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DETERMINATION OF Mn⁵⁶

IN REACTOR EFFLUENT WATER

by

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DETERMINATION OF Mn^{56}
IN REACTOR EFFLUENT WATER

INTRODUCTION

The isotope Mn^{56} is the major short half-life constituent of reactor effluent water. It has a half-life of 2.59 hours⁽¹⁾ and decays by emission of a 2.86 mev maximum beta to stable Fe^{56} . This report describes a rapid method for the quantitative determination of Mn^{56} in a radiochemically pure form for use as a routine control procedure. The procedure requires the separation of Mn^{56} from other activities including Na^{24} , Si^{31} , P^{32} , Cu^{64} , Sr^{91-92} , Ba^{139} and the rare earths.

Because of the rather short half-life of Mn^{56} , the length of a procedure for its analysis must be short and the possible methods for its isolation are reduced considerably.

SUMMARY

A carrier-precipitation procedure has been developed which successfully separates Mn^{56} from other radioisotopes in reactor effluent water. It involves addition of Mn^{++} carrier to the sample followed by oxidation to MnO_4^- , removal of radioactive cations by stirring with Dowex 50 cation resin, and precipitation as $MnO_2 \cdot xH_2O$. The $MnO_2 \cdot xH_2O$ is dried and weighed and its radioactivity measured by beta counting.

Although the manganese dioxide precipitate does not have a definite molecular formula, it was demonstrated that under the conditions of the procedure the percent manganese in the precipitates varied only slightly. The chemical and radiochemical yields could therefore be determined from the weight of precipitate obtained.

The possibility of any Mn^{56} occurring as MnO_2 in reactor effluent water was shown to be unlikely. When reactor effluent water samples were treated with a reducing agent, which would reduce MnO_2 to Mn^{++} , prior to carrying out the Mn^{56} analysis no increase in Mn^{56} content was observed.

Decay curves of about 40 Mn^{56} analyses of reactor effluent water have demonstrated that radioactive contamination due to other elements is negligible.

A self-absorption and self-scatter curve for $Mn^{56}O_2 \cdot xH_2O$ was prepared by using a Mn^{56} spike prepared from reactor effluent water. For samples of interest a correction for self-absorption and self-scatter will be unnecessary.

DISCUSSION

This procedure for Mn^{56} analysis is a modification of a standard Mn analytical procedure(2) with the addition of an ion exchange purification step.

A 10 ml portion of reactor effluent water is used for analysis. It is placed in a 250 ml beaker with 1 ml conc. HNO_3 , 1 ml of Mn carrier (7 mg/ml as $MnSO_4$), and the solution is cooled to about $15^\circ C$. Approximately 0.5 grams of $NaBiO_3$ is added and the solution swirled for about one minute. The slurry is diluted to about 100 ml, 2 grams Dowex 50 resin (50-60 mesh) added and the mixture stirred for 2-3 minutes with a glass-propeller paddle driven by an air-motor. The mixture is filtered, the residue washed with 10-20 ml of distilled water and the combined filtrate and washings stirred as above with a second 2 gram portion of resin. The mixture is then filtered, the filter washed and the filtrate and washings placed in a 250 ml beaker. To this solution is added 3 ml of 6N NaOH and 1 ml of 3% H_2O_2 . The mixture is stirred, then placed in 100 ml Bosteroid centrifuge tubes and centrifuged. The supernatant liquid is siphoned off and the precipitate washed with about 80 ml of H_2O and centrifuged again. The $MnO_2 \cdot xH_2O$ is placed on a weighed one inch counting dish, dried, weighed and counted in a standard GM mica-window counter. The chemical and radiochemical yields are determined from the weight of precipitate and the counting rate of the sample.

As an alternate method for isolating the manganese an acid precipitation procedure was studied.

After the resin treatments 10 ml of conc. HNO_3 and 1 ml of 3% H_2O_2 are added. The solution is brought to a boil, cooled slightly and 2 grams $KBrO_3$ added, then boiled for two minutes. The precipitated $MnO_2 \cdot xH_2O$ is centrifuged, washed, centrifuged and plated in the same manner as described previously. The

Mn content of the precipitate is slightly higher by this procedure and is reasonably constant.

This procedure requires that none of the Mn^{56} be present as $Mn^{56}O_2$. A study was therefore conducted to determine if any Mn^{56} did actually exist as $Mn^{56}O_2$. Duplicate aliquots of two reactor effluent water samples were analyzed; one of each set by the above procedure and one with the addition of 0.5 ml of 3% H_2O_2 and boiling just prior to the bismuthate oxidation step. The effect of the H_2O_2 would be to reduce any MnO_2 to Mn^{++} by the reaction:

As may be noted from the data in Table I, no apparent increase in the Mn^{56} content of the samples was observed with this treatment. The counting rates recorded are corrected for decay and chemical yield.

TABLE I

<u>Number</u>	<u>c/m Mn^{56} (regular procedure)</u>	<u>c/m Mn^{56} (H_2O_2 Treatment)</u>
1	3308	3144
2	3866	3716

CHEMICAL ANALYSIS OF PRECIPITATES AND RADIOCHEMICAL RECOVERY

To determine the reproducibility of the procedure and the chemical composition of the manganese dioxide precipitates a number of analyses were performed on each of several reactor effluent water samples.

The samples were analyzed for Mn^{56} by beta-counting and for Mn by the "Bismuthate Procedure" (2).

In Table II the results obtained from the chemical analysis for Mn of 23 samples carried through the regular procedure and seven carried through the alternate HNO_3 - $KBrO_3$ precipitation step are given.

TABLE II

<u>Regular Procedure</u>		<u>HNO₃-KBrO₃ Precipitation Step</u>	
<u>Sample</u>	<u>Fraction Mn in Precipitate</u>	<u>Sample</u>	<u>Fraction Mn in Precipitate</u>
Sample I			
1	0.4617	1	0.4917
2	0.4565	2	0.5227
3	0.4789	3	0.5086
4	0.4681	4	0.5079
5	0.4864	5	0.5325
6	0.4707	6	0.5126
		7	<u>0.5252</u>
Sample II			
1	0.4444	Average = 0.5145 Standard Deviation = 2.47%	
2	0.4783		
3	0.4792		
4	0.4707		
5	0.4800		
6	0.4543		
Sample III			
1	0.4452		
2	0.4701		
3	0.4477		
4	0.4421		
5	0.4670		
Sample IV			
1	0.4659		
2	0.4718		
3	0.4617		
4	0.4874		
5	0.4813		
6	<u>0.4889</u>		
Average = 0.4678			
Standard Deviation = $\pm 3.78\%$			

The data in the above table give the fraction of Mn present in the manganese dioxide precipitate as $0.4678 \pm 3.78\%$ standard deviation for the regular procedure and $0.5145 \pm 2.47\%$ standard deviation when the HNO₃-KBrO₃ precipitation step is employed. Although the HNO₃-KBrO₃ precipitation step gives a precipitate of composition closer to MnO₂, the extra time it requires would probably make it less desirable for routine use.

Replicate analyses for Mn⁵⁶, by the regular procedure, were performed on

three samples of reactor effluent water. The results obtained from these analyses are summarized in Table III.

The value 0.4678 given in Table II for the fraction Mn in the precipitate was used in making chemical and radiochemical yield corrections. One ml of Mn carrier (7.710 mg/ml Mn) was used so a yield of 100% would weigh 16.48 mg.

TABLE III

Sample I

<u>Number</u>	<u>mg MnO₂</u> <u>Precipitate</u>	<u>Observed</u> <u>c/m</u>	<u>Time</u> <u>Counted</u>	<u>Percent</u> <u>Chemical Yield</u>	<u>(Corrected for decay</u> <u>and chemical yield)</u> <u>c/m Sample</u>
1	11.9	719.8	1805	72.2	998.5
2	10.1	585.4	1815	61.3	998.8
3	10.7	593.0	1825	64.8	998.8
4	11.8	588.1	1845	71.6	981.9
5	11.6	560.2	1855	70.4	994.9
6	11.0	466.6	1925	66.7	998.9

Average = 995.3

Standard Deviation = 0.62%

Sample II

<u>Number</u>	<u>mg MnO₂</u> <u>Precipitate</u>	<u>Observed</u> <u>c/m</u>	<u>Time</u> <u>Counted</u>	<u>Percent</u> <u>Chemical Yield</u>	<u>(Corrected for decay</u> <u>and chemical yield)</u> <u>c/m Sample</u>
1	13.4	1132.5	1735	81.3	1410
2	13.1	956.6	1805	79.5	1375
3	13.4	886.2	1815	81.3	1302
4	14.7	961.1	1830	89.2	1377
5	13.4	798.5	1840	81.3	1316
6	13.9	779.9	1850	84.3	1293

Average = 1346

Standard Deviation = 3.26%

Sample III

<u>Number</u>	<u>mg MnO₂</u> <u>Precipitate</u>	<u>Observed</u> <u>c/m</u>	<u>Time</u> <u>Counted</u>	<u>Percent</u> <u>Chemical Yield</u>	<u>(Corrected for decay</u> <u>and chemical yield)</u> <u>c/m Sample</u>
1	12.6	3407.6	1445	76.5	4458
2	13.2	3505.7	1455	80.1	4576
3	13.5	3526.4	1505	81.9	4707
4	13.1	2739.4	1600	79.5	4822
5	12.8	2391.2	1610	74.6	4499
6	13.0	2837.6	1540	78.9	4596

Average = 4610

Standard Deviation = 2.66%

The results given in Table III indicate the precision that can be expected for the procedure. On replicate analyses of the samples the standard deviation of the counting rates, corrected for decay and radiochemical yield, varied from 0.62 to 3.26%.

Decay rate measurements were made on at least one precipitate from each of the above samples. The decay curves showed the samples to be of high radiochemical purity. A typical decay curve for Mn^{56} separated from reactor effluent water is shown in Figure 1.

SELF-ABSORPTION AND SELF-SCATTER DETERMINATION

Due to the short half-life of Mn^{56} it was impractical to obtain it from Oak Ridge National Laboratory. A spike was therefore prepared by separating the isotope from reactor effluent water. The spike obtained had a specific activity of about 10^3 c/m/ug and 4145 c/m/100 λ of solution.

Five ml of the Mn^{56} spike was added to 500 ml of 0.01192 M $MnSO_4$ thus giving a solution of 1266 c/m/mg of Mn. This Mn solution was oxidized to MnO_4^- , and precipitated as manganese dioxide by the regular procedure. Various amounts of the moist precipitate were placed on one inch counting dishes and the samples dried, weighed, counted and analyzed for Mn by the bismuthate procedure⁽²⁾.

The normalized self-absorption and self-scatter curve obtained from these measurements is shown in Figure 2.

DISCUSSION OF RESULTS

Manganese dioxide was chosen as a precipitant because of its insolubility and ease of drying on stainless steel counting dishes. Although the percentage composition of Mn in the dioxide precipitate does not represent any definite molecular formula, the fact that this percentage can be stated with a small standard deviation justifies its use in making radiochemical yield calculations.

The percent manganese in a manganese dioxide precipitate certainly is not

FIG.1 TYPICAL DECAY CURVE FOR Mn^{56} SEPARATED
FROM REACTOR EFFLUENT WATER

FIG. 2 Mn^{56} AS MANGANESE DIOXIDE ON STD. 1" DISH
(4.5 cm²) SELF ABSORPTION — SCATTER FACTOR
SHELF ONE OF MICA WINDOW COUNTER

constant for all methods of precipitation, but for a definite precipitation procedure it appears reasonably constant. The seven manganese dioxide precipitants obtained by using the $\text{HNO}_3\text{-KBrO}_3$ precipitation step, listed in Table II, had a reasonably constant Mn content. Manganese dioxide precipitated from more dilute or more concentrated Mn solutions than those described here was found to have essentially the same Mn content. When samples containing twice or half as much carrier as that used in the above experiments were carried through the procedure the Mn contents found in the precipitates were, within experimental error, the same as those given in Table II.

It is obvious from the self-absorption and self-scatter curve that little or no correction is necessary for these phenomena. The lack of self-scatter in this curve may be due to the fact that the dry precipitate actually exists as small particles which cover a relatively small area of the plate. The self-scatter phenomenon is most prominently exhibited by very thin uniform sources.

The Dowex 50 resin used (50-60 mesh, 8% crosslinkage) was found to be superior to resins of lower crosslinkage. When Dowex 50 resin of 1-2% crosslinkage was used, radiochemical contamination of 1 to 5% was generally observed.

The results given in Table III indicate that in replicate samples a standard deviation of 0.62 - 3.26% can be expected for the procedure. Also, the chemical yield obtained does not appear to influence the chemical composition of the precipitation.

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Methods

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References

- (1) Hollander, J. M., Perlman, I., and Seaburg, G. T., "Table of Isotopes", Rev. Modern Physics, Vol. 25, No. 2, (April 1953); pp. 493.
- (2) Kolthoff, I. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis. New York: The Macmillan Company, 1947; pp. 709-10.

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