A MEASUREMENT OF LOW LEVEL CESIUM ISOTOPE CONCENTRATION IN A FRESH WATER LAKE[1]

Supplement To

Final Report (COO-1795-3)
To The
UNITED STATES ATOMIC ENERGY COMMISSION
Contract No. AT(11-1)-1795
Modification No. 1-1

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LIST OF ABBREVIATIONS AND NOMENCLATURES

NCFC	ammonium hexacyanocobalt II ferrate II
KCFC	potassium hexacyanocobalt II ferrate II
AMP	ammonium molybdophosphate
TPB	sodium tetraphenylboron
hexone	3/1 methylisobulylketone-cyclohexane
ZrP	zirconium phosphate

INTRODUCTION

Extensive measurements of radioactive cesium-137 concentrations in aqueous and various environmental samples have been made. However, relatively little work has been done on measuring total cesium in environmental samples, and even less on measuring cesium in fresh water. Considerable work has been done by Folsom (1970), on stable cesium analysis in sea water, but generally these methods do not apply to the low levels of cesium found in the natural fresh water system. Methods for concentrating and counting cesium-137 are relatively numerous (Finston and Kinsley, 1961), when compared to methods of total cesium analysis (Yamagata, 1965). Feldman and Rains (1964) offer procedures for concentration and flame photometric determination of cesium in water and biological samples.

Cesium has been shown to be concentrated considerably with increasing trophic levels (Gustafson, 1966; Pendleton, 1962). This biological amplification introduces a possible hazard, not only to the higher trophic level organisms but also to man, using the organisms for food. Stable cesium levels must be known to better understand the dynamics of cesium in the ecosystem. Also stable cesium has become of practical importance with its use as the main constituent in the photoelectric cell.

This study was originally designed to develop a method of total cesium analysis that was applicable to the analysis of total cesium in fresh water. Numerous methods using proconcentration and detection have been suggested but few apply to the very low fresh water concentrations encountered in most lakes and streams. Initially efforts were directed toward a direct chemical method for total cesium analysis. Pursuit of this type of method proved to be quite futile considering available detection methods. An alternative to the direct method of cesium analysis has been hypothesized and was incorporated into the design. This indirect method of obtaining total cesium concentration consists of analysis of a biological factor or factors of the fresh water system in question, for both cesium-137 and total cesium. Yellow perch (*Perca flavescens*) and largemouth bass (*Micropterus salmoides*) were chosen for this use. Using cesium concentrations in the fish and the cesium-137 content of the water, the total cesium could be calculated with more accuracy and precision than the direct methods of cesium determination. This method, based on the specific activities being equal for the fish and the water, shows promise to be a good method of isotope determination (Nelson, 1967).

Considerable methodology was developed for the collection of cesium samples from fresh water lakes. Methods for cesium analysis in whole fish also were improved.

METHODS AND MATERIALS

Methods were developed for preconcentration of cesium from lake water and analysis of cesium isotopes in fish. Direct methods of cesium analysis also were explored.

Ion Exchange Materials

In the past decade a number of ion exchange materials have been studied in terms of selectivity for alkaline earth elements. The majority of the highly specific exchangers fall in the class of inorganic anionic exchangers. The group most suited to column operation is the complex cyanides of heavy metals. These complex cyanides have an affinity for the alkaline earths in the following order:

$$Cs > Rb > K > Na > Li$$

The complex cyanides, using cobalt as the heavy metal, are the strongest cesium sorbents (Kourim, et al., 1964).

The alkali metals are bound with increasing strength according to their increasing ionic radii, with cesium having the largest ionic radius of the series (Tananajev, et al., 1957).

Some other ion exchange materials available for use with cesium are ammonium molybdophosphate (AMP) used as a batch absorber and quite specific for cesium (Feldman and Rains, 1964), and zirconium phosphate. The zirconium phosphate is suited to column operation but is much less specific for cesium in the presence of potassium and sodium (Macek, et al., 1963). Dowex 50, a strongly acid cation-exchanger also has been applied to cesium uptake, however, it is not nearly specific enough for cesium uptake from water containing relatively large concentrations of other alkali metals.

The chemical stability of the complex cyanides in general is as follows: Quite stable in mild alkaline solutions and in neutral solutions, but soluble in concentrated H_2SO_4 and shows tendency to peptize in other strongly acid solutions (Kourim, et al., 1964). The most structurally stable of the complex cyanides are the copper and zinc forms. Zirconium phosphate is stable in strong acids and neutral solutions but breaks down somewhat in strong alkaline solutions. It is structurally very stable and excellent for use in columns. Ammonium molybdophosphate (AMP) is a microcrystaline substance that is structurally quite stable. It is chemically stable in strong acid to neutral solutions but dissolves readily in alkaline solutions. A number of the ion exchange materials suited to column use were tested in the laboratory for cesium uptake. Potassium hexacyanocobalt II ferrate II (KCFC), ammonium hexacyanocobalt II ferrate II (NCFC) and zirconium phosphate (ZrP) were studied in respect to uptake of cesium at various flow rates through the column. The columns were prepared using 1.0 inch by 2.67 inch polystyrene vials. The bottom of the vial was removed and a polyethylene porous (120μ) disk was placed in the bottom. Five grams of the ion exchange material were slurried in distilled water until saturated. This soaked resin was poured into the vial and another polyethylene porous disk (120μ) was placed on top of the resin. The columns were stored under distilled water until used. Figure 1 is a photograph of columns prepared using NCFC. The NCFC, KCFC, and ZrP were obtained commercially from Bio Rad Laboratories. The AMP was prepared using a procedure described by Folsom (1970). The copper and zinc ferrocyanides were prepared using a method described by Kourim, *et al*. (1964).

Ion Exchange Field Apparatus

In order to preconcentrate enough cesium-137 on a five gram ion exchange column to facilitate a statistically accurate count in a reasonable counting time, it was estimated that at least four hundred liters of water must be passed through the column. As it was not feasable to transport this volume of water to the laboratory, a constant flow apparatus was designed and built to operate in the field. This system was built completely of

Figure 1.--Five-gram NCFC ion exchange columns used for cesium-137 determinations.


#1
tergreen
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Wintergr
11-21-

polyethylene to minimize the loss of cesium due to adsorption on the container walls. A polyethylene (20 gal.) container fitted with a polyethylene valve at the bottom and a micro-switch float assembly at the top served as a constant head reservior. The float was set to maintain a desired head in the container and thus to produce a suitable flow rate through the column. The micro-switch was connected to the lead of a submersible 12 volt water pump contained in a plexiglas frame surrounded by plankton netting. The netting functioned as a primary filter to keep large particles out of the system. The pump outlet was connected through one half inch tygon plastic tubing to a check-valve. The check-valve was connected to a volume recording flow meter. From the flow meter the water passed through two in-line filters and into the 20 gallon container. When the water level reached the preset level, the micro-switch breaks contact and the flow of water into the container stops. After approximately ten liters of water had run out through the ion exchange column the micro-switch is actuated and the container is refilled to the preset level. Two 12 volt auto batteries connected in parallel were used for electrical power to run the pumps. Two identical systems were set up to facilitate duplicate sampling of the lake simultaneously. A photograph of the entire duplicated system is shown in Figure 2.

Figure 2.--Photograph of ion exchange field apparatus designed for preconcentration of cesium from fresh water.

Cesium Determination in Water

Radiocesium was determined by preconcentrating the cesium on a five-gram column of NCFC and counting the columns on a solid scintillation well type gamma counter. Ion exchange columns were used with the continuous flow field apparatus. Approximately 475.0 liters of lake water per sample were passed through the column to concentrate the cesium.

Methods of direct total cesium analysis were attempted but none gave a satisfactory result. Several methods were tested. A batch absorption of cesium was attempted using the method proposed by Feldman and Rains (1964). The greatest emphasis was on a method proposed by Folsom (1970) and other similar methods. Generally they consisted of using a column preconcentration of cesium, an acid digestion of the ion exchange resin, extraction with AMP and a liquid-liquid extraction into an organic solution suitable for flame emission analysis for cesium. A slight variation of this method involved preconcentration of cesium on an ion exchange column and an extraction directly from the acid solution of the resin into an organic solution. A number of different compounds were tested for their cesium extracting abilities. One of these methods was described by Flynn (1970) involving the use of a phenol nitrobenzene mixture.

With the failure to find a suitable direct method for total cesium analysis, an indirect method was devised.

Fish samples that consisted of yellow perch and largemouth bass were taken by hook and line from the study lake. These fish were analyzed for cesium-137 and total cesium. With the specific activity of the cesium-137 in the fish and the cesium-137 concentration of the water the total cesium concentration was calculated for the water. This was done assuming the specific activity of the cesium-137 was the same in the fish and the lake water (Nelson, 1967).

$$\frac{^{137}\text{Cs in pCi/g in fish}}{\text{Total Cs in ng/g in fish}} = \frac{^{137}\text{Cs in pCi/ml in water}}{\text{Total Cs in ng/ml in Water}}$$

Both perch and bass were used in this analysis to allow a means of comparing specific activities. If the assumption that there is no discrimination for either cesium-137 or stable cesium in the aquatic system is true, the specific activities should not vary significantly between the perch and the bass. By measuring both the cesium-137 and the total cesium in the perch and bass and then testing the means of the specific activity of the fish statistically and showing them to be equal would lend considerable strength to the assumption.

The lake chosen for testing this assumption was Wintergreen Lake. It is located in Kalamazoo County T1S, R9W, Section 8, Lat. 42, Lon. 85 and elevation 890 Ft.

Cesium Determination in Fish

The analysis of cesium in whole fish is largely involved with preconcentrating the cesium and getting it into a matrix suitable for the detection equipment available. Feldman and Rains (1964) proposed a method of cesium analysis in tissue ash samples. This method was used as a basis for the method used for fish analysis in this study. Whole fish were frozen, cut into small pieces, weighed and placed in the digestion flask. A wet nitric acid digestion was used to dissolve the fish using about 3ml of concentrated nitric acid per gram wet weight of fish. AMP was used as a scavenger in the fish solution to collect the cesium isotopes; 4.0 mg per gram wet weight of fish were used. The AMP was collected by centrifugation and then dissolved in 1.0N sodium hydroxide. This solution was made acidic using powered tartaric acid and again extracted with AMP using 0.4mg/g of fish. This AMP was collected and counted to determine cesium-137 concentrations in a solid scintillation gamma counter. The AMP was then dissolved in 1.0N NaOH and extracted into a 3/1 methylisobutylketone-cyclohexane solution of sodium tetraphenylboron (TPB) (0.1N). This organic solution of TPB was retained for flame emission analysis for cesium at 8521Å. A Jerrell-Ash model 82-800 atomic absorption instrument was used. The instrument was equipped with an infrared blazed grating and a red sensitive photomultiplier, R446. A compressed air and hydrogen gas flame was used.

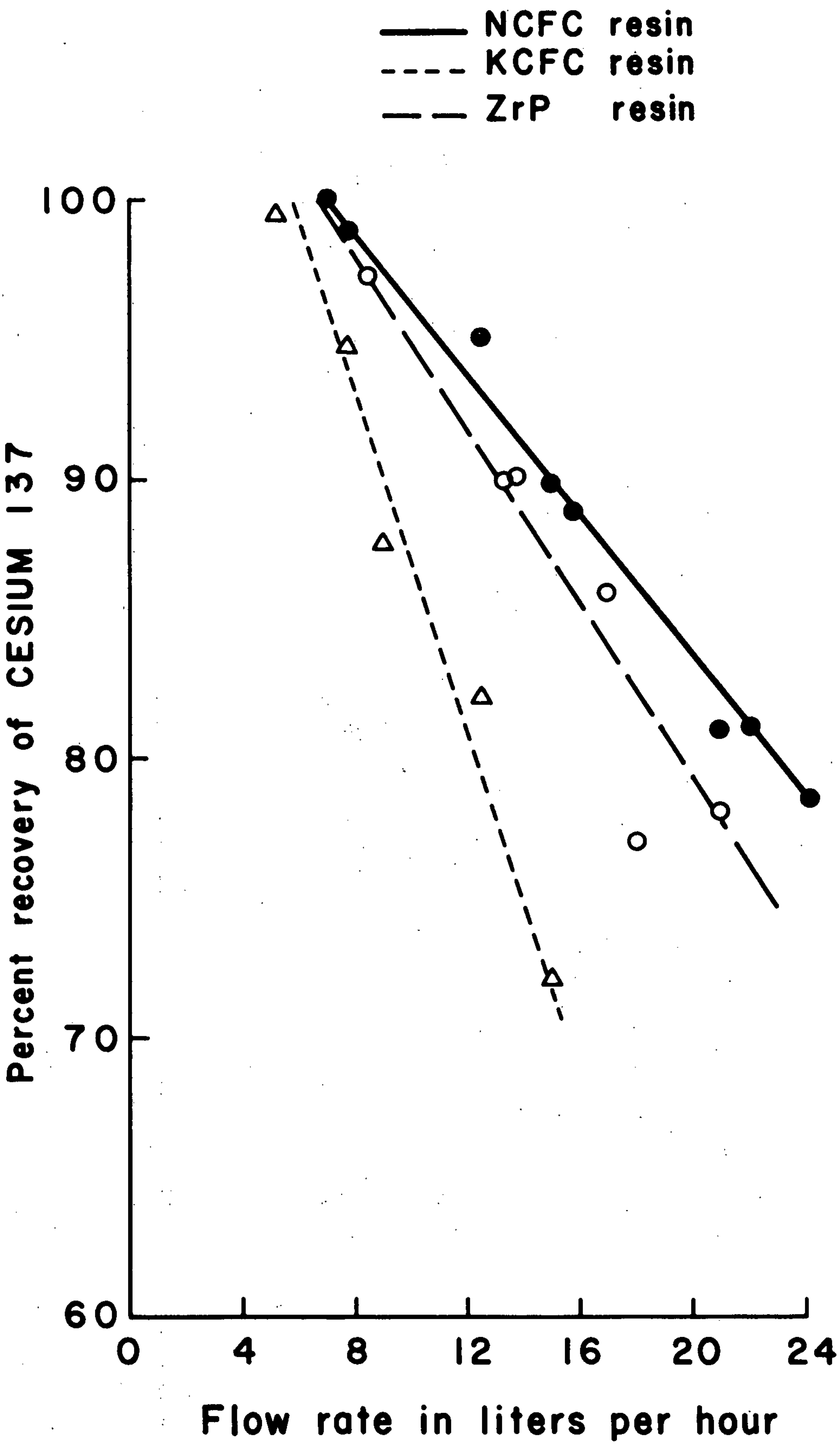
RESULTS

Flow rate versus percent recovery of cesium-137 was studied for three of the ion exchange materials suited to column use. NCFC, KCFC, and ZrP were the three resins tested. Results of the tests are shown graphically in Figure 3. These results were determined using five-gram columns of each type of resin. Six liter distilled water samples were spiked with a known cesium-137 activity. The water was run through the column and the flow rate determined using a timer. The columns were counted in a 3" NaI(Tl) crystal and percent recovery of cesium-137 calculated.

$$\text{Percent recovery} = 100\text{X}\ \frac{\text{cpm on column}}{\text{cpm in spike}}$$

A linear relationship between flow rate in liters per hour and percent recovery was found between five and thirty liters per hour, varying among resins. From Figure 3 it can be seen that the ammonium hexacyanocobalt II ferrate II ion exchange resin has the least decrease in percent recovery for increased flow rate of the three exchangers examined. Because of this percent recovery and also

Figure 3. Percent recovery for ion exchange resins versus flow rate in liters per hour for cesium.


NCFC resin
KCFC resin
ZrP resin
100
90
80
70
60
0
4
8
12
16
20
24
Percent recovery of CESIUM 137
Flow rate in liters per hour

because the NCFC resin offers a method of potassium removal (Petrow and Lavine, 1967), the NCFC resin was used for preconcentration of cesium isotopes. The ion exchange columns were tested using cesium-137 spiked water samples loaded with K^+, NH_4^+, and Na^+ to test the effect of interfering ions on the uptake of cesium. The K^+ concentration used was 2000 mg/liter, Na^+ was 4000 mg/liter and the NH_4^+ concentration was 500 mg/liter in the six liter samples. These high concentrations were used to approximate the total amount of the ion that would be encountered in 100 gallons of lake water. The spiked water samples were run through the columns at approximately seven liters per hour. The K^+ and Na^+ gave no decrease in percent recovery for the NCFC or the KCFC, however when 2000 mg/liter K^+ were run through the ZrP resin only 8 per cent recovery of the cesium was obtained. The NH_4^+ samples, when run through the NCFC and KCFC columns showed a slight depressing effect on the percent recovery of Cs. The percent recovery of Cs on the NCFC with 500 mg/liter NH_4^+ was 91.0% while the percent recovery on the KCFC was 93.0%. This depressing effect was considered quite unimportant in this application of the resin. The levels of NH_4^+ in fresh water are usually very low, only 30-60 μg/liter as reported by Vetter (1938).

The determination of cesium-137 in Wintergreen Lake was accomplished using NCFC resin in five gram columns and the continuous flow ion exchange apparatus. These columns of NCFC resin were tested at approximately 15 liters/hr. and were counted at 0.662 Mev for cesium-137 long enough to give 95% accuracy. The average concentration of cesium-137 in Wintergreen Lake in November 1970 is given in Table 1.

Elution of cesium from the NCFC columns was also attempted. Thallium nitrate, sodium hydroxide, and nitric acid were tried in varying concentrations and at various temperatures, but no satisfactory results were obtained. Results of elution attempts are given in Table B-5 in the appendix.

Total Cesium Analysis of Water

The results of the various direct methods for total cesium in fresh water are mainly negative. The one procedure common to all of the methods examined, is the final step; the quantative detection of the cesium. Flame emission analysis is the most sensitive widely available method of cesium detection. The Jarrell-Ash model 82-800 instrument used was one of the most sensitive available. The detection limit of cesium in hexone TPB solution was approximately 0.05 mg/liter. In order to obtain reproducible readings at least 0.1 mg/liter of cesium should be used. To preconcentrate cesium in fresh water so that enough cesium is collected to give a detectable amount of cesium on an ion exchange column is not difficult, however the handling of the cesium once it has been collected is

TABLE 1.--Cesium isotope levels ± 1 S.E. in fish and water of Wintergreen Lake November 1970.

	Largemouth Bass	Yellow Perch	Lake Water
Total Cesium	36.56±3.31 ng/g	33.0±2.21 ng/g	21.16 ng/Liter*
^{137}Cs	0.438±0.033 pCi/g	0.343±0.017 pCi/g	0.236±0.0024 pCi/Liter
Concentration factor of total cesium over lake water	1727	1560	

*Value calculated using specific activity of fish and cesium-137 concentraction of water.

quite difficult. For flame emission analysis the cesium must be in a solution that is fairly low in total solids and as low as possible in interfering ions.

The methods investigated were generally involved with preconcentration of cesium on an ion exchange material specific for cesium, a series of purification steps, and a final extraction into an organic solution to be aspirated into the flame emission instrument. The majority of the methods were based on one method described by Folsom (1970). This method uses a complex cyanide resin, AMP, and the tetraphenylboron hexone solution to accomplish analysis of Cs in sea water. Individual steps of the procedure were examined using cesium-137 spikes to determine percent recoveries. The average values of percent recovery are given in Table 2. Another method tested involved the extraction of the cesium directly from a sulfuric acid digest solution of the ion exchange resin. A number of extractants were examined for their ability to absorb cesium. A list of these compounds and percent recoveries of cesium-137 are given in Table 3. Batch methods of cesium concentration using AMP as a scavenger (Feldman and Rains, 1964), gave no detectable cesium-137. AMP is not extremely specific for cesium uptake in the presence of interfering ions, such as K^+ and Na^+. Because of this and also because large volumes of water are difficult for batch absorptions using a microcrystaline

TABLE 2.--Percent recovery of cesium-137 in steps of analysis of water.

Step of Procedure	Percent Recovery of ^{137}Cs
Digestion of ion exchange resin in H_2SO_4	100
Extraction of Cs from digested resin using AMP	51.0±19
Solution of AMP in 1.0N NaOH	50.0±10
Extraction of Cs into 0.1N Tetraphenylboron in hexone	30.7±9

Total %-recovery of Cs for entire method is 7.7%

TABLE 3.--Cesium extractants tested for use on acid digest of ion exchange resin.

Extractant	Solvent	Percent Recovery of Cs
Phenol 37.6% wt./wt.	Nitrobenzene	0.0
Orthophenylphenol 1.0N	Carbon tetrachloride	0.0
Picric acid 0.1N	Carbon tetrachloride	0.0
2,4,5, trichlorophenol 1.0N	Carbon tetrachloride	0.0
Thenoyltrifluoroacetone 1.0N	Carbon tetrachloride	0.0
4-sec-butyl-2-(methylbenzyl)phenol 0.1N	Carbon tetrachloride	14.0
Sodium Tetraphenylboron 0.1N	3/1 Hexone	5.0

exchanger, this method was not considered a feasable solution to the problem of cesium analysis in fresh water.

Cesium Isotopes Analysis of Fish

Nine largemouth bass and ten yellow perch samples were digested in nitric acid and analyzed for cesium-137 and total cesium. The average values of the concentrations obtained are given in Table 1. Concentration factors of cesium in the fish over the cesium concentration in the lake water also are given in Table 1. Individual values of specific activity in the perch and bass are given in Table 4. Average specific activites of the yellow perch and largemouth bass were calculated and a pooled-t statistical comparison of means was performed. The evidence indicated that there was no significant difference between the specific activities of the bass and perch with $P < 0.5$. The data for the pooled-t test are given in Table 5. Six largemouth bass were cut in half (dorsal-ventral longitudinally) and each half was treated as a separate sample. The specific activities were calculated for each half and a paired-t comparison of means was run on the results. The evidence indicated that the subsample means were equal with $P < 0.1$. This indicates that there is no great variation in the procedure used for fish analysis. The data for the paired-t test performed are given in Table 6.

The method used for determination of cesium in fish was examined in terms of total percent recovery of cesium.

TABLE 4.--Specific activites of perch and bass from Wintergreen Lake November 1970.

Sample Code	Specific Activity in pCi/ng
Largemouth Bass	
Wi-1	0.010
Wi-2	0.008
Wi-5	0.012
Wi-7	0.011
Wi-8	0.015
Wi-13	0.015
Wi-16	0.009
Wi-21	0.012
Wi-22	0.014
Yellow Perch	
Wi-3	0.010
Wi-4	0.010
Wi-10	0.017
Wi-11	0.015
Wi-14	0.008
Wi-15	0.008
Wi-17	0.009
Wi-18	0.009
Wi-19	0.008
Wi-20	0.009

TABLE 5.--Statistical data for pooled-t on specific activity.

Largemouth Bass	Yellow Perch
$n = 9$	$n = 10$
$\Sigma X_1 = 0.105$	$\Sigma X_2 = 0.103$
$\bar{X}_1 = 0.0117$	$\bar{X}_2 = 0.0103$
$s_1^2 = 0.000054$	$s_1^2 = 0.000058$
Calculated $t = 0.408$	Critical value $t_{(.5,17)} = 0.689$

TABLE 6.--Statistical data for paired-t on half-fish samples.

Sample 1	Sample 2
$n = 6$ pairs	
$\Sigma X_1 = 0.078$	$\Sigma X_2 = 0.083$
$\bar{X}_1 = 0.013$	$\bar{X}_2 = 0.0138$
$s_d^2 = 0.0000065$	
Calculated $t = 1.73$	Critical value $t_{(.1,5)} = 2.015$

The critical step was found to be the first batch ion exchange using AMP to remove the cesium from the digested fish solution. A sample of four fish was used. Multiple extractions using AMP were performed on the acid fish solutions until no more cesium-137 activity was removed. Two extractions proved to be sufficient for this purpose. Using the total cesium-137 activity obtained from both extractions, a percent uptake of cesium was calculated for each of the fish. The average value was 82.8±2.3% for the multiple extractions. The same acid solutions with cesium removed by multiple extractions were then spiked with a known activity of cesium-137. The spiked solution was again extracted with AMP and percent recovery calculated, the average value being 71.2 ± 1.67%. For an estimate of the actual percent uptake using one AMP extraction, an average was taken of the two methods, giving a value of 77.0%. This value was used in calculating cesium concentrations in the fish. The data used for this calculation are given in Table 7.

Fish samples were taken two weeks after the lake had overturned and within one week of the cesium-137 determination on the lake water. The date of water sampling was November 23, 1970. Water samples were taken from surface to bottom for analysis of K^+ and Na^+ by flame emission. The K^+ and Na^+ concentrations demonstrated that the lake was in a state of thorough mixing. The values of

TABLE 7.--Initial extraction of cesium with AMP from acid fish solution.

Spiked Samples	Multiple Extractions
72.0%	86.0%
70.5%	83.6%
73.3%	82.6%
69.0%	79.0%
X = 71.2±1.67%	X = 82.8±2.3%

Average of Two Methods:

77.0±3.79%

K^+ and Na^+ concentration were 5 mg/Liter and 6.4 mg/Liter respectively for all five depths tested demonstrating that the lake water was a homogenous mixture during the sampling period.

DISCUSSION

NCFC ion exchange columns were used for cesium isotope preconcentration for a number of reasons. The NCFC columns showed the best percent recovery for increasing flow rates of the three resins tested. This NCFC resin also has a low level of potassium in its structure and offers a method of potassium removal by passing ammonium nitrate through the column, to elute the potassium and leave the Cs (Petrow, *et al.*, 1967). This resin also exhibits great selectivity for cesium over potassium and sodium. This factor is very important when working with lake water that contains considerable concentrations of these elements. The NCFC resin also exhibits good structural stability when used in columns for preconcentration of cesium.

The methods of direct determination of total cesium that were tested showed little promise for use in fresh water of low cesium content. Most methods that are now being used for total cesium analysis were designed for water of a significantly higher cesium concentration than exists in the lake that was examined. These methods were designed for use in salt water and contaminated water such as reactor effluents and are simply not sensitive enough to give precise results in low cesium waters. Methods of direct total cesium determination proved to be quite unreliable when used with low cesium concentrations. Values of percent recovery for individual steps of procedures and total percent recovery for the steps tested showed that the methods are not suitable for the low total cesium concentration in most fresh water lakes and streams.

The limiting step in the use of direct methods of total cesium analysis is the last, the quantative detection of the cesium. Flame emission is the most widely used and is currently the best method. Neutron activation analysis could prove to be a more sensitive method of detection, allowing that a procedure would be available to preconcentrate the cesium in a matrix that is suitable for this method.

Nelson (1967) used specific activity of cesium for calculation of concentration of cesium isotope in fish. Using this method for calculating concentrations seemed to be an analytically reliable procedure. Comparing the specific activity in two species of fish and supporting the evidence that these values are equal does strengthen the argument that the specific activity is constant. Assuming that the specific activity is the same in the water, one needs only cesium-137 activity of the water to calculate the total cesium concentration of the water. The level of cesium-137 in age 3 perch was substantially lower in Wintergreen Lake in 1970 than in Finnish lakes in 1963 (Kolehmainen, et al., 1966). Values of cesium-137 found by Kolehmainen are given in Table 8. Some of this difference could be explained by the level of fallout receding greatly since then. The Clinch River Study (1967), established that 69 to 92 percent of the cesium-137 was associated with suspended particles. With the input of cesium-137 being reduced and because the cesium-137 is largely associated with particulates (Nelson, D. M., et al., 1970) which settle to the bottom making the cesium-137 unavailable the levels of cesium-137 in the fish would decrease. In addition there may be minor losses of soluble and suspended cesium-137 from the lake resulting from terrestrial and semi-aquatic organisms using the lake. In this sense the lake becomes a source rather than a sink for cesium-137 according to Gustafson (1966).

In calculating the total cesium concentration in Wintergreen Lake, a weighted average of the mean values of specific activity for the perch and bass was used. The calculated value seems quite reasonable considering Wintergreen Lake. The lake has a large input of foreign material from the water fowl that use the lake. This would tend to increase the amount of trace elements found in the water and fish. Sreekumaran, et al. (1968) gives values of cesium in western American rivers and lakes which agree

TABLE 8.--Cesium-137 in fish in Finnish lakes compared to Wintergreen Lake fish.

Lake and Fish	Age	Cesium-137 in nCi/kg Fresh Wt.
Finnish lakes*		
Perch (*Perca fluviatilis*)	3	16.1
	5	25.1
Pike (*Esox lucius*)	3	15.8
	4	16.2
Burbot (*Lota vulgavis*)	. .	1.53 3.28
	. .	
Wintergreen Lake		
Perch (*Perca flauescens*)	3	0.343
Bass (*Micropterns salmoides*)	3	0.438

*Kolehmainen, *et al*., 1966.

TABLE 9.--Cesium in western American rivers and lakes and Wintergreen Lake

Locality	Date	Cesium in μg/liter
Lake Mead*	28-1-67	0.057
Colorado River, end of Iceberg Canyon*	29-1-67	0.022
Colorado River at Moreles Dam*	21-2-67	0.023
Wintergreen Lake (This Study)		0.021

*Sreekumaran, _et al_., 1968.

favorably with the values obtained (Table 9). Assuming that there is no preferential uptake of either of the cesium isotopes, this method should be a sound determination of total cesium. Further work should be done to test the soundness of the specific activity assumption. More diverse biological components of the aquatic system could be tested and variations due to changing food habits might be explored.

REFERENCES CITED

REFERENCES CITED

Amphlett, C. B., L. A. McDonald, J. S. Burgess and J. C. Manard. 1959. Synthetic inorganic ion-exchange materials-III. The separation of Rubidium and Cesium on zirconium phosphate. J. Inorg. Nucl. Chem. 10:69.

Boni, A. L. 1966. Rapid ionexchange analysis of radiocesium in milk, urine, seawater, and environmental samples. Anal. Chem. 38 (1):89-92.

Clinch River Study. 1967. Comprehensive report of the Clinch River study. ORNL-4035.

Crowther, P. and F. L. Moore. 1963. Liquid-liquid extraction of cesium with 2-thenoyltrifluoroacetone. Anal. Chem. 35:2081.

Edgington, D. N., M. M. Thommes and C. I. Harrison. 1968. Separation of cesium and rubidium by the ferrocyanide of copper, zinc and zirconium. Argon National Lab Radiological Physics Division Annual Report ANL-7615.

Egan, B. Z., R. A. Zingare, and B. M. Benjamin. 1965. Extraction with 4-sec-butyl-2(α-methylbenzyl) phenol (BAMBP). Inorg. Chem. 4:1055.

Feldman, C. and T. C. Rains. 1964. The collection and flame photometric determination of cesium. Anal. Chem. 36:405.

Finston and Kinsley. 1961. The Radiochemistry of cesium. National Academy of Science, National Research Council Nuclear Science Series.

Flynn, W. W. 1970. A rapid solvent extraction method for the determination of cesium-137 in environmental materials. Anal. Chem. Acta 50:365.

Folsom, T. R. 1970. Some reference methods for determining radioactive and natural cesium for marine studies. Reference methods for Marine Radioactive Studies, Annex IV, I.A.E.A. Vienna.

Folsom, T. R. 1970. Personal communications.

Gustafson, P. F. 1966. Comments on radionuclides in aquatic ecosystems. Radioecological Concentration Processes Pergamon Press, London 1040.

Gustafson, P. F. 1967. Cesium-137 in fresh water fish during 1954-1965. Symposium on Radioecology 249.

Horner, Crouse, Brown, and Weaver. 1963. Cesium recovery. Nucl. Sci. Eng. 17:240.

Kahn, B., D. K. Smith and C. P. Straub. 1957. Determination of low concentrations of radioactive cesium in water. Anal. Chem. 29:1210.

Kolehmainen, S., Häsänen and J. K. Miettinen. 1966. ^{137}Cs levels in fish of different limnological types of lakes in Finland during 1963. Health Physics 12:917-922.

Kourim, V., J. Rais and B. Million. 1964. Exchange properties of complex cyanides-I. J. Inorg. Nucl. Chem. 26:1111-1115.

Maeck, W. J., M. E. Kussy and J. E. Rein. 1963. Adsorption of elements on inorganic ion exchangers from nitrate media. Anal. Chem. 35:2086.

Mohanrao, G. J. and T. R. Folsom. 1963. Gamma-ray spectrometric determination of low concentrations of radioactive cesium in sea water by a nickel ferrocyanide method. Analyst 88:105.

Nelson, D. J. 1967. The prediction of ^{90}Sr uptake in fish using data on specific activities and biological half lives. Radiological Concentration Processes Pergamon Press, London 843.

Nelson, Donald M., G. P. Romberg and W. Prepejchal. 1970. Radionuclide concentrations near the big rock point nuclear power station. Argonne National Laboratory.

Palmer, H. E. and T. M. Beasley. 1967. Fe-55 in the marine environment and in people who consume ocean fish. Radioecological Concentration Processes. Pergamon Press, London 1040.

Pendleton, R. C. and W. C. Hanson. 1958. Absorption of cesium-137 by components of an aquatic community. 2nd UN Geneva Conference. Pergamon Press, London.

Pendleton, R. C. 1962. Accumulation of cesium-137 through the aquatic ecosystems. Radioecological Concentration Processes. Pergamon Press, London.

Petrow, H. G. and H. Lavine. 1967. Ammonium hexacyanocobalt ferrate as an improved inorganic exchange material for determination of cesium-137. Anal. Chem. 39:360.

Prout, W. E., E. R. Russell and H. J. Groh. 1965. Ion exchange absorption of cesium by potassium hexacyanocobalt II ferrate II. J. Inorg. Nucl. Chem. 27:473-479.

Ross, W. J. and J. C. White. 1964. Determination of cesium and rubidium after extraction with 4-sec-butyl-2-(α-methylbenzyl) phenol. Anal. Chem. 36:1998.

Sekine, T. and D. Dyrssen. 1969. The solvent extraction of alkali metal tetraphenylborates. Anal. Chem. Acta. 45:433-446.

Smit, J. vanR., W. Robb, and J. J. Jacobs. 1959. Cation exchange on ammonium molybdophosphate-I. The Alkali Metals. J. Inorg. Nucl. Chem. 12:104-112.

Sreekumaran, C., K. C. Pillai and T. R. Folsom. 1968. The concentration of lithium, potassium, rubidium, and cesium in some western American rivers and marine sediments. Geochimica et. Cosmochimica Acta. 32:1229-1234.

Tananejev, I. V. and Gluskova. Zh. Neorg. Khim. 2:281.

Vetter, H. 1937. Limnologische Untersuchungen über das Phytoplankton und seine Bezihungen zur Erüahung des Zooplanktons in Schleinese bei Langenangen am Bodensee. Int. Rev. Hydrobiol. 34:499-561.

Yamagata, N. 1965. Review on the analytical methods for the stable and radioactive cesium. Dept. of Radiological health. The Institute of Public Health, Tokyo UDC. 543.036:546.36.

APPENDICES

APPENDIX A

LITERATURE REVIEW

APPENDIX A

LITERATURE REVIEW

Radioisotope accumulation in our environment was not considered extremely important until the advent of the atomic and hydrogen bombs and more recently the thermal nuclear power plant. Considerable effort is now being asserted to understand the cycling of the biologically active isotopes in our ecosystems. One of the most important parameters controlling the radioisotope dynamics is the stable isotope of the element.

Cesium, at. wt. 132.905; at. no. 55; m. p. 28.5 C; B. P. 690 C; sp. gr. 1.873 (20 C) valence 1, was spectrographically discovered in 1860. Cesium occurs in lepidolite, polucite (hydrated silicate of aluminum and cesium) and is the most electropositive and most alkaline element. Cesium has recently become one of the chief components in the photoelectric cell. It also has been found that it may have application in ion propulsion systems. Trace amounts of cesium-137 from fallout and thermal nuclear plants are present throughout the world.

Cesium-137 is found as a result of the following decay scheme:

$$^{137}\text{I} \xrightarrow[\text{min}]{19} {}^{137}\text{Xe} \xrightarrow[\text{min}]{3.4} {}^{137}\text{Cs} \xrightarrow[\text{years}]{30.5} {}^{137}\text{Ba (stable)}$$

A 30.5 year half life allows sufficient time for considerable biological accumulation. Cesium has been compared to potassium in biological reactivity.

Ion Exchange Materials

Several papers have been published on the complex cyanides and their use as sorbers of the alkali metals. Petrow, et al. (1967) describes NCFC as an improved resin for use with cesium; Prout, et al. (1964) discusses KCFC as a cesium sorber; Mohanrao, et al. (1963) used nickel ferrocyanide for cesium-137 determinations. Kourim, et al. (1964) and Edgington, et al. (1969) review and compare many of the forms of complex cyanides.

Yamagata (1965) reviews many of the ion exchangers used in cesium work while Maeck, et al. (1963) compares zirconium exchangers at different pH values and Amphlett, et al. (1958) discusses separation of rubidium and cesium on zirconium phosphate resin. Feldman and Rains (1964) used AMP as a cesium scavenger in water and biological samples while Kahn, et al. (1957) used a precipitation method of cesium determination with AMP being formed and Van, et al. (1959) described AMP as an exchanger for alkali metals using an asbestos mixture to facilitate its use in column form.

Cesium Analysis in Water

Methods of cesium analysis have been largely involved with areas of relatively high cesium concentration. Much of the preconcentration processes were involved strictly with cesium-137 in reactor effluents. Methods of total cesium analysis are offered by Feldman and Rains (1964), but results of tests on this method showed it to be not nearly sensitive enough for low levels of cesium found in water of this southern Michigan area. Folsom (1970) gives many methods, but all are designed for sea water. Yamagata (1965) gives a summary of methods of cesium analysis but most apply to higher levels than are present here. He also covers methods of cesium analysis in biological materials and gives a fairly complete reference. Feldman and Rains (1964) offer a method of cesium analysis in biological samples that was used with some alterations in this study and gave favorable results. Methods were also examined using a liquid-liquid extraction of cesium from the acid solution of the ion exchange resin used for preconcentration. Flynn (1970) reports a rapid solvent extraction using a phenol nitrobenzene solution. Sekine and Dyrssen (1969) discuss the use of tetraphenylborates for use with alkali metals; Horner, *et al*. (1963) used substituted phenols in a suitable diluent for recovery of cesium. The use of 4-sec-butyl-2-(-methylbenzyl) phenol (BAMBP) as a cesium extractant is discussed by Egan, et al. (1964) and Ross and White (1964) also report the use of BAMBP. Crowther and Moore (1963) used 2-thenoyltrifluoroacetone for liquid-liquid extraction of cesium.

Specific Activity

Specific activity has been used by Nelson (1967) to predict ^{90}Sr uptake in fish. Nelson (1967) also used specific activity data to calculate cesium-137 levels in white crappies. He showed the specific activity of stroutium in the water to be very close to that in the fish samples. Using results from Pendleton, et al. (1958) on equilibration time between cesium in fish flesh and water the fish were sampled at a time that would reflect the concentration of cesium in the water. Pendleton reported about 10-12 days for equilibration between the cesium in fish flesh and in the water. Other investigators have indicated the equality of specific activity of cesium in fish and their surroundings (Folsom, et al., 1967 and Palmer and Beasley, 1967).

APPENDIX B

METHODS AND MATERIALS

APPENDIX B

METHODS AND MATERIALS

The methods of direct total cesium analysis are of three major types: The first and most common involves preconcentration of cesium on ion exchange columns, digestion of ion exchange resin, extraction with AMP, solution of the AMP, and finally liquid-liquid extraction into an organic phase suited to flame emission photometery. The method of NCFC digestion is given in Table B-1. The procedure for preparation of cesium analysis from digested resin is given in Table B-2. A method proposed by Folsom (1970) is given in Table B-3. The second type of method uses the same preconcentration method employing an ion exchange column. The resin is digested in acid and a liquid-liquid extraction is performed directly on the acid solution. Various extractants were examined for their extraction power of cesium. A list of extractants and percent recovery of cesium-137 is given in Table B-3. The third method involves a batch absorption of cesium. AMP was added directly to a volume of water, slurried and collected. This AMP was dissolved and the cesium was

TABLE B-1.--Digestion procedure for complex cyanide resins.

1. Dry a 5g resin sample for 8 hrs. at 70 C.
2. Place dry resin in 500ml boiling flask; add 10ml conc. H_2SO_4.
3. Boil gently with reflux condenser for 1-4 hours, until residue is pink-purple color.
4. Allow to cool.
5. Add 50ml of distilled water slowly; bring to a gentle boil.
6. Continue refluxing 1-3 hours, until resin is completely in solution.
7. Cool solution.

TABLE B-2.--Procedure for AMP extraction of Cs form acid solution of resin.

1. Place resin solution in a 200ml Pyrex beaker.
2. Put solution on a magnetic stirrer.
3. Adjust pH to approximately 2.5 with 5N NaCH and remove pH electrodes.
4. Add AMP (2.5g) and stir for 30-60 min.
5. Remove stirring bar and allow AMP to settle.
6. Decant the clear liquid from the top.
7. Place the slurried AMP in a 50ml centrifuge tube and centrifuge.
8. Decant the supernatant and discard.
9. Dissolve AMP in about 20Ml 1.0N NaOH.
10. Place solution in a sepratory funnel and add 20ml 0.1N tetraphenylboron in hexone and shake.
11. Separate upper organic layer and retain for flame emission analysis.

TABLE B-3.--Method for CS analysis of sea water samples (Folsom, 1969).

1. Dried ion exchange granules are covered with 5 times their weight in conc. H_2SO_4, heated slowly for about 20 minutes.
2. More H_2SO_4 is added to rinse the walls of the container, and heating is increased until white fumes appear. Heating is continued to dryness.
3. The dish is cooled and .05 N nitric acid is added and heat applied to dissolve most of the residue.
4. Small amounts of residue are removed by filtering through Whatman no. 41 paper and collecting in a plastic beaker.
5. 5 grams of AMP is stirred into the cold solution for 10 minutes with a magnetic stirrer.
6. AMP is settled over night and supernatant then is decanted off.
7. The beaker is refilled with 0.05 $NHNO_3$ and allowed to settle again over night and decanted.
8. AMP is washed into centrifuge tube and centrifuged.
9. The supernatant is decanted off and AMP is hardened in oven for 10 minutes at 60°.
10. Sample is counted on NaF crystal for Cs concentration.
11. AMP is transferred to a 250 ml centrifuge tube and 40ml 2 M NaOH is added to dissolve the AMP.
12. After centrifuging the iron hydroxide residue is packed down and the supernatant is transferred into a plastic beaker containing 20ml of glacial acetic acid and the residue is washed with 10ml of 0.5 N NaOH.
13. Powdered AMP is stirred into the solution that now has a pH = 4. Stir for 15 minutes and then centrifuge. Add 50mg more AMP and stir and again centrifuge.
14. This ppt. is dissolved in 5ml 1 M NaOH and washed with deionized water into a separatory funnel.
15. 10ml of 0.025 N TPB solution is added.
16. Shake vigorously for 1 minute and allow to stand over night.
17. Separate organic layer and retain for flame emission analysis.

extracted into an organic solution. This method was described by Feldman and Rains (1964) and is given in Table B-4.

Elution techniques were also attempted to remove the cesium from the ion exchange columns. Table B-5 gives the results of these elution tests. These attempts were not successful as can be seen by the results for all but one ion exchange resins. The one exception, ZrP gave very good elution values at 77 C. ZrP was not specific enough to use for cesium concentration in the presence of K^+ and Na^+, so this elution capability was of little use in this study. It does offer an excellent method of laboratory separation of alkali metals in "clean" solutions (Amphlett, 1958). The procedure used for elution of cesium from ZrP is given in Table B-6.

Resins used in column form were prepared using 5 grams dry weight of 20-50 mesh material. This 5 grams of resin was slurried in 50ml of distilled water and allowed to soak for at least 24 hours. The resin was then placed in polystyrene vials (obtained from Dynalab Corp.) 30mm x 70mm with the bottoms removed and fitted with polyethylene porous disks. A column similar to this was described by Boni (1966). This size and shape of column and amount of resin proved to be a good compromise between percent uptake of cesium and flow rate necessary for large quantities of water to be preconcentrated. A photograph of the column is shown in Figure 1.

TABLE B-4.--Batch absorption of Cesium from water samples (Feldman and Rains, 1964).

1. Transfer 8 liters of water to a wide-mouthed battery jar which can be drained through a stop cock in the bottom.
2. Adjust the pH to 6-7 if necessary. Add 800mg of AMP and stir for 10 minutes.
3. Add 25 mg of Al^{+3} solution and heat to 40 C while stirring.
4. Allow solution to cool and AMP to settle out.
5. Siphon off as much of the supernatant liquid as can be removed without disturbing the residue.
6. Stir the remaining liquid vigorously and drain the resulting slurry through the stop cock. Transfer the slurry to the required number of 50ml centrifuge tubes. Centrifuge and combine.
7. Count AMP for ^{137}Cs level. Dissolve AMP in 1.0 N NaOH (10-15ml).
8. Adjust pH to 3.5 with tartaric acid and extract with 50mg of AMP.
9. Dissolve this AMP in 1.0 N NaOH and extract into 10ml of 0.1 N TPB hexone solution and retain for flame emission analysis.

TABLE B-5.--Complex cyanide ion exchange resins.

Resin Form	Mesh Size	Weight of Resin	Flow Rate	% Uptake of ^{137}Cs	Eluting Solution	% Elution
$K_2[CuFe(CN)_6]$	20-40	5.0g	10.6L/hr.	57.4	15M HNO_3	39.0
$K_2[ZnFe(CN)_6]$	20-40	2.5g	8.0L/hr.	67.0	15M HNO_3	29.0
$K_2[CoFe(CN)_6]$	20-50	5.0	15.0L/hr.	83.0	0.1M $TlNO_3$	0.0
$NH_4[CoFe(CN)_6]$	20-50	5.0g	15.0L/hr.	80.0	1.0M NaOH	0.0
Zirconium Phosphate	20-50	5.0g	16.0L/hr.	86.0	0.5M NH_4NO_3	99.5 @77 C

2

TABLE B-6.--Procedure for elution of Cs from zirconium phosphate resin.

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1. 5 gm columns of zirconium phosphate spiked with ^{137}Cs and counted to determine exact ^{137}Cs content were used.
2. The column was suspended above a 300ml beaker on a plexiglas sheet fitted with a hole to set the column in. This apparatus was placed in a Sargent drying oven at 77 C.
3. A 100ml capacity addition buret was placed on top of the drying oven with the stem extending down to the top of the ion exchange column.
4. The ion exchange column was allowed to equilibrate with the oven temp.
5. 100ml of 0.5 N NH_4NO_3 hot water soln. is then added to the addition buret.
6. The stop cock is then adjusted to give an approximate flow rate of 40ml per hour.
7. The column was then dried and counted to determine % elution of the ^{137}Cs spike.

The ion exchange columns were operated on the continuous flow constant head ion exchange apparatus I designed and built for field use. The unit was built in duplicate so two samples could be taken simultaneously or so two types of ion exchange materials could be compared. Detailed photographs are given in Figure B-1 to supplement the earlier description.

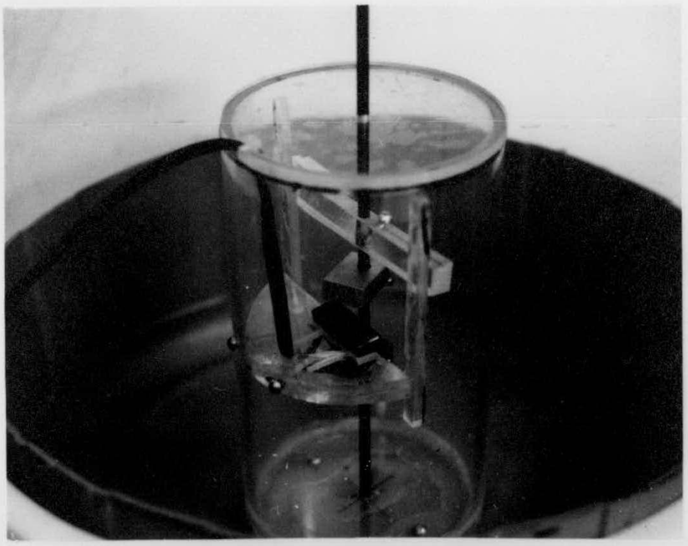
The filtration system designed to clean the lake water of particulate matter before it was passed through the ion exchange column was an essential part of the system. Two in-line filters were used to remove the bulk of the material before the water entered the reservoir and a final filter removed traces of matter just before the water passed through the column. All three of the filters were built completely of inert plastic material to minimize absorption of cesium. Soft polyethylene funnels, 11.0cm in diameter, were fitted with plexiglas rings. These rings had four holes drilled through them for brass nuts and bolts. A piece of rubber gasket material was used between the funnels for the in-line filters. The actual filtering material consisted of a porous polyethylene disk (90μ pore size). This disk was 9.0cm in diameter so it would fit down inside one of the funnels. Polyethylene filter floss, purchased at an aquarium supply house, was used as the filtering material. Filter floss was used in varying amounts depending on the size of the particulate matter

Figure B-1.--Ion exchange apparatus photographs.

A. Micro-switch apparatus

B. Battery and flow meter box

C. Complete apparatus operating on Wintergreen Lake November 1970



to be filtered. The final filter was built using the same materials. The difference was that only one funnel was used and the polyethylene porous disk was cut 11.5cm in diameter and was clamped to the rim of the funnel with the plexiglas rings. Photographs are shown of the two types of filters in Figure B-2.

Flow Rate and Percent Uptake of Cesium

The flow rate and percent recovery data for the ion exchangers were determined using six-liter distilled water samples. Five-gram columns were prepared as described earlier. These columns were counted for background radiation and placed on the outlet of a ten-liter glass battery jar. The cesium-137 spike was counted and placed in six liters of water in the battery jar. The stop cock was then adjusted to the required flow rate and a timer started. The time of flow was recorded for the six liters of water and an average flow rate calculated. The column was counted at 0.662 Mev for cesium-137 and percent recovery determined and all the samples were run at room temperature. Using this apparatus, flow rates up to 30 liters/hr. were obtained. A photograph of the apparatus used is shown in Figure B-3.

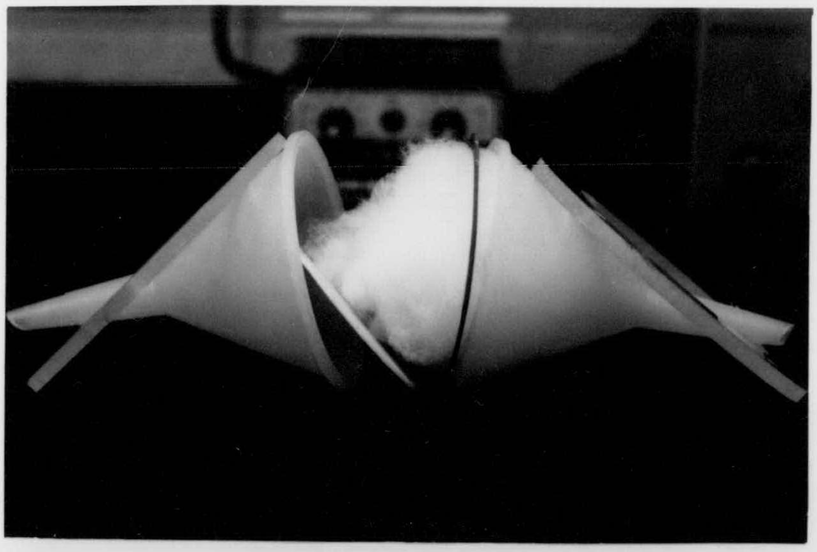
The NCFC, KCFC and ZrP ion exchange resins were purchased from Bio Rad Laboratories. The other two forms of complex cyanide resins, Zn and Cu, were prepared by a method described by Kourim, *et al*. (1964). Methods of

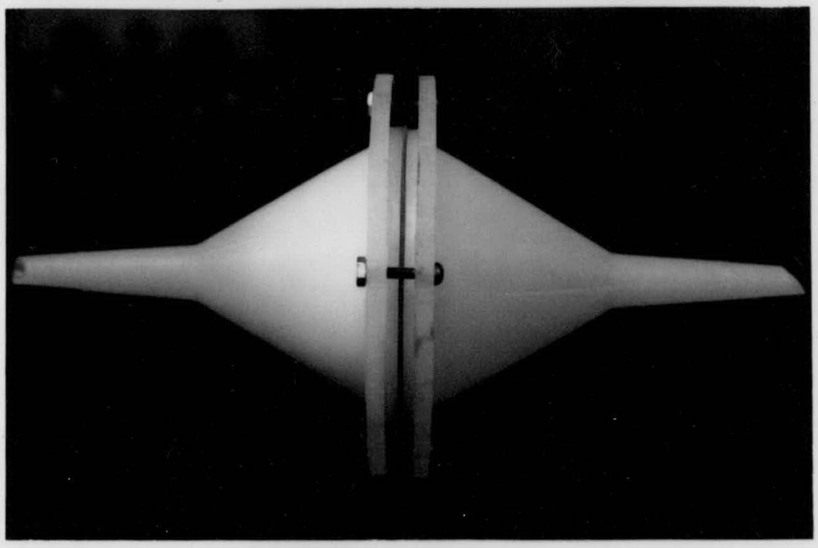
Figure B-2.--Photographs of filters.

A. Disassembled in-line primary filter

B. Assembled in-line filter

C. Final filter





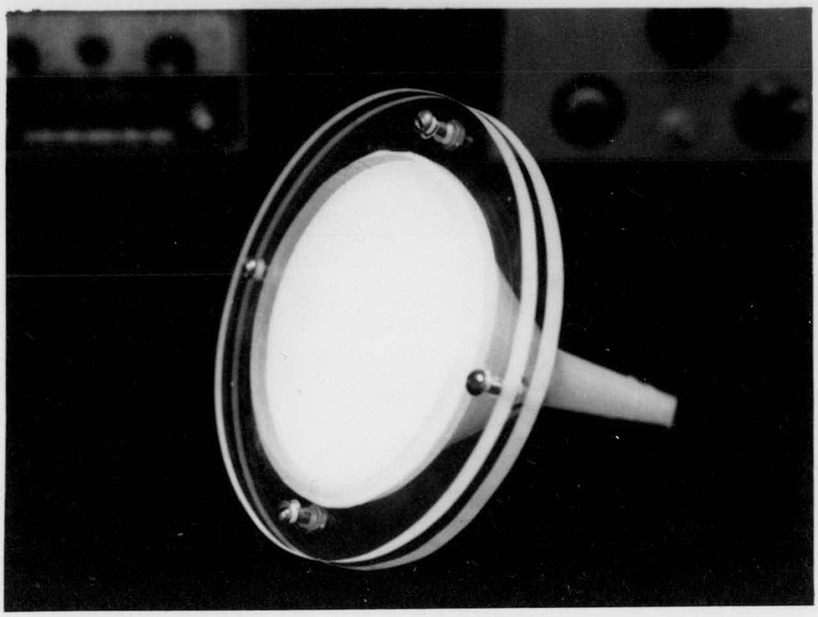
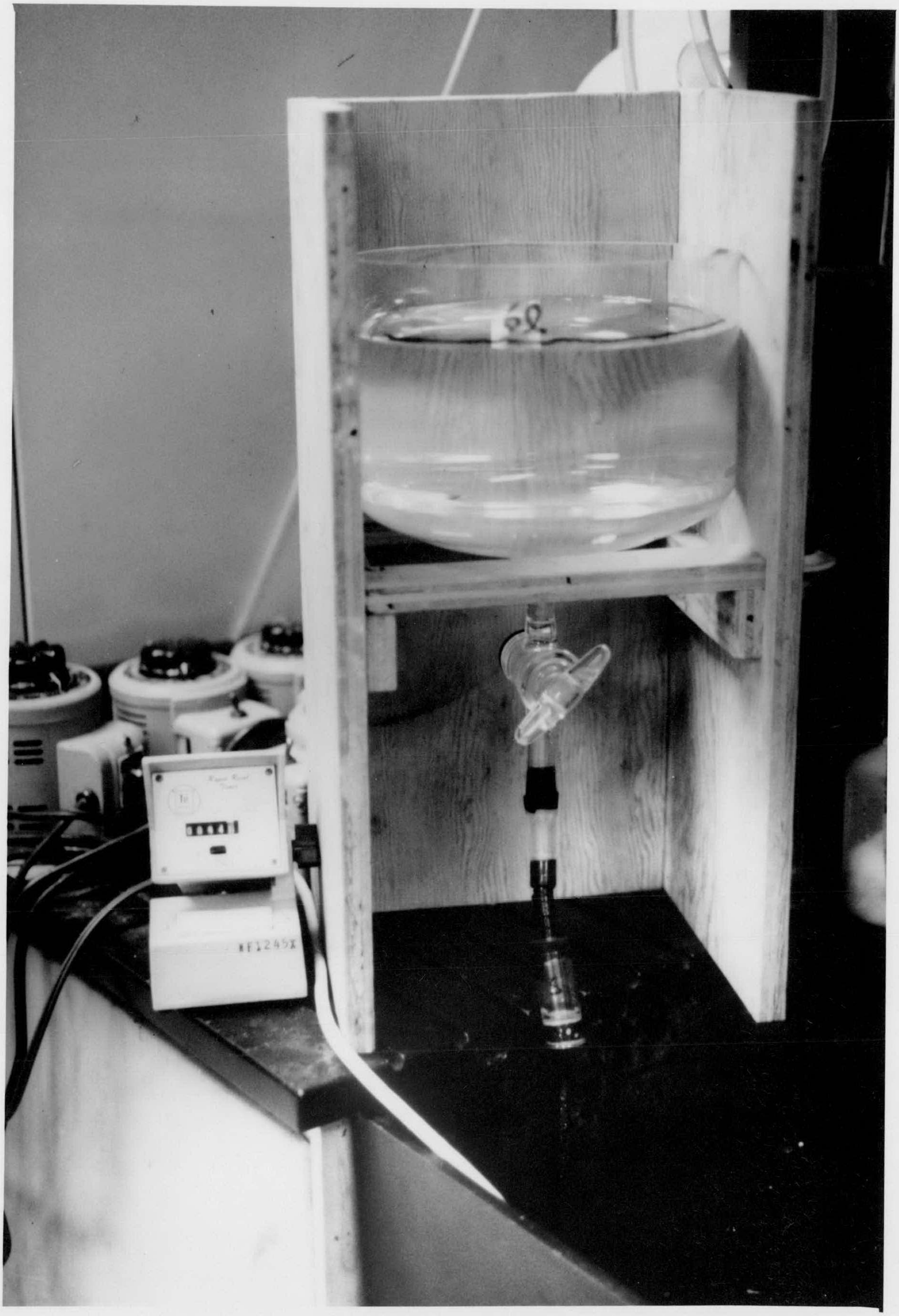


Figure B-3.--Photograph of flow rate versus uptake apparatus used in lab studies.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preparation are given in Table B-7. The AMP was first purchased from Bio Rad Laboratories but Folsom (1970) reported considerable contamination of cesium in this product. He gives a method which was used for preparation of AMP and is given in Table B-8. Chemicals used for preparation of ion exchange materials were obtained from Mallinckrodt and were all reagent ACS grade.

Counting Radiocesium

Cesium-137 counting was done by means of a single channel solid scintillation counter. A three inch NaI(Tl) crystal with a 1.25 inch by 2 inch well was used (Harshaw). This crystal was connected to a Tracerlab single channel spectrometer and a NMC scaler.

A 0.05 Mev window was used to give a good signal to background ratio. Columns and counting vials were 1.0 inch diameter to insure consistent counting geometry. The counting efficiency averaged about 17.0% for cesium-137 standard. The efficiency was determined daily.

Counting times were determined using the following formula: (Overman and Clark, 1960)

$$T_s = \frac{R_{s+B} + \sqrt{(R_b)(R_{s+b})}}{(G^2)\ (R_s{}^2)}$$

where:

T_s = sample time (min)
R_s = sample rate (min)

TABLE B-7.--Preparation of complex cyanides of Zn and Cu (Kourim, *et al.*, 1964).

1. 0.1 M solution of potassium ferrocyanide (167ml) was added slowly to 0.1 M zinc nitrate (500ml) while stirring.
2. The mixture was heated on a hot plate magnetic stirrer for 1-2 hours.
3. After cooling the mixture was filtered through no. 1 Whatman paper in a Buchner funnel.
4. The precipitate was washed twice with 9.3 M $NaNO_3$ and then with water.
5. The material was then placed in a drying oven and dried at 70 C overnight and ground to mesh size 20-50. The Cu form of the resin was prepared exactly the same substituting 0.1 M copper nitrate for zinc nitrate.

TABLE B-8.--Preparation of AMP (Folsom, 1969).

Sol. 1.--81g NH_4NO_3 + 81g citric acid + 102g $(NH_4)_6MO_7O_{24}$ + 2140ml H_2O

Sol. 2.--391ml 70% HNO_3 + 455ml H_2O

Sol. 3.--Pour Sol. 1 slowly into Sol. 2 stirring without heat

Sol. 4.--100g $(NH_4)_2HPO_4$ + 2000ml H_2O

1. To Sol. 3 in a 4 liter pyrex beaker add 2ml of Sol. 4 and heat to a boil while stirring.
2. After cooling solution allow AMP formed to settle to bottom of beaker.
3. Decant the supernatant into another 4 liter beaker and discard AMP that was made in step 1.
4. To supernatant in 4 liter beaker add 100ml of Sol. 4 and bring to boil while stirring.
5. Allow to cool and filter solution through Whatman no. 4 filter paper.
6. Wash the AMP with two 1 liter solutions of .1 N NH_4NO_3.
7. Place the AMP in drying oven at 70 C overnight and store in dry place.

R_b = bkgd rate (min)

R_{s+B} = total rate (min)

G = percent error (0.05)

$$T_b = T_s \Big/ \frac{R_{s+b}}{R_b}$$

where:

T_b = bkgd time (min)

Thus, the determination of cesium-137 activity was significant at the 95% level.

Fish Collection

The majority of the fish taken for analysis including perch and bass were age three and of fairly uniform weights. Some larger bass were taken for subsampling procedures in the lab to test the variation of the method. Fish samples were taken at least two weeks after fall overturn and within one week of the water samples of cesium-137 concentration. The perch and bass were all taken by hook and line.

Study Site

Wintergreen Lake was chosen as the study site due to its high cesium levels in fish and water compared with other lakes in the area. This lake in Kalamazoo County has been managed as a waterfowl refuge for many years. It is a part of the W. K. Kellogg Biological Station, Michigan State University. It may be speculated that the relatively high concentrations of alkali metals Na, K, and Cs is in part due to the large number of waterfowl that regularly occupy the lake. The lake can be termed eutrophic and typically dimictic. The presence of large numbers of waterfowl and some agricultural drainage has contributed to its natural tendency toward enrichment. The availability of fish in the lake also make it ideal for this type of study as adequate samples are easily obtained.

At present, another study is being performed on the lake. The concentrations of cesium through the trophic levels are being examined by D. Eyman.

Fish Digestion

All perch were treated individually except two samples where two fish were combined. Bass were either digested individually or halved for subsamples. Prior to digestion the fish were cut into pieces small enough to fit through the neck of the digestion flask.

A wet oxidation method of digestion was employed. This allowed a low temperature (130 C) digestion to minimize cesium loss due to volitilization. Digestions were executed in 3 and 5 liter round bottom two-necked boiling flasks. These flasks were fitted with reflux condensers and electrical heating mantles. The method of nitric acid digestion of whole fish is given in

Table B-9. A photograph of the digestion apparatus is shown in Figure B-4.

Cesium in Whole Fish

The concentration of the cesium from the acid solution of the fish was accomplished using AMP. The batch absorption of cesium using AMP and successive clean-up steps were described by Feldmand and Rains (1964). Some changes have been made in the procedure to accommodate whole fish analysis. The procedure is given in Table B-10.

The final sodium hydroxide solution of the AMP is extracted into organic solution and retained for flame emission analysis of cesium.

Flame Emission Analysis

Basically, it involves the aspiration of a solution containing the element to be analyzed into the flame, the element is first atomized and is said to be in the ground state. This means that the electrons are at their normal energy level. The thermal energy in the flame excites some of the electrons to a higher energy level. This excited state is not a stable state for the electrons, so they keep losing energy and falling back into the ground state. In this process, the atom emits energy at a wavelength characteristic to the element. Flame emission measures this energy and from the amount of energy emitted

TABLE B-9.--Nitric acid digestion procedure for fish.

1. Cut fish into pieces to fit boiling flask neck.
2. Determine wet weight of sample.
3. Place fish pieces in boiling flask.
4. Add approximately 3.0ml of conc. HNO_3 per gram of fish.
5. Allow oxidation to proceed 3-4 hours with no heat applied.
6. Reflux the solution approximately 8 hours allowing excess water and acid to be distilled off until about 2ml of acid are left per gram of fish.
7. Add sufficient conc. HNO_3 to bring back to original volume.
8. Reflux with stop cock closed for approximately 4-6 hours until no oil can be seen floating on the surface. Additional acid should be added if oil is not digested.
9. Allow to cool and remove from flask rinsing with distilled water into a plastic beaker at least twice the volume of the digest.
10. Allow to cool to room temp. and proceed with AMP collection of Cs.

Figure B-4.--A photograph of a three liter digestion apparatus, used for wet oxidation of whole fish.

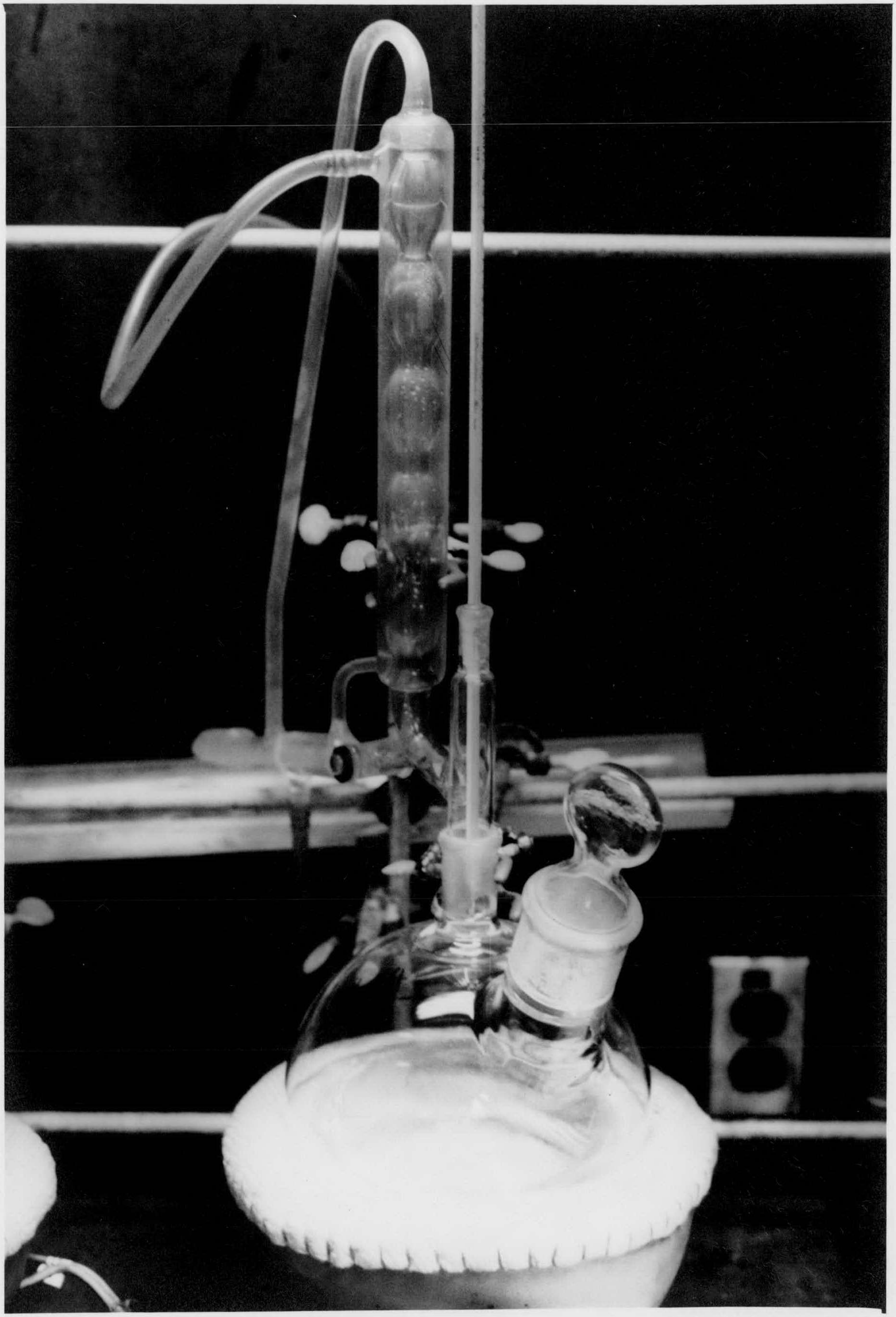

TABLE B-10.--Cs collection and preparation for flame emission analysis.

1. To the acid solution of fish tissue add 4mg AMP/gm wet wt.
2. Stir solution 15-30 minutes and allow to settle overnight.
3. Pour off supernatant and collect AMP in 50ml centrifuge tubes.
4. Collect AMP in one tube and count ^{137}Cs.
5. Dissolve AMP in 1.0 N NaOH (approximately 15ml per gram).
6. Adjust pH of solution to 3.5 using powdered tartaric acid.
7. Add 0.4mg AMP/gm wet wt. and stir for 15 minutes.
8. Collect AMP in centrifuge tube and again count ^{137}Cs.
9. Dissolve AMP in 1.0 M NaOH (about 10ml).
10. Place 10ml NaOH Cs soln. in separatory funnel with 10ml 0.1 N TPB and shake vigorously for 1-2 minutes.
11. Allow layers to separate overnight.
12. Retain organic layer for flame emission analysis.

a quantitative estimation of the amount of the element in the sample can be calculated.

Cesium is best suited to flame emission due to its ratio of ground state to excited state atoms (7×10^2 at 3000 K). Atomic absorption depends on having many atoms in the ground state to be excited.

The instrument used in this study was a model 82-800 Jerrell-Ash equipped with an infrared grating and a red sensitive photomultiplier (R446). The detection limit for cesium in hexone TPB solution was approximately 0.05mg/liter. An air-H_2 flame was used for cesium. Standards were prepared using CsCl. One hundred mililiters of NaOH solution standard was extracted with 0.1N TPB in 3/1 hexone solution.

APPENDIX C

DATA TABLES

TABLE C-1.--Flow rate and percent recovery of cesium-137.

Resin Type	Flow Rate Liters/hr.	CPM in Spike		Percent Recovery
NCFC	7.0	270.0	270.0	100.0
	7.7	87.2	86.1	99.0
$(NH_4)_2[CoFe(CN)_6]$	12.5	187.0	178.0	95.2
	15.7	111.4	100.3	90.0
	15.79	107.0	96.1	89.0
	20.9	306.0	248.0	81.0
	24.8	262.0	219.0	83.6
	28.8	354.0	290.0	81.9
KCFC				
	5.26	126.6	126.0	99.5
$K_2[CoFe(CN)_6]$	7.72	136.0	129.0	94.8
	9.0	136.6	119.9	87.7
	12.56	141.0	116.0	82.2
	14.4	114.0	80.9	71.0
	15.0	128.0	89.6	70.0
ZrP				
	8.65	147.3	143.0	97.3
$ZrO_2P_2O_5.3H_2O$)	13.32	150.0	135.0	90.0
	13.5	173.5	155.5	90.0
	15.6	177.0	163.0	92.0
	16.98	158.0	137.0	86.0
	18.0	139.0	108.0	77.0

TABLE C-2.--Percent recovery of cesium-137 on AMP from acid digest of NCFC.

Sample No.	mg AMP Used	Percent Recovery
1	200	37.0
2	300	69.0
3	500	68.7
4	100	41.0
5	100	40.0
		$\bar{X} = 51.0 \pm 19.0\%$

TABLE C-3.--Cesium recovered when AMP was dissolved in NaOH.

mg AMP	Vol. NaOH	Percent Recovery
200	10ml	40.0
300	10ml	65.0
500	10ml	51.0
100	10ml	45.0
		$\bar{X} = 50.0 \pm 10.0\%$

TABLE C-4.--Cesium recovered from NaOH with TPB in hexone.

Vol. NaOH	Vol. TPB	Percent Recovery
10ml	10ml	36.4
10ml	10ml	23.6
10ml	10ml	34.2
10ml	10ml	28.7
		$\bar{X} = 30.7 \pm 9.0\%$