Designation: D8027 − 16

Standard Practice for Concentration of Select Radionuclides Using MnO_2 for Measurement Purposes[1]

This standard is issued under the fixed designation D8027; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice is intended to provide a variety of approaches in which manganese oxide (MnO_2) can be used to concentrate radionuclides of interest into a smaller volume counting geometry or exclude other species that would otherwise impede subsequent chemical separation steps in an overall radiochemical method, or both.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1129 Terminology Relating to Water
D7902 Terminology for Radiochemical Analyses

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminologies D1129 and D7902.

4. Summary of Practice

4.1 These practices describe different processes through which MnO_2 can be used to concentrate specific radionuclides of interest into a smaller volume counting geometry or exclude other species that would otherwise impede subsequent chemical separation steps in an overall radiochemical method, or both.

4.2 Published studies (**1-5**)[3] have addressed in detail the various manners in which hydrous manganese dioxides can be synthesized and the variety of crystal forms of hydrous manganese dioxide that can result. The literature describes the following general categories in which hydrous manganese dioxide can be prepared.

4.2.1 *Guyard Reaction:*

$$3Mn^{2+} + 2MnO_4 + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

4.2.2 By the reduction of permanganate with reducing reagents such as hydrogen peroxide (H_2O_2) or hydrogen chloride (HCl).

4.2.3 By the oxidation of Mn(II) salt under alkaline conditions with oxidizing reagents such as potassium chlorate ($KClO_3$), H_2O_2, ozone (O_3), or ammonium persulfate ($(NH_4)_2S_2O_8$).

4.3 The presented practices are not meant to address every possible approach to the generation and use of MnO_2 but are meant to present some more typical practices that may be generally useful.

5. Significance and Use

5.1 This practice is applicable to the separation of specific radionuclides of interest as part of overall radiochemical analytical methods. Radionuclides of interest may need to be quantified at activity levels of less than 1 Bq. This may require measurement of less than 1 fg of analyte in a sample which has a mass of a gram to more than several kilograms. This requires concentration of radionuclides into a smaller volume counting geometry or exclusion of species which would impede subsequent chemical separations, or both. MnO_2 has shown good selectivity in being able to concentrate the following elements: actinium (Ac), bismuth (Bi), lead (Pb), polonium (Po), plutonium (Pu), radium (Ra), thorium (Th), and uranium (U) as noted in the referenced literature (see Sections 4 and 8). The MnO_2 can be loaded onto a variety of substrates in preparation for use or generated in-situ in an aqueous solution. The presented processes are not meant to be all encompassing of what is possible or meant to address all limitations of using MnO_2. Some limitations are noted in Section 6, Interferences.

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

6. Interferences

6.1 MnO_2 is able to achieve a very good decontamination factor from monovalent cations in solution as evidenced by 8.3 below in which it is used in seawater. However, in the case of elevated concentrations of divalent cations, for example barium, the recovery of analytes of interest can be significantly reduced (**6**). Additionally in the case of seawater, the recovery of analytes such as uranium may also be substantially reduced. In such cases the use of an isotopic tracer can be very important to correct for such reduced recovery. The MnO_2 separation is also very conducive to being easily repeated to achieve a second stage of separation from potentially interfering species.

7. Reagens

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without increasing the background of the measurement.

7.1.1 Some reagents, even those of high purity, may contain naturally occurring radioactivity, such as isotopes of uranium, radium, actinium, thorium, rare earths and potassium compounds or artificially produced radionuclides, or both. Consequently, when such reagents are used in the analysis of low-radioactivity samples, the activity of the reagents shall be determined under analytical conditions that are identical to those used for the sample. The activity contributed by the reagents may be considered to be a component of background and applied as a correction when calculating the test sample result. This increased background reduces the sensitivity of the measurement.

7.2 *Ammonium hydroxide, 15 M NH_4OH,* (concentrated reagent).

7.3 *Ammonium hydroxide, 6 M NH_4OH*—Add 400 mL of concentrated ammonium hydroxide to 400 mL water. Dilute to 1 L with water and mix well.

7.4 *Bromocresol purple pH indicator*—Add 0.1 g bromocresol purple in 18.5 mL of 0.01 M sodium hydroxide (NaOH) solution. Dilute to 250 mL with water and mix well.

7.5 *Hydrogen peroxide, 30 % H_2O_2.*

7.6 *Iron chloride, $FeCl_3$.*

7.7 *Potassium permanganate, $KMnO_4$.*

7.8 *Potassium permanganate, 0.5 M $KMnO_4$*—Add 79 g of $KMnO_4$ to 750 mL water. Dilute to 1 L with water and mix well.

7.9 *Sodium hydroxide, 0.01 M NaOH*—Add 0.1 g NaOH to 250 mL water.

8. Procedure

8.1 *Use of MnO_2 Generated in-situ to Pre-Concentrate Sample Analytes:*

8.1.1 The precipitation of MnO_2 from a water sample may be most conveniently performed on a volume of 0.1 to 2 L but larger volumes are possible (**7 and 8**). Any isotopic tracers should be added and the valence states of the tracers and analyte species allowed to equilibrate before proceeding.

8.1.2 Add to the water sample approximately 10 mg of $KMnO_4$ and allow to dissolve. Optionally, approximately 2 mg of $FeCl_3$ may also be added to improve the obtainable separation factor.

8.1.3 The pH indicator bromocresol purple may be added to the water sample to provide a color indicator in the following step of raising the pH.

8.1.4 Add to the water sample approximately 1 mL of about 30 % H_2O_2.

8.1.5 The precipitation step to follow is best performed at ambient temperature if a period of one or more days is available to allow for complete settling and development of the precipitate. Alternatively the promptness of the precipitation can be assisted by gently heating the water sample, for example to approximately 70–80°C.

8.1.6 Add sufficient 6 M NH_4OH to the water sample to raise the pH to about 8. If bromocresol purple was added in the prior step this pH would be indicated by a color change to purple. The needed pH change could also be measured through use of pH test strip or pH meter.

8.1.7 Following complete development and settling of the precipitate the supernate may be removed by aspiration or careful decantation. The small amount of MnO_2 precipitate may be optimally isolated into a small pellet by transferring the bottom layer containing the precipitate (about 50 mL) to a centrifuge tube and centrifuging. The precipitate may be further washed up to two times with water and centrifugation repeated.

8.1.8 An alternative to centrifugation is filtration through a 0.45 µm filter but may require more time to accomplish the filtration in a careful manner.

NOTE 1—A similar procedure can be used on acid leachates of sediment samples but care should be taken when adding 6 M NH_4OH to strong acid solutions.

8.1.9 The washed MnO_2 precipitate and the incorporated analytes of interest and associated isotopic tracers may be taken through further separative steps, for example extraction chromatography, or may be transferred to a suitable counting geometry.

8.2 *Use of MnO_2 Impregnated Resin Beads:*

8.2.1 A typical radiochemical separation geometry is the use of a column into which an aqueous sample can be poured and excellent contact made with a supported extraction media. MnO_2 has also been found to be quite amenable to this approach (**9-13**). MnO_2 loaded resin can be made or purchased commercially for use in such column geometry. This approach allows the amount of MnO_2 loaded resin to be readily adjusted

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.