Sulfite Detection possibilities

ZRT

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1. Colorimetric detection of sulfite by TMB-O2-Co3O4 nanoparticles

* From Quin, Yang, Ma, et al. (2014) Colorimetric Detection of Sulfite in Foods by a TMB-O2-Co3O4 Nanoparticles Detection System, J. Agric. Food Chem. 62, 25, 5827-5834.
* Rough sketch of procedure:
  + Add 80uL of sample, 150uL of 5mM TMB, 120uL of Co3O4 NPs solution (1.0 mg/mL) to 2.65 mL of 0.2M acetic acid-acetate buffer solution (pH 4.0) and mix thoroughly.
  + Maintain solution at 40 deg C (in water bath) for 10 min
  + Move solution to ice bath for 10 min to terminate the reaction
  + Perform adsorption spectroscopy measurement at 652 nm
  + For controls, use DI water instead of sample
* Materials:
  + TMB – 3,3’,5,5’-tetramethylbenzidine (<https://www.sigmaaldrich.com/US/en/product/mm/613544>)
  + Co3O4 NP (nanoparticles) (you might be able to purchase these directly, rather than synthesize them as in the paper - <https://www.sigmaaldrich.com/US/en/product/aldrich/637025?gclid=CjwKCAjwtIaVBhBkEiwAsr7-c6Nc4umkWiUe_-KnNebS8IdSjh3ve_DxcMd40ugIdyh09J_iaf1PBBoC5qgQAvD_BwE> )
  + Acetic acid-acetate buffer solution (anywhere should have this – probably could get it from the Harvard stockroom)
  + Ethanol (same thing – should be fairly easy to get)
  + *If you wanted to synthesize the NPs yourself, the cobalt(II) acetate tetrahydrate is also available for purchase (*[*https://www.sigmaaldrich.com/US/en/product/sigald/208396*](https://www.sigmaaldrich.com/US/en/product/sigald/208396)*)*
* Instruments:
  + Water bath
  + Ice bath
  + Centrifuge
  + Autoclave (will oven work?)
  + oven
* Preparation of Co3O4 nanoparticles:
  + “hydrothermal method as described in the literature (ref 27)”
  + 0.5 g of Co(CH3COO)2.4H2O dissolved in 25 mL of ethanol
  + Add 2.5 mL of ammonia solution; stir vigorously
  + After stirring for 10 min, transfer to autoclave
  + Seal autoclave and hold at 150 deg C for 3 hr; then let cool to room temperature naturally
  + Separate product via centrifugation and wash several times with DI water and ethanol until pH of supernatant is ~7
  + Dry at 60 deg C for 4 hr
* Sensitivity:
  + Linear relationship between \Delta A\_{652 nm} vs. Sulfite concentration from ~0-16 uM sulfite, then saturates at higher concentrations.

1. Fuchsin reagent and spectrophotometry

* Mentioned in Frederiksen & Finster (2003) Sulfite-oxido-reductase is involved in the oxidation of sulfite in Desulfocapsa sulfoexigens during disproportionation of thiosulfate and elemental sulfur, Biodegradation, 14, 189-198. (<https://link.springer.com/content/pdf/10.1023/A:1024255830925.pdf>)
* Page 193: “Sulfite was instead determined spectrophotometrically by use of fuchsin reagent (Packmayr 1960, Bak & Pfenning 1987).”
* Note though: “Thiosulfate and sulfide interfere with this sulfite assay.” So, this probably isn’t super useful…

1. Novel NIR fluorescent probe to detect sulfite/bisulfite

* Relevant paper: Zeng et al. (2020) A novel mitochondria-targetted near-infrared fluorescent probe for selective colorimetric detection of sulfite and its application in vitro and vivo. Food Chemistry, 318, 126358. (<https://www.sciencedirect.com/science/article/pii/S0308814620302156>)
* Probe is easily synthesized, gives colorimetric and fluorescence changes aat 690 nm after reaction with sulfite from 3.13-200 uM; excellent selectivity
* Procedure to prepare probe:
  + (E)-3-(4-(dimethylamino)phenyl)acrylaldehyde (180 mg, 1.03 mM) put in round bottom flask and dissolved in 10 mL ethanol.
  + Add 456 mg, 1.23 mM of 1-benzyl-4-methylquinolin-1-ium iodide to flask
  + Mixture is catalyzed by piperidine (ZRT question: how much??) at room temperature for 10 hr.
  + Then solution placed in rotavap and the purple solid was dissolved in CH2Cl2.
  + Collect organic layer and wash three times with water
  + Dry via anhydrous Na2SO4
  + Rough product is refined by silica-gel column with CH2Cl2/MeOH eluent
* Procedure to test samples:
  + Probe dissolved in ethanol, prepared at 1 mM stock solution
  + Probe solution (10 uM) and different sulfite solutions were prepared by diluting with PBS solution (pH 7.4) at room temp as the test solution, which was prepared to measure UV-Vis absorption and fluorescent spectra.
  + Test solution shaken well and detected after 30 min
  + Results obtained by detecting fluorescence intensity at emission of 690 nm
  + The same volume of sulfite could be replaced by various anions to detect interference, using same conditions.

1. Ion chromatography

* This has been done in the literature, but as we are all non-experts in IC, I think to be a viable option, we would need a collaborator with an already-established procedure for sulfite quantification

1. Raman or FT-IR

* Maybe possible? Are these quantitative?