Determination of Manganese in nanomaterial

Introduction

Two methods have been developed to suite the analysis of manganese in solutions of nanomaterial. In the first method, called the "Formaldoxime method", Mn^{2+} forms a matte brownish red complex with formaldoxime at pH = 9.3. In the second method, called "Permanganate" method, Mn^{2+} is oxidized to MnO_4^- to give a purple color. UV absorption at 450 nm respective 525 nm is finally used to establish the Mn^{2+} concentration. Both methods can be used for the determination of Mn^{2+} but they have some different features.

Formaldoxime method

Solutions

Formaldoxime reagent (FR)

Dissolve 2.0 g hydroxylamine hydrochloride in 45 ml deionized water, add 1.0 ml formaldehyde solution (37%) and make up to 50 ml with water.

Ammonium hydroxide buffer (AHB)

Mix 4.0 ml 6 M HCl with 3.4 ml conc. ammonia (density 0.90 g/ml) and if necessary adjust the pH to 9.6. **Caution**: the reaction is highly exothermic. Prepare the buffer in a protective fume hood and actively cool it during the preparation.

Method

1. Mix a sample of nanomaterial solution with water so that the final concentration of manganese in the solution is between 0.015 mM and 0.150 mM and the total volume is 1.000 ml.
2. Add 100 µl AHB and 100 µl FR and mix and make sure that 9.1<pH < 9.4 in the final solution.
3. Allow the reaction to proceed for 1 hour and read the absorbance at 450 nm in a 1 ml/1 cm cell. The absorbance at 450 nm for a 0.150 mM solution is ~ 1.5 AU.
4. For the calibration curve use the same procedure but replace the sample by at least three volumes of a ~ 1.0 mM manganese standard (including zero) and note exact concentration.

5. Make a calibration curve for absorbance against added µmoles manganese.
6. Calculate the concentration manganese in the sample by dividing µmoles found by volume of sample.

Alternative method for very stable particles

Nanomaterials with high stability could first be treated with concentrated HCl to facilitate the release of manganese.

For [Mn] ≤ 1.5 mM:

1. mix 200 µl sample and 200 µl 1.0 M HCl and incubate the solution for 10 min. Filter the solution through a 10 kDa spinfilter (e.g. Amicon Ultra – 0.5 mL 10 kDa) at 12000 x g for 5 min.
2. Mix in the following order: 200 µl filtrate, 700 µl H2O, 100 µl AHB, 100 µl 1.0 M NaOH and 100 µl FR. Allow the reaction to proceed for at least 10 min and read the absorbance at 450 nm. Remember that this measurement will now correspond to 100 µl sample.

For [Mn] ≤ 3,0 mM:

- As above but mix 100 µl filtrate, 850 µl H_2O, 100 µl AHB, 50 µl 1.0 M NaOH and 100 µl FR. Remember that this measurement will now correspond to 50 µl sample.

For [Mn] ≤ 6,0 mM:

- As above but mix 50 µl filtrate, 925 µl H_2O, 100 µl AHB, 25 µl 1.0 M NaOH and 100 µl FR. Remember that this measurement will now correspond to 25 µl sample.

Comments

- No interference was observed for gadolinium
- The reaction rate for forming the colored complex with manganese in nanomaterial is much slower compared to standards as showed in Figure 1 below.
- If particles are subjected with the formaldoxime method, the “color” could be filtered through a 10 kDa ultrafilter, suggesting that the complex is not attached to the nanomaterial.
- The color that is developed with the method could not be “decolorized” with DTPA or EDTA (50 times excess).

- If Mn^{2+} is chelated with DTPA or EDTA the color was NOT developed according to the method.
- Addition of sodiumbisulfite to “decolorize” samples was not necessary and did not interfere the analysis.

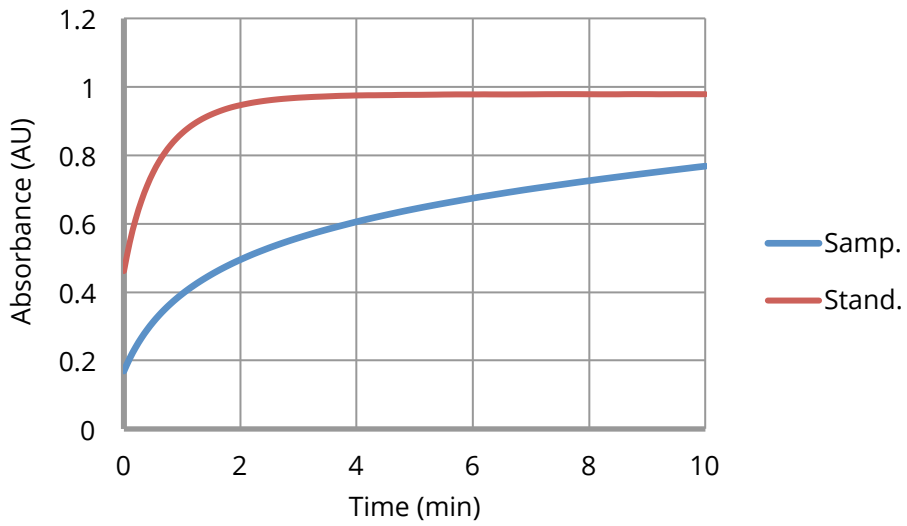

Figure 1. Plot comparing the absorance increase over time between standard samples (Stand.) and nanomaterial (Samp.)

Permanganate method

Solutions

Concentrated phosphoric acid (85 %) (CP)

Potassium periodate solution (PS)

Dissolve 60 mg KIO_4 in 10 ml deionized water

Sodium bisulfite reagent (BS)

Dissolve 10 mg sodium bisulfite in 10 ml deonized water.

Method

1. Pipette a 50 µl sample for manganese concentrations 2 – 10 mM in and 500 µl for manganese concentrations down to 0.2 - 2 mM into a 4 ml “crimp top glass vial”.
2. Mix the sample with PS to a total volume of 1.20 ml.
3. Add 100 µl BS and 50 µl CP and mix.

4. For the calibration curve, use the same procedure but replace the sample with the 100 µl, 200 µl and 500 µl of a 1.0 mM manganese standard.
5. Seal the vials and them on a heated shaker board at 100° C for 5 min.
6. Allow the solution to cool and read the absorbance at 525 nm in a 1 ml/1 cm cell.
7. Make a calibration curve for absorbance against added µmoles manganese.
8. Calculate the concentration manganese in the sample by dividing µmoles found by the sample volume.

Comments

- The addition of BS is necessary, especially if the samples are colored.
- The Permanganate method is harsher and can be used even if Mn^{2+} is complexed with EDTA or DTPA.
- Chloride is a supposed interference of the method but can be removed by the addition of $AgNO_3$. Even if the chloride (from $MnCl_2$ standards) was removed by precipitation with $AgNO_3$, no interference was observed from chloride in the standard.
- Only minor difference was observed in the manganese determination between the formaldoxime and permanganate methods (< 2 % difference).
- The permanganate method is about 5 times less sensitive compared to the formaldoxime method.
- If “spinfilters” are used for sample preparation, make sure that they are washed because they may contain glycerol that interferes with the method.

References

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http://www.chemteach.ac.nz/investigations/documents/manganese_steel_nocolorimeter.pdf