

Article

A Straightforward Route to Tetrachloroauric Acid from Gold Metal and Molecular Chlorine for Nanoparticle Synthesis

Shirin R. King, Juliette Massicot and Andrew M. McDonagh *

School of Mathematical and Physical Sciences, University of Technology Sydney, 15 Broadway, Ultimo NSW 2007, Australia; E-Mails: shirin.r.king@student.uts.edu.au (S.R.K.); jmassicot@live.fr (J.M.)

* Author to whom correspondence should be addressed; E-Mail: andrew.mcdonagh@uts.edu.au; Tel.: +61-2-9514-1035 (ext. 1035).

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Abstract: Aqueous solutions of tetrachloroauric acid of high purity and stability were synthesised using the known reaction of gold metal with chlorine gas. The straightforward procedure developed here allows the resulting solution to be used directly for gold nanoparticle synthesis. The procedure involves bubbling chlorine gas through pure water containing a pellet of gold. The reaction is quantitative and progressed at a satisfactory rate at 50 °C. The gold(III) chloride solutions produced by this method show no evidence of returning to metallic gold over at least twelve months. This procedure also provides a straightforward method to determine the concentration of the resulting solution using the initial mass of gold and volume of water.

Keywords: gold chloride; HAuCl₄; chlorine; gold nanoparticles

1. Introduction

Research involving gold nanoparticles has increased significantly over the last two decades, creating with it the need for high purity gold chloride (generally in the form of tetrachloroauric acid) as a starting material for the nanoparticle synthesis. Many synthetic methods utilize aqueous solutions of gold(III) chloride for this purpose. Although gold chloride can be purchased from commercial suppliers, we have found that this can increase laboratory costs significantly, especially when larger quantities of gold

nanoparticles are being prepared. Furthermore, solutions of gold(III) chloride can be quite unstable, rapidly returning to metallic gold unless kept under appropriate conditions (e.g., pH < 4 with excess chloride ions) [1]. Here we report a straightforward method to produce highly stable aqueous solutions of gold(III) chloride using gold metal and molecular chlorine as starting materials. The method can be scaled from the millilitre scale to litre scale and requires no expensive reagents.



The reaction of metallic gold with chlorine is shown in Equation (1). This chemistry was applied to industrial processes as early as the 19th century to dissolve gold from gold-bearing ores [2–4], and although chlorination was quickly replaced by cyanidation in the gold mining industry, research into the use of halogens, in particular chlorine, bromine and iodine, has made a resurgence in recent decades due to environmental concerns associated with cyanide use [5,6]. A number of the industrial procedures for ore extraction use chlorine gas injected into the reaction chamber or alternatively water that contains dissolved chlorine gas [7], while other methods employ the reaction between sodium hypochlorite, hydrochloric acid and sodium chloride (Equation (2)) to generate chlorine gas *in situ* [8,9].



Of course, *aqua regia* (formed from nitric and hydrochloric acids) has been used for centuries to dissolve gold and form gold(III) chloride, but this process requires cumbersome workup procedures (such as boiling down and repeated hydrochloric acid dilution/concentration cycles to remove nitric acid).

Thus, the method that we report here offers several advantages over the above-mentioned procedures. Importantly, we show that the known reaction of gold with chlorine can be used in a straightforward method to produce high purity and highly stable gold(III) chloride solutions that can be used directly (without further workup procedures) for gold nanoparticle synthesis. In comparison to solutions prepared from commercially available gold(III) chloride, this method offers a significant reduction in expense, ease of concentration determination and is scalable.

2. Experimental Section

2.1. General

Gold pellets (99.99%, ~250–360 mg, AGS Metals, Sydney, Australia), hydrochloric acid (36%; RCI Labscan, Pathumwan Bangkok, Thailand), potassium permanganate (BDH) and sodium thiosulfate pentahydrate (Ajax Chemicals, Sydney, Australia) were all used as received. Ultrapure Milli-Q water (Sartorius, Dandenong South, Australia; 18.2 MΩ cm) was used as the reaction solvent. UV-visible spectra were recorded using an Agilent Technologies Cary 60 UV-Visible spectrophotometer (Mulgrave, Victoria, Australia) with 0.1 M aqueous HCl as the solvent. Inductively coupled plasma mass spectrometry was performed with an Agilent Technologies 7500cx series ICP-MS (Mulgrave, Victoria, Australia) with sample introduction via a micromist concentric nebuliser (Glass expansion) and a Scott type double pass spray chamber cooled to 2 °C. The sample solution and the spray chamber waste were carried with the aid of a peristaltic pump. ICP-MS extraction lens conditions were selected to maximise the sensitivity of a 1% HNO₃:HCl solution containing 1 ng/mL of Li, Co, Y, Ce and Tl. Gold and

manganese stock solutions were obtained from Choice Analytical (Thornleigh, Australia). Baseline nitric acid (HNO₃) was purchased from Seastar Chemicals Inc. (Sidney, BC, Canada). Calibration standards were prepared in 1% nitric acid. Oleylamine-stabilised gold nanoparticles were prepared by the literature method [10]. The concentration of chlorine in solution was measured using the iodometric titration method [11].

2.2. Synthesis of Tetrachloroauric Acid (HAuCl₄)

A laboratory-scale reaction apparatus was assembled as shown in Figure 1. Hydrochloric acid (14 mL, 36%, 0.16 mol) was placed in a pressure-equalizing dropping funnel, and slowly added drop-wise to a side-arm flask containing potassium permanganate (3.0 g, 19 mmol). The resulting chlorine gas (see Equation (3)) was passed into a two-neck round-bottom flask containing 100 mL Milli-Q water and one pellet of gold (~250–360 mg). Undissolved/unreacted chlorine gas was bubbled through a solution of sodium thiosulfate (1.1 g, 7.0 mmol) in 50 mL of water. The reaction mixture was stirred at the selected temperature (25–70 °C) until all of the gold dissolved. The resulting solution of tetrachloroauric acid can be used without further treatment. UV-Vis (λ_{\max} , nm [ϵ , 10⁴ M⁻¹·cm⁻¹]): 226 (3.5), 313 (0.54).

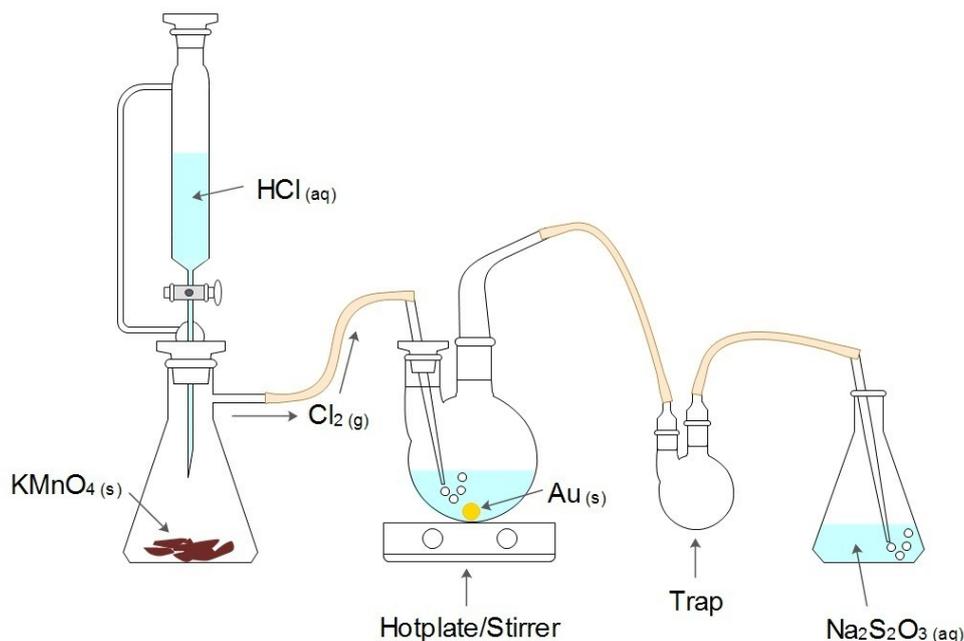


Figure 1. Apparatus for the synthesis of aqueous tetrachloroauric acid.



2.3. Measurement of Reaction Times

The rate at which gold dissolved was measured by weighing the gold pellet at regular intervals. The pellet was removed from the reaction vessel using a clean glass spoon, rinsed with acetone and allowed to completely dry, and then weighed before returning to the reaction mixture. For experiments using

flattened gold pellets, the pellets were placed between layers of cotton fabric or sheets of polycarbonate and mechanically pressed to a thickness of ~1 mm.

2.4. Synthesis of Citrate-Stabilised Gold Nanoparticles

The citrate method was used to synthesise aqueous gold nanoparticles from the tetrachloroauric acid synthesised as above. All glassware was cleaned with aqua regia, then rinsed and steeped in Milli-Q water prior to use. Aqueous tetrachloroauric acid (6.85 mL, 14.6 mM) was added to a 100 mL volumetric flask and diluted with Milli-Q water to make a 1.00 mM solution. The contents of the volumetric flask were poured into a 250 mL conical flask containing a magnetic stirrer bar, and heated to 90 °C. While stirring vigorously, a freshly prepared solution of tri-sodium citrate (114 mg, 10.0 mL, 38.8 mM) in Milli-Q water was quickly added to the conical flask. The solution was heated for a further 15 min, allowing it to turn a deep burgundy colour, indicating the presence of small gold nanoparticles.

3. Results and Discussion

The oxidation of gold metal to form aqueous solutions of gold(III) chloride was reliably and reproducibly achieved through introduction of chlorine gas to water containing the gold metal. The reaction is quantitative and no manganese-containing by-products (which may have arisen from the chlorine production process) were detected (see Table S1). Thus, the concentration of the gold(III) chloride solutions can be reasonably accurately calculated from the mass of the gold metal and the final volume of water.

The UV-visible spectrum of the resultant gold(III) chloride solution is shown in Figure 2 and displays the expected peaks for a solution at pH 1.05. The absorption bands at 313 and 226 nm are assigned to ligand-to-metal charge transfer [12,13]. It is important to note that the UV-visible spectrum is highly dependent on pH [14]. Therefore, accurate determination of concentrations of aqueous gold(III) chloride solutions using UV-visible spectroscopy requires an accurate determination of pH (and of course knowledge of the molar absorptivity at that particular pH).

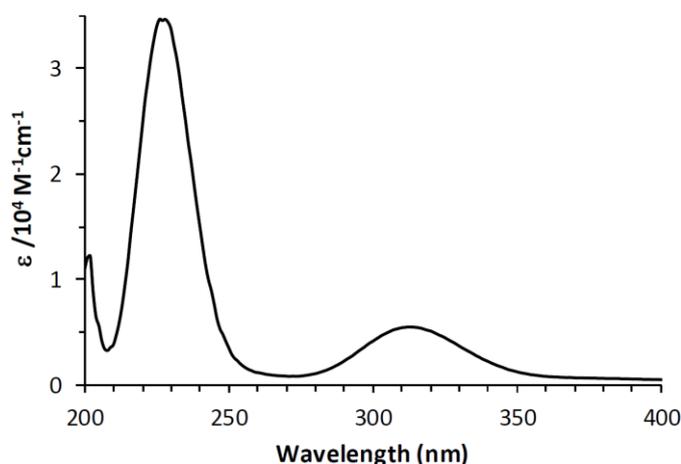


Figure 2. UV-Vis spectrum of H[AuCl₄] in 0.1 M aqueous HCl.

At room temperature, the reaction proceeded at a moderate rate and the rate of reaction could be significantly increased by increasing the reaction temperature (Figure 3). The rate at 50 °C was

significantly greater than that at room temperature and although the rate at 70 °C was greater than that at 50 °C, it was only marginally so. We attribute this to the reduction in solubility of chlorine gas at elevated temperatures [15].

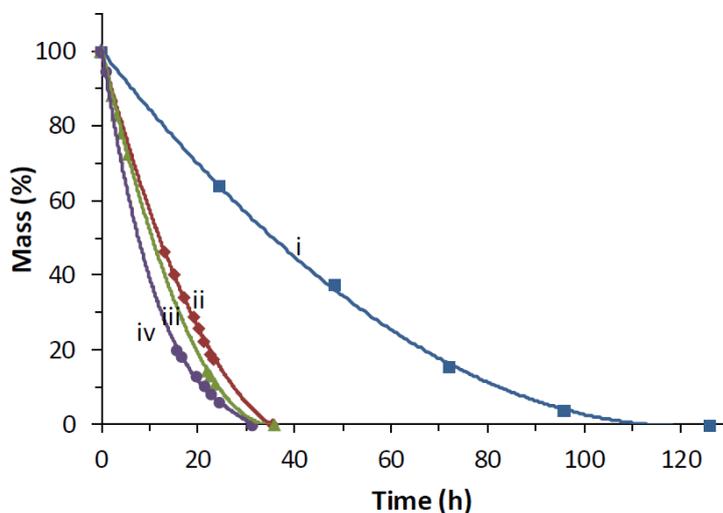


Figure 3. Reaction times at different temperatures, expressed as the percentage remaining of the initial mass of gold as a function of time: (i) 281 mg pellet at room temperature; (ii) 268 mg pellet at 50 °C; (iii) 319 mg pellet at 60 °C; (iv) 357 mg pellet at 70 °C. Note: pellets were used as-received from the supplier hence the range of masses used.

The effect of surface area of the gold pellet is also an important factor influencing reaction times. The data shown in Figure 3 were obtained using reasonably spherical (as purchased) gold pellets. Mechanical flattening of the gold pellets to thicknesses <1 mm resulted in significantly shorter reaction times whereby the flattened pellets dissolved in ~12 h at 50 °C (*ca.* 35 h for spherical pellets). However, care needs to be taken to prevent any metallic contamination of the gold during the flattening process. This may be accomplished by placing the gold between layers of cotton fabric or sheets of polycarbonate prior to the mechanical flattening process.

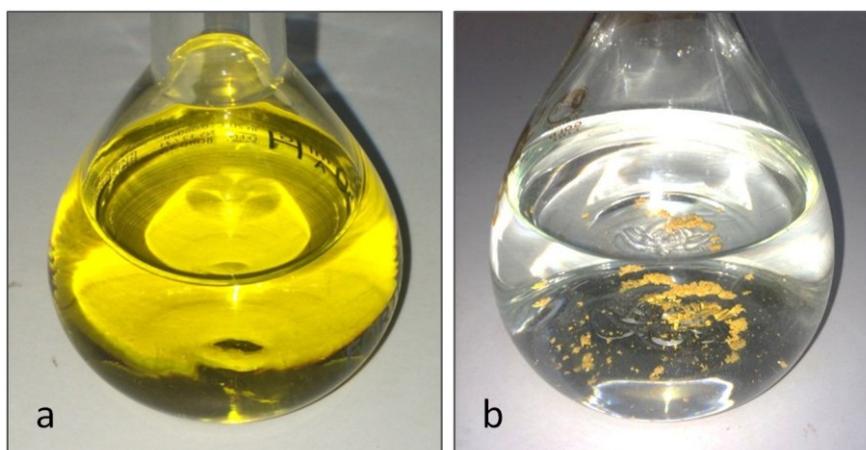


Figure 4. Photographs of gold(III) chloride solutions prepared by: (a) chlorine gas method; and (b) sodium hypochlorite/hydrochloric acid method (where precipitation occurred ~2 weeks post-synthesis).

The aqueous gold(III) chloride produced by this method is quite stable; no metallic gold precipitation was evident within at least twelve months of synthesis and the UV-visible spectra were invariant over this time (Figure S1). The stabilisation of the gold chloride was achieved without the addition of a source of excess chloride ions, such as sodium chloride, which would have made the gold chloride unusable for some nanoparticle synthesis methods due to the extreme sensitivity of many gold nanoparticles to ionic impurities [16]. The dissolved chlorine concentration of a three month old solution kept in a tightly stoppered flask was measured by iodometric titration to be 8.9×10^{-3} M. This concentration is somewhat lower than the chlorine saturation concentration of 0.08 M at 20 °C [15] and comparable to previous reports of gold chloride solutions with dissolved chlorine [17–19]. The solution pH was 1.6–1.8, where molecular chlorine is expected to be the predominant species [17], and well within the pH range required for gold chloride stability (<pH 4) [1]. Furthermore, the as-prepared gold(III) chloride solution can be directly freeze-dried to produce solid gold(III) chloride (note: the powder is highly hygroscopic, and must therefore be stored under strictly anhydrous conditions). In contrast, gold(III) chloride solutions prepared using sodium hypochlorite as oxidant followed by purification by extraction into diethyl ether, solvent removal and redissolving in pure water or dilute aqueous HCl were found to be significantly less stable over time (see Figure 4).

To test the suitability of the gold(III) chloride solutions for direct use in nanoparticle synthesis, citrate-stabilised aqueous gold nanoparticles were synthesised, which are known to be extremely sensitive to ionic impurities. The formation of the nanoparticles progressed as described in previous literature [20], and remained in a stable colloidal suspension, confirming the high purity of the gold(III) chloride solutions produced by the chlorine gas method. We also used the gold chloride solution as starting material to prepare organic-soluble oleylamine-stabilised gold nanoparticles [10]. This synthesis also proceeded as described in the literature method to yield stable nanoparticles. Scanning electron microscope images and UV-visible spectra of the particles are shown in the Supplementary Information (Figures S2–S4).

4. Conclusions

Aqueous solutions of gold(III) chloride of high purity and stability can be reliably synthesised from gold metal and molecular chlorine via a straightforward procedure. The reaction was found to proceed at a satisfactory rate at 50 °C, and progressed at a faster rate when the gold pellets were flattened compared to the as-purchased spherical beads.

Gold(III) chloride solutions prepared by this method did not precipitate any metallic gold within at least twelve months of synthesis. ICP-MS analysis confirmed the absence of any manganese contamination that may have arisen from the chlorine production process, and the purity of the gold chloride solution was further demonstrated through its direct use in the synthesis of stable aqueous citrate-stabilised as well as oleylamine-stabilised gold nanoparticles. The use of gold metal as the starting material allows for accurate determination of the final gold(III) chloride concentration from the mass of gold and the volume of water.

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Author Contributions

Shirin R. King: sample preparation, data analysis and writing the manuscript. Juliette Massicot: development of the process and data analysis. Andrew M. McDonagh: supervision of the first and second authors and writing the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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