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## A RAPID CHEMICAL SEPARATION FOR RADIOMANGANESE

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### Abstract

A simple and rapid radiochemical separation method has been developed to separate radiomanganese from neutron-irradiated sample materials. The method is based on manganese oxide precipitations from basic and acidic media and has been successfully used in activation analysis applications for trace stable manganese. This radiochemical procedure is readily adaptable for the determination of radiomanganese species in other materials.

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In radiochemistry, the most frequently used method of separating manganese has been by perchlorate precipitations of the manganese<sup>(1-6)</sup> carrier added to a solution of the irradiated materials. It is often necessary to repeat the perchlorate precipitation several times to achieve the degree of purification needed for the separation of radio-manganese (either 2.6-h Mn<sup>56</sup> or 310-d Mn<sup>54</sup>). If the sample is a large aqueous solution, the MnO<sub>2</sub> is difficult to precipitate quantitatively by the perchlorate method. Hence, other methods of manganese separation and precipitation have been evaluated with respect to interests concerned with degree of radiochemical purification and the time required to separate the manganese species.

The formation of MnO<sub>2</sub> in a basic medium met these conditions of time and purity. Thus, the separation method was investigated further.

### Experimental

A current problem concerned with the determination of trace manganese in water by an activation analysis method, involving the Mn<sup>55</sup>(n,γ)Mn<sup>56</sup> reaction, provided a need for the study reported here. The sample volumes used varied from 10 ml to 100 ml of water. Each sample was neutron irradiated in approved plastic bottles in the ORNL Graphite Reactor for four hours and then returned to our laboratory for processing. Depending upon the volume, centrifuge tubes and beakers were used to precipitate the manganese dioxide. In each test, a solution of manganese carrier (as manganese nitrate, containing 10 mg/ml) was added as Mn(NO<sub>3</sub>)<sub>2</sub>. Holdback carriers of Cu, Fe, Na, and Ba were also added. A known amount of cobalt carrier (cobaltous nitrate, 10 mg/ml) was sometimes added as a carrier when cobalt was also to be determined in the sample. This initial

solution was made basic with either 2 M NaOH or 2 M NH<sub>4</sub>OH. Due to the chemical reaction with the added peroxide, the use of NaOH was preferred. Upon the addition of NaOH, Mn(OH)<sub>2</sub> was formed (a light pink precipitate) and 10 drops of 30% solution H<sub>2</sub>O<sub>2</sub> was added dropwise and the solution stirred until MnO<sub>2</sub> was completely precipitated. After the reaction was complete, the solution was heated to near boiling to coagulate the precipitate. The mixture was then centrifuged and the supernatant liquid discarded. The separated MnO<sub>2</sub> precipitate was then washed in 6 M HNO<sub>3</sub>; the mixture centrifuges and the wash liquid discarded. The MnO<sub>2</sub> precipitate was then dissolved in 2 ml formic acid, HCOOH; 5 ml conc. HNO<sub>3</sub> was then added and the solution heated to boiling. Solid HClO<sub>3</sub> was then added cautiously in small amounts; after each addition, the solution was boiled. Sufficient KClO<sub>3</sub> was added until the MnO<sub>2</sub> is completely precipitated. The mixture was then centrifuged and the supernatant liquid discarded. The precipitate of MnO<sub>2</sub> was then washed with 2-3 ml conc. HNO<sub>3</sub>; the mixture centrifuged and the wash liquid discarded. The MnO<sub>2</sub> precipitate is filtered, washed, dried, and mounted for counting.

The precipitate of the manganese carrier and radiomanganese may be counted either by beta, gross gamma, or gamma spectrometry. In our study, gamma spectrometry was used to determine the purity of radiochemical separations.

#### Data

The manganese radioactivity in water sources varies greatly depending on a number of factors. The water source utilized in this study was processed river water and some of the samples had manganese added for back-

water valve prevention device.<sup>(7)</sup> The data given below (Table I) shows the manganese content in tap water and gives some of the results obtained in analyses involving the addition of stable manganese to distilled water. The yield of the radiochemical of the separation method is also shown in Table I.

### Discussion

This method of separating radiomanganese from large volumes of water is rapid since it only requires about 30 minutes to analyze duplicate samples. This speed is essential because of the half-life of  $Mn^{56}$  (2.58 hr.)  $MnO_2$  precipitates as the basic oxide from a large volume much faster than the acid perchlorate; thus, shortening the analysis time and giving better chemical yields of the added stable manganese carrier. The preferred use of NaOH brings the manganese down rapidly as  $MnO_2$  without the violent effervescence which occurs when  $NH_4OH$  is employed. However, there are occasions where  $NH_4OH$  should be used instead of NaOH; for example, if much radioactive copper is present in the neutron-irradiated water,  $NH_4OH$  will aid in removing the copper by complexing it (and its holdback carrier). The use of cobalt carrier in the basic oxide precipitation of manganese permits the quantitative precipitation of cobalt along with manganese. It can be separated from manganese during the acid perchlorate step and quantitatively determined.

Many other elements can be precipitated in the basic peroxide method, but most of these will dissolve and be removed by the  $HNO_3$  acid-wash step.

Any residual contamination in the initial  $MnO_2$  precipitate can be removed by the perchlorate precipitation. In analyzing water samples, the

TABLE I  
Manganese Concentration in Valve Water Samples

<u>Sample</u>	<u>Stable Mn Found, 10<sup>-3</sup> µg/ml</u>
Natural Water-A	1
-B	1
Valve Water	
Leak 1A	16
1B	17
Valve Water	
Leak 2A	47
2B	49

TABLE II

Mn Tracer Determination by Activation  
Analysis and Chemical Separation

Sample		Chemical* Yield, %	Stable Mn Found $10^{-3}$ $\mu\text{g/ml}$	Mn Added $10^{-3}$ $\mu\text{g/ml}$
Tap Water	1	54.2	<1	0
	2	62.0	<1	0
	3	60.2	1	0
	4	59.6	1	0
Distilled Water	1	59.0	6	5
	2	51.0	5	5
	3	69.9	5	5
	4	76.5	5	5
	5	80.1	20	20
	6	78.8	19	20
	7	82.5	21	20
	8	80.1	20	20

\*Theoretical chem. yield: 16.6 mg  $\text{MnO}_2$ .

primary contaminant is  $\text{Na}^{24}$  which is completely separated by either the acid or basic precipitation of manganese and the acid washes. Greater than  $10^6$  counts of sodium-24 have been added to test the procedure, and it was found that complete decontamination could be achieved by this procedure.

The data in Table I shows that a leak in the back-prevention device had occurred, permitting manganese to seep into the natural water chamber. This process is described in detail elsewhere. Most of the data in Table I was obtained by gross gamma counting and then checked on a gamma-ray spectrometer for contamination. Appendix I shows a step-by-step procedure for use in the separation of radiomanganese.

#### Conclusions

This method appears to be useful in the determination of manganese in water samples where a radiochemical separation is required. Since it is rapid, there is only a small loss of time from the end of the neutron irradiation until the sample may be counted for its manganese radioactivity, thus, having a better counting rate so that better statistics can be obtained for the  $\text{Mn}^{56}$  measurement. This procedure is now being used routinely in the analysis of manganese in water. It may be applied to manganese in many other materials, either nonradioactive or radioactive.

#### References

1. Leddicotte, G. W., Manganese, Neutron Activation Analysis (Isotopic-Carrier) Method No. 5-11480 (1960), ORNL Master Analytical Manual, TID-7015.
2. Bowen, H. J. M., and Cawse, P. A., Atomic Energy Research Establishment, Harwell, Berkshire, England, Report No. AERE-R2925 (1959).

3. Bowen, H. J. M., J. Nuclear Energy 3, 18-24 (1956).
4. Albert, P., Caron, M., and Chaudron, G., Comp. Rend. 236, 1030 (1953).
5. Talbot, J., Albert, P., Caron, M., and Chaudron, G., Rev. Met. 50, 817 (1953).
6. Meinke, W. W., Chemical Procedures Used in Bombardment Work at Berkeley, USAEC Report AECD-2738 (1949).
7. Y. Wellwart, L. C. Bate, W. T. Mullins, J. R. Stokely, G. W. Leddicotte, "Stable Isotope Trace-Activation Analysis Methodology Use in Water Flow Studies," presented at the 14th Southeast Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, November 1-3, 1962.

## APPENDIX A

## Manganese-Chemical Separation - Alkaline-Acidic Procedure

Target Material: Tap Water

Yield: Approximately 85%

Degree of Purification: Factor of  $10^5$  from other activities;  $10^6$  from  $\text{Na}^{24}$

Advantages: Fast and good separation

Time: 30 minutes for duplicates

Procedure:

1. To 10.0 ml aliquot in a 50-ml centrifuge tube, add 10.0 mg Mn as carrier in  $\text{Mn}(\text{NO}_3)_2$  solution form, 1 ml.
2. Add holdback carriers: Cu, Fe, Zn, Co, as solutions in approximately 5 mg amount.
3. Dilute to 15-20 ml with  $\text{H}_2\text{O}$ .
4. Add 2 M NaOH dropwise until the solution is basic - universal indicator.
5. Add 10 drops of  $\text{H}_2\text{O}_2$ , 30% solution.
6. Heat cautiously until near boiling.
7. Centrifuge and discard supernatant.
8. Wash precipitate with 6 N  $\text{HNO}_3$ .
9. Dissolve precipitate in 2 ml  $\text{HCOOH}$ .
10. Add 5 ml  $\text{HNO}_3$  conc. and heat to boiling.
11. Add  $\text{KClO}_3$  solid - in small amounts to a not boiling solution; add until the precipitation of  $\text{MnO}_2$  is complete.
12. Boil after each addition.
13. Centrifuge and discard supernatant.
14. Wash ppt. with 2-3 ml  $\text{HNO}_3$  conc.
15. Transfer to tared filter paper - Munktell 00 - filter, wash with  $\text{H}_2\text{O}$ , alcohol, and ether. Mount and count.

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