



# Comparison of oxysilver nitrate and oxysilver bisulfate, Part I: Synthesis and physicochemical properties



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## ABSTRACT

Multivalent silver complexes of oxysilver nitrate (OSN) and oxysilver bisulfate (OSBS) were prepared with excellent purity and yield through ozone oxidation of  $\text{AgNO}_3$  or  $\text{Ag}_2\text{SO}_4$  solutions, respectively. An inorganic chemical synthesis method for making oxysilver nitrate was also used to generate material (OSC) for comparison of the methods. The complexes were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental analyses (EA), cyclic voltammetry (CV), and X-ray photoelectron spectroscopy (XPS). The XRD structural refinement for OSBS is presented here for the first time. SEM showed that OSBS had significantly larger particles than OSN or OSC. Through a comparison of OSBS, OSN, and OSC using the XRD, XPS, EA and also differential scanning calorimetry (DSC) data, it was discovered that the OSC was actually a mixture of oxysilver nitrate and oxysilver bisulfate, meaning that the inorganic chemical synthesis method did not make a pure oxysilver nitrate product as has been reported previously. The solubility/stability of OSN and OSBS in water was examined, and it was determined that both OSN and OSBS decompose on contact with water with no sign of initial dissociation, but that OSBS does so much more rapidly than OSN. Stability of the two products under reaction conditions was also examined, and both products were determined to be reasonably stable under acidic/ozonation conditions. OSN demonstrated better thermal stability, as measured by DSC and thermogravimetric analysis (TGA). In addition, accelerated storage stability studies demonstrated that OSN could be stored with refrigeration, but that storage of OSBS without substantial product breakdown could not be achieved. OSC appeared to be the least stable material of the three. The inconsistent composition and poor stability of OSC have implications for the applications in which it is used, such as wound dressings.

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## 1. Introduction

It has long been known that oxidation of silver(I) ions in solution leads to the formation of argentic oxysilver salts which contain silver in the (I), (II), and (III) oxidation states and have the formula  $[\text{Ag}_7\text{O}_8]^+\text{X}^-$  [1]. The first oxysilver salt was described by

*Abbreviations:* a, lattice constant (in XRD); AAS, atomic absorption spectroscopy; ANOVA, analysis of variance; B, isotropic displacement parameter (in XRD); BE, binding energy; DSC, differential scanning calorimetry; FWHM, full width half maximum; I, intensity (in XRD); ICP, inductively coupled plasma; KPS, potassium persulfate; LPM, liters per minute; ND, not detected; N/A, not applicable; OSBS, oxysilver bisulfate (by ozonation); OSC, oxysilver compound (by inorganic chemical synthesis); OSN, oxysilver nitrate (by ozonation); QPA, quantitative phase analysis; R-factor, residual index; RPM, rotations per minute; RT, room temperature; SEM, scanning electron microscopy; SG, space group; TGA, thermogravimetric analysis; UV–Vis, ultra violet/visible spectroscopy; WP, weighted pattern; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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Ritter in 1804 [2] and further studies have been reported by many investigators through the centuries [3].

Traditionally,  $\text{Ag}_7\text{O}_8\text{X}$  salts have been electrodeposited from silver(I) solutions by electrochemical routes (e.g. by anodic polarization of a platinum electrode) [4,5]. Photocatalytic synthesis methods to generate oxysilver salts have also been developed [6–10]. However, both electrolysis and photocatalysis give extremely low yields at high cost due to the use of Pt electrodes and the consumption of the photocatalyst.

More extensive investigations have explored the application of inorganic oxidizers to prepare oxysilver complexes. Some strong chemical oxidizers such  $\text{K}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and  $\text{F}_2$  have successfully been used to oxidize aqueous solutions of  $\text{Ag}(\text{I})$  to produce  $\text{Ag}_7\text{O}_8\text{X}$ . A series of argentic oxysilver complexes with high oxidation state silver ( $\text{Ag}_7\text{O}_8\text{X}$ , where  $\text{X} = \text{NO}_3$  [3,11–15],  $\text{ClO}_4$  [4],  $\text{BF}_4$  [16],  $\text{F}$  [17], and  $\text{HSO}_4$  [14,18–23]) have been reported. This chemical route is much better than the electrolysis/photocatalysis procedures in terms of decreased costs. However, the introduction of

chemical oxidants can lead to impurity formation via side reactions, as will be demonstrated in this work.

Recently, the use of ozone has proven attractive for metal oxidation. Several authors have investigated the application of ozone for synthesis of high oxidation-state silver products [24,25]. Waterhouse et al. reported that  $\text{Ag}_7\text{O}_8\text{X}$  salts ( $\text{X} = \text{NO}_3$ ,  $\text{ClO}_4$ ,  $\text{HSO}_4$ ) have been synthesized successfully by passing an ozone/oxygen mixture through aqueous solutions of different AgX species [26]. Nishimura et al. reported that pH has an effect on the ozone oxidation of silver(I) species to form oxysilver salts [27]. Although ozone production is a fairly energy intensive procedure, its rapid and quantitative reactions with metal ions result in high purity and yield of products. Ozone oxidation also makes it possible to scale-up oxysilver complex production. In the present study, high purity oxysilver nitrate (OSN) and oxysilver bisulfate (OSBS) were synthesized via ozonolysis with pH control by modifying Waterhouse's [26] and Nishimura's [27] methods, and were compared to oxysilver compound (OSC) generated by an inorganic chemical oxidation method [28]. A further intention of the present work was to investigate various properties of oxysilver salts. The X-ray diffraction (XRD) structural refinement for OSBS is presented here for the first time; a comparison of particle sizes for OSBS, OSN, and OSC is provided; high resolution fitted X-ray photoelectron spectroscopy (XPS) spectra are provided for all three compounds; and bulk elemental analyses (EA) are provided for the three compounds. In addition, the compounds are examined for their behavior in water by basic solubility testing, by cyclic voltammetry (CV), and by collecting species present in solution and as precipitate at various time points. Furthermore, the stability of the products maintained under reaction conditions is examined for the first time. As well, the thermal stability and storage stability of the materials are compared.

## 2. Experimental

### 2.1. Compound synthesis

Silver nitrate ( $\text{AgNO}_3$ ) and silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) were purchased from Alfa Aesar and used without further purification. Double distilled water ( $\text{ddH}_2\text{O}$ ) was used throughout. The ozone generator used was an Absolute Ozone Model Atlas 30, which used a corona discharge method to generate the ozone from tank oxygen (welding grade, 99.6% pure), which was purchased from Air Liquide.

The following procedure was applied to  $\text{AgNO}_3$  and  $\text{Ag}_2\text{SO}_4$  to produce OSN and OSBS, respectively: The silver(I) salt ( $\text{AgNO}_3$  or  $\text{Ag}_2\text{SO}_4$ ) was dissolved in  $\text{ddH}_2\text{O}$  to make a 1.0 mol/L solution (unless otherwise indicated) which was refrigerated overnight. The next day, the solution was transferred to a duty vessel placed in an ice-bath. The vessel was equipped with a magnetic stir bar (~360 rpm), temperature sensor, and pH probe. The initial pH was measured and determined to be just below 4 in each run described in this study. Ozone was generated from dry oxygen (at a pressure of 20 psi) passed through the ozone generator and bubbled into the reaction vessel at ~4 lpm via a ceramic disperser. Shortly after the ozone generator was turned on, the pH invariably started to drop. When the pH dropped down to ~3.50, cold KOH solution (0.05 M or 0.5 M, kept on ice) was added drop-wise to the reactor through a peristaltic pump to bring the pH up to ~3.90. This was repeated as necessary to maintain the pH of the reaction solution between 3.5 and 3.9. The reaction temperature was kept between 1.8 and 5.6 °C by regularly adding ice to the ice-bath. When the pH didn't appear to be changing anymore, the ozone generator was stopped. (As noted in the results section, some runs were performed without pH control, meaning that the pH was

allowed to drop throughout the experiment, with no KOH addition. In these situations, the reaction was stopped when the pH was no longer dropping.) Oxygen was bubbled through the solution for an additional 15 min in order to remove remaining ozone from the reaction solution. The product was filtered, washed as needed, and dried. The water content of the product was measured via Karl Fischer titration using an 831 KF Coulometer with an 860 KF Thermoprep (Metrohm). This method was used for water content measurements reported elsewhere in this study as well.

For comparison, oxysilver compound (OSC) was synthesized using the inorganic chemical oxidizer method described in Djokic [28]. 75.57 g potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , KPS) was dissolved in 1.7 L  $\text{ddH}_2\text{O}$  (pH ~3.25). A 0.71 mol/L  $\text{AgNO}_3$  solution was prepared in 375 mL  $\text{ddH}_2\text{O}$  in a separate beaker (pH ~5.75). 500 mL  $\text{ddH}_2\text{O}$  was added to a separate flask equipped with an overhead stirrer (450 rpm). The KPS and  $\text{AgNO}_3$  solutions were connected to the container of  $\text{ddH}_2\text{O}$  using transfer lines with metering pumps. The  $\text{AgNO}_3$  and KPS solutions were added simultaneously to the  $\text{ddH}_2\text{O}$ , with stirring, at rates of 44 mL/min and 9.9 mL/min, respectively. A black precipitate formed immediately. After the addition was complete (pH ~1.73), the reaction mixture was stirred for an additional hour (500 rpm). The product was filtered, washed with 40 mL of  $\text{ddH}_2\text{O}$ , and dried.

### 2.2. Physicochemical analyses of products

The products were submitted for X-ray diffraction (XRD); scanning electron microscopy (SEM); X-ray photoelectron spectroscopy (XPS); thermogravimetric analysis (TGA); differential scanning calorimetry (DSC); and elemental analyses for N, S, and Ag content.

XRD data was collected at the University of Alberta (Department of Earth & Atmospheric Sciences, X-ray Diffraction Laboratory) on a Rigaku Ultima IV with a  $\text{Co K}\alpha$  tube, an Fe filter, and a D/Tex detector. Scanning was performed between 10 and  $120^\circ 2\theta$ . Quantitative phase analysis (QPA) for composition, mean microstrain, and crystallite size of oxysilver nitrate was performed using a Rietveld analysis software – TOPAS 4.2 [29]. This entailed direct convolution of the instrument and sample contributions to the diffraction profiles followed by the double integral method of Balzar [30] to separate the crystallite size from the mean microstrain effect. As the structural parameters for OSBS have not previously been measured, a very high purity batch of OSBS was generated following the steps described in Section 2.1, except that the  $\text{Ag}_2\text{SO}_4$  solution used was 0.02 M, KOH was not added (i.e. the pH was not controlled and was allowed to drop continuously during the reaction, reaching a final pH of 2.63), and a shorter reaction time was used (i.e. the reaction was not allowed to approach completion, with a yield of 49%). This batch was then submitted for XRD analysis as described for OSN, except that diffraction data was collected between 10 and  $140^\circ 2\theta$  (0.95–10 Å) with a  $0.02^\circ$  step size, in order to provide high quality data for structure refinement. Both OSN and OSBS have the same crystal structure and  $Fm-3m$  space group, therefore  $\text{Ag}_7\text{O}_{11}\text{N}$  – OSN [31] was used as the starting model for structure refinement. Lattice parameters were refined without constraints, and oxygen atom positions refined were restrained within sulfur–oxygen and oxygen–oxygen bond distances. Occupancies were constrained to the structural formula, and Ag and S displacement parameters were refined. The OSC was also analyzed by XRD as described for OSN to determine its composition.

SEM imaging was obtained at the Alberta Centre for Advanced MNT (Microsystems and Nanotechnology) Products (ACAMP) using a Hitachi Model S3700N to determine particle size following a method based on OPPTS 830.7520 [32]. Briefly, powders (OSN and OSBS synthesized without pH control, and OSC) were attached directly to aluminum supports by sprinkling the powders onto carbon tape. Sputter coating was not necessary. Images were taken at

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