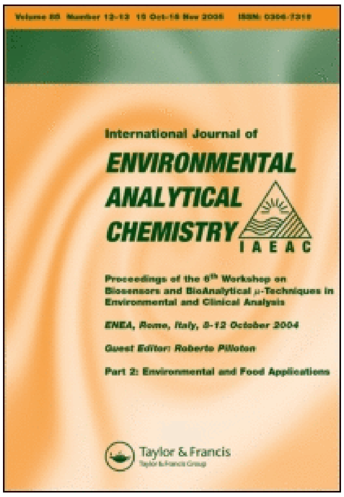

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Preparation of Ultrapure Potassium Peroxydisulfate

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Peroxydisulfate salts are effective oxidants for refractory organic material, including humic substances, but their usefulness in trace metal determinations is limited by the presence of impurities in commercial preparations. Peroxydisulfates were synthesized chemically and electrolytically, and assayed accurately in admixture with side products and starting materials. Even without elaborate environmental controls, the non-electrochemical route was adapted readily to the preparation of potassium peroxydisulfate containing $<6\,\mathrm{ng\,g^{-1}}$ of Zn, and $<3\,\mathrm{ng\,g^{-1}}$ of Cu and Pb. A key step in the synthesis was the purification of H_2O_2 by fractional recrystallization.

KEY WORDS: Peroxydisulfate, hydrogen peroxide, trace analysis, oxidizing agents, digestion, metals.

INTRODUCTION

The accuracy and precision of most trace analytical techniques are generally not limited by the sensitivity of the methods employed. More often, the method is limited by the size and variability of the blank. Recent acceptance of this notion has been accompanied by a lively controversy in the literature.[1] Experience has shown that great care must be exercised in choosing equipment, reagents, and handling procedures.[2] Analysts working at ultratrace levels ($\mathrm{ng\,g^{-1}}$ region and below) may find that commerically available reagents are not pure enough for their application. Even reagents labeled as "ultrapure" may contain unacceptable levels of some elements especially when relatively large quantities are needed for sample work up.[3] Purity with respect to contaminants may vary from one lot to another and among various suppliers. This situation confronts the analyst with the alternatives of purification, or synthesis from ultrapure starting materials.

A review article[4] and a monograph[5] describing the current technology of reagent purification have appeared. Unfortunately, the available methodology is generally inapplicable to thermally labile or highly reactive compounds. For these compounds, direct synthesis from purified starting materials is the only way to obtain a purified product. Preparation of ultrapure peroxydisulfate[6] salts is a case in point. Direct synthesis from ultrapure starting materials appears to be the best if not the only way to obtain a contamination-free product.

Peroxydisulfate at 100 °C in aqueous solution effectively destroys refractory organic matter such as humic and fulvic substances.[7,8] Since these materials complex some metals very strongly,[9] their destruction is desirable if complete recovery of the metals is to be achieved.[10-12] Boiling a sample in the presence of peroxydisulfate offers several advantages over other methods. For example, digesting a sample in the presence of hydrogen peroxide or perchloric acid leaves residual oxidizing capacity unless metals are added as catalysts.[13] This can be a potential problem when one is working with readily oxidized complexing agents such as the dithiolate reagents.[14] Irradiation with ultraviolet light is effective but slow, and it requires the use of fused silica reaction vessels. It also may be difficult to implement without exposing the sample to potential sources of contamination.

Digestion of a sample with a peroxydisulfate salt avoids these difficulties. Peroxydisulfates disproportionate rapidly in aqueous solution at 100 °C and a pH less than 2, in the absence of reductants, leaving no residual oxidizing capacity,[15]

$$2S_2O_8^{2-} + 2H_2O = O_2(g) + 4HSO_4^-.$$

Unfortunately, our preliminary experiments showed that commercially available preparations contain relatively large amounts of some heavy metals, especially iron and zinc (Table 1).

Table 1 Analysis of peroxydisulfate salts

Lot no.	*Ni*	*Fe*	*Cu*	*Zn*	*Pb*
743732[a]	0.15(0.02)	1.36(0.71)	0.06(0.09)	0.09(0.03)	0.18(0.18)
714508[a]	0.07(0.09)	1.40(0.70)	0.02(0.04)	0.09(0.04)	0.05(0.01)
743791[b]	0.59(0.04)	0.13(0.06)	0.03(0.02)	0.16(0.04)	0.16(0.12)
Purified	—	1.20(0.06)	<0.003	<0.006	<0.003

Results are in 10^{-6} g metal/1 g salt.
Values in parentheses are standard deviations for $n = 3$.
[a] Fisher reagent grade potassium peroxydisulfate.
[b] Fisher reagent grade ammonium peroxydisulfate.

Electrolytic[16] and non-electrolytic[17–19] methods of preparing peroxydisulfate salts have been reported. In the electrolytic approach, the peroxide linkage is created by the electrochemical oxidation of precursors containing only O (II−). While appealing in its simplicity, electrolysis involves electrodes and cell materials which are obviously potential sources of contamination. An ultrapure product is unlikely unless one addresses these problems. Non-electrolytic methods offer the possibility of controlling contamination by working with purified starting materials in a clean environment. We studied both approaches to the synthesis of peroxydisulfates.

EXPERIMENTAL

Concentrated hydrogen peroxide, 88% by weight, was obtained through the fractional distillation of 30% (w/w) hydrogen peroxide (Fluka Chemical Co. Inc.). The distillation was carried out at 3×10^{-2} torr and 40 °C in a conventional borosilicate glass apparatus.[20] The water and small amounts of peroxide carried over during the distillation were trapped using a liquid nitrogen trap. A second trap filled with oil acted to protect the pump from peroxide attack. Even so, the pump oil was changed frequently to avoid potential deterioration of the seals. The liquid nitrogen trap also prevented oil vapors from reaching the hydrogen peroxide concentrate.

Anhydrous hydrogen peroxide greater than 98% (w/w) was obtained by three-fold fractional crystallization of the 88% concentrate over liquid nitrogen.[19] When hydrogen peroxide-water mixtures are frozen under controlled conditions, a pure solid forms with the exclusion of water. The sheath of ice formed on the outside of the crystal can be easily removed using centrifugation. Fractional crystallization also removes inorganic impurities. Should further purification be necessary, low temperature sublimation is a viable approach.[21]

CAUTION should be used when working with concentrated solutions of hydrogen peroxide. At vapor concentrations greater than 26 mol %, hydrogen peroxide detonates on contact with heated surfaces or in the presence of catalytic substances. Mixtures with organic matter are extremely explosive. Only use clean, inert materials (borosilicate glass, teflon, polyethylene, etc.), and low temperatures and pressures, when working with concentrated peroxide solutions. Never use oxidizing cleaning solutions such as chromic acid to prepare surfaces that will be in contact with the peroxide. Consult the literature before proceeding with this experiment.[13]

Chlorosulfonic acid was purified by conventional distillation in a borosilicate glass apparatus.

A saturated solution of potassium carbonate was purified by extraction with ammonium pyrrolidinecarbodithoic acid (APDC) into chloroform. We found that a continuous extractor provided an effective means of purification. The extractor was allowed to run for three days with periodic addition of APDC. By proceeding in this manner, we were able to reduce Fe, Cu, Zn and Pb from 2.5 ppm, 0.03 ppm, 0.08 ppm and 0.35 ppm, to less than 0.06 ppm, 0.01 ppm, 0.003 ppm and 0.008 ppm, respectively, based on the dry weight of the salt.

Chemical synthesis of potassium peroxydisulfate

The synthesis of potassium peroxydisulfate was accomplished by means of a 2:1 stoichiometric reaction between chlorosulfonic acid and anhydrous hydrogen peroxide. The reaction was carried out by the slow addition of hydrogen peroxide (12.8 g) to purified chlorosulfonic acid (87 g) in a teflon reaction vessel with constant stirring in an ice bath. After the addition was complete, the reaction vessel was placed into a vacuum desiccator connected to an aspirator to remove the bulk of the HCl gas produced as a by-product of the reaction,

$$HSO_3Cl + H_2O_2 = H_2SO_5 + HCl(g)$$

$$HSO_3Cl + H_2SO_5 = H_2S_2O_8 + HCl(g).$$

After four hours, the pressure was lowered to 3×10^{-3} torr. Once HCl evolution was complete, cooling the product to 0 °C in an ice bath resulted in immediate crystallization. Using this approach, we have been able to obtain a product assaying $58 \pm 0.61\%$ by weight peroxydisulfuric acid, $16.8 \pm 0.34\%$ peroxymonosulfuric acid, and $0.181 \pm 0.55\%$ hydrogen peroxide ($n = 3$). The remainder of the product is most likely sulfuric acid.

CAUTION must be exercised at this step. Peroxymono- and peroxydisulfuric acids are strong oxidizers. Rapid and uncontrolled reactions can occur when they are placed in contact with oxidizable materials or in the presence of water. Failure to take appropriate precautions could result in an explosion.

This intermediate product (60 g) was then mixed slowly with stirring into an ice slurry prepared from purified water (Barnstead Nanopure II). A saturated solution of potassium carbonate containing 0.2 mol of K^+ (10% excess) was added slowly while maintaining the temperature below 10 °C in an ice bath. The resulting mixture was allowed to stand for 15 minutes at 0 °C. The salt was quickly collected by vacuum filtration onto a 0.4 μm Nuclepore membrane, washed with 20 mL of ice water to remove more soluble potassium salts and dried under a Class 100 clean air hood. We obtained a product assaying $99 \pm 0.05\%$ ($n = 3$) by weight potassium peroxydisulfate. The yield based on the peroxydisulfuric acid starting material was 46.3%. Table 1 lists the amount of impurities remaining in the salt using this method as compared to some commercial preparations. Although a substantial amount of iron still remains in the product, the other elements were reduced considerably. We demonstrate the workability of this approach and suggest it as a model for obtaining ultrapure potassium peroxydisulfate.

Electrosynthesis of ammonium peroxydisulfate

The cell design and operation for the electrolytic synthesis was simple. The cell consisted of a fritted glass Gooch crucible of 30 mL capacity filled with a saturated solution of ammonium sulfate (76 g/100 mL). The filled crucible was placed into a 150 mL beaker containing a solution made from equal weights of sub-boiling distilled sulfuric acid and purified water. A coiled platinum wire anode (0.5 cm diam. by 4 cm) was placed into the saturated ammonium sulfate solution. A lead cathode (5 cm by 5 cm) was placed into the sulfuric acid solution. The entire cell was placed into an ice bath to maintain a temperature less than 10 °C. The electrodes were connected to a 12 volt D.C. power supply capable of supplying a high current density.[22] After 45 minutes of electrolysis, the solution became cloudy with the production of ammonium peroxydisulfate, $(NH_4)_2S_2O_8$. After five hours, the reaction was stopped and the product vacuum filtered and washed with 10 mL of 95% ethanol. It was dried overnight in a vacuum desiccator over sulfuric acid. The product obtained assayed $90.2 \pm 1.3\%$ ($n = 3$) by weight ammonium peroxydisulfate.

The electrolysis can be carried out with very little attention. This is a definite advantage over chemical methods of synthesis. An obvious concern about contamination exists in part due to the choice of cell materials. However, it should be reasonable to expect cationic impurities to migrate toward the cathode and away from the area of product formation. The chemicals used in the synthesis can be obtained or produced in high purity so that future experimentation with cell materials and design could lead to a useful approach.

Assay procedures

Anhydrous H_2O_2 preparations may be assayed by direct titration with 0.1 M potassium permanganate in a solution that is 25% (v/v) sulfuric acid according to the equation

$$5H_2O_2 + 2MnO_4^- + 6H^+ = 5O_2 + 2Mn^{+2} + 8H_2O.$$

In order to distinguish between different oxidizing species in mixtures potentially containing hydrogen peroxide, peroxymonosulfuric acid, peroxydisulfuric acid or a combination of any of the three, the following analysis procedure was developed.[23,24] The reaction mixture (300 to 500 mg) was added to a 150 mL ice slurry containing

10 mL of concentrated sulfuric acid. Unreacted hydrogen peroxide was titrated with 0.1 M ceric sulfate solution to the faint blue ferroin endpoint

$$H_2O_2 + 2Ce^{4+} = O_2 + 2Ce^{3+} + 2H^+.$$

The ceric sulfate does not react with either peroxymono- or peroxydisulfuric acid. The titration can also be carried out using 0.2 M potassium permanganate although the darker endpoint can cause difficulties with determining the endpoint of the following titration. Immediately following the titration of the hydrogen peroxide, 10 mL of a 10% (w/w) iodide solution is added to the mixture. At 0 °C, the peroxymonosulfuric acid liberates I_2 from I^-

$$2I^- + HSO_5^- + 2H^+ = I_2 + HSO_4^- + H_2O.$$

Peroxydisulfuric acid does not liberate iodine rapidly at 0 °C due to kinetic factors. The iodine liberated is titrated to the starch-iodine endpoint using 0.1 M sodium thiosulfate

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-.$$

The total oxidant titer of a second aliquot of sample was determined by adding 0.3 to 0.5 g of sample to 50 mL of a 0.1 M ferrous sulfate solution. The solution was diluted to 150 mL and boiled for 30 minutes allowing for the complete oxidation of the ferrous ion

$$2Fe^{2+} + H_2O_2 + 2H^+ = 2Fe^{3+} + 2H_2O,$$

$$2Fe^{2+} + HSO_5^- + 2H^+ = 2Fe^{3+} + HSO_4^- + H_2O,$$

$$2Fe^{2+} + H_2S_2O_8^- + H^+ = 2Fe^{3+} + 2HSO_4^-.$$

The solution was then cooled to room temperature in an ice bath and the excess ferrous ion titrated to the ferroin endpoint with 0.1 M ceric sulfate solution. Peroxydisulfuric acid was determined as the difference between the total oxidant titer and the sum of the hydrogen peroxide and peroxymonosulfuric acid concentrations.

The analysis of peroxydisulfate salts for heavy metal content was carried out by weighing out replicate 10 to 20 g portions of the salt into a 250 mL quartz Erlenmeyer flask followed by decomposition at 300 °C in a muffle furnace. The decomposed salt was then cooled and dissolved into purified water and the metals precipitated with APDC. The precipitates were then analyzed using energy dispersive X-ray fluorescence spectrometry.[11] The results are compared in Table 1 with trace metal levels found in a commercial preparation.

CONCLUSIONS

The synthesis from purified starting materials yields a product in which the concentrations of representative heavy metals have been reduced by 1–2 orders of magnitude relative to the commercial preparations. This degree of purity was achieved under ordinary laboratory conditions using careful cleaning and handling procedures. We expect even higher purity could be achieved using clean-room technology. The material we synthesized is already sufficiently pure to be used in gram amounts for determining submicrogram quantities of several metals.

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