CLUSTERING OF GOLD ATOMS IN ACETONE:

NON-AQUEOUS METAL COLLOIDS

by

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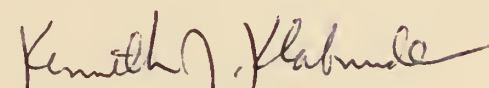Manhattan, Kansas

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for Melinda

I. <u>HISTORICAL SECTION</u>

I.1. Introduction and Ancient History

The term "colloid' was coined by T. Graham to describe
suspensions of small particles in a liquid (1). His investi-
gations on suspensions of sulfur, prussian blue and casein with
respect to their diffusion rates in water (which is slow) led him
to differentiate between them and such substances as KOH, $MgSO_4$
and sugar (which diffuse rapidly). He referred to the former as
colloids and the latter as crystalloids. The different behaviors
of these two classes of substances toward a semipermeable membrane
(such as hog intestine) was also striking: crystalloids in
solution would pass readily through the membrane, but colloids
would not. This made it possible to separate the two. This
process is called dialysis.

"Colloid" eventually took on the more general meaning of any
dispersed system, in general one in which the dimensions of the
dispersed phase range from approximately 1 nm to approximately
500 nm (10-5000 A). (2)

Colloidal particles cannot be seen by ordinary optical
microscopes, nor are they filterable by ordinary means.

The following table summarizes the various types of colloidal
systems, along with their common names:

Table I (3)

Dispersion medium	Dispersed phase	Common names
Gas	Liquid	Fog, Mist, Aerosol
Gas	Solid	Dust, Fume, Smoke, Aerosol
Liquid	Gas	Foam
Liquid	Liquid	Emulsion
Liquid	Solid	Sol, Colloidal solution
Solid	Liquid	Gel, Solid emulsion
Solid	Solid	some Alloys, Glasses

The main topic of this thesis is gold colloids or sols; with special emphasis on those in non-aqueous dispersion medium. It is well at this point to discuss the history of gold colloids.

Man's fascination with gold is older than recorded history. Since gold is found almost exclusively in the elemental form in nature, and is soft, easily worked and does not tarnish, it was probably the first metal with which early humans became acquainted. Its fascination still holds, and even today gold is synonymous with wealth. This fascination led people to believe early on that gold also had magical and mysterious properties. In most early alchemical schemes, gold was the center of atten- tion. Efforts were directed towards synthesizing gold from cheaper materials, or towards freeing other "base" metals from the impurities which were believed to differentiate them from gold. Gold was the "perfect" metal, and other metals and materials could theoretically be "perfected', at which point they would become gold. It was only natural at this point to ascribe great medicinal powers to gold, and, not incidentally, to the reagent capable of transmuting base metals into gold. As Roger Bacon (1214?-1294) said: "For the medicine which could remove all

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impurities and corruptions from base metal so that it could become the purest silver or gold is considered by the wise to be able to remove the corruptions of the human body to such a degree that it could prolong life through many ages." (4)

The first recorded efforts in this area were by the ancient Chinese. In about 142 A.D. a work appeared called Ts'an t'ung ch'i by one Wei Po-yang. In it, he gives the primary aim of Chinese alchemy: "Longevity is of primary importance in the grand triumph.... The men of the art, feeding on [gold], attain longevity." (5)

There are references in the Pao-pu-tzu of Ko Hung (281?-361? A.D.) to the consumption of Chin i (gold fluid) to prolong life. (6) It is doubtful that this was a colloidal solution (or even if it actually contained gold), since aqua regia was unknown to the early Chinese alchemists. They did, however, make use of Hg amalgams, and it is possible that they were able to form some sort of dispersion using this.

The discovery of true colloidal gold had to wait until the discovery of aqua regia, which is the only solvent which can be employed to dissolve gold under ordinary conditions. The first record of aqua regia appears in Summa Perfectionnis Magisterii, commonly ascribed to Geber. (7) Geber is the Latin form of the name of Jabir ibn Hayyan, the most celebrated of Arabic alchemists, who is supposed to have been active in the ninth century. In all probability, Summa Perfectionnis Magisterii was written by a practicing Spanish alchemist in about 1310. It was

frequently quoted and copied by others. (8)

In medieval Europe, as in ancient China, there was an interest in the medicinal properties of gold. Various recipes for aurum potabile (drinkable gold) appeared in the literature of the time. In many cases these contained no gold at all, as in the recipe of Arnold de Villanova (1235-1311), which called for quenching a hot gold plate in a bucket of wine. (9) In general, though, aurum potabile consisted of what we call today colloidal gold. A solution of gold in aqua regia (in which it exits as $AuCl_3$ or $HAuCl_4$) was reduced by treatment with ether or ethereal oils (10). It was usually then treated with chalk to neutralize it and make it fit for consumption. Fabulous curative powers were attributed to these solutions, especially towards heart disease. In many astrological schemes, the sun controlled the heart and the sun was also mystically associated with gold. (11)

In 1618 Franciscio Antonii published "Panacea Aurea: Auro Potabile" (12) which was about colloidal gold. Antonii was a physician and his book centered on the use of aurum potabile in the treatment of venereal diseases, dysentery, epilepsy, tumors, etc. He claimed to have successfully treated many patients (13). In 1676, Johann Kunckels published a book entitled, "Nützliche Observationes oder Anmerkungen von Auro und Argento Potabile" (14). In this treatise Kunckels noted that preparations usually called "drinkable gold" actually contained metallic gold in a clear, slightly pink solution. Thus he concluded that the gold must be in pieces so small that the eye could not detect them.

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He also attributed curative power to these preparations.

In 1718 a treatise on colloidal gold appeared entitled, "<u>Aurum Potabile oder Gold Tinctur</u>" by Hans H. Helcher, a doctor of medicine (15). In it he described primarily the medicinal use of colloidal gold, but most important to modern readers, he pointed out that the addition of boiled starch would noticeably increase the stability of the preparation. This was confirmed by later workers who investigated the action of so-called protective colloids, polymeric, lyophilic materials which when adsorbed onto the surface of colloids, tended to stabilize them.

Gold colloids were mentioned by J. Juncker in 1730 (16), and also by P.J. Macquer in 1789 (17). In 1802 Richter published "<u>Ueber die neuren Gegenstande der Chymie</u>" (18), in which he mentioned that the colors of purple gold solutions and ruby glass were due to the presence of finely divided gold (19). He correlated the color of gold solution with particle size, saying that the pink or purple solutions contained the finest particles, and that the gold color appeared only after the particles had grown to a certain size (20). A Mrs. Fulhame published in 1794 an account of how she had used a colloidal gold solution to dye silk cloth, resulting in various shades of purple (21).

A parallel development to that of colloidal gold was the development of the so-called Purple of Cassius. Addition of a solution of stannous chloride to one of auric chloride results in the precipitation of stannic hydroxide and the reduction of gold to tiny particles which precipitate in various shades of

brown, purple, blue or red. This reaction is also used as the basis for a very sensitive qualitative test for gold. The sample is dissolved in aqua regia and boiled, then added to a saturated solution of stannous chloride. It has been shown that 10 p.p.b. can be detected by this method (23).

J.R. Glauber mentioned the precipitation of a purple material by tin from a gold/aqua regia solution (24). In 1684, A. Cassius described completely for the first time this reaction (25). The materials prepared in this way found extensive use as agents for coloring red glass. Often this color does not appear when the gold reagent is added to the glass, but annealing the glass just below its melting point brings out a brilliant ruby red color (26).

I.2. First Scientific Investigations

The first thorough scientific investigation of gold sols was
carried out by Michael Faraday and published in 1857 (22). The
principal object of Faraday's study was the properties of light.
To this end he studied gold and silver leaf, and various films of
these metals. In conjunction with this he studied gold sols made
by several methods, all of which were reductions of $AuCl_3$ in
aqueous solution with various reducing agents: phosphorus in
ether, phosphorus in carbon disulfide, phosphorus alone, etc. He
also studied aerosols produced by sparking a gold wire with the
discharge from a Leyden condenser. He concluded from his investi-
gations that the gold is actually present in the elemental form,
and that the color of the colloidal solution is a function of the
particle size. He added NaCl solutions to the gold sols and
observed that the color changed from red to purple, and was
accompanied by flocculation. He also studied the filtration of
these sols and found that they could pass through filter paper
unchanged. He also discovered the phenomenon of light scattering
by colloids: when a beam of light was passed through a dilute
gold sol, the beam was visible as a cone of light where it passed
through the sol. This phenomenon is called the Tyndall cone
effect.

All of the gold sols known up to this point had two things
in common: they were formed by the reduction of $AuCl_3$ and they

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were in aqueous solution. This has continued to be the favored method for the production of gold sols, but some other methods have been used as well.

In 1898, Bredig described a method for the formation of metal hydrosols by the use of an electric arc (27). Two electrodes made of the metal of interest, are brought close together under water. High voltage (40-50 V, 5-10 A) was applied across the electrodes, and the arc formed generated colloidal metals from the electrodes. Colloids of lead, tin, gold, platinum, bisimuth, antimony, arsenic, thallium, silver and mercury have been prepared by this method (28,29,30). It has been found by these workers that some sols are more stable when formed in dilute acid or base solutions. Mindel and King investigated Pt sols formed by the Bredig method and determined that the particles were stabilized by platinic oxide and hexa-hydroxyplatinic acid, which were formed from hydrolysis of water and not from atmospheric oxygen (31). Bredig also attempted to form organosols by his method, but these efforts were unsuccessful due to the decomposition of the solvents under experimental conditions. Svedberg modified Bredig's apparatus somewhat, by striking the electric arc in a glass tube under the surface of the liquid. A small hole was placed in the side of the tube near the arc ends of the electrodes. Gas was passed through the tube and out the small hole, bubbling up through the liquid and carrying with it the small metal particles generated by the arc. Svedberg was able to use this method to prepare some stable metal

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organosols, using liquid methane, ether and isobutanol at low temperatures. Svedberg also used a slightly different method, in which electrodes such as those of Bredig are used in conjunction with a large induction coil and a large condenser. Fragments of the metal of interest are placed in the bottom of the vessel holding the solvent, and the arc from the discharge soon forms a sol (32,33,34). This method was also used for the production of organosols. Mayer obtained a patent on the use of a high voltage (100-200 kV) discharge to evaporate metal wires in liquid media. The liquid used was 48% betaine or 48% benzidine in water. Using gases instead of liquids as the dispersion medium yields aerosols (75). Bredig and Haber used a high voltage discharge to disintegrate cathodes of Pb, Sn, Bi, Sb, As, Th, and Hg in a aqueous NaOH solution (77). Kimura used a modified form of Kohlschutter's apparatus (arcing metal electrodes in an air stream) to form aerosols of Pt, An, Ag, Al, Ni, Fe, Cn. When these aerosols were swept into water by a has stream, hydrosols were formed (78,79). Karioris, Fish and Royster made metal aerosols by exploding metal wires in air and other gases with high voltage (1-18 kV) (80).

In 1935, Pauli, Russer and Brummer made stable gold sols by electrically sputtering gold metal into an aqueous HCl solution. Pauli and Schild also used this method for the production of a Pt sol (81,82).

Matsumura reported the formation of colloidal silver in the following way: a mixture of $AgNO_3$ solution and MgO was pulverized and kneaded into a paste. Dilute acetic acid was added to

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dissolve MgO, and the resulting colloidal solution of Ag was filtered and then electrodialyzed to remove excess ions (83).

Kimoto, Kamiya, Nonoyama and Uyeda noted that aerosols could be produced by evaporation of various metals (Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Sn, Au, Pb, and Bi) from a hot tungsten wire into a chamber containing He or Ar from 1 - 30 tons pressure. They found that at low pressures, smaller particles were formed, and at higher pressures, larger particles. N. Wada used this method with Ar gas and confirmed the earlier findings (84,85).

In 1983, K. Kimura and S. Bandow reported on the formation of metal colloids both by codeposition of gold vapor and ethanol vapor in a cold matrix and by the evaporation of metal into a gas stream which is then bubbled through a cold solvent (usually ethanol) (35). This work was unknown to this author until 1985. Efforts to replicate Kimura's and Bandow's work in our laboratory have thus far met with limited success.

I.3. Aqueous Metal Sols

This has been the most common route to metal colloids in aqueous dispersion media. Typically the metal halide (occasionally the oxide) is the starting material, and a variety of substances have been used as reducing agents.

Faraday's methods of reducing gold chloride have already been mentioned.

Gutbier reported in 1908 that a 0.1% sols of $AuCl_3$ neutralized with Na_2CO_3 could be reduced to colloidal gold when treated with hydrazine hydrate, hydroxylamine hydrochloride or phenyl-hydrazine hydrochloride. In his study, dilute sols resulted in a red color, while more concentrated sols were blue (36,41).

Thomae reduced $AuCl_3$ solutions with K_2CO_3 and formaldehyde, and also replicated Faraday's work with an ethereal solution of phosphorus (37).

Hydrogen peroxide was used as a reducing agent for aqueous $HAuCl_4$ by Doerinckel. He found that addition of a small amount of preformed gold colloid would facilitate the formation of a uniform sol. He also found that the particle concentration was proportional to the amount of "seed" colloid used (38).

Zsigmondy also studied this "seeding" phenomenon. He added $AuCl_3$ solution to a gold sol in the presence of a reducing agent and found that the reduced gold was deposited on the particles already present, increasing their size. This would later lead to

important conclusions about the mechanisms of particle nucleation and growth. Zsigmondy studied this experiment with the aid of the slit ultramicroscope, about which more will be said later (39). Reitstötter also studied the seeding phenomenon (47) as did Zakowski. Zakowski found that particle growth occurred in 2 stages: slow growth, in which the size of the particles does not increase very fast, and a fast growth period. The first stage can be thought of as an induction period. Zakowski found that increasing the surface area of the "seeds" or increasing the temperature or exposure to U.V. light shortens the induction period (53).

Svedberg studied the reduction of metal salts and oxides in solution by a stream of gas bubbles. He found that AgO was reduced by H_2 at 50 degrees C. He also reported reduction of $AuCl_3$ in solution by CO, SO_2 and formaldehyde (40).

In 1914 Gutbier and Weingärtner reported that $AuCl_3$ could be reduced by an aqueous starch suspension under basic conditions. It was found that the starch macromolecules were adsorbed on the surface and helped to stabilize the colloid. Moving-boundary electrophoretic measurements indicated that the starch-coated colloid behaved approximately like a neat starch solution (42).

Colloidal gold and silver were obtained by Granert by heating a basic solution of the protalbin or lysalbin acid salt of silver or gold, and dialyzing the resulting sol to remove excess ions. Again, it was found that the long macromolecules adsorbing on the surface of the particles tended to stabilize

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them. Granert exploited this fact by stabilizing Au, Pt, Pd, Ir
and Ag colloids with serum albumin. He used hydrazine hydrate to
reduce the salts of these metals in a solution containing the
serum albumin (43).

An interesting method for the reduction of gold salts was
reported by Donau in 1915. He made a blue gold hydrosol by
playing the reducing portion of a hydrogen flame across the
surface of an auric chloride solution (44). Halle and Pribram
proposed that the reducing species in this instance was HNO_3
formed in the water by the oxidation of atmospheric N_2 by the
heat of the flame (45). Donau also used a spark discharge just
under the surface of a $AuCl_3$ solution, and found that this forms
a red hydrosol (44).

Groll reported that in the reduction of $AuCl_3$ by H_2O_2 in
aqueous solution the pH of the solution had an effect on the
color of the colloid formed. At low pH, the sol would be red,
while in more basic solutions, the color would be blue (46).

During the early years of the 20th century, research in gold
colloids was stimulated by the discovery that the cerebrospinal
fluid of a person infected with syphillis would precipitate
certain gold colloids, while that of a healthy individual would
not. This was used as the basis for a diagnostic routine known
as the Lange colloidal gold test. One problem with the test was
the near-impossibility of repeatably making identical gold
colloids. Much work was done in an effort to standardize the
preparation of colloidal gold used for this purpose. Black

published a reductive method which he found to be reproducible (48). Speidel and Smith reviewed various preparations of colloidal Au for this purpose, and found that it was very important that both the water and glassware used be completely free from any contaminants (49). Manheim and Bernhard described the use of an electric arc for the preparation of the colloid, and found that it was also useful for the Lange test (50). Nicol reported that equimolar amounts of urea and H_2O_2 would reduce gold chloride to form a red colloid suitable for the Lange test (51).

Domanitzkii found that almost any unsaturated hydrocarbon could be used to reduce $HAuCl_4$ in aqueous solution. He used acetylene, allene and 2-methyl-2-butane, and found that they also worked for the reduction of AgCl to a silver colloid (54).

One of the more bizarre reducing agents used has been wine, as reported by Iwase in 1930. He found also that Japanese sake did not work as well as wine (55). Other plant materials have also been used as reducing agents: Iwase used aqueous plant leaf extracts for this purpose, and N. von Veimarn used extracts from pea petals, cloves, azaleas, peonies, roses and chrysanthemums to form a red gold sol (56,57). Rimini reported that adding $AuCl_3$ solution dropwise to a fresh aqueous yeast suspension, followed by extensive filtration and treatment with NaOH, more filtration and neutralization with HCl resulted in a bluish gold colloid, but one that was only stable for approximately one week (58). Liversidge also published an account of AuCl, reduction by a yeast, aspergillus oryzae, to form a gold sol (59).

A silent electric discharge was used by Miyamoto to reduce
an $HAuCl_4$ solution (60). A similar method was used by Pavlov to
make colloidal gold, copper, silver, and lead from $AuCl_3$, Cu^{+2}
salts, $AgNO_3$ and $Pb(OAc)_2$ solution, respectively. A four to
five cm. layer of distilled water was carefully added on top of
an electrolyte solution in a partially filled U-tube. A Pt
cathode was suspended above the water layer, and a Pt anode was
immersed in the electrolyte in the other limb of the U-tube. A
potential sufficient to form an arc between the cathode and the
water layer was then applied. This was supposed to form O_2^-
anions which then diffused through the water and reacted with the
cations which have migrated to the cathode. The reduction by O_2^-
was unaffected by other anions present (61).

Galecki reported that silver sols could be prepared from AgO
or $AgNO_3$ using Na_2CO_3, K_2O, CO_3, KOH, NH_3, ethereal solutions of
P, aqueous H_2SO_4, or hydrazine hydrate. He also investigated the
light sensitivity of the Ag sols formed (62).

Sodium citrate was used to reduce $AuCl_3$ in aqueous solution
by Scherre in 1950. He found that the stability of the resulting
red sol could be improved by the addition of ascorbic acid
(vitamin C), which was presumably adsorbed on the surface of the
gold particles (63).

Suito and Ueda discovered an interesting correlation between
the absorbtion spectra of gold sols formed by reduction with a
formalin solution and the particle size as determined by electron
microscopy (64).

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The growth of colloidal gold particles in a gold trichloride/ hydroxylamine/dilute HCl solution was studied by Turkevich, Stevenson and Hillier. They found that the particle size distribution curve was determined by two separate kinetic processes: nucleation and growth. Using the assumption that the spread of the particle size distribution is directly proportional to the spread in time of nuclei formation, they were able to analyze the particle size distribution curves and obtain data about the rates of particle growth and nucleation (65,66). This group made extensive use of the electron microscope.

Suito and Ueda also used the electron microscope to study the crystalline morphology of colloidal gold reduced with salicylic acid at room temperature. Their investigation showed that most particles had a threefold symmetry azis and were flat. They noted Moire fringes and surmised that these were due to the presence of step defects which were slightly offset one from another as the step grew angularly about the center of the crystal. Interestingly, it was noted that some of the flat crystals had holes in the center. Based on the threefold symmetry, they concluded that growth occurred on the (111) plane (67).

Chiang and Turkevich confirmed the work of Suito and Ueda and also observed holes in the center of platelike particles with approximately 1000 A diameters (the particles). Chiang and Turkevich also noted that the platelike form is not the first one produced, but is the result of aggregation and rearrangement of

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the smaller particles that were initially formed. They also produced some platelike particles of platinum and palladium (68).

Fabrikanos, Athanassiou and Leiser reported the preparation of stable gold and silver hydrosols by reduction with disodium ethylenediaminetetraacetate (69).

In 1969, Machalov, Groisberg, and Palikov reported the formation of colloidal Au, Ag, Pd, Os, Rh, Pt, Sn, Te and Tl from their nitrates using KBH_4 as a reducing agent in an aqueous solution of pH 9 containing 5% gelatin at 40 C. The products initially formed in the reaction were unstable and decomposed to form the colloids. It was found that the addition of a small amount of poly (vinylalcohol) increased the stability of the colloids (70).

Brede, Mehnert, Franke, Roschke and Herrmann obtained a patent on a process for the production of gold colloids by light. An aqueous mixture containing a metal salt, an aromatic or aliphatic substituted ketone as a light acceptor, an alcohol as a proton donor, and a detergent to stabilize the colloid formed, was irradiated for 60 minutes with light from a Xe lamp ($\lambda = 350$ nm). With an aqueous solution of $HAuCl_4$, isopropanol and benzophenone they formed a gold sol with particle size of approximately 100 nm which absorbed light of $\lambda = 560$ nm. Using sunlight, and irradiating for 180 minutes resulted in the forma-tion of a gold colloid with a particle size of approximately 50 nm which absorbed at $\lambda = 540$ nm (107).

I.4. Protective Colloids

Protective colloid is a term used to describe macromolecular or polymeric substances which stabilize other colloids (usually inorganic) by adsorption on the surface. This effect has been known for a long time. Faraday noted that gold sols are more stable in gummy gelatinous liquids (22). Lottermoser noted that albumin prevented the coagulation of silver sols by electrolytes (71). Gutbier, Huber and Kuhn reported in 1916 that the reduction of $AuCl_3$ in a very dilute solution of icelandic moss with hydrzine hydrate gave a very stable gold sol. They noted that the sol thus formed could be precipitated by the addition of alcohol and then reversibly solvated by the distillative removal of the alcohol. This method also worked for making colloids of palladium from the reduction of $PdCl_2$ (72). Granert found that gelatin and serum albumin made good protective colloids for silver and gold sols, respectively (43). Gutbier and Weingaertner used starch as a protective colloid for silver (42). Wegelin used gelatin as a protective colloid for the stabilization of several metal sols which he formed by grinding the metal with a soluble solid (76). Rimini used glucose to stabilize a gold sol formed by reduction of $AuCl_3$ with a fresh yeast suspension (58). Gum arabic and gelatin were used to stabilize silver sols by Miyamoto (60). Scherre used ascorbic acid to stabilize a gold hydrosol (63). The use of polyvinyl alcohol as a protective colloid was reported

by Machalov, Groisberg and Palikhov for the stabilization of Ag, Au, Pd, Os, Rh, Pt, Sn, Te, and Td sols (70).

Natanson was able to make stable copper sols in acetone/toluene/1-pentanol mixtures by agitation of Zn powder with $CaCl_2$ in the solution. No stable sols could be produced without the use of 0.001 - 0.01% natural latex or collodion as a protective colloid (73). Chu and Friel prepared colloidal cobalt in tetrahydrofuran dispersion medium by reduction of $CoCl_2$ with sodium naphthalide. They postulated that the cobalt sol was stabilized by adsorbed naphthalene (74). Rampino and Nord stabilized colloidal palladium with polyvinyl alcohol and found that it was an efficient catalyst for the reduction of quinone and m-bromonitrobenzene to hydroquinone and m-bromoaniline in the presence of H_2 (86). Uno, Ichiji and Kobayashi reported that the coagulation of frozen Au, Pt, and As_2S_3 sols upon thawing was prevented by the presence of alcohols, sugars or urea. For alcohols, it was found that the protective action was increased with an increase in the number of -OH groups present (87).

Jirgensons studied the protective action of various PVP (polyvinylpyrrolidone) fractions on silver sols and found that lower molecular weight fractions were more protective against coagulation by electrolyte addition than the higher fractions (88). Fujii and Sugiura compared the protective abilities of polyvinyl alcohol to those of gelatin and found that PVA did not protect inorganic colloids as well as gelatin against coagulation by electrolytes (89). Kubal used Na or K polyalkylacrylate both

as reducing agents for AgNO3 and as protective colloids for the resultant Ag colloids (90). Colloidal Pd protected with poly (N-vinyl - 2-pyrrolidinone) was used for selective catalytic hydrogenation of cyclopentachine in alcohol solutions by Hirai, Chawanya, and Toshima (91).

The fact that long-chain molecules are adsorbed on small metal particles with concomitant stabilization of these particles has been exploited by biochemists as a labeling technique for biomolecules. Faulk and Taylor reported stabilizing Au sols with several types of antibodies which rendered the antibodies visible in the electron microscope (92). They also reported the use of colloidal Au as a label on rabbit anti-salmonellae serum (antibody), which retained full biological activity and allowed them to see the binding sites on the cell surface with the aid of an electron microscope. They also discussed the possibility of using two different particle sizes for a double labelling technique (93).

Lee and Meisel performed surface-enhanced Raman spectroscopy experiments on Au and Ag colloids stabilized with poly (vinyl alcohol) (PVA), Carbowax 20 M, and poly (vinylpyridine) (PVP). The bands observed by this experiment showed that PVA was absorbed through unhydrolyzed OAc groups, Carbowax by C-O-C groups and PVP by the pyridine π - system, giving flat ring coordination to the metal surface (108).

I.5.   Non-Aqueous Metal Sols

Compared with the amount of work done on metal colloids in aqueous dispersion media, the amount of literature dealing with non-aqueous systems is quite small.

Bredig attempted to make metal sols in organic liquids with his high voltage electric arc but found that the high potential needed to generate the arc tended to decompose the organic solvents (27). Svedberg was able to make sols of Fe, Cu, Ag, Al, Ca, Pt, Au, Zn, Sn, Cd, Sb, Tl, Bi and Pb in liquid methane, ether, isobutyl alcohol and other solvents at low temperatures. He modified Bredig's apparatus by the use of an alternating current and by placing small grains and pieces of the metal of interest in the bottom of the ceramic vessel used to hold the liquid. The discharge was then propagated among these small pieces and tiny particles of metal (colloidal) passed into the dispersion medium (94). Another method exploited by Svedberg used a gas flow to carry a metal aerosol formed by an electrical discharge between electrodes of the metal of interest into the organic solvent dispersion medium (34). Williams and Skogstrom reported in 1926 that a small amount of H_2O would stabilize colloidal P_2O_5 in nitromethane dispersion medium (95). P.P. von Weimarn prepared colloidal Au by pouring a weak solution of $AuCl_3$ in glycerol into boiling glycerol and then rapidly cooling the solution after the appearance of a red color. Apparently the

glycerol functions both as a reducing agent and as the dispersion medium (52). Natanson reported the production of colloidal Cu in an acetone/toluene/1-pentanol solvent by reduction of $CuCl_2$ with Zn powder (73). Janek and Schmidt formed a gold/citrate hydrosol and added this to a solution of propanol with a small amount of toluene or nitrobenzene in a closed tube. The tube was then heated until one phase was formed, and then cooled. When two layers formed again, it was found that the Au colloid was in the alcohol-rich layer. This method also worked with t-butanol to yield a highly concentrated alcosol (96). Marinescu reported that sonication (treatment with ultrasound) of alkali metals and their alloys at their melting point in kerosene yielded pyrophoric colloids (97). Gibson and Baldwin noted that the subjection of 200 V across a U-tube containing a two-phase system composed of H_2O/acetone/diethyl ether in the ratio of 12:19:10 would cause the migration of colloidal As_2S_3, Au and bentonite (a clay mineral) from the H_2O-rich phase to the ether-rich phase (98). Gold organosols were prepared by Yamakita. He used 52 different dispersion media--fats, organic acids, alcohols, aldehydes, ketones, ethers, and various hydrocarbons and hydrocarbon deriva- tives (halogen, $-NO_2$ and $-NH_2$). The dispersion media were also the reducing agents for the starting material, Au_2O_3. He had the most success with fats and higher fatty acids which were weakly reducing. He reported particle sizes of approximately 300 A, determined by ultramicroscopy (99). In 1947, M.D. Marshall of Monsanto Chemical Co. obtained a patent on a process for forming

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SiO$_2$ sols in organic dispersion media. The first step was formation of the hydrosol. Then a miscible organic solvent (boiling point greater than 100 C) was added in an amount sufficient to precipitate the inorganic salts present. The salts were then removed by filtration, and the water removed by distillation. This method was successful for SiO$_2$ in butyl acetate, ethyl acetate, toluene and hydrocarbon oil fraction with boiling point 116 C (100).

Khibvidze found that Pb sols in ethanol could be formed merely by shaking Pb powder in ethanol for an extended period. His studies revealed that an initially very fine dispersion would aggregate at first, but after prolonged agitation would again become fine. Initially coarse sols formed finer sols upon prolonged shaking (101). Van der Waarden studied the stabilization of carbon black in hydrocarbons by the addition of aromatic compounds with long aliphatic side chains. He postulated that these additives acted as a protective colloid for carbon black (102).

Colloidal cobalt in THF was reported by Chu and Friel. CoCl$_2$ was reduced with sodium naphthalide to form colloidal Co (74). Broadbent, Campbell, Bartly and Johnson reduced RhO$_7$ with H$_2$ gas in various solvents: p-dioxane, ethanol, glacial acetic acid and water. In acetic acid, they produced a black, air-sensitive rhodium colloid that was an efficient hydrogenation catalyst (103). Kukushova and Radulova produced colloidal Au in a number of turpentine oils, turpentines, lavender oil, rosemary

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oil, nitrobenzene and asphalt mixtures. The product was used to paint gold lines on ceramic products. Few details were given (104). Ledwith reported the formation of blue Au organosols in diazoethane mixtures with: diethyl ether, toluene, benzene, cyclohexane, chloroform, carbon tetrachloride and bromobenzene. The diazoethane reduced $AuCl_3$ (1% solution in water) which was added dropwise to the organic solvent mixture (105). Blumencron reported that reduction of $AuCl_3$ in olive oil fractions formed an organosol which could be injected with few harmful side effects for the treatment of arthritis (106). Colloidal Pd was produced in alcohol solutions by the reduction of $PdCl_2$ poly (N-vinly-2-pyrrolidimone), which also served as a protective colloid. Particle sizes of 18-56 A were reported (91).

Some other non-aqueous systems have also been mentioned in the sections dealing with electrical discharge methods, protective colloids and miscellaneous methods, respectively. The interested reader should see the appropriate sections for the work of Natanson (73); Chu and Friel (74); Hirai, Chawanya and Toshima (91); Svedberg (32,33,34); and Kimura and Bandow (35).

II.   RESULTS AND DISCUSSION SECTION

II.1.   Preparation of Metal Sols

In this study, the metal vapor technique was used for the production of colloidal metals in organic dispersion media. The equipment and general techniques of metal vapor chemistry have been covered extensively by other authors (109,110,111).

The system comprised of gold and acetone was the one studied most extensively. Silver/acetone and copper/acetone were also found to form colloids by this method. Gold/ethanol and AgCl/ethanol were attempted but did not result in stable colloidal solutions. Neither did Ag/DMF or Cu/DMF.

Typically a small amount of metal (0.002 – 0.2 g) was vaporized and co-condensed with acetone vapor (41 – 199 mL). After an extensive period of trial and error, it was found that stable sols would only result if the matrix were warmed up slowly. Various liquid nitrogen/solvent slush baths were tried, as were various lengths of time with the slush baths. In general, it was found that merely pouring out the liquid nitrogen from the dewar surrounding the reactor and then replacing the cold, empty dewar would slow the warming sufficiently to form a stable sol, and this was adopted as the "standard" method.

II.2. Concentration Studies - Gold / Acetone

It was necessary to investigate the influence that concen-
tration had on the products (colloid) formed, particularly with
regard to particle size and particle size distribution. The
simplest and most direct way to gain information about the
particle sizes of metal colloids is through electron microscopy.
Indeed, gold colloids were one of the first subjects to occupy
the attention of early workers in electron microscopy (115,116,
117,118). Electron microscopy gives images of the particles
under investigation, and therefore gives information not only
about particle size and size distribution, but also particle
morphology, degree of agglomeration and deformities. Electron
microscopy has therefore been used to check the validity of other
particle size determination methods: small angle x-ray scattering
(119,120,123), absorption spectroscopy (121), ultracentrifugation
(122), and ultrasonically-induced optical birefringence (124).
The morphology of colloidal Au particles was studied by Suito and
Ueda. They found that under certain conditions, the particles
would adopt a threefold symmetry, indicating growth on the
crystallographic [111] plane (125,126). Colloidal gold was used
in conjunction with electron microscopy to probe certain cellular
functions (127,128). In this context the colloidal Au is useful
because it renders visible cellular structures which would
otherwise be invisible to the electron microscope. Electron

microscopy has been used to study the growth of colloidal gold particles (129,130) and the most important and thorough work in this area has been by Turkevich et. al. (133,134,135). Recently electron microscope studies of the structures formed when colloidal gold aggregates have been undertaken. It has been determined that these structures are scale invariant or fractals, which can be described by a fractal dimension $d_f = 1.75 - 2.05$. These structures are in agreement with computer simulations in which the clustering of the particles is modeled as a diffusion-controlled process (131,132).

The study undertaken here is similar to that of Turkevich et. al. (65,66) in the studies of gold hydrosols.

The first study undertaken had as its object the investigation of the effect of gold concentration on the particle size. Turkevich's group reported that small $HAuCl_4$ concentrations resulted in comparatively larger colloidal particles with a broad particle size distribution, and at higher $HAuCl_4$ concentrations, the mean particle size decreased and the particle size distribution narrowed.

Our investigations on gold organosols revealed the reverse effect: a direct relationship between gold concentration and particle size.

Turkevich's explanation for the inverse size/concentration relationship observed in his aqueous Au colloids is not directly spelled out, but it is evidently due to the belief that a certain critical concentration of reduced auric ions is necessary in

order that they will agglomerate into a stable particle. Due to the statistical nature of physical events, this local concentration will occur more readily in a concentrated solution, leading therefore predominately to nucleation rather than the slower step of particle growth.

We believe that our opposite finding is a result of several factors. In the frozen matrix, nucleation and particle growth are probably favored about equally at the beginning. As the temperature of the matrix increases and it begins to melt, the single atoms and smallest particles are most mobile due to their small size. Collisions leading to particle growth are more common in a concentrated matrix, and thus the size increases. This dependence on particle growth is confirmed by the observed increase in polydispersity with increasing concentration.

The effects of solvent viscosity and other factors are discussed in the next section.

In our investigations with the electron microscope, several interesting features were revealed: First, the particles display no well-defined shape, in contrast with some of Turkevich's samples (66) which show either a trigonal, crystalline outline or a simple spherical shape. Secondly, our particles do not have similar optical density throughout: some areas of a single particle appear to be darker (have a higher electron cross-section) than others. It is interesting to note that, in those photographs which show the particles to be agglomerated, there is still space between the individual particles. This is believed

to be the result of organic material adsorbed on the surfaces of the particles. This adsorbed material would have a much smaller electron cross-section than the gold of the particles themselves, and thus would be transparent. Further evidence for this adsorbed organic layer was given by our unsuccessful attempts to obtain SEM photographs of the gold samples. The samples were applied to the metal stages used and then the sample was coated with a vapor-deposited coating of gold (a standard SEM procedure for biological samples). Good photographs could not be obtained due to excessive noise levels emanating from the particles themselves but not the background. At the time, the operator attributed this to a capacitance effect produced when the organic-coated metal particle was again coated with metal, creating a spherical microcapacitor which had an inhibitive effect on the secondary electron emission.

FIGURE 1

Gold / Acetone Colloid

160,000 X

MTF-82-S-01

1.8×10^{-5} $\dfrac{\text{g Au}}{\text{mL acetone}}$

mean particle size: 20 A
median particle size: 20 A

FIGURE 2.   Particle size distribution, MTF-82-S-01.

FIGURE 3

Gold / Acetone Colloid

250,000 X

MTF-80-S-01

$$2.7 \times 10^{-4} = \frac{g \ Au}{mL \ CH_3COCH_3}$$

mean particle size: 53 A

median particle size: 50 A

FIGURE 4. Particle size distribution, MTF-80-S-01.

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FIGURE 5

Gold / Acetone Colloid

250,000 X

MTF-82-S-02

9.1×10^{-4} $\dfrac{\text{g Au}}{\text{mL } CH_3COCH_3}$

mean particle size: 80 A
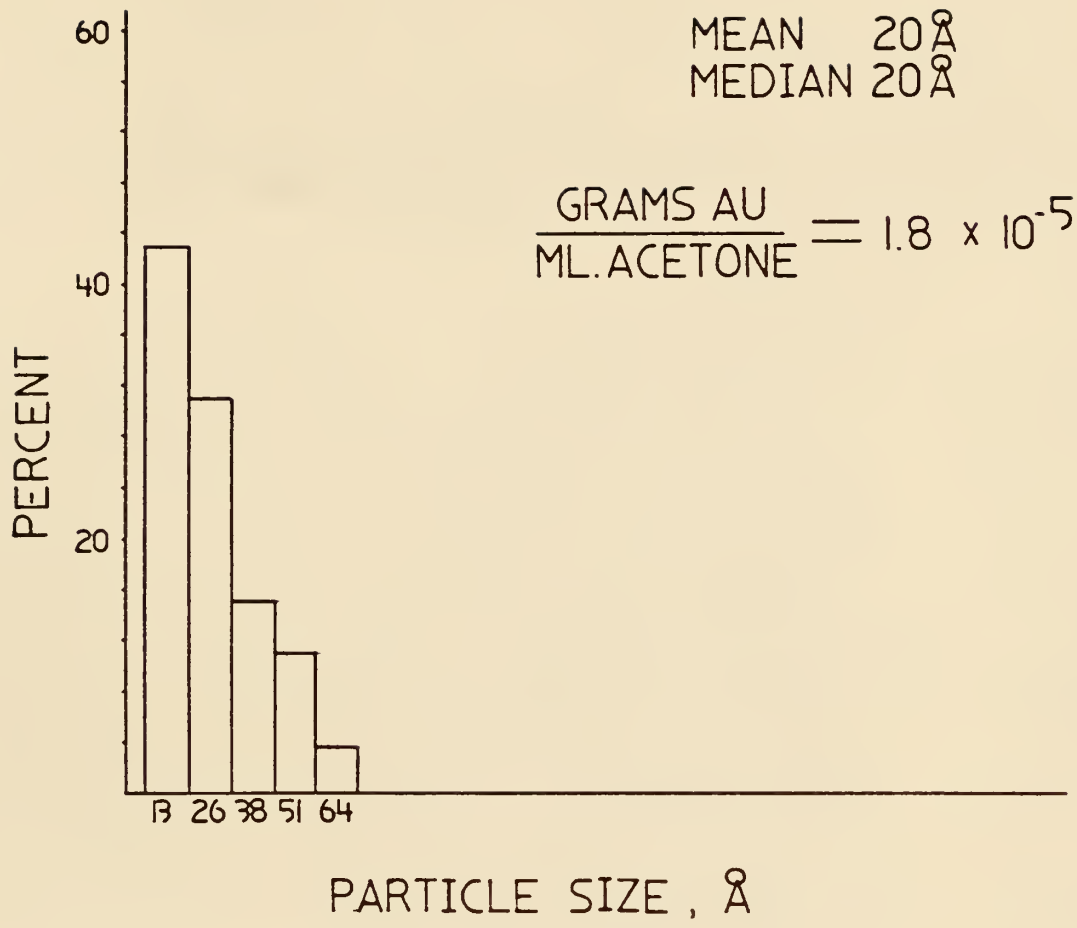
median particle size: 60 A

FIGURE 6.   Particle size distribution, MTF-82-S-02.

FIGURE 7

Gold / Acetone Colloid

160,000 X

MTF-112-S-01
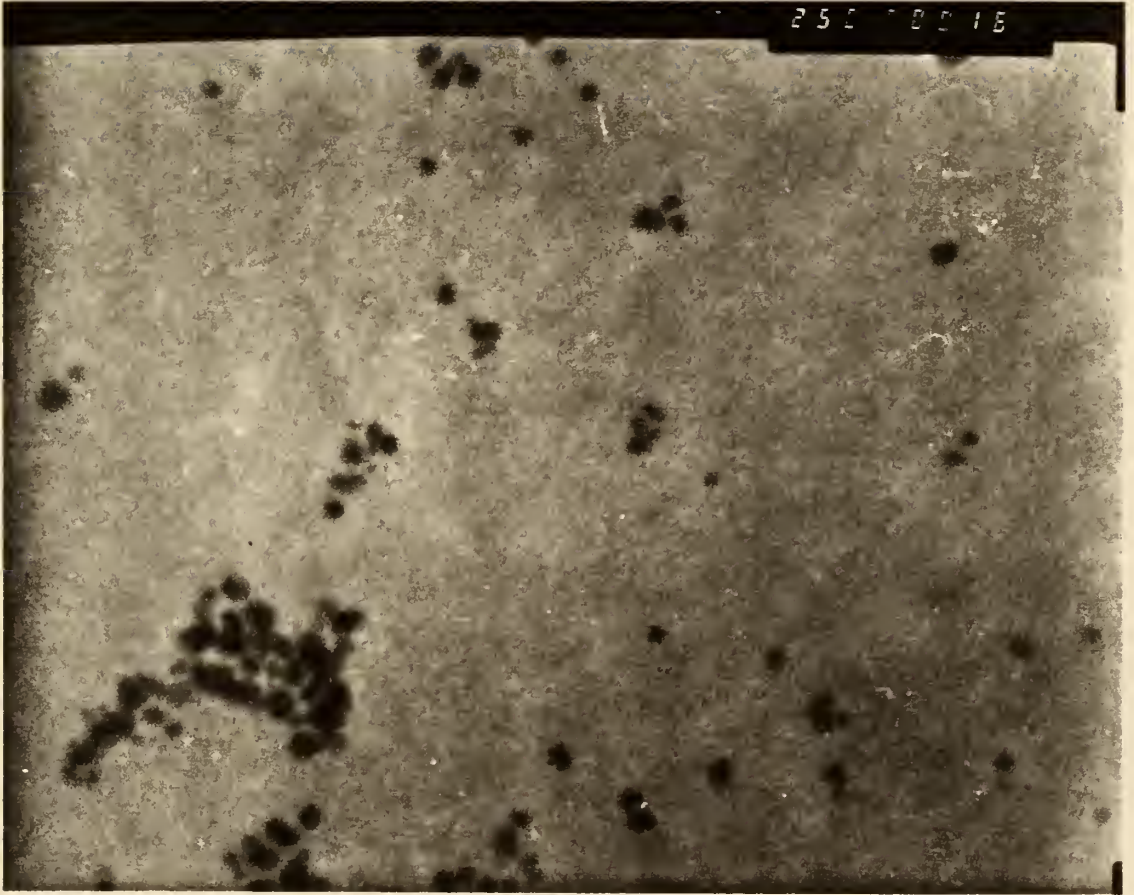
$$5.3 \times 10^{-5} = \frac{\text{g Au}}{\text{mL CH}_3\text{COCH}_3}$$

mean particle size: 40 A

median particle size: 38 A

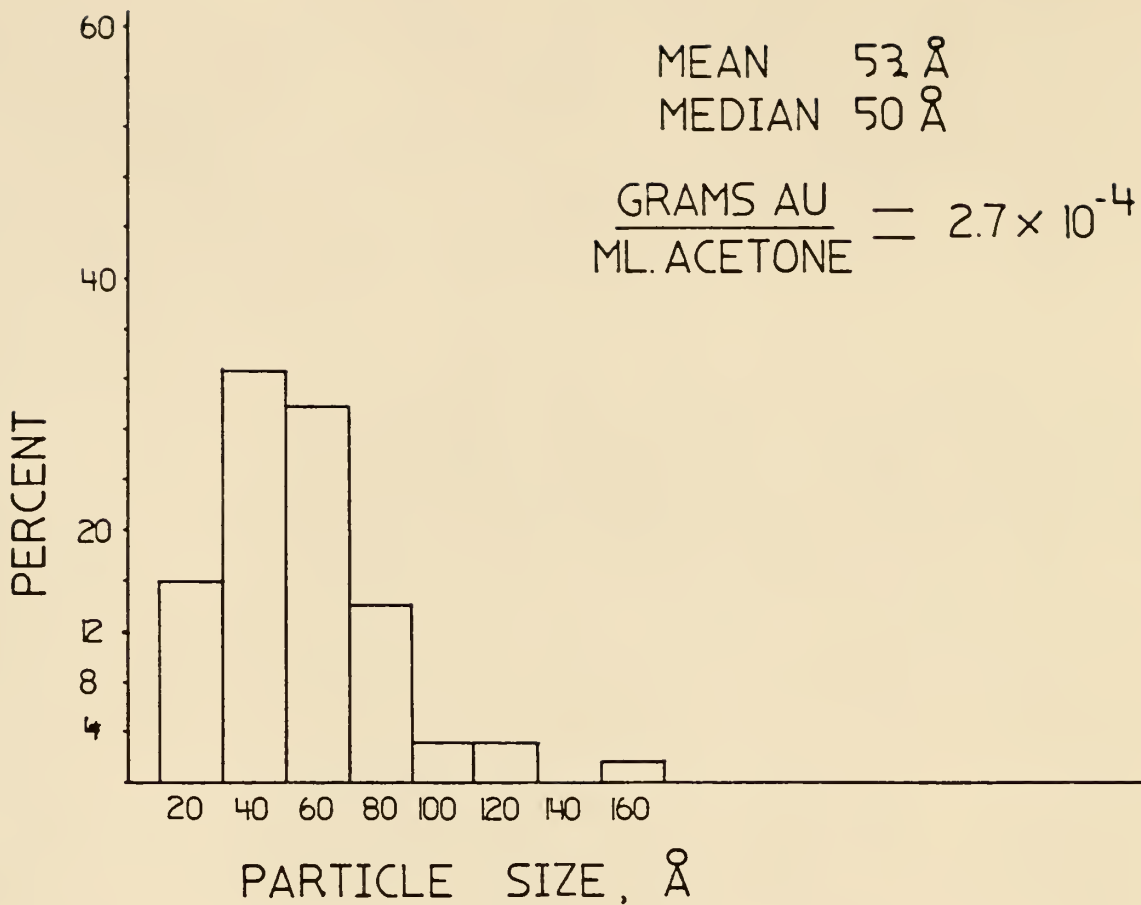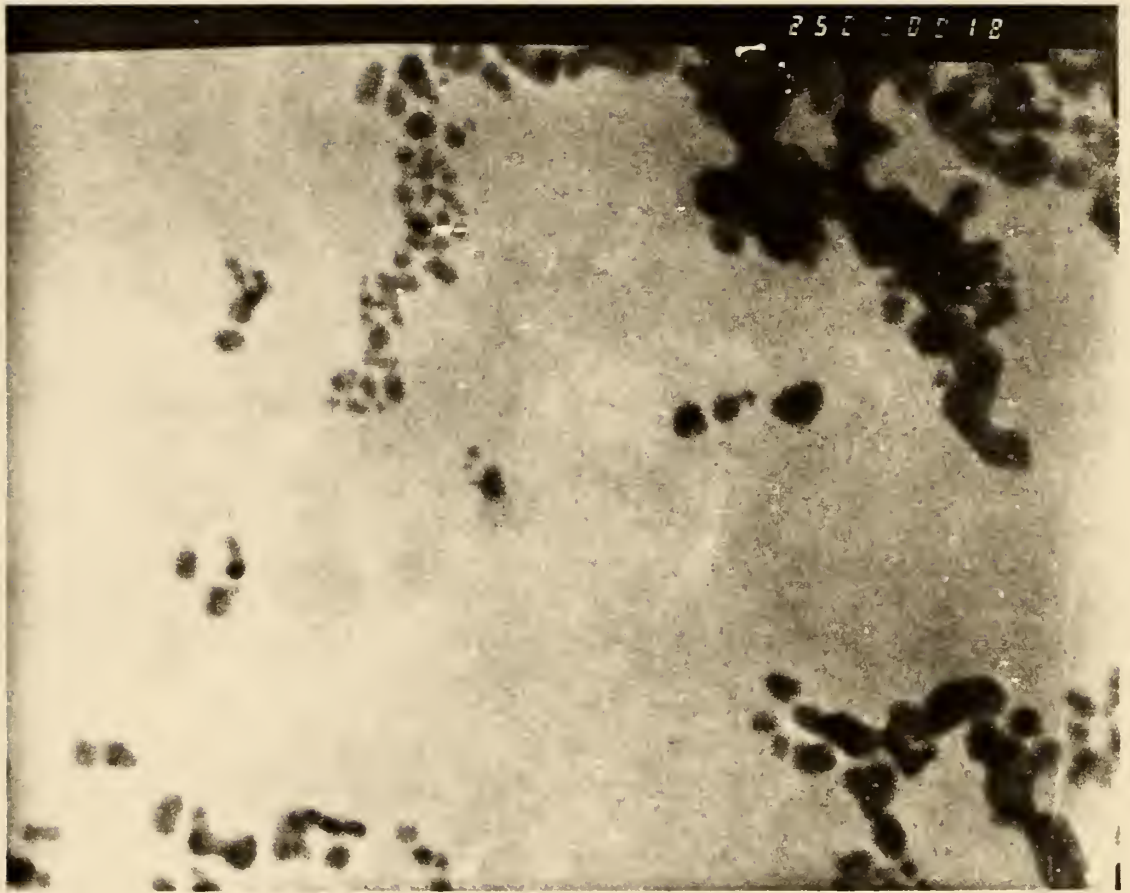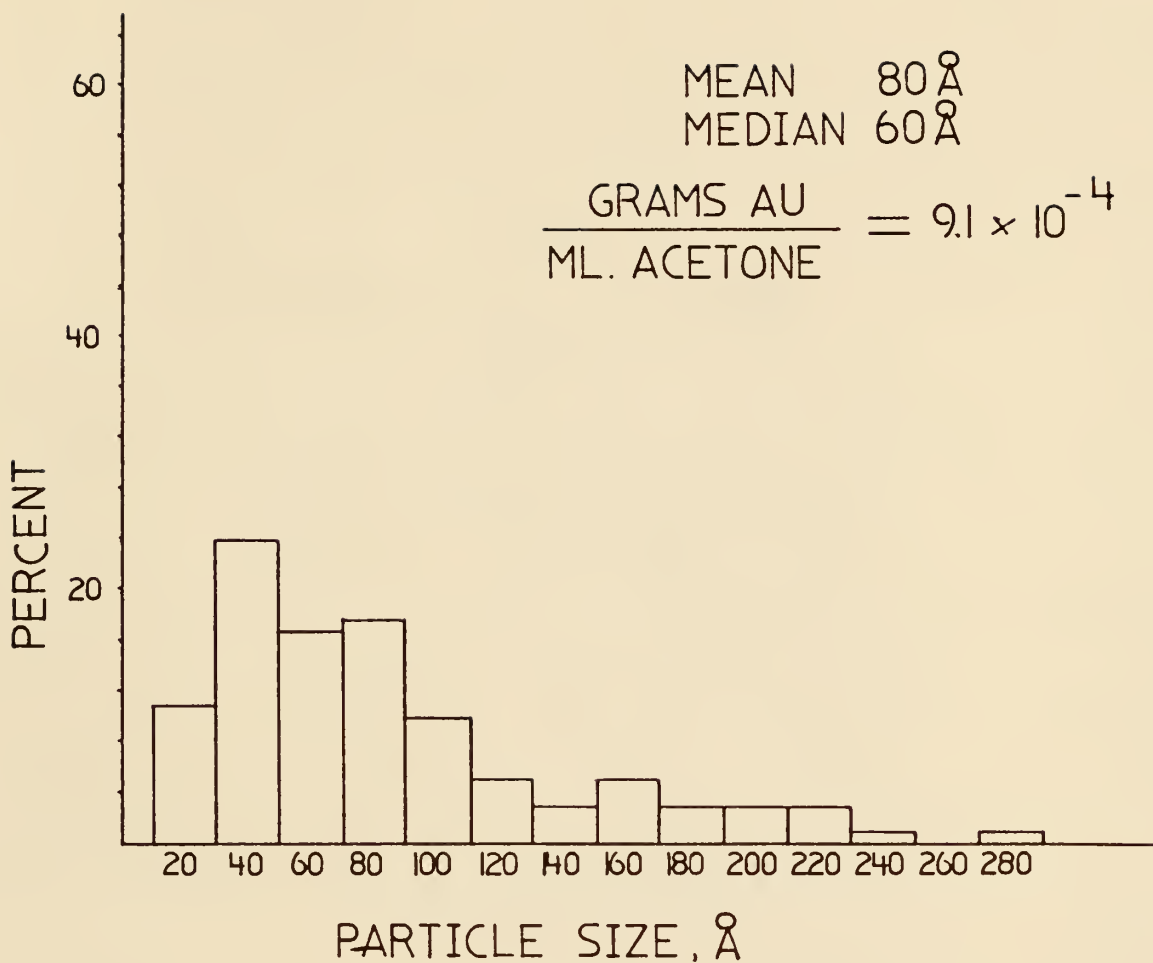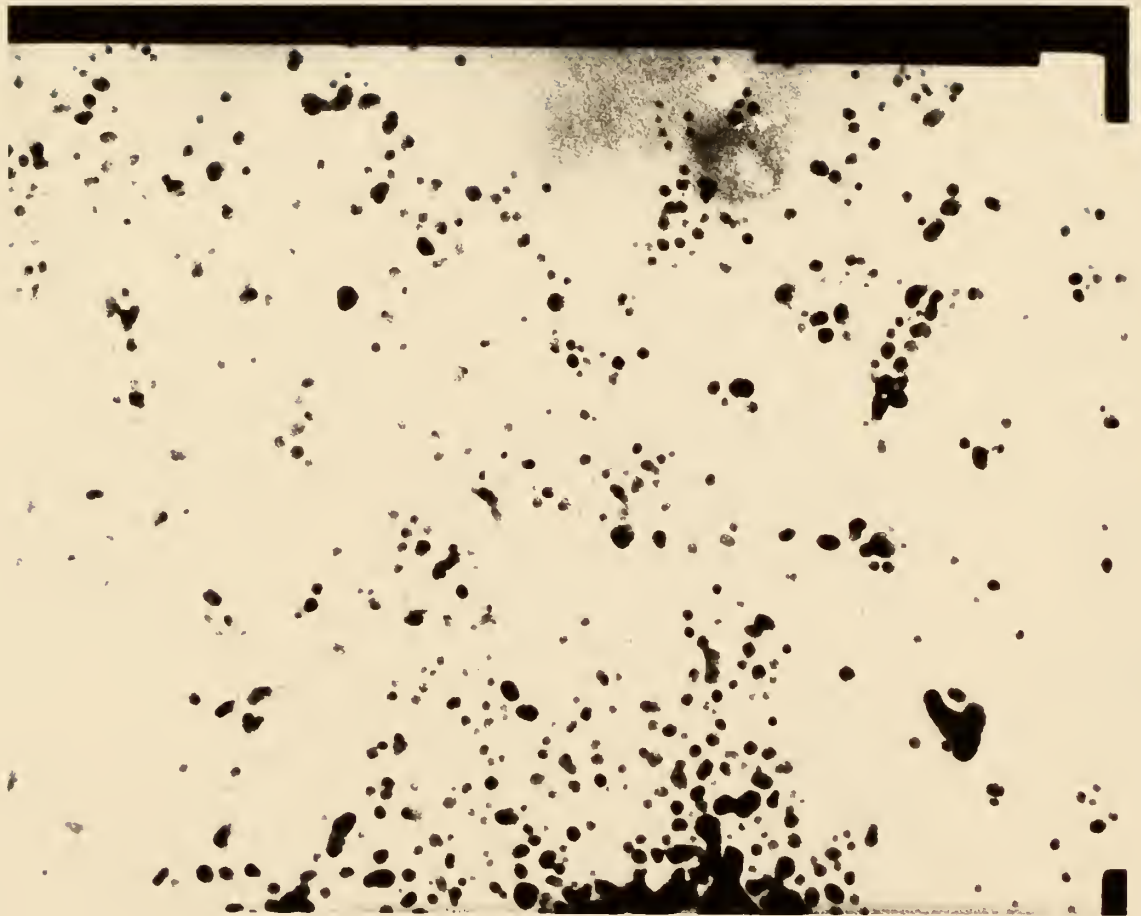$$\frac{\text{g Au}}{\text{mL acetone}} = 5.27 \times 10^{-5}$$

MEAN = 40 A

MEDIAN = 38 A
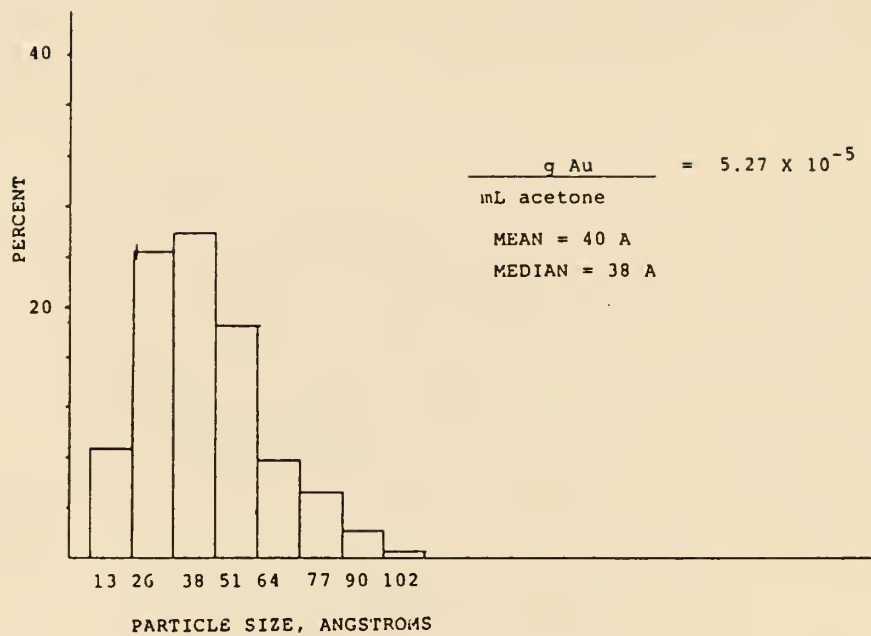
FIGURE 8.   Particle size distribution, MTF-112-S-01.
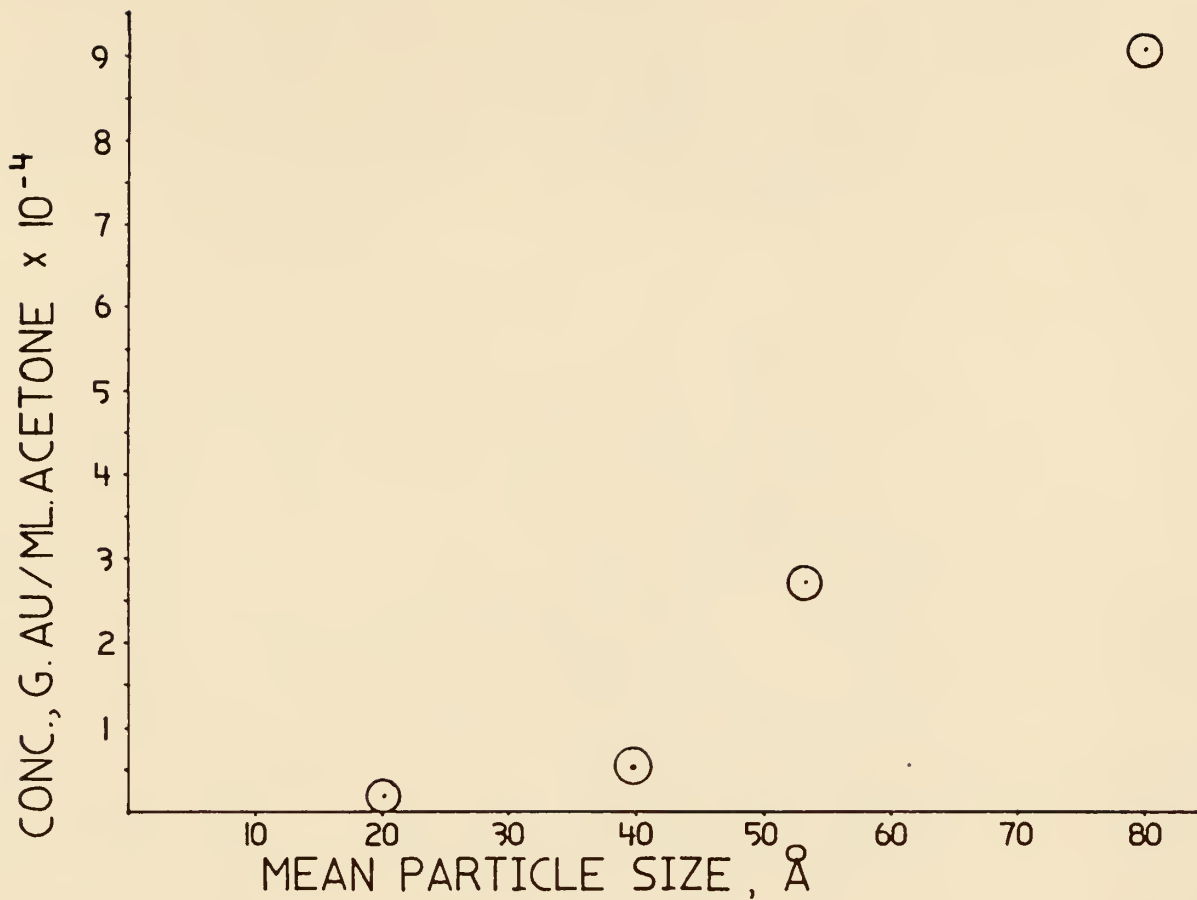
FIGURE 9. Concentration vs. Particle size, Gold Colloids:
MTF-82-S-01, MTF-80-S-01, MTF-82-S-01, and MTF-112-S-01.

II.3. Concentration Studies – Silver / Acetone

These experiments were carried out in almost exactly the same way as those with gold. The "standard" warmup method was used (1 hour warmup under static vacuum with a cold, empty dewar surrounding the reaction vessel).

The differences between gold and silver colloids formed is striking: while the color of the gold colloid solution is a very dark purple, the silver colloid solution is black. Also, the silver colloid is light sensitive. Samples which were exposed to the light would gradually turn a light gray, and the particles would precipitate as a spongy, gray mass after exposure to light for approximately 48 hours. Samples which were kept in the dark were stable indefinitely (up to 6 months).

The electron microscope reveals even more striking differences: the silver colloid particles are much larger than those of gold. It is also interesting to note the banded patterns in individual particles. At this time it is not known whether these striations are due to alternating layers of crystallites (each layer being the twin of the layers above and below it) or whether they are due to alternating layers of silver and organic material. The latter explanation seems more likely. It is not known whether the banded pattern is related to the light sensitivity of the colloid.

FIGURE 10

Silver / Acetone Colloid

250,000 X

MTF-125-S-01

$$\frac{g\ Ag}{mL\ acetone} = 1.57 \times 10^{-3}$$

mean particle size: 258 A

median particle size: 240 A

PERCENT

$$\frac{g\ Ag}{mL\ acetone} = 1.57\ X\ 10^{-3}$$

MEAN = 258 A
MEDIAN = 240 A

PARTICLE SIZE, ANGSTROMS
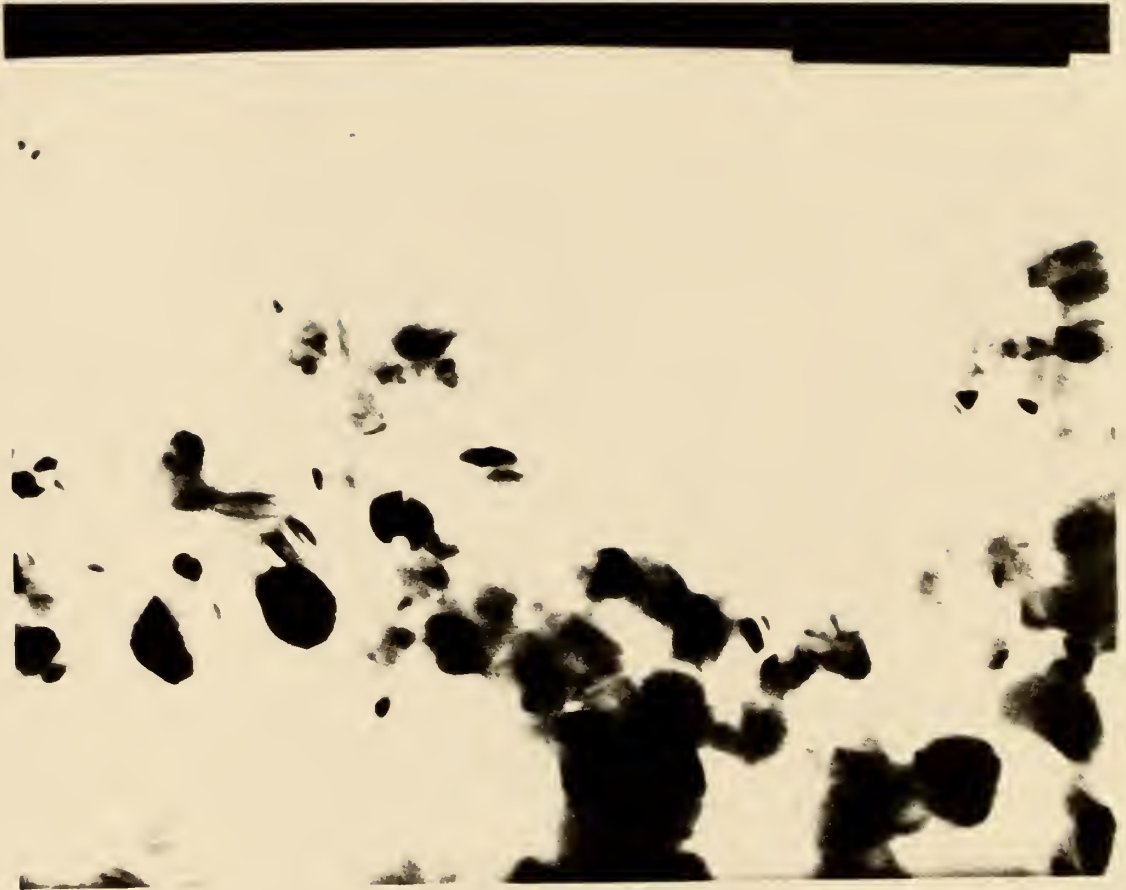
FIGURE 11.   Particle size distribution, MTF-125-S-01.

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FIGURE 12

Silver / Acetone Colloid

250,000 X

MTF-127-S-02

$$\frac{g\ Ag}{mL\ acetone} = 1.6\ X\ 10^{-3}$$

mean particle size: 376 A

median particle size: 260 A
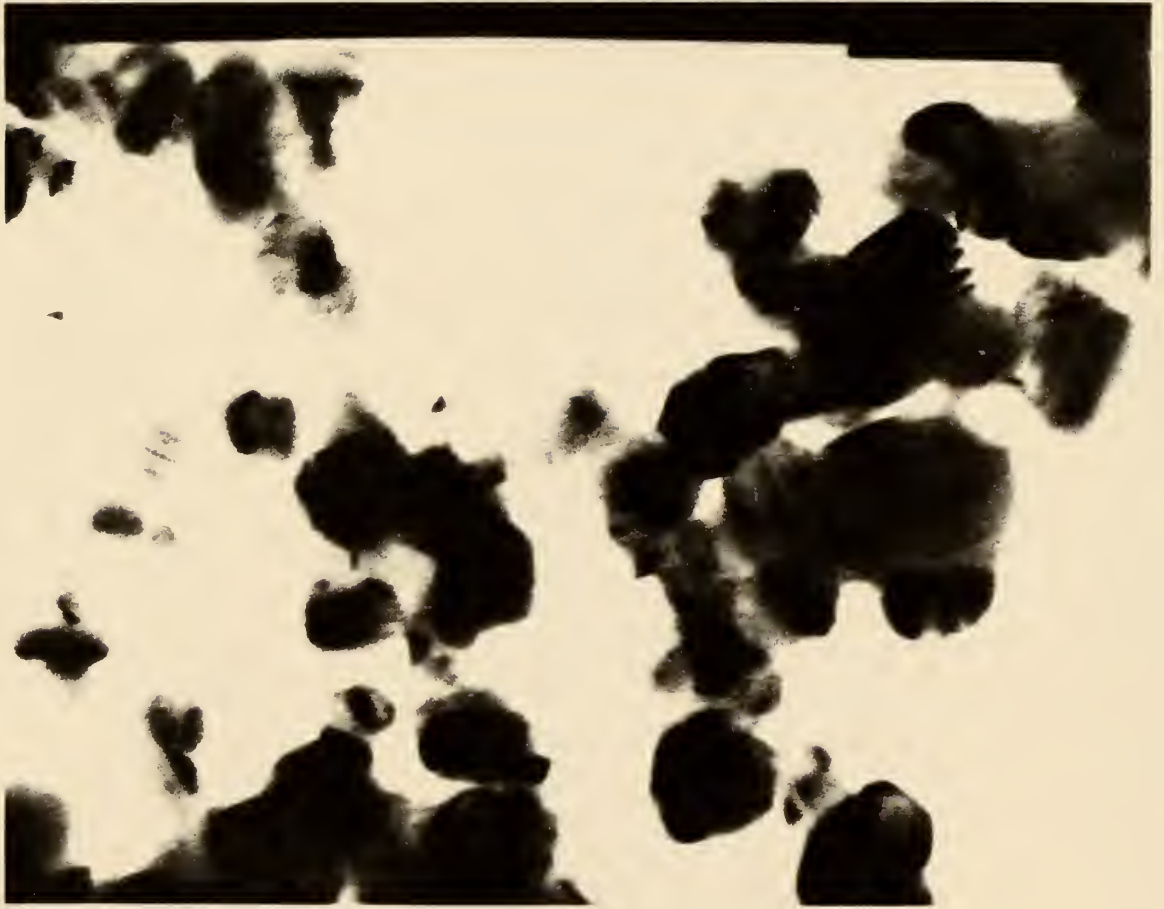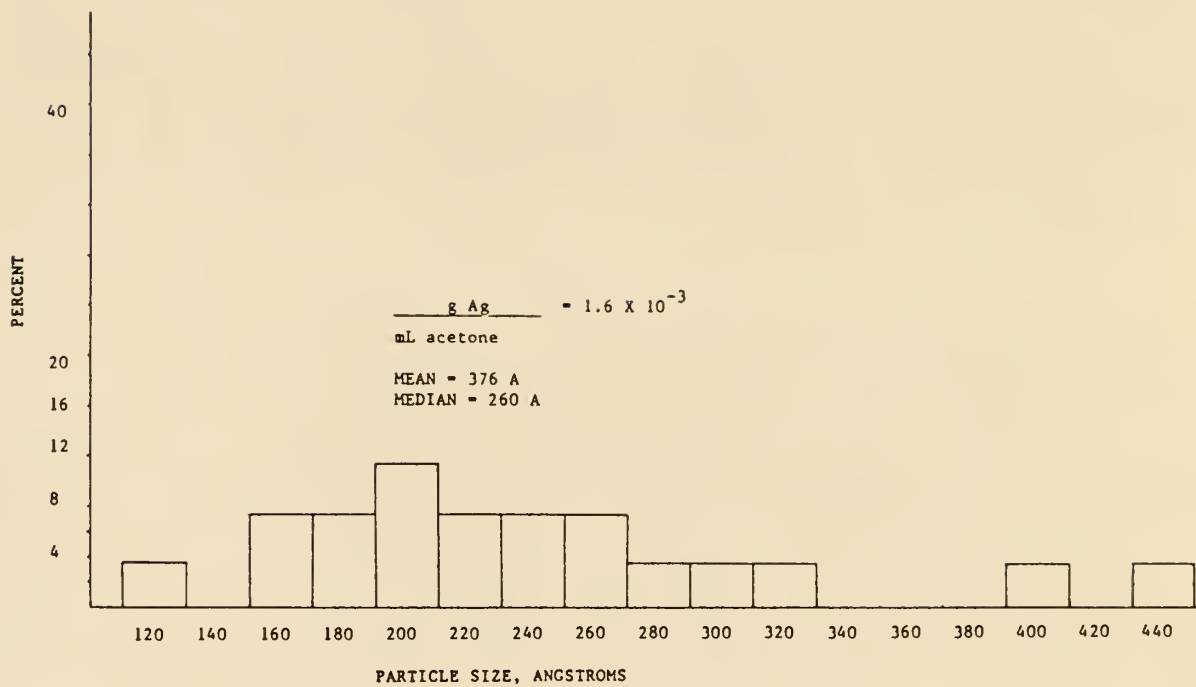
FIGURE 13.   Particle size distribution, MTF-127-S-02.

FIGURE 14

Silver / Acetone Colloid

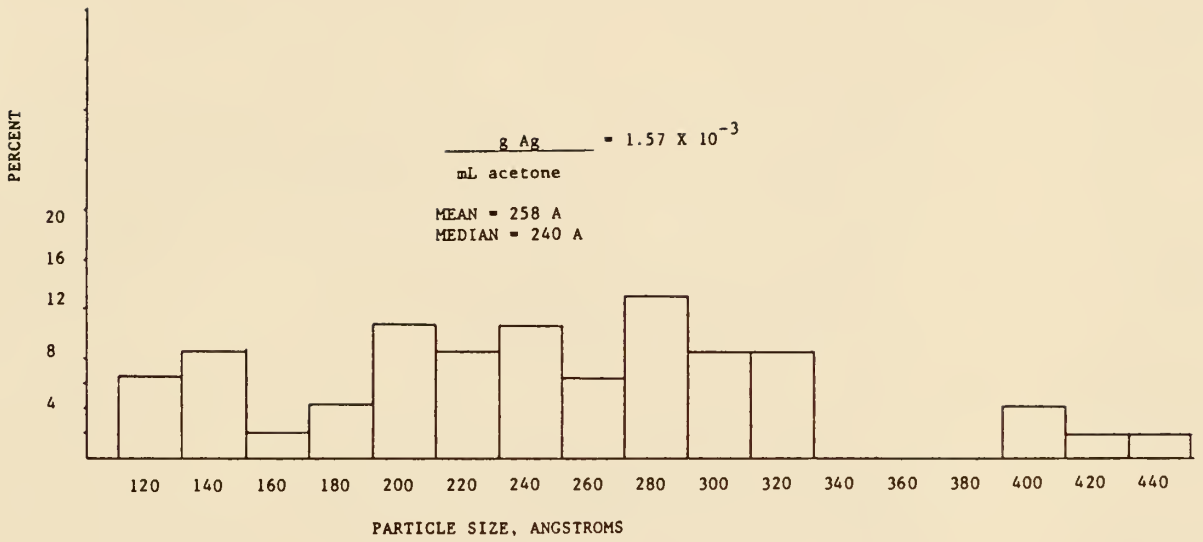160,000 X

MTF-113-S-01

$$\frac{g\ Ag}{mL\ acetone} = 2.1\ X\ 10^{-3}$$

mean particle size: 316 A

median particle size: 319 A
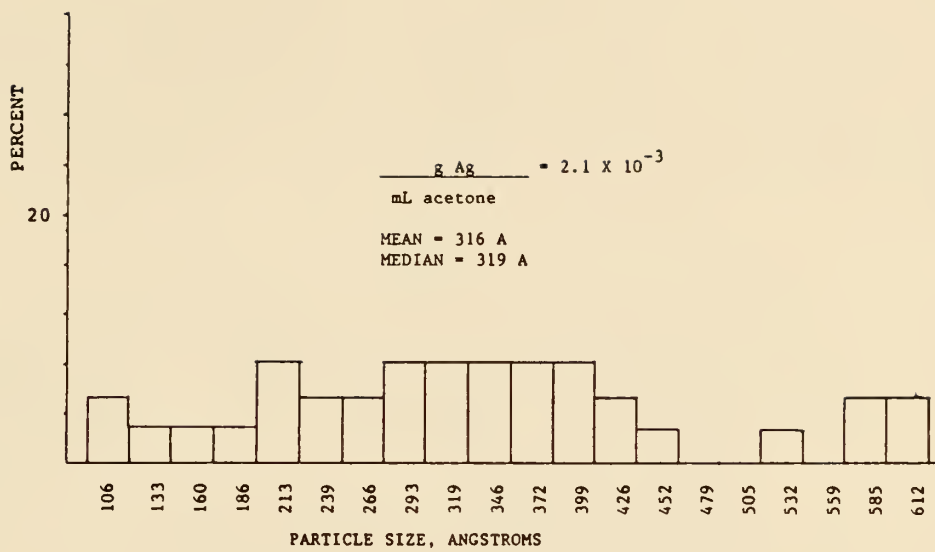
FIGURE 15.   Particle size distribution, MTF-113-S-01.
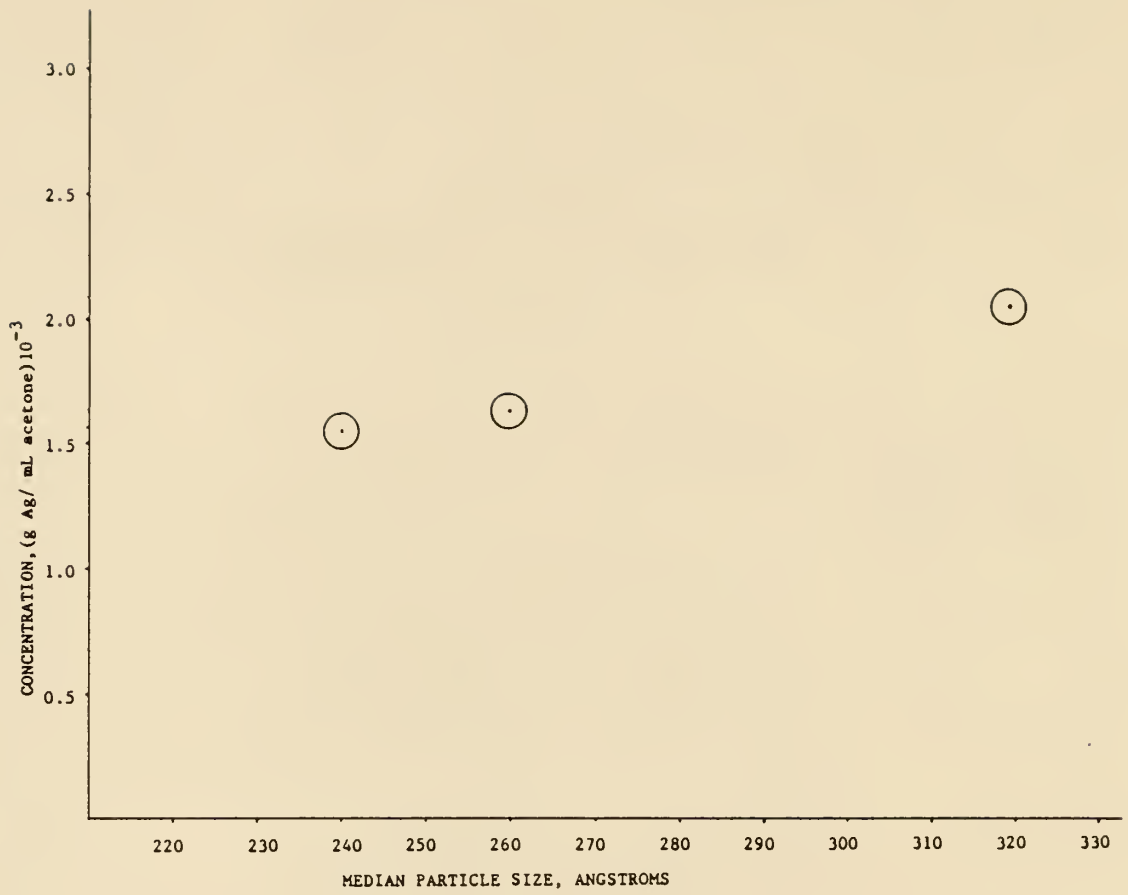
FIGURE 16.   Concentration vs. Particle size:

MTF-113-S-01, MTF-127-S-02, and MTF-125-S-01.

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Silver colloids showed a particle size dependence on concentration similar to that of gold. In these experiments, the concentrations of silver used were much greater than the amount of gold used in the previous studies of gold colloids, thus the particles were much larger. Since the silver sols were very polydisperse, median particle sizes were used in the correlation with concentration.

Klabunde and co-workers have studied the clustering of metal atoms in organic solvent matrices extensively. The systems most studied were Ni/alkane and Co/alkane. In (149) it was reported that the use of a large excess of pentane over Ni (>300:1, mole ratio) resulted in the formation of very small (<30 A) nonferromagnetic crystallites, while a smaller excess of pentane (<100:1) over nickel gave larger (780 A) ferromagnetic particles (particle sizes determined by soft x-ray scattering). In (148), Klabunde et. al. reported findings similar to these with respect to the question of ferromagnetism/nonferromagnetism in small particles formed from nickel atoms co-condensed with various other alkanes, but reported no size differences; however, such differences may have been overlooked with the size determination method used (H_2 chemisorbtion and nitrogen BET adsorbtion isotherms, spherical particles assumed). Electron photomicrographs of similar samples showed the assumption of spherical geometry to be invalid for some of the samples (153). The present study supports these earlier findings. The crucial question to be answered for all these systems has to do with the mechanism by which the organic

solvent moderates the clustering of the metal atoms and limits the clusters to a certain size.

Some of the first work toward addressing this question was performed by Klabunde et. al. (153). This investigation revealed the morphology of small nickel particles formed from the warmup of different organic matrices to be different.

In (154), Klabunde, Davis, Hattori and Tanaka discussed the factors influencing cluster growth from a metal atom/organic solvent dispersion. These factors are: (1) metal atom-solvent binding strength; (2) M_2-solvent, M_3-solvent, M_4-solvent,...$M_{(x)}$ solvent binding strengths; and (3) the viscosity of the solvent at the temperature at which the clustering takes place. M-M bond dissociation energy is not a factor since at these low temperatures, the clustering is probably irreversible.

There is another factor involved, and that is the reaction of the metal clusters with the solvent molecules. This has been observed experimentally (148,149,154,155) by the recovery of fragments of the original organic solvent used from the dry metal powder. The effect of matrix dilution and varying warmup conditions suggests the existence of competing reactions: metal clustering and cluster reaction with solvent. Once a small cluster reacts with an organic molecule to form a strongly bonded organic fragment, that "coordination site" is no longer available for the addition of another metal atom or small cluster. Thus the reaction with solvent inhibits the growth of the cluster. This works the other way too: once the cluster has reached a

certain size, it will be less reactive toward the solvent. The
combination of these two effects limits the final size of the
particles formed by encouraging a certain amount of nucleation
and then moderating the growth rate until all the limiting
reagent (metal) is used up.

The situation for gold and silver sol formation is believed
to be quite similar.

II.4. Concentration Studies - Copper / Acetone

The copper/acetone system was not very amenable to study, and few experiments were carried out with it. In most instances, black colloid was formed initially, but one which turned olive green and flocculated in less than 12 hours. One very dilute reaction mixture resulted in a stable green colloid. An interesting observation with this sample was that addition of a small amount of H_2O resulted in the formation of bubbles. A simple flame test revealed that the gas evolved was either H_2 or CH_4. This same experiment was tried with the gold and silver sols, with the same result.

No experiments were carried out to determine whether the color change and subsequent precipitation of the colloid was a result of light sensitivity, as was the case with silver.

II.5. Warmup Studies — Gold / Acetone

Davis and Klabunde reported that for the co-condensation of
nickel and alkane vapors, a temperature staged (slow) warmup of
the frozen matrix formed a nonferromagnetic metal powder with
crystallite sizes of < 30 A, whereas a direct warmup of the
frozen matrix resulted in the formation of larger (> 80 A)
ferromagnetic crystallites (149).

The experiments performed for the gold/acetone colloid system
support this earlier work. It was found that, without exception,
a fast (< 1 hour) warmup resulted in the formation of a flocculent
purple/gold mass that was definitely not colloidal, small gold
crystallites being visible. However, experiments with tempera-
ture-staged warmups always resulted in stable gold sols.

A series of organic solvent slushes, methanol/liquid N_2
(-95 C), ethanol/liquid N_2 (-117 C) and pentane/liquid N_2
(-130 C) were placed around the reaction vessel and left in place
for one hour, at which time they were removed and a cold, empty
dewar which had contained liquid N_2 was placed around the reactor
and left for one hour. During this procedure, a static vacuum
was maintained over the warming matrix until meltdown was
complete. A similar series of experiments was also performed in
which the slush baths were left around the reactor overnight.

No clear-cut trend relating warmup temperature to particle
size was established, other than the general trend stated above.

The explanation proposed for the lack of evidence for such a trend involves the difficulty of controlling the metal/acetone ratio in the matrix. As was seen in the previous sections, the metal/acetone ratio also has an effect on the resulting particle size, and this must be held rigidly constant in any experiments on the effects of temperature staging on particle size.

FIGURE 17

Gold / Acetone Colloid

250,000 X

MTF-89-S-01

$$\frac{g\ Au}{mL\ acetone} = 5.6\ X\ 10^{-4}$$

Warmup conditions: pentane/LN_2

slush overnight

mean particle size: 48 A

median particle size: 40 A

WARMUP CONDITIONS: pentane/ LN_2 slush overnight

CONCENTRATION: $\dfrac{g\ Au}{mL\ acetone}$ = 5.6 X 10^{-4}

MEAN = 48 A
MEDIAN = 40 A

PERCENT

PARTICLE SIZE, ANGSTROMS
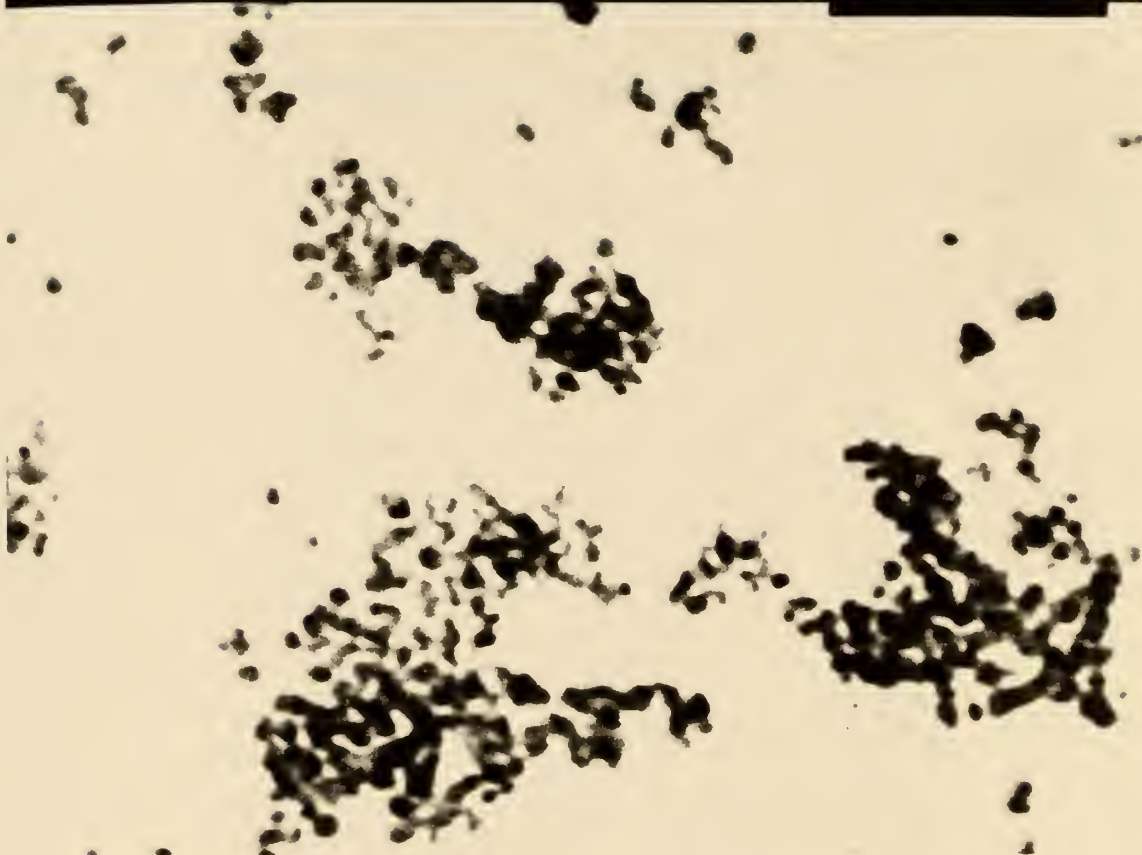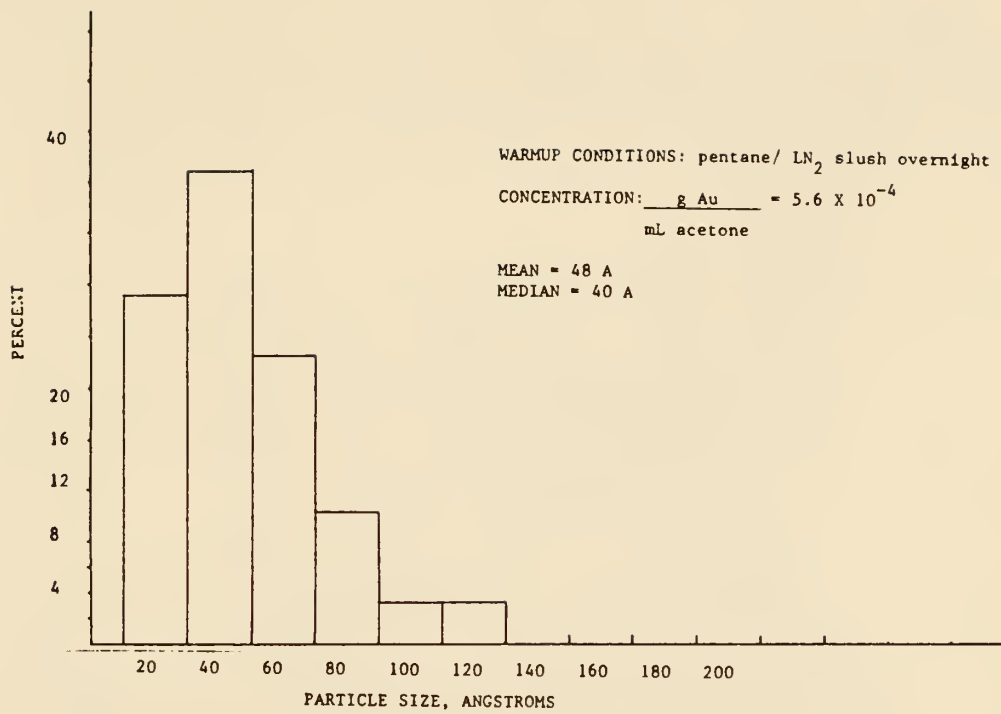
FIGURE 18.   Particle size distribution, MTF-89-S-01.

FIGURE 19

Gold / Acetone Colloid

250,000 X

MTF-90-S-01

$$\frac{g\ Au}{mL\ acetone} = 9.6\ X\ 10^{-4}$$

Warmup conditions: ethanol/LN_2

slush overnight

mean particle size: 34 A

median particle size: 40 A

WARMUP CONDITIONS: ethanol/ LN_2 slush overnight

CONCENTRATION: $\dfrac{\text{g Au}}{\text{mL acetone}}$ = 9.6 X 10^{-4}

MEAN = 34 A
MEDIAN = 40 A
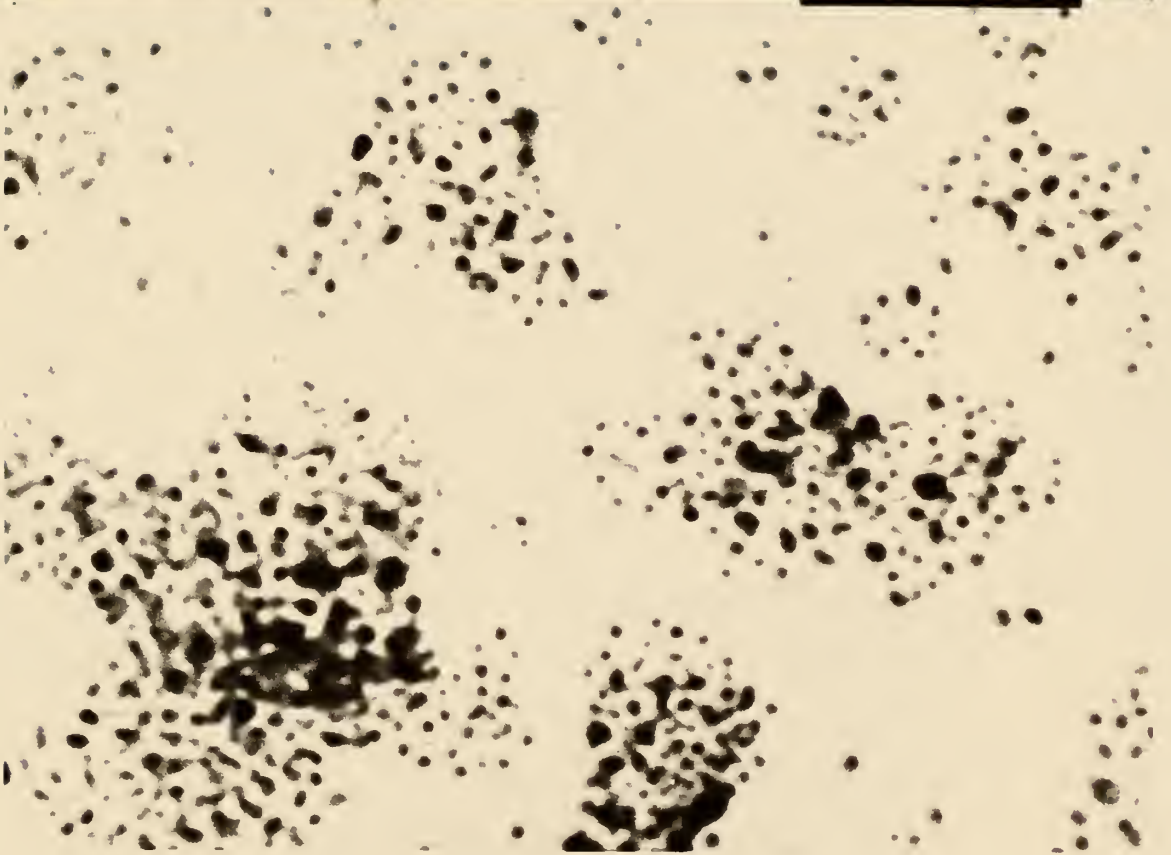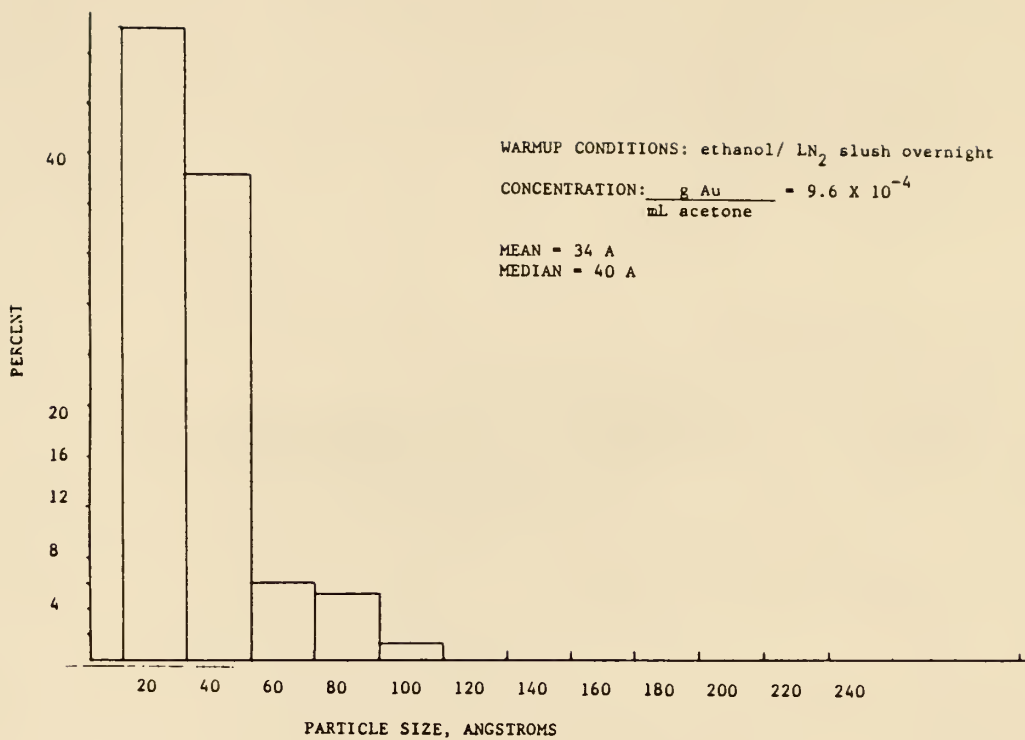
FIGURE 20.   Particle size distribution, MTF-90-S-01.

FIGURE 21

Gold / Acetone Colloid

250,000 X

MTF-91-S-01

$$\frac{g\ Au}{mL\ acetone} = 9.3\ X\ 10^{-4}$$

Warmup conditions: methanol/LN_2

slush overnight

mean particle size: 60 A

median particle size: 60 A

WARMUP CONDITIONS: methanol/ LN_2 slush overnight

CONCENTRATION: $\dfrac{g\ Au}{mL\ acetone}$ = 9.3 X 10^{-4}

MEAN = 60 A
MEDIAN = 60 A

PARTICLE SIZE, ANGSTROMS
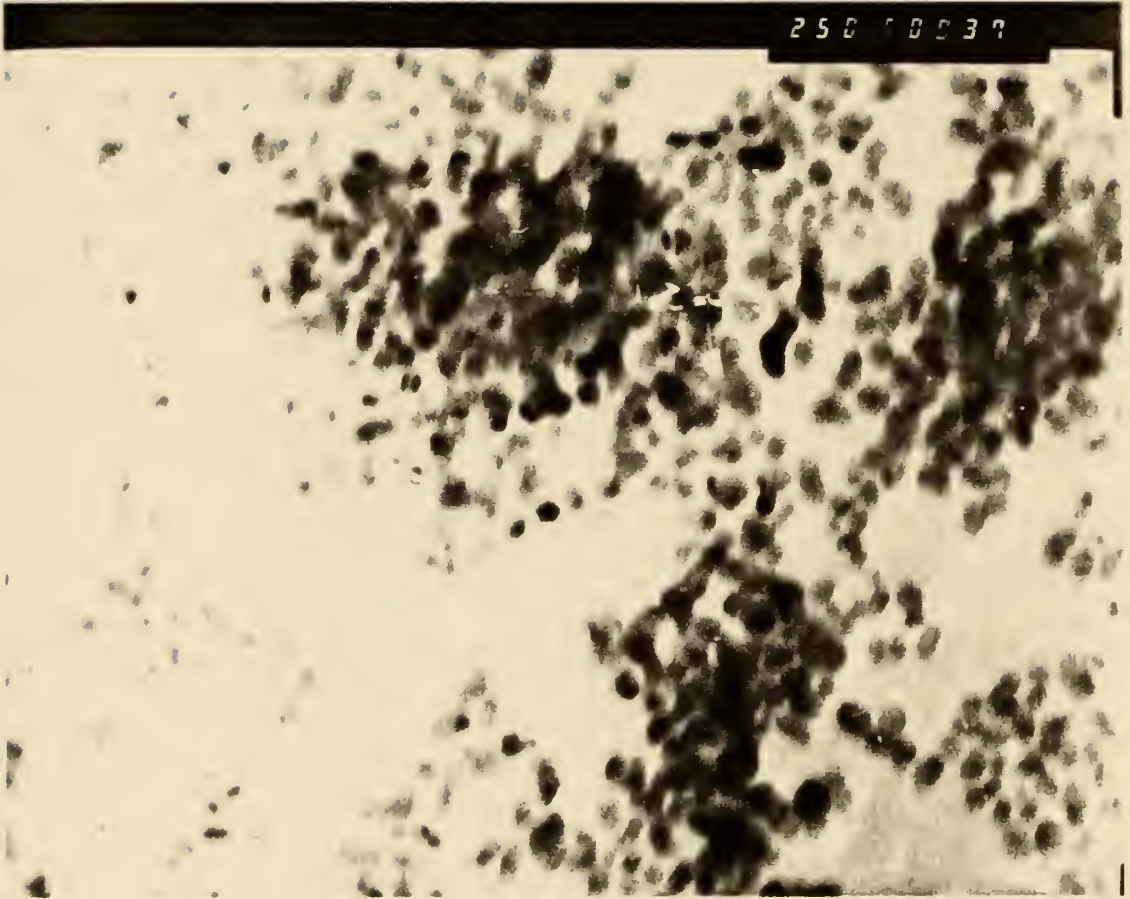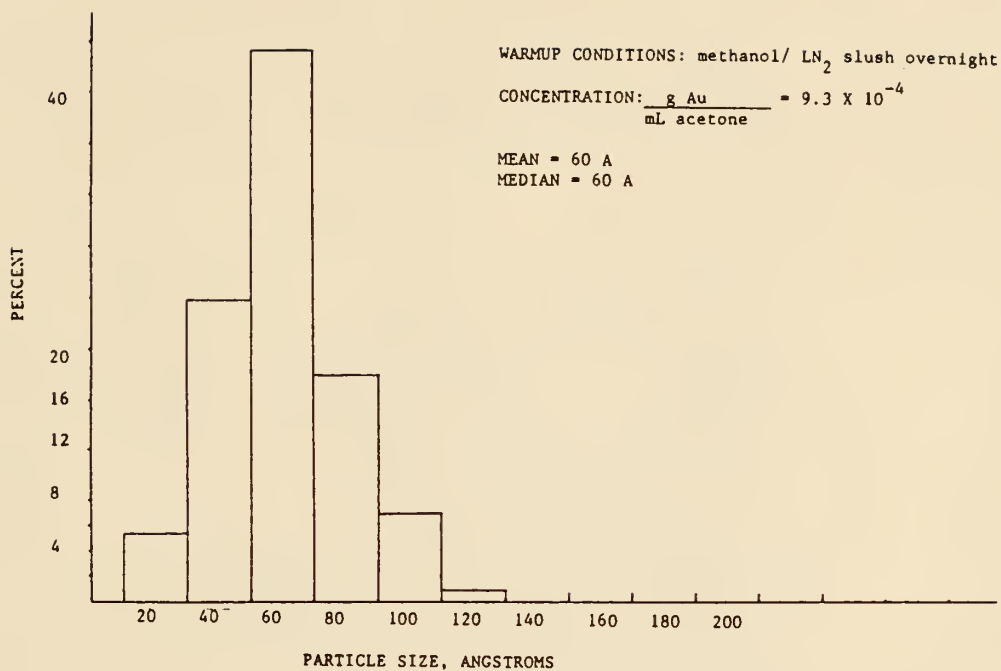
FIGURE 22.   Particle size distribution, MTF-91-S-01.

FIGURE 23

Gold / Acetone Colloid

250,000 X

MTF-88-S-02

$$\frac{g\ Au}{mL\ acetone} = 2.5 \times 10^{-3}$$

Warmup conditions: pentane/LN_2

slush, one hour

mean particle size: 68 A

median particle size: 60 A

WARMUP CONDITIONS: pentane/ LN_2 slush, one hour

CONCENTRATION: $\dfrac{g\ Au}{mL\ acetone}$ = 2.5 X 10^{-3}

MEAN = 68 A
MEDIAN = 60 A
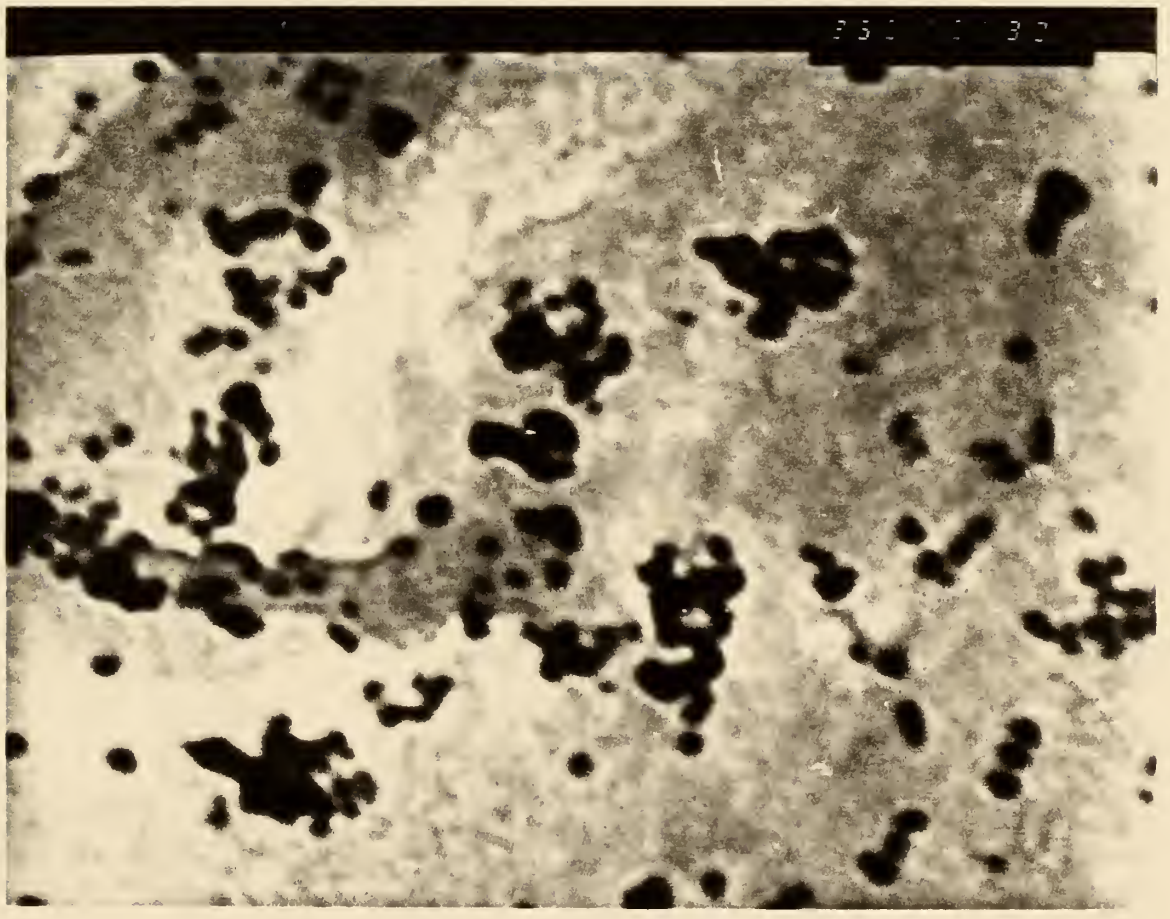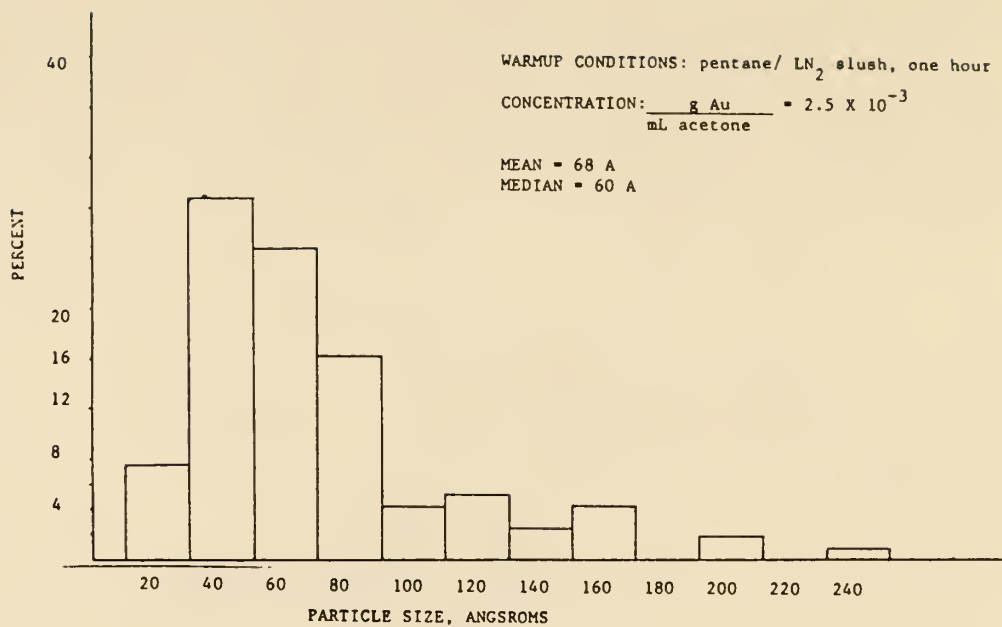
FIGURE 24. Particle size distribution, MTF-88-S-02.

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FIGURE 25

Gold / Acetone Colloid

250,000 X

MTF-86-S-01

$$\frac{g\ Au}{mL\ acetone} = 6.5\ X\ 10^{-4}$$

Warmup conditions: ethanol/LN$_2$

slush, one hour

mean particle size: 48 A

median particle size: 40 A

WARMUP CONDITIONS: ethanol/ LN_2 slush, one hour

CONCENTRATION: $\dfrac{g\ Au}{mL\ acetone}$ = 6.5 X 10^{-4}

MEAN = 48 A
MEDIAN = 40 A

PERCENT

PARTICLE SIZE, ANGSTROMS
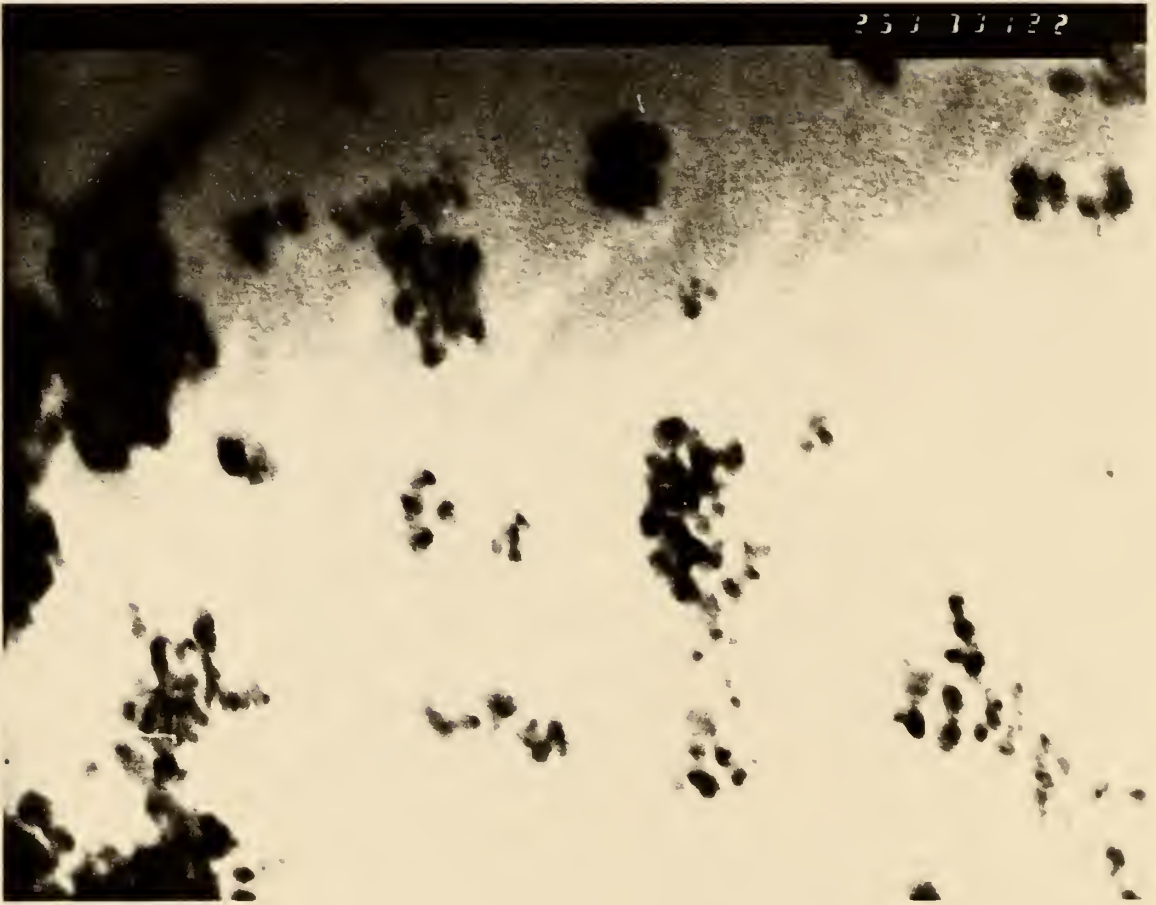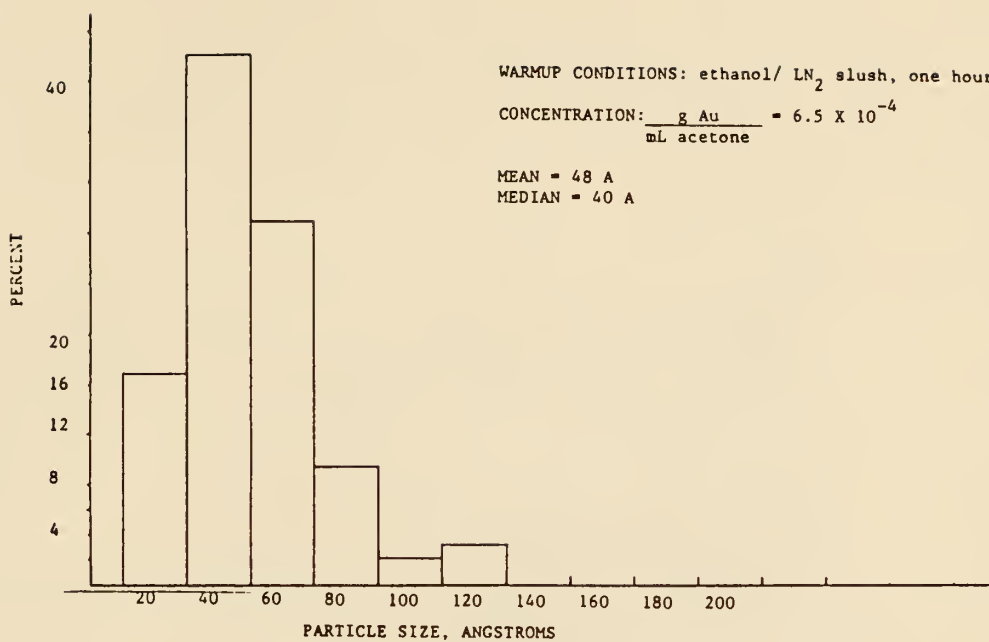
FIGURE 26.   Particle size distribution, MTF-86-S-01.

FIGURE 27

Gold / Acetone Colloid

250,000 X

MTF-88-S-01

$$\frac{g\ Au}{mL\ acetone} = 5.4\ X\ 10^{-4}$$

mean particle size: 38 A

median particle size: 40 A

WARMUP CONDITIONS: methanol/ LN_2 slush, one hour

CONCENTRATION: $\dfrac{g\ Au}{mL\ acetone}$ = 5.4 X 10^{-4}

MEAN = 38 A
MEDIAN = 40 A
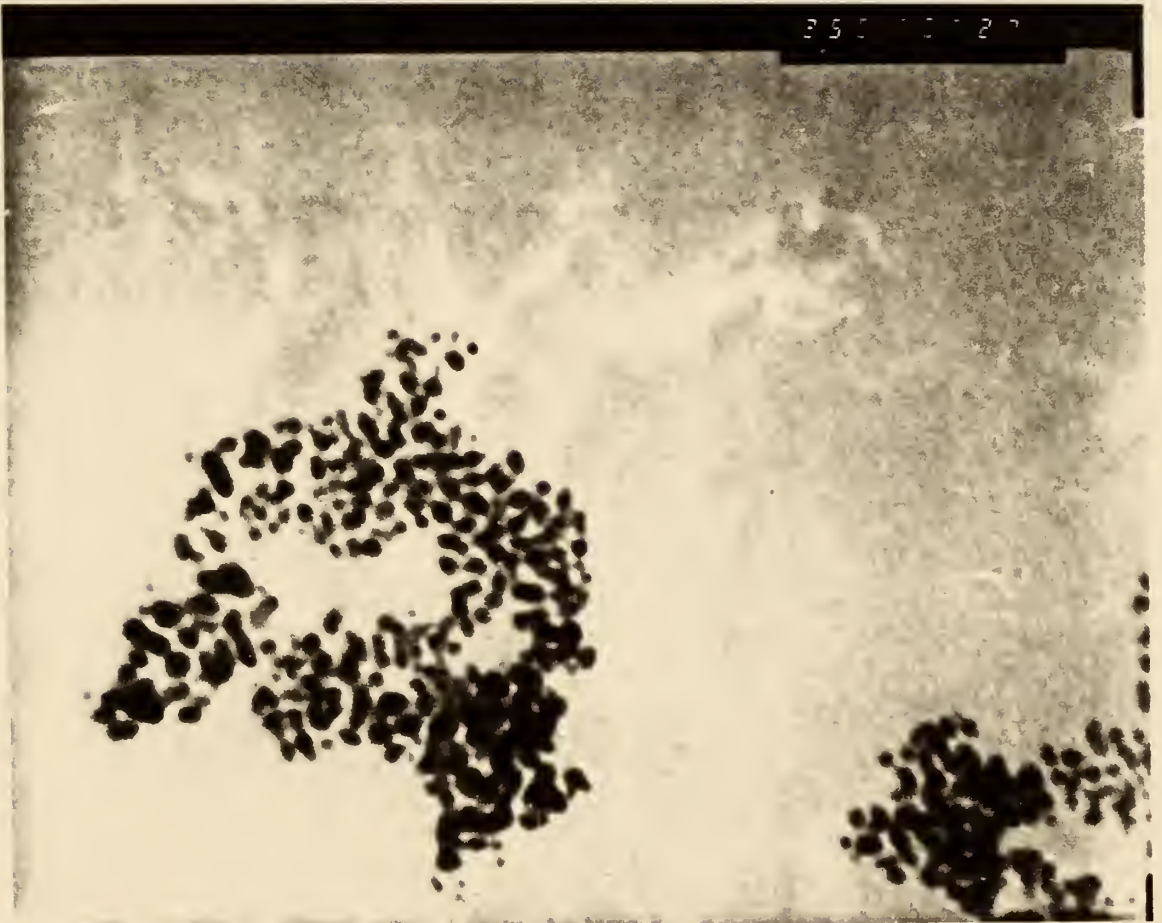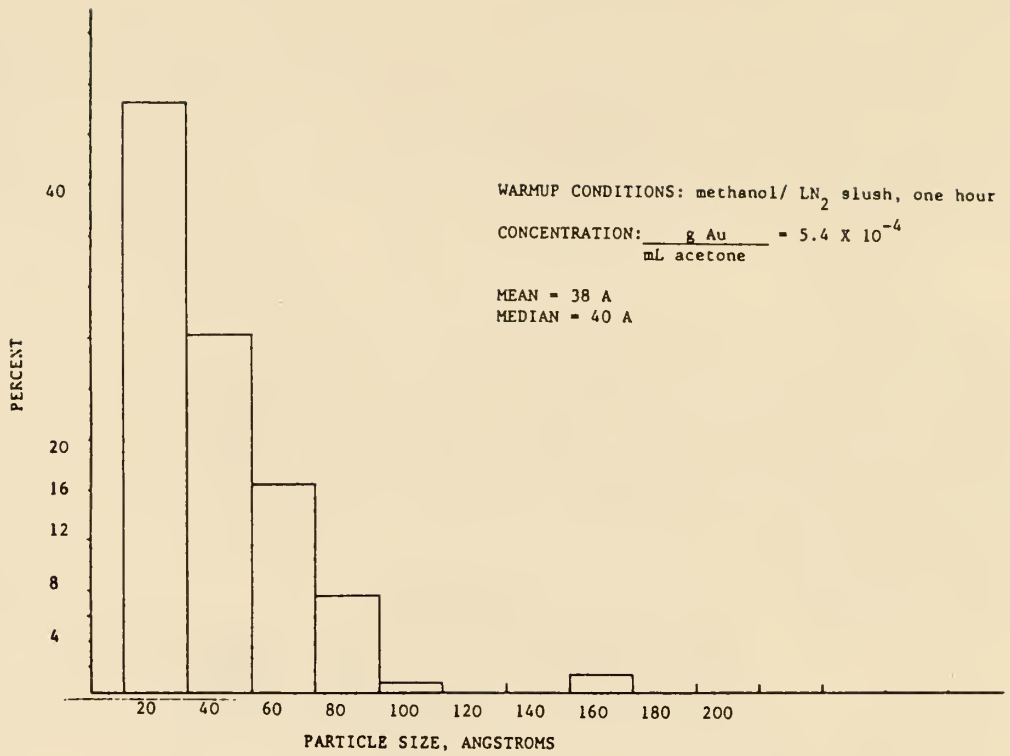
FIGURE 28. Particle size distribution, MTF-88-S-01.

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## II.6. Spectroscopic Studies – Gold / Acetone Sols

A. UV-visible

UV-visible spectra were recorded for gold sols only. The absorptions attributed to the gold sol particles occurred at 706 nm and at 572 nm. The absorption at 572 nm was attributed to plasmon absorption by the conductive particles (136,137,138).

Visible absorption spectra have been used as a method of determining particle size in gold colloids, smaller red particles absorbing in the range 500-550 nm and blue sols absorbing in the range 580-650 nm (for aqueous sols) (139,140). Jeppeson and Barlow reported that a red gold colloid absorbed at 525 nm. Electron microscopy revealed that the particles formed were smaller than 40 A (141). This method is not a foolproof way of obtaining particle size, however. The color of the sol is very sensitive to such things as the concentration of reagents used to make it, pH, electrolyte additions and additions of adsorbed substances such as proteins (142,143,144,145).

II.6. Spectroscopic Studies – Gold / Acetone Sols

B. Nuclear Magnetic Resonance

The solvent (acetone) was evaporated from a gold colloid under vacuum and collected in a trap at 77K. The ^{1}H NMR of this solvent showed only a singlet due to the six equivalent hydrogens on acetone. No other species were detected, even when the acetone peak was blown up until it was off the scale.

4.0   3.0   2.0   1.0   0.0   -1.0

PPM
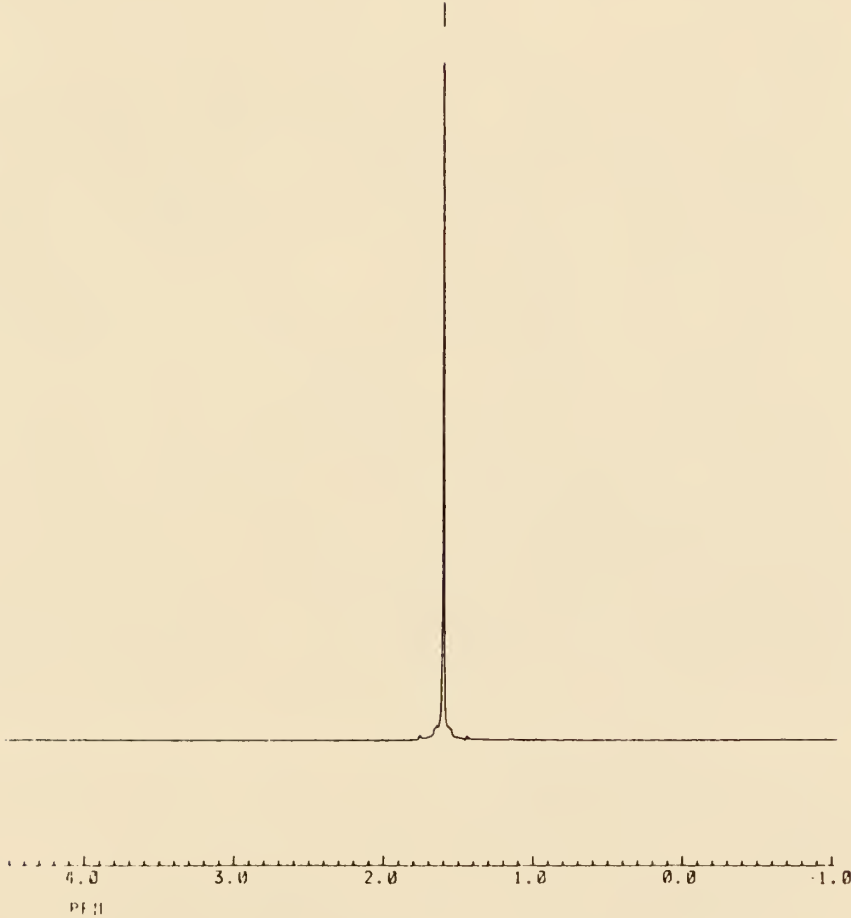
FIGURE 29. ^{1}H-NMR spectrum of acetone

removed from gold colloid solution.

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ACETONE AFTER REACTION WITH AU

FIGURE 30. Appearance of Figure 29 magnified 128 times.

II.7. Electrophoresis – Gold / Acetone Sols

The phenomenon of electrophoresis, the movement of charged
particles or macromolecules in response to an electric potential
was discovered by Reuss and reported in 1809. He thrust two
glass tubes into a lump of moist clay, placed a layer of sand in
the bottom of each tube, and filled the tubes partially with
water. He then applied the direct current generated by 74
silver/zinc cells across the clay by means of electrodes immersed
in the water. The positively charged side of this system became
cloudy due to the migration of negatively charged particles
through the sand layer. The water in the negatively charged side
rose, demonstrating the phenomenon of electro-osmosis (164).

Picton and Linder studied the movement of the boundaries of
colloidal As_2S_3, shellac, Fe_2O_3 and hemoglobin solutions confined
in a U-shaped tube and subjected to a direct current. They
reported that reversal of the current reversed the direction of
the migration (165,166).

Hardy showed that negatively charged denatured colloidal egg
albumen could be made positive by the addition of acid. The
concentration of acid needed to reduce the particle's mobility to
zero was called the "isoelectric point" (167).

Svedberg and Tiselius extended the utility of this method
for the separation of proteins, by the use of ultraviolet
radiation which made the proteins fluoresce. This fluorescence

could then be photographed, and intensity measurements made at various points in the apparatus allowed a quantitative estimation of the boundary positions of different proteins (168).

Prideaux and Howitt noted that when albumin, gelatin or casein were adsorbed upon gold sols, the electrophoretic velocities of the sols matched those of the neat proteins (169). This observation pointed to the importance of the colloidal particles' surface condition in the electrophoresis experiment. Prideaux and Howitt exploited this finding by electrophoresing various agar sols which were rendered visible by the addition of a purple gold sol (170).

Tiselius ushered in the era of preparative electrophoresis. He constructed the familiar U-tube apparatus from rectangular glass curvettes that were joined by flat ground glass surfaces. A desired protein fraction (for example) could be isolated from solution after electrophoretic separation merely by sliding out the section of the apparatus containing that fraction (171). Preparative electrophoresis is now a widely-used technique, especially in the biological sciences. Nowadays it is generally carried out on paper sheets or gel films rather than in solution.

Philpott developed a cylindrical lens optical system which improved the location of boundaries between components in an electrophoretic separation by displaying them as peaks. An added benefit of this system was that the relative concentrations of the components were reflected by the peak heights. This lens system also found use in ultracentrifugation (172).

Pt electrodes

filler tube

CELL FOR SOLUTION
ELECTROPHORESIS :

PATH LENGTH = 223 mm
POTENTIAL = 12.6 VDC

pyrex glass construction

PTFE
stopcock
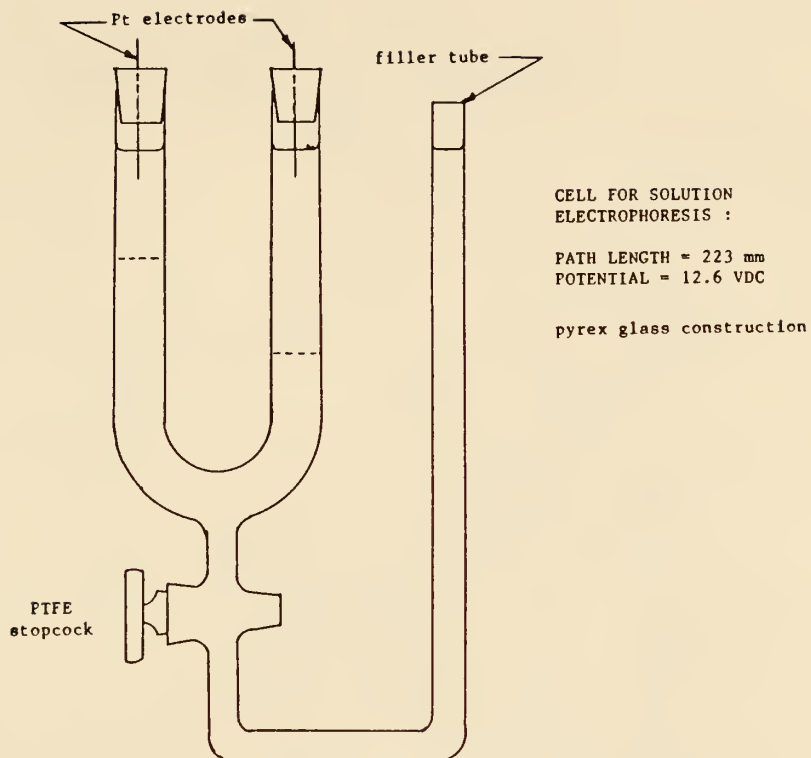
FIGURE 31.   Diagram of electrophoresis cell used for
determination of electrophoretic velocities.

In the present study, experiments were carried out in a U-tube apparatus similar to that described by Burton (173). Neat acetone was placed in the U-tube, until the limbs were approximately half-full. The gold/acetone colloid was run in under the neat acetone by means of a stopcock in the bottom of the U-tube, carefully so that a sharp boundary was maintained between the clear acetone and the dark purple colloid. Next, platinum wire electrodes were placed in the top ends of the tube, and a direct current applied across them. The boundary was marked at the beginning of the experiment, and again at the end, and the distance and time recorded.

The raw data for the electrophoresis experiment is recorded here:

TABLE 2

Sample #	Electrophoretic Velocity toward (+) electrode
MTF-90-S-01 (gold/acetone)	1.7 μ/S
MTF-91-S-01 (gold/acetone)	2.2 μ/S
MTF-86-S-01 (gold/acetone)	1.2 μ/S

The relation between electrophoretic mobility (the electrophoretic velocity divided by the potential gradient) and the surface properties of the particle (usually modeled as an ionic double layer for aqueous colloid systems) is a classical problem in colloid science. The Helmholtz-Smoluchowski equation can be

$$\frac{U}{X} = \frac{\epsilon \zeta}{4 \pi \eta}$$

considered as the oldest solution to this problem. In this

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equation:

   U = electrophoretic velocity

   X = strength of the applied dc field

   ς = electrokinetic potential

   ϵ = dielectric constant of the medium

   η = viscosity of the medium (Stokes) (174)

The validity of this expression has been long known to be
rather restricted, and much refinement has been carried out. In
1924, Hueckel published a detailed calculation of the electro-
phoretic retardation force, which can be thought of as analogous
to the retardation force which develops in an electric motor to
counter the applied force. On the basis of this modification,
Hueckel came up with the following modified equation (175):

$$\frac{U}{X} = \frac{\epsilon \varsigma}{6 \pi \eta}$$

The apparent contradiction between these two expressions was
resolved by Henry, who took into account the deformation of the
applied dc field by the presence of the particles. This expres-
sion was originally derived for an insulating particle, but there
is strong theoretical evidence (supported by experiment) that
even metallic particles can be treated as insulators in electro-
phoresis (176). Henry's expression is:

$$\frac{U}{X} = \frac{\epsilon \varsigma}{6 \pi \eta} f_1 (ka)$$

The dimensionless product ka is a measure of the ratio between
the particle radius and the thickness of the (ionic) double

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layer. In the limit ka→∞(when the double layer is very thin compared with the radius), f_1 (ka) = 3/2 and the result is the Helmholty-Smoluchowski equation. In the limit ka→0, f_1 (ka) = 1 and Hueckel's result is obtained.

Application of any of these expressions to the gold/acetone colloid system poses a number of problems. First of all, these equations are all predicated on the DLVO theory of stabilization for colloidal particles, in which the formation of a tightly adsorbed layer of ions is supposed to account for the charge on the particle, and an outer, more loosely attracted layer of counterions stabilizes the particle in solution by repelling the similarly charged outer layers of other particles, preventing coagulation (177). Although the gold/acetone system must contain some kind of positively charged species to preserve electrical neutrality and to allow electrophoresis to occur, the nature of this species is unknown, as is the nature of the charged particle interface. Also, the theoretical models have usually been tested in aqueous systems. Their validity for non-aqueous systems (different dielectric constant, different viscosity) is unknown. One serious difficulty in all the theoretical models is that of the two quantities which they relate, ζ-potential and electro- phoretic mobility, only one, the electrophoretic mobility, can be directly determined. ζ-potential can be determined by other methods, for example by streaming potentiometry, but the theory here shares many features of electrokinetic theory, and therefore methods for determination of ζ-potential are not completely

theory-independent.

The Hueckel equation for small ka is the one most likely to be applicable to electrophoresis in non-aqueous media (184):

$$\frac{U}{X} = \frac{\epsilon \, \zeta}{6\pi\eta}$$

solving for ζ :

$$\zeta = \frac{U}{X} \, \frac{6\pi\eta}{\epsilon}$$

For the gold/acetone system the values are:

η = kinematic viscosity of acetone = 0.400 centipoise (178)

X = potential gradient for U-tube = 0.568 V/cm

ϵ = dielectric constant for acetone = 20.7

Solving for the three samples tested obtains the following values:

TABLE 3

MTF-90-S-01	ζ =	-840 mV
MTF-91-S-01	ζ =	-1080 mV
MTF-86-S-01	ζ =	-590 mV

These values are much higher than those usually reported for gold sols in aqueous solution (180).

TABLE 4

Sample	$\dfrac{U}{X} \dfrac{cm^2}{V\ S}$ x 10^{-5}	ζ (mV)	Author
Colloidal gold	40	−58	Whitney & Blake
Colloidal gold	32	−32	Burton
Pt sol	30	−44	Whitney & Blake
Pt sol	20	−30	Burton
Colloidal Pb	12	−18	Burton

The reasons for these great deviations are at present unknown, and it is unknown whether these are true values or if this is a case where the generally accepted equations do not apply. It is also possible that our experiment set-up was too crude to produce good results, but as was stated above, the design is very similar to that which Burton used to determine the ζ-potential for gold sols in the table above.

It is possible to calculate the charges on the particle from the ζ-potential by the following expression.

$$\zeta = \frac{e}{E}\ \frac{(r_1 - r)}{r\ r_1}$$

where:

    e = charge (coulombs)

    r_1 = radius of particle and tightly adsorbed ionic layer

    r = radius of particle

    E = dielectric constant of the medium

For the gold colloid system, we can calculate the charge on

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the individual particles, assuming the value $(r_1 - r)$ to be 3 A:

$$e = \frac{E\ r_1\ r\ \gamma}{(r_1 - r)}$$

TABLE 5

Sample #	av. particle size, A	charge, coulombs
MTF-90-S-01	34 A	7.3×10^{-7}
MTF-91-S-01	60 A	2.8×10^{-6}
MTF-86-S-01	48 A	9.9×10^{-4}

The origin of the particle's charge is presently unknown. It may be due to some unknown capacitance effect associated with the metal atom reactor, although Klabunde and co-workers' experience with the formation of small nickel and cobalt particles seems to rule this out (148,149). Although the nickel and cobalt particles are of colloidal dimensions, there apparently exists no mechanism for stabilizing them in solution.

Henglein and co-workers and Meisel and co-workers have reported that for systems of aqueous gold colloids containing a small amount of acetone and 2-propanol, gamma irradiation by ^{60}Co produced free radicals which transferred an electron to the colloid particle. This electron had a high enough potential to reduce H_2O, and its transference to the gold particle extended it lifetime so that it could react with H_2O in a diffusion-controlled way. In effect, the gold colloid catalyzed the reduction of H_2O by the acetone free radical (156,157,158,159,160,161). It is known that free radicals can be formed by high temperatures and

trapped in frozen organic matrices (162,163). Under our experi-
mental conditions, radicals could be formed in the gas phase by
contact with the hot crucible, then trapped by the cold matrix on
the reactor walls. Warmup would then release these free radicals
to transfer their electrons to the metal clusters.

It is also possible that the charge is formed by static
electricity. This was proposed by some of the early authors on
the subject (167).

II.8. Miscellaneous Observations - Metal Sols

Conductance Measurements

The conductance of various gold/acetone colloids were measured and compared with neat acetone, as well as various concentrations of NaI in acetone and in a gold/acetone colloid.

TABLE 6

Solution	Conductance (M ohms $^{-1}$ cm^{-1}) (23 °C)
Neat Acetone	4.5
MTF-80-S-01	2.5
MTF-82-S-01	2.5
MTF-82-S-02	2.8
MTF-86-S-01	2.8
MTF-88-S-01	2.0
MTF-88-S-02	7.4
MTF-89-S-01	6.0
MTF-90-S-01	5.1
MTF-91-S-01	not enough sample
1.5 M NaI/Acetone	>20,000
0.15 M " "	12,000
0.015 M " "	2,100
0.0015 M " "	290
0.075 M NaI/MTF-88-S-02	6,000
0.0075 M NaI/ " "	1,100
0.00075 M NaI/ " "	130

These experiments were undertaken to understand the nature of the counter ions that the electrophoresis experiment indicates must be present. The fact that the colloids' conductance is approximately the same as that of neat acetone indicates that this counterion must be present in extremely tiny amounts, or perhaps it is only formed when the direct current is applied. In light of the very small potential gradient used, however, this seems unlikely.

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Temperature Sensitivity

A small sample of gold/acetone colloid was placed in a test tube heated in an oil bath from 23°C to approximately 150°C (at which point it was boiling). Another sample was placed in a test tube and placed in a beaker of water at 19°C and this placed in a refrigerator and cooled to 3°C. This test tube was then placed in liquid nitrogen and the colloid frozen solid. This was then allowed to thaw at room temperature. Both samples remained as stable sols after return to room temperature, and remained stable indefinitely. This is evidence for polymer stabilization (151) since charge-stabilized gold colloids always precipitate when subjected to freezing or boiling (182).

Addition of Water

A curious phenomenon was observed upon the addition of a small amount of water to either the gold/acetone, silver/acetone or copper/acetone sols. Bubbles were evolved which a simple flame test revealed to be either H_2 or CH_4. This phenomenon ceased after a certain amount of water was added, and the colloid then precipitated. It is difficult to explain this. Henglein and co-workers reported that the free radicals generated by [60]Co γ-irradiation of acetone in an aqueous gold colloid would reduce water to form H_2 (156-161). The presence of similar radicals in the gold/acetone colloid system transferring electrons to the gold particles could account for those particles' charge. These electrons would then be available to reduce water when it was

added. We have no direct evidence for radical formation, however.

Light Sensitivity - Silver/Acetone Sols

All the silver/acetone sols investigated were initially a
dark black or purple/black color. After 3-4 days exposure to
light, they gradually turned gray and the metal precipitated as a
spongy light colored mass. When the colloids were kept in the
dark however, they retained their dark color and remained stable
indefinitely (up to six months). This phenomenon needs further
investigation.

II.9. Film Formation - Gold / Acetone Films

Elemental Analyses

Samples were prepared for elemental analysis by removing the solvent under vacuum into a cold trap. The dry residue was subjected to a dynamic vacuum of approximately 5×10^{-3} mm Hg for approximately one hour at room temperature to remove all traces of solvent. The resulting dry residue was then scraped from the Schlenk tube into a small vial and sent to Galbraith Laboratories for metal, carbon, and hydrogen analyses. Oxygen was determined by difference. The results of analyses are summarized in the following table.

TABLE 7

Sample #	% C	% H	% Metal	% O (by difference)
MTF-110-S-01	9.69	1.14	82.78 (Au)	6.39
MTF-127-S-01	17.42	2.76	62.81 (Au)	17.01
MTF-132-S-01	6.15	0.81	81.45 (Au)	11.59
MTF-130-S-01	0.62	<0.01	(Ag) (not enough sample for determination)	

Except for MTF-130-S-01, these were all mixed samples, that is, they contained material from several different reactions; therefore no general trends regarding concentration can be found. Klabunde and co-workers found that for Ni and Co co-condensed with various organic solvents (pentane, hexane, toluene, THF, and heptane), either slow warmup conditions or a large excess of

organic species resulted in the incorporation of more carbon and hydrogen in the resultant powder (112,113,114). It is very likely that this same effect is operative for the metals in this study, especially since a correlation between matrix concentration and particle size similar to that noted in (112) was also observed in the present study (_vide_ _supra_).

Klabunde, Davis and Severson (148,149) reported the incorporation of alkane fragments in nickel and cobalt powders formed by vacuum deposition of these metals in cold alkane matrices. In their experiments, it was found that the alkane (pentane, hexane, heptane, octane and 2,2- and 2,3-dimethylbutane) was cleaved into smaller hydrocarbon fragments as a result of reaction with small growing metal particles. ESCA ion-beam etching experiments revealed the carbon to be present as sp^2- and sp^3- hybridized forms dispersed throughout the small metal particles (148). Pyrolysis experiments on the nickel powders revealed that only CO_2, CH_4 and H_2 were evolved upon heating to 600°C. CO_2 was evolved between 150 and 300°C. Above 300°C, only CH_4 and H_2 were evolved.

Products evolved by hydrogenation and hydrolysis of the Ni-pentane powder were very similar, and the product distributions from these experiments were also very similar (149). Products found were CH_4, C_2H_6, C_3H_{10}, and C_5H_{12}. No species containing more than five carbons were found. From these experiments, it was concluded that the pentane fragmentation occurred during the codeposition - warmup procedure and not during the product workup.

The results obtained through pyrolysis/mass spectrometry of the powders obtained by solvent evaporation from the gold/acetone

and silver/acetone samples stand in contrast to these earlier results. The gold powder was pyrolized in a Pyrex glass tube and the volatile products evolved were inlet directly into the mass spectrometer. The temperature was gradually raised from room temperature through $300\,^{\circ}C$, and the mass spectrum recorded at regular intervals. The most striking thing about the products evolved was their high molecular weight, and the presence of repeating units of 12, 14, 15, and 17 daltons indicating the loss of carbon, $-CH_2$, CH_3 and $-OH$ groups.

The open, low pressure pyrolysis equipment used seems to preclude the polymerization or oligomerization of acetone during the pyrolysis experiments, rather, it seems that the high molecular weight products are formed during the matrix codeposition-warmup procedure. It seems that these high molecular weight products formed are of varying sizes, so exact characterization seems to be out of the question. The best we can hope for is to identify functionalities. More detailed infrared data is needed for this.

The above interpretation of the pyrolysis/M.S. experiment is supported by the literature on polymer stabilization of colloidal particles. As was discussed in the Historical section, colloids are stabilized in solution in one of two ways: either by the absorption of ionic species in solution in the form of double layers, relying on electrostatic repulsions to stabilize the particles, or by absorption of lyophilic high molecular weight molecules such as starches, proteins, gelatins, PVA, etc. (in

aqueous solution) (150,151,152). The role of these so-called

"protective colloids" is reviewed in the Historical section (<u>vide</u>

<u>supra</u>).

The mass spectra obtained from the pyrolysis/M.S. experiment

for the gold/acetone colloid are reproduced on the following

pages.

It is evident that the amount of volatile organic material

given off peaks at about 240 – 300 °C, and decreases at higher

temperatures.
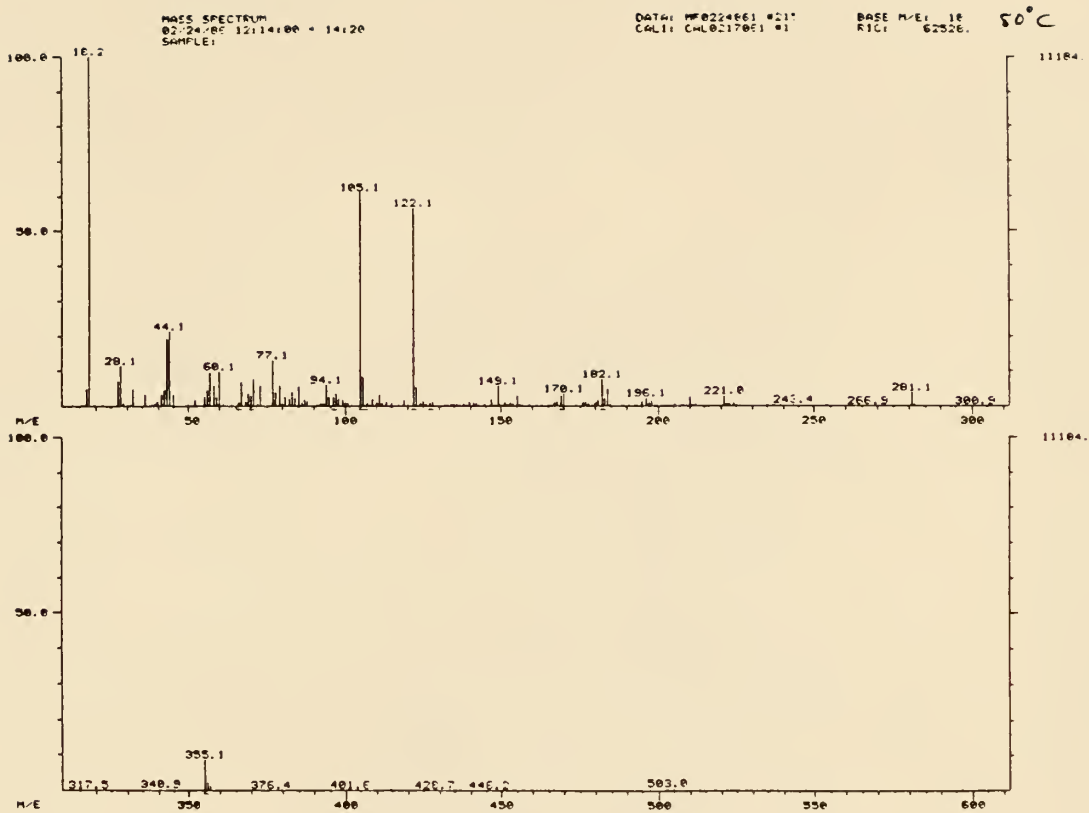
FIGURE 32. Mass spectrum of gold colloid film powder
pyrolyzed at 80 °C, directly into M.S.

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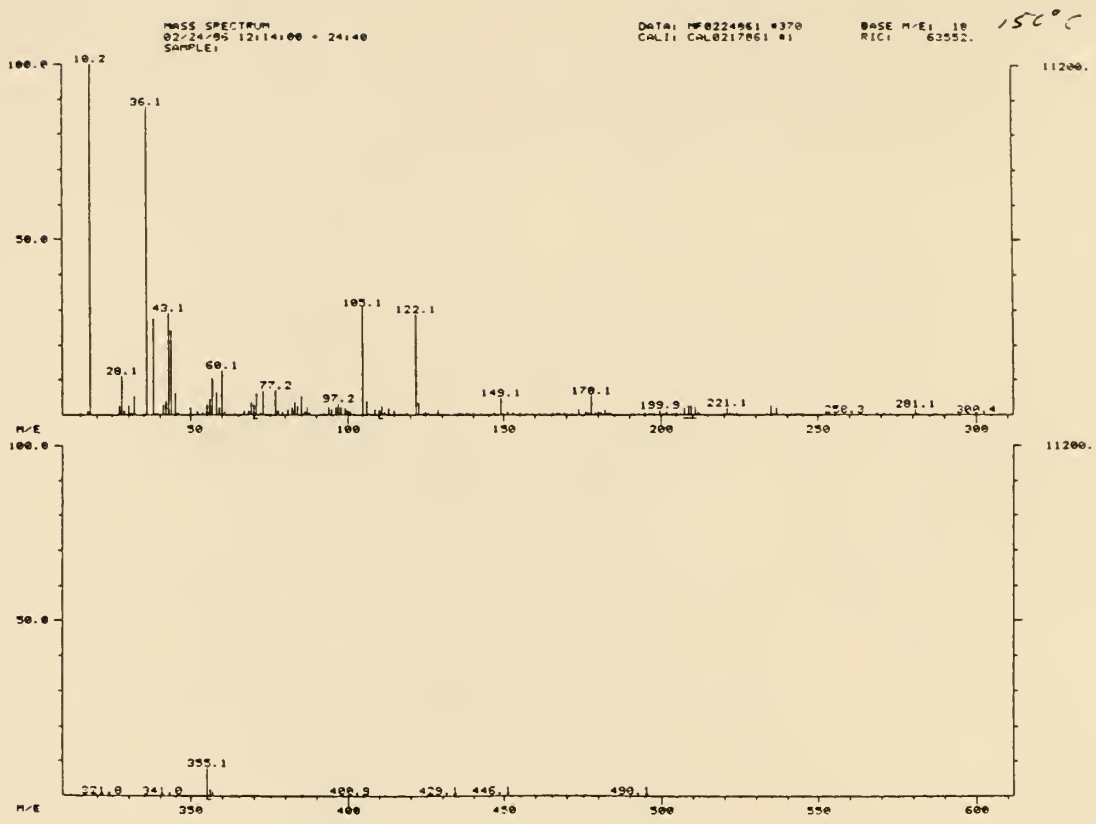
FIGURE 33.   M.S. of gold colloid film powder

pyrolyzed at 150 °C.
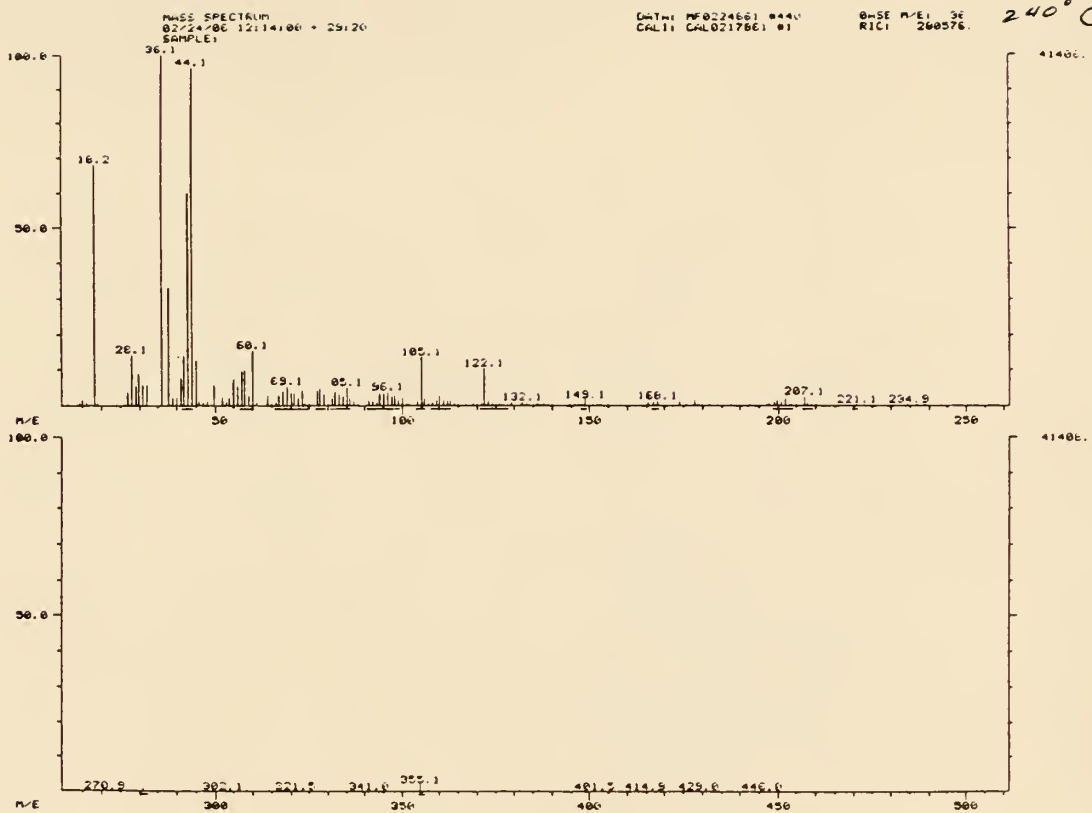
FIGURE 34. Gold colloid film powder pyrolyzed at 240 °C.

MASS SPECTRUM
02/24/85 12:14:00 + 33:20
SAMPLE:

DATA: MF0224851 #504
CAL: CAL0217961 #1

BASE M/E: 207
PIC: 436272.
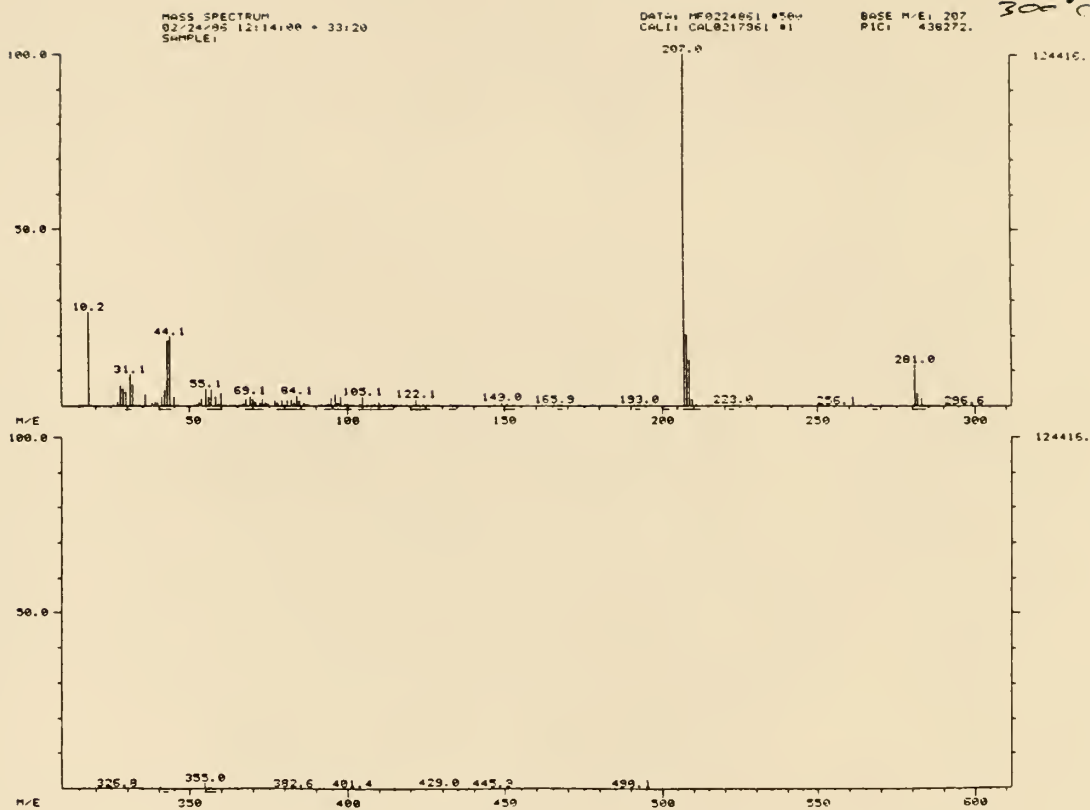
300°C

FIGURE 35.   Gold colloid film powder pyrolyzed at 300°C.

In an effort to gain more understanding of the nature of the organic material adsorbed onto (or incorporated into) the colloidal gold particles, an experiment similar to the one outlined in the preceding section was performed, with the exception that a closed-tube pyrolysis apparatus was used, and the volatiles evolved during heating the sample were then swept into a G.Ci column (six foot Porapak Q) with He gas. These products were characterized by mass spectrometry upon elution.

Under the conditions used in these experiments, high molecular weight organics are probably broken down by the combination of high temperature and pressure in the closed pyrolysis tube. The important thing to note is that many of the organic molecules evolved contain <u>more</u> carbon atoms than the original material, acetone. This stands in direct contrast to the earlier reported work of Klabunde et. al. on the organic molecules evolved in the hydrogenation or hydrolysis of Ni/alkane powder, which were never observed to contain more carbon atoms than the starting alkane (149). This is further, indirect evidence for the formation of high molecular weight organics from the acetone present in the frozen matrix. It is important to note, however, that there is no <u>direct</u> evidence for the presence of such species.

The data from the chromatograms and mass spectra for both the gold/acetone and silver/acetone colloid film powders are

summarized in the following table.

TABLE 8

MASS SPECTRA: eI, 35 eV

Sample, Conditions	Column Temp. Program	Species Observed (in order of elution)
Au film powder, pyrolyzed 8 min @ 180°C injected 20 s.	At I + 6.2 min T --> 100°C. At I + 35 min T --> 150°C. Porapak Q 6' long	CH_4, CO_2, C_2H_4, H_2O, C_3H_6, CH_3OH, C_4H_4, C_3H_8, C_3H_7OH, C_4H_8, CH_3COCH_3
Au film powder, pyrolyzed 30 min @ 250°C injected 20 s.	Same as above.	C_4, CO_2, C_2H_4, H_2O, C_3H_6, CH_3OH, C_4H_4, C_3H_8, C_4H_8, another C_4H_8, $CH_3-C \equiv N(?)$, CH_3COCH_3
Au film powder, pyrolyzed 23 min @ 360°C injected 20 s.	Same as above.	CH_4, CO_2, C_2H_4, $H_2CO(?)$, H_2O, C_3H_6, C_4H_4, C_3H_8, C_4H_8, another C_4H_8, $CH_3C \equiv N(?)$, CH_3COCH_3
Ag film powder, pyrolyzed 8.8 min @ 180°C injected 20 s.	Same as above.	CO_2, H_2O
Ag film powder, pyrolyzed 1 hour @ 250°C injected 20 s. (Some noise in spectrum due to contact between column and furnace)	Same as above.	CO_2, C_2H_4, $C_3H_6(?)$, C_4H_4, C_3H_8, C_4H_8
Ag film powder, pyrolyzed 9 min @ 360°C injected 20 s.	Same as above.	CO_2, C_2H_4, $C_3H_6(?)$, C_4H_4, C_3H_8, C_4H_8, CH_3COCH_3
Au film powder w/ several drops d6-acetone added, excess allowed to evaporate, pyrolyzed 8 min @ 180°C. injected 20 s.	Same as above.	CO_2, H_2O, C_3H_6, C_4H_4, $C_3H_8(?)$, C_4H_8, another C_4H_8. (no deuterated species observed)

TABLE 8 (continued)

MASS SPECTRA: eI, 35 eV

Sample, Conditions	Column Temp. Program	Species Observed (in order of elution)
Same sample as above, pyrolyzed 30 min @ 250°C. injected 20 s.	Same as above.	CO_2, C_2H_4, C_3H_6(?), C_4H_4, C_3H_8, C_4H_8, CH_3COCH_3 (no deuterated species observed)
Same sample as above, pyrolyzed 23 min @ 360°C. injected 20 s.	Same as above.	CO_2, C_2H_4, H_2O, C_3H_6, C_4H_4, C_3H_8, C_4H_8, CH_3COCH_3, (no deuterated species observed)

It is interesting to note that the silver colloids contain much less organic material than the gold colloids. Since there is a higher metal/acetone ratio in all the silver colloids prepared, this is not surprising. Klabunde and co-workers noted that Ni/pentane powders in which the Ni/pentane ratio was high contained less carbon and hydrogen than those powders in which the corresponding Ni/pentane ratio was low (149). This effect was also noted for cobalt (148). The reason for this is not clear, but it probably has to do with the competition between metal particle growth and metal particle reactions with the organic solvent molecules initially present.

II.12. Infrared Studies – Gold / Acetone Films

Infrared spectrophotometry of the dry gold colloid residue (acetone removed under vacuum) yielded some useful information. The dry residue was ground with dry KBr powder and then compressed into a pellet. Due to the very weak absorbances, the desired regions of the sample were scanned numerous times, and the absorbances added together by the computer data station (Perkin-Elmer 1330). Due to limitations on the computer's memory space, only portions of the spectrum could be repetitively scanned in this manner.

Perhaps the most important observation was that of a gold-carbon stretch at 570 cm^{-1}. The only gold-carbon stretching frequencies reported in the literature are for mononuclear gold (I) and gold (III) compounds in which the carbon is present in the form of a methyl group. Nonetheless, there seems to be good agreement and it is not evident that there are any other possibilities to which this absorbance can be attributed. Puddephatt reports that Au-C stretching frequencies (for methyl groups) range from 457-591 cm^{-1}, depending on other ligands present (146). Nakamoto lists three Au-C stretches (147):

Compound	ν (Au-C), cm^{-1}
$[(CH_3)_2 \, Au \, Cl]_2$	571, 561
$[(CH_3)_2 \, Au \, Br]_2$	561, 550
$[(CH_3)_2 \, Au \, I]_2$	550, 545

The IR spectra are reproduced on the following pages, along with their assignments.

It is evident from this data that there is a significant amount of organic material incorporated with the gold colloid particles. Even vacuum pumping on this material for up to one hour at pressures as low as 20 mm Hg failed to remove it. We can also conclude that at least some of this material is chemisorbed rather than physisorbed on gold, due to the presence of a gold-carbon stretch in the IR.
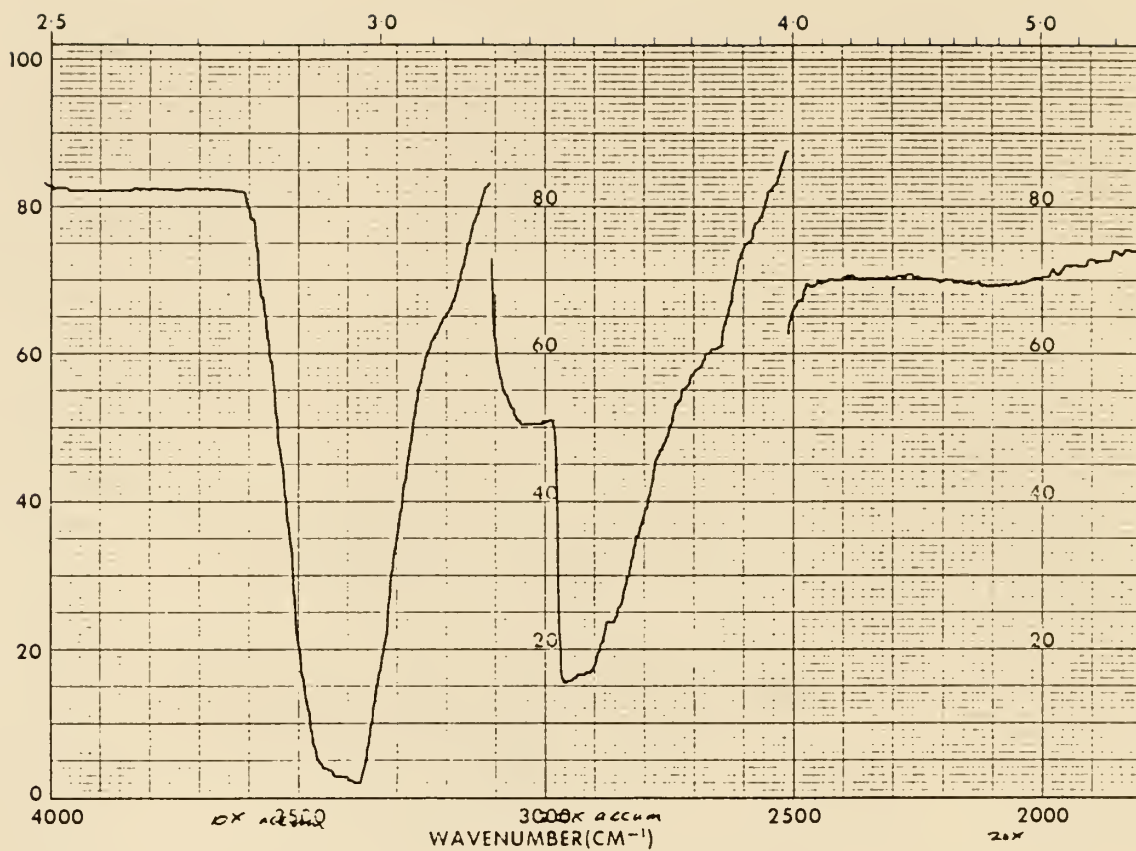
FIGURE 36. IR spectrum of gold colloid film powder,

$3420 \text{ cm}^{-1} = \nu \text{ O-H (water)}$

$2960 \text{ cm}^{-1} = \nu \text{ C-H}$

$3040 \text{ cm}^{-1} = \nu \text{ C-H (olefinic)}$
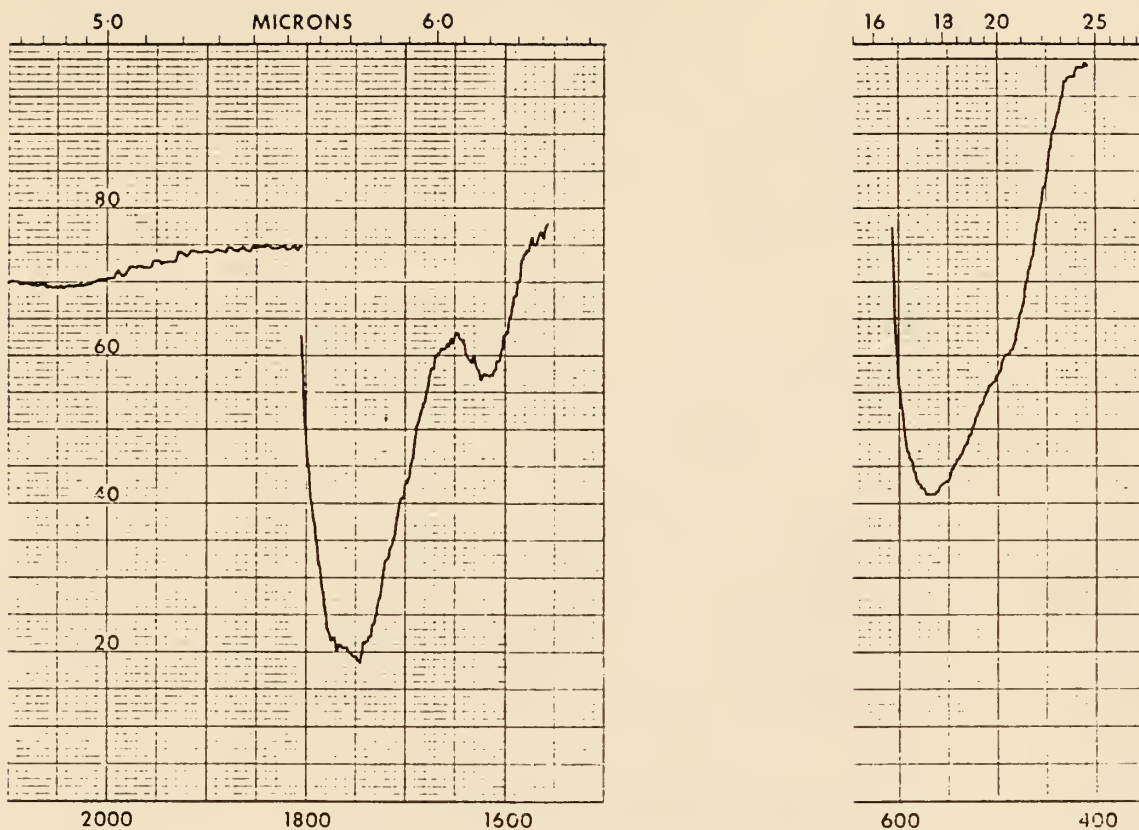
FIGURE 37. IR spectrum of gold colloid film powder,

$$1760 \text{ cm}^{-1} = \nu \text{ C=O}$$

$$1620 \text{ cm}^{-1} = \nu \text{ C=C}$$

$$570 \text{ cm}^{-1} = \nu \text{ Au-C}$$

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II.13. General Conclusions

The gold/acetone, silver/acetone and copper/acetone sols
described in this thesis appear to be stabilized by a combination
of adsorbed organic material and an accumulation of electrons on
the particle. The process responsible for the formation of the
organic material is probably also the moderating reaction which
slows down the clustering of metal atoms such that small particles
are formed rather than a mass of metal. This clustering process
is affected by the concentration of metal atoms and the warmup
conditions imposed on the frozen matrix, a slow warmup and/or
small concentration of metal atoms favoring the formation of
smaller particles. These sols are extremely stable, samples
exhibiting stability for over 1 year.

III. <u>FUTURE DIRECTIONS</u>

Surface-enhanced Raman scattering would seem to be the tool most applicable to study of the absorbed organic material on the surface of the particles. Such a method has been used for the study of materials absorbed on the surfaces of aqueous gold colloids, including probing the nature of electron donor and acceptor sites and specific absorption of TTF and TCNQ on a gold colloid surface (183).

The light sensitivity of the silver colloid clearly needs further investigation. This process appears to be slow enough for kinetic and quantum yield studies, and it would be interesting to find out if the silver colloid is sensitive to specific wavelengths.

IV. EXPERIMENTAL SECTION

IV.1. Equipment and Parameters

Metal vapor reactions were carried out in a reactor composed
of a top and bottom which are commercially available from Kontes –
Martin Glass Company. The reactor bottom was a three-liter glass
resin kettle (Kontes part no. 61200) which was mated to the
reactor head (Kontes part no. 613200) by a 4 1/4 inch ground
glass flange. The top also has four 24/40 standard taper ground
glass joints of which two serve for the introduction of water
cooled hollow copper electrodes. The other two are used for
product recovery, attachment to a vacuum system, and for intro-
duction of the solvent vapor (See diagram).

The vacuum line was of a standard configuration, and included
both fixed and demountable solvent traps, a vacuum/inert gas
manifold, mercury manometer, and thermocouple pressure gauge
(Arthur F. Smith & Co.). All valves were of the greaseless,
teflon and glass type (J. Young Ltd.). Two oil diffusion pumps
and two mechanical vacuum pumps (Sargent-Welch Co.) complete the
vacuum system (See diagram).

Electron photomicrographs were obtained with either a
Hitachi HU-11B transmission electron microscope or a JEOL JEM-100C
transmission electron microscope. Negatives were produced and
developed by Mr. Larry Seib of the KSU Physics Department.
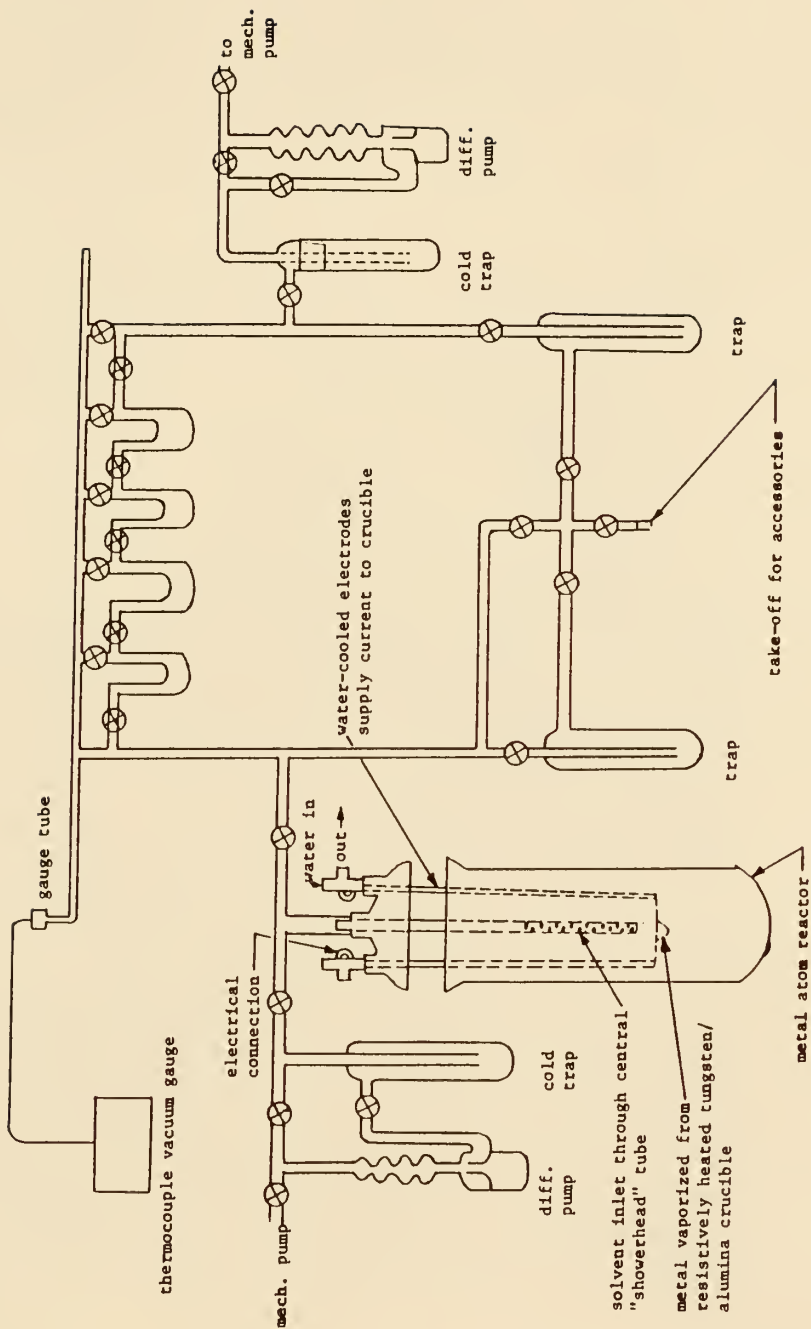
FIGURE 38. Diagram of vacuum system and metal atom reactor.

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Prints were made by KSU Photo Services.

Ultraviolet and visible spectra were collected on a Cary-14 spectrophotometer.

Proton NMR spectra were obtained on the Chemistry Department Bruker 400 MHz instrument with the kind assistance of Mr. David D. Devore of the KSU Chemistry Department.

Infrared spectra of the solid particles obtained after solvent evaporation were recorded on a Perkin-Elmer 1330 IR spectrophotometer with data station.

Scans were accumulated either 20 or five times and added together and stored on the data station's memory. A correction program entitled FLAT was used to correct for the sloping baseline resulting from the pressed KBr pellets used.

Electrophoresis measurements were obtained with a solution electrophoresis cell constructed by the author after a design by Burton (173). Electrophoretic mobilities were measured with a Seiko Chronograph Wristwatch against millimeter graph paper.

The solid material obtained from the removal of the dispersion medium by vacuum distillation was pyrolyzed in the following way: The solid material was contained in a concentric trap constructed of stainless steel tubing and Swage-lok ^{TM} fittings. This trap comprised one loop attached to a four-way injection valve. The other loop connected to the chromatography column and ultimately the mass spectrometer (Finnegan Model 4000 quadrupole GC-MS, ionization energy 35 eV, used in electron impact mode). The mass spectra of the pyrolysis products were

recorded as the material eluted from the column.

X-ray photoelectron spectra of the dry colloidal particles were collected by Dr. Peter M.A. Sherwood, Mr. Kevin Robinson and Mr. Guy Wilson of the KSU Chemistry Department on a VSW 100 C/ Apple instrument.

Elemental analyses for metal, carbon and hydrogen were carried out by Galbraith Laboratories of Knoxville, TN.

Electron paramagnetic resonance spectroscopy was carried out on the departmental Varian/IBM instrument by Dr. Ileana Nieves-Fontana.

IV.2. Summary of Reactions

Page# in Notebook	Mass of Metal Evaporated	Volume of Solvent	Comments
p. 25	0.2609 g Au	50 mL EtOH	orange green matrix --> pptd black solid.
p. 27	1.1810 g Au	50 mL EtOH	red matrix, turned green, black sol, pttd 24 hours.
p. 29	AgCl 0.7402 g	25 mL EtOH	yellow matrix-->orange sol lg. pink particles.
p. 31	AgCl	EtOH	orange/red matrix
p. 31	Au 0.0912 g	65 mL EtOH	greenish matrix-->purple sol-->pptated.
p. 33	Au 0.0844 g	100 mL EtOH	greenish matrix-->purple sol-->pptated - 2 hrs.
p. 37	Au 0.0271 g	90 mL EtOH	purple sol-->pptated - 2 hrs.
p. 39	Au 0.8179 g	100 mL EtOH	bubbling observed in warmup.
p. 43	0.0265 g Au	140 mL Acetone	purple-brown sol-<u>stable</u> (MTF-41-S-01).
p. 47	Ag 0.4812 g	120 mL Acetone	black sol, black matrix pptated (not protected from light).
p. 49	Au 0.1946 g	55 mL Acetone	purple sol (MTF-49-S-01).
p. 61	Au 0.0847 g	136 mL Acetone	purple liq.
p. 63	Au 0.0284 g	66 mL Acetone	purple liq (MTF-63-S-01).
p. 65	Au 0.0817 g	44 mL Acetone	purple liq (MTF-65-S-01).
p. 67	Au 0.0269	103 mL Acetone	purple liq (MTF-67-S-01)
p. 70	Cu 0.1477 g	66 mL Acetone	green-black matrix, black sol-->ppted, green powder
p. 71	Cu 0.3075 g	56 mL Acetone	green-black matrix, green sol-->pptated (MTF-74-S-01).
p. 73	Au 0.0562 g	160 mL Acetone	purple sol.
p. 80	Au 0.0222 g	82 mL Acetone	bubbles on warmup, cold, empty dewar warmup (MTF-80-S-01).
p. 81	Au 0.0024 g	135 mL Acetone	v. dilute purple (MTF-82-S-01).
p. 82	Au 0.0886 g	97 mL Acetone	purple sol.
p. 83	Au 0.0114 g	180 mL Acetone	spectral grade acetone stable ^ 1 hr.

Page# in Notebook	Mass of Metal Evaporated	Volume of Solvent	Comments
p. 84	Au 0.0202 g	76 mL Acetone	spectral grade acetone stable indefinitely (MTF-84-S-01).
p. 85	Au 0.0286 g	137 mL Acetone	pressure fluctuations --> pptated.
p. 86	Au 0.0530 g	81 mL Acetone	ETOH slush warmup (MTF-86-S-01).
p. 86	Au 0.0116 g	138 mL Acetone	MeOH slush-->pptated.
p. 87	Au 0.0441 g	81 mL Acetone	MeOH slush (MTF-88-S-01).
p. 88	Au 0.3673 g	147 mL Acetone	pentane slush (MTF-88-S-02).
p. 89	Au 0.0466 g	83 mL Acetone	pentane slush overnight (MTF-89-S-01).
p. 90	Au 0.1095 g	114 mL Acetone	EtOH slush overnight (MTF-90-S-01).
p. 91	Au 0.0587 g	63 mL Acetone	MeOH slush overnight (MTF-91-S-01).
p. 99	Cu 0.1033 g	58 mL Acetone	black colloid-->pptated.
p. 105	Cu 0.0530 g	44 mL Acetone	black colloid when cold pptated on warmup.
p. 107	Ag 0.3550 g	89 mL Acetone	black colloid-->pptated.
p. 108	Ag 0.0142 g	41 mL Acetone	reddish matrix black colloid-->pptated.
p. 108	Cu 0.0521 g	108 mL DMF	bubbled during warmup formed yellowish matrix.
p. 111	Ag 0.1046 g	74 mL DMF	bubbled during warmup formed silver sponge.
p. 112	Au 0.0105 g	199 mL Acetone	purple sol.
p. 113	Ag 0.2010 g	95 mL Acetone	airlessly handled but exposed to light. Color change from purple/black to gray.
p. 114	Cu 0.0439 g	79 mL Acetone	green sol handled airlessly.
p. 125	Ag 0.2502 g	159 mL Acetone	greenish matrix, stored in dark--retains dark coloring when stored in dark.
p. 126	Cu	83 mL Acetone	green sol-reacted w/H_2O to release bubbles--> flame test revealed gas to be H_2.
p. 127	Ag 0.1770 g	107 mL Acetone	black colloid, stored dark.
p. 129	Ag 0.0130 g	96 mL Acetone	black colloid, stored dark.
p. 130	Ag 0.0316 g	95 mL Acetone	black colloid, stored dark.

Au - Concentration Study:
    MTF-80-S-01
    MTF-82-S-01
    MTF-82-S-02
    MTF-112-S-01

Au - Preliminary Study:
    MTF-63-S-01
    MTF-65-S-01
    MTF-67-S-01

Au - Warmup Studies:
    MTF-86-S-01
    MTF-88-S-01
    MTF-88-S-02

Au - Warmup Studies - Slushes:
    MTF-89-S-01
    MTF-90-S-01
    MTF-91-S-01

Ag - Concentration Study:
    MTF-125-S-01
    MTF-127-S-01
    MTF-129-S-01
    MTF-113-S-01 (not exposed to light)

Ag Colloid - Exposed to Light:
    MTF-113-S-01
    (J00288 not exposed)
    (J00289 exposed 1 day)

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CLUSTERING OF GOLD ATOMS IN ACETONE:

NON-AQUEOUS METAL COLLOIDS

by

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ABSTRACT

Gold atoms, when co-condensed with acetone or other organic vapors in a cryogenic matrix at low pressure and subsequently warmed up slowly, will cluster in a controlled way to yield colloidal particles of gold suspended in the organic liquid. this method has been found to work also for silver, and less successfully with copper.

The colloidal particles were found to form conductive metal films when the solvent is removed by evaporation.

The colloids were characterized by electron microscopy, electrophoresis, UV-visible and NMR spectroscopy.

The films were characterized by pyrolysis/gas chromatography-mass spectrometry, and infrared spectroscopy.

It was concluded that the colloidal particles were stabilized by a combination of adsorbed solvent and by a buildup of negative charge on the particles.