric procedure were also given in a Fisher Scientific technical data brochure (TD-138) and may be found in: (1) A. L. Hensley & J. E. Barney II, "Spectrophotometric Determination of Fluoride with Thorium Chloranilate, " (2) L. Fine and E. A. Wynne, "A New Colorimetric Method for General Fluoride Determinations," Microchemical Journal (in press), and (3) W, Funasaka, M. Kawane, T. Kojima and Y. Matsuda., "Separation of Fluoride Ion by use of Ion-Exchange Resin," Japan Analyst 4: 514-517 (1955). When values for chloride and fluoride are subtracted from total halogen results using mercuric nitrate, the difference should represent the combined concentrations of bromide and iodide. The fluoride concentration was often below the sensitivity limit of the thorium chloranilate procedure, that is below 0.01 , ppm --hence it could not be separated from iodide and bromide. Fluoride was reported separately as being below 0. 01 ppm. in each case. During the course of the analytical procedures, an attempt was made to determine iodide using the tentative method given in Standard Methods (pp. 123-124). Because of the low concentration of iodide, it was impossible to reproduce results with any accuracy using this procedure.

Total iron (dissolved and suspended) was determined, using the 2, 2', 2" - Tripyridyl method (cf. pp. 128-130, Standard Methods). To free iron in an organic form, samples were digested with hydrochloric acid. The tripyridyl procedure is specific for ferrous iron. Iron found in samples of natural waters which have been exposed to air is in ferric

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or oxidized form. Ethylenediamine and hydroxylamine sulfate were used to reduce ferric iron to the ferrous state. Ferrous ions are then chelated with 2, 2', 2" tripyridyl to give a reddish-purple complex that can be measured colorimetrically. A filter photometer was used at a transmittance of 555 m μ . It was found that the only 2, 2'. 2" tripyridyl which could be relied upon was that supplied by **K** & **K** Laboratories of Long Island, New York.

Five ions were determined utilizing flame spectrophotometric analysis. A Beckman DU-4 spectrophotometer, supplemented with a spectral scan adaptor and a Bristol recorder, was employed. The 5 ions were calcium, magnesium, potassium, sodium, and strontium.

Calcium was recorded through a spectro-range of $525-575$ m μ with a maximum peak of line spectra at $564 \text{ m}\mu$. It was necessary to maintain a slit opening of O. 01 mm with a sensitivity of 3 and a zero suppression of 1 on the photomultiplier of the Bristol recorder during an increase through a spectral-band of $525-575$ m μ at an analyzer increased speed rate of 3. Calcium maintains a comparatively linear relationship when **compared** to a series of reference standards. Thus, interpretation of calcium unknowns may be accomplished by direct comparison of the peak intensity of the unknown with that of a reference standard analyzed on the same day.

Magnesium measurements were made in a similar manner on the flame spectrophotometer with a slit opening of 0.02 mm and through a spectro-range of 286-284 mu at a decreased analyzer speed of 10.

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Sensitivity on the Bristol recorder was maintained by setting the photomultiplier at 4· while the zero suppressor was at 1. Magnesium, unlike calcium, has a non-linear relationship between concentration and emission when compared at the peak intensity of 285 $m\mu$. Hence it was necessary to interpolate from a standard curve to compensate for differences between the reference standard and the unknown sample.

Potassium was measured with the Beckman DU-4 spectrophotometer using the flame attachment. In this case the slit opening was maintained at 0.25 mm through a spectro-band of $725-775$ m μ , A maximum intensity was reached at a wave length of $768 \text{ m}\mu$. The photomultiplying system was maintained at a sensitivity of 3 and the zero suppression at 4. The analyzer was set at an increased speed rate of 3. Unlike magnesium, potassium maintains a linear emission-concentration relationship so that the concentration could be determined directly from reference standards.

Sodium is similar to magnesium in that concentration is nonlinear at peak intensity (589 m μ). It was recorded through a spectroband extending from 580 to 600 m μ at an analyzer speed rate of 3. The photomultiplication system was maintained at a sensitivity of 1 and the zero suppressor was set at either 4 or 5. The slit opening was maintained at 0.01 mm.

Strontium was recorded through a spectro-range of $456 - 465$ m μ and with a peak line spectral-emission at 460.7 m μ . A slit opening of 0.01 mm, a sensitivity of 3, and a zero suppression on the photomultiplier of 1 or 2 were maintained. The analyzer speed rate was 3 .

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Strontium maintains a linear relationship between concentration and emission intensity. It was impossible to interpret most of the unknowns because values fell below the detectable limit of 0.01 ppm.

For the flame analyses, two gas sources were used. In the analysis of calcium, magnesium, potassium and sodium an acetyleneoxygen flame source was used, however check comparisons were made with the hydrogen-oxygen flame source, The hydrogen-oxygen flame source was used for strontium in order to obtain a more clearly defined peak.

For analyses of soluble and total phosphorus we utilized the method outlined in the "Determination of Water Quality" (Research Report No. 9, U. S. Fish and Wildlife Service, pp. 79-81), This uses ammonium molybdate and stannous chloride for measurement of orthophosphate.

A similar procedure using ammonium molybdate was employed for the determination of dissolved silica (cf. pp. 186-190, Standard Methods). In this procedure silica is distinguished from phosphate by use of an oxalic acid solution which decomposes the phospho-molybdate complex. To increase the sensitivity of the silico-molybdate method, a reducing agent consisting of recrystallized 1-amino-2-napthol-4 sulfonic acid and sodium sulfite is employed. This makes the method sensitive to about 0. 02 ppm of silica.

Sulfate was analyzed by the turbidimetric procedure outlined in Standard Methods (pp. 197-198). The procedure was accurate to an **approximate±** 5 percent in a range of concentration less than 10 ppm.

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Two procedures outlined in Standard Methods were used for nitrogen. The Kjeldahl method of digestion was used in conjunction with direct nesslerization procedure (pp. 127-148, Standard Methods). Organic nitrogen was converted by Kjeldahl digestion to an ammonium compound which was measured colorimetrically after nesslerization. In the absence of interfering substances this method had a reproducibility of between \pm 0.005 and \pm 0.01 ppm.

Manganese was determined by the periodate method given in Standard Methods (pp. 137-139). For this determination samples were collected in polyethylene bags of 5-gallon capacity. After concentrated sulfuric and nitric acids were added, 2 liters of water were concentrated by boiling for each analysis. At this point the procedure outlined in Standard Methods is carried to completion. When the photometer is used with a filter having a maximal transmittance at 525 m μ , the relative error in the determination is generally not more than 1 percent. The manganese concentration was found to be below 5 ppb in most of the samples tested.

Zinc was determined using diphenylthiocarbazone. This is the "mixed color" method, given as a tentative method in the 10th edition of Standard Methods (pp. 212-214). It was necessary to use 500 cc_a . of water for the reaction with the diphenylthiocarbazone to obtain enough color for comparisons with reference standards. The filter photometer was used with a filter having a maximum transmittance at 525 m μ . Reproducibility was within \pm 0.002 milligrams of the true value.

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Discussion

The data (Tables 2 and 3) reflect regional characteristics in the chemical properties previously known from analyses of surface waters. Waters of the Upper Peninsula were of lowest ion-content, and the most highly mineralized waters were from southeastern Michigan. Local characteristics of the drift and underlying rock formations and differences in the depth of the water sources probably account for the range of variation. In most instances hatchery samples agreed well with analyses of nearby domestic water supplies (cf. Michigan Department of Health, Engineering Bulletin No. 4).

Certain of the data, however, appear unusual and deserve special comment. Samples from the Thompson Hatchery all have a high magnesium-calcium ratio and the water from Station No. 9 (Thompson **Creek** above bulkhead) was unusually high in phosphorus. This value was so high that we suspected that the sample had been contaminated. Unusually high magnesium-calcium ratios were noted at Marquette and in Sample No. 32 from **Davies** Trout Pond near the Paris Hatchery. The latter sample was so high in magnesium that we suspect some sort of error. Water from Station 42 (Wolf Lake; artesian well) and Stations 44 and 45 (Drayton Plains) had an exceptionally high halogen (chloride) content. This might indicate contamination by domestic drainage.

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Table 1. --Source of water supply samples

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Table 1. -- (Continued)

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Table 1. -- (Continued)

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Table 1. --(Concluded)

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Table 2.--Field analyses of water samples at hatchery sites, made at time of

Table 3.--Laboratory analyses of water samples from hatchery sites.
(For sites, see Table 1)
Results are in parts per million unless noted otherwise. ppb = parts per

VAnalyses for strontium and flueride, made for all 48 samples, were all less than 0.01 ppm.

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Table 3.--(Concluded).

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 $\sqrt[2]{\text{tr}} = \text{less than } 0.02 \text{ ppm.}$