END
DATE
FILMED
11-86

1.0

1.1

1.25

4.5
2.8
2.5
3.2
2.2
3.6
4.0
2.0

1.8

1.4   1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

AD-A172 483

DTIC
ELECTE
OCT 0 3 1986
S
D

Technical Report No. 5

"Living Colloidal Metal Particles
from Solvated Metal Atoms.
Clustering of Metal Atoms in
Organic Media 15."

by

M. T. Franklin and Kenneth J. Klabunde
for publication
in an American Chemical
Society Chemistry Series Book entitled
"High Energy Methods in Organometallic Chemistry,"
editor, K. Suslick

Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

September 23, 1986

86 10   2 20

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Living Colloidal Metal Particles from Solvated Metal Atoms. Clustering of Metal Atoms in Organic Media 15.		5. TYPE OF REPORT & PERIOD COVERED Technical
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. T. Franklin and K. J. Klabunde		8. CONTRACT OR GRANT NUMBER(s) N00014-1-85-K0821
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Kansas State University Manhattan, Kansas 66506		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1596
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE September 1986
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

free atoms, solvated, nonaqueous colloids, metal particles, clustering, electrophoresis, living colloids, gold, palladium, films.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A review of preparative methods for metal sols (colloidal metal particles) suspended in solution is given. The problems involved with the preparation and stabilization of non-aqueous metal colloidal particles are noted. A new method is described for preparing non-aqueous metal sols based on the clustering of solvated metal atoms (from metal vaporization) in cold organic solvents. Gold-acetone colloidal solutions are discussed in detail, especially their preparation, control of particle size (2-9 nm), electrophoresis measurements, electron microscopy, GC-MS, resistivity, and related studies. Particle stabilization involves both electrostatic and steric

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-LF-014-6601

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

LIVING COLLOIDAL METAL PARTICLES FROM SOLVATED METAL ATOMS

CLUSTERING OF METAL ATOMS IN ORGANIC MEDIA 15.

Matthew T. Franklin

and Kenneth J. Klabunde*

Department of Chemistry

Kansas State University

Manhattan, Kansas 66506

Abstract

A review of preparative methods for metal sols (colloidal metal particles) suspended in solution is given. The problems involved with the preparation and stabilization of non-aqueous metal colloidal particles are noted. A new method is described for preparing non-aqueous metal sols based on the clustering of solvated metal atoms (from metal vaporization) in cold organic solvents. Gold-acetone colloidal solutions are discussed in detail, especially their preparation, control of particle size (2-9 nm), electrophoresis measurements, electron microscopy, GC-MS, resistivity, and related studies. Particle stabilization involves both electrostatic and steric mechanisms and these are discussed in comparison with aqueous systems.

Introduction

Graham coined the term "colloid" to describe suspensions of small particles in a liquid.[1] Such particles are generally considered to be from 1 to 5000 nm in diameter and are not easily precipitated, filtered, or observed by ordinary optical microscopes. The topic of this paper is metallic colloidal particles, often called metal sols, with special emphasis on non-aqueous media. Some history of gold sols is appropriate.

Gold has held the attention of mankind for thousands of years. Attempts to make the "perfect metal" (gold) from imperfect metals was the realm of alchemists, and over the centuries great medicinal powers were ascribed to gold. And as early as 300 A.D. there are references to the consumption of gold fluid to prolong life.[2] It is doubtful that this was a colloidal solution of gold since aqua regia[3] was unknown to early Chinese alchemists, and more likely amalgums of Hg-Au were actually consumed. Centuries later more recipes for aurum potabile (drinkable gold) appeared which were aqueous gold colloid solutions prepared by dissolving gold in aqua regia followed by treatment (chemical reduction of $AuCl_3$ or $HAuCl_3$ to Au metal particles) with ethereal oils. These solutions were usually then treated with chalk to neutralize the acid before being consumed. Fabulous curative powers were attributed to these solutions, especially toward heart disease. And in 1618 Antoni published Panacea Aurea: Auro Potabile[4] which centered on the treatment of venereal diseases, dysentery, epilepsy, tumors and more with drinkable gold. Additional similar books appeared,[5] and Helcher pointed out that the addition of boiled starch noticeably increased the stability of the preparation. In 1802 Richter[6] mentioned that the shades of color in purple gold solutions and ruby glass were due to the presence of finely divided gold. He correlated the colors with particle

size in a qualitative way.[4] And Fulhame[7] noted in 1794 that she would dye

silk cloth various shades of purple with colloidal gold solutions. Cassius[8]

and Glauber[9] were also involved in using colloidal gold as a coloring agent.

Faraday published the first scientific investigations of gold sols.[10]

He usually reduced aqueous solutions of $AuCl_3$ with phosphorous. However, he

also experimented with sparking gold wires. He concluded that gold was

present in the solutions as elemental gold, and that color depended on

particle size. He also discovered flocculation by addition of an

electrolyte NaCl. Other workers also used sparking of metals under water to

produce sols of Pb, Sn, Au, Pt, Bi, Sb, As, Tl, Ag, and Hg.[11,12] As the

years passed aqueous colloidal gold was studied extensively. The classic

work of Svedberg,[13] Zigmondy,[14] Kohlschutter,[15] and Turkevich[16] must be

noted. Zigmondy,[14] using a slit microscope, was able to study the "seeding"

phenomenon and found that gold particles already present preferentially grew

as more gold salt was reduced. This and related work[17,18] improved our

understanding of particle nucleation and growth.

Non-Aqueous Colloidal Metal Solutions

It has been difficult to prepare colloidal gold in non-aqueous media

due to limitations in preparative methods (low salt solubilities, solvent

reactivity, etc.), and the fact that the low dielectric constant of organic

solvents has hindered stabilization of the particles. In aqueous solution

the gold particles are stabilized by adsorption of innocent ions, such as

chloride, and thus stabilized toward flocculation by the formation of a

charged double layer, which is dependent on a solvent of high dielectric

constant. Thus, it seemed that such electronic stabilization would be poor

in organic media.

In spite of these difficulties, some limited successes have been reported. Svedberg[13] struck an electric arc in a glass tube under organic liquids. Gas flow through the tube carried some of the metal particles into the solution (liquid methane or isobutanol were used). Mayer used a similar method using very high voltage with organic-water mixtures.[19] More recently, Kimura and Bandow reported a similar method where metals were evaporated and swept into a cold trap containing ethanol, with some success.[20]

Additional successes have been reported: Svedberg[21] used an alternating current discharge to disperse small pieces of metal; Natanson[22] obtained colloidal copper in an acetone/toluene/1-pentanol mixture by reducing $CuCl_2$ with zinc powder; Janek and Schmidt[23] added a gold/citrate aqueous sol to an alcohol/toluene mixture followed by heating and cooling and found that some gold colloidal particles remained in the alcohol rich layer; Marineseu[24] reported that sonication of alkali metals at their mp in kerosene yielded pyrophoric colloids; Yamakita[25] used fats, organic acids, alcohols, and other organics as reducing agents for Au_2O_3 and obtained success especially with fats and fatty acids; and Ledwith[26] was able to reduce $AuCl_3$ in water with diazoethane followed by mixing with organics which gave some gold particles in the organic phase.

Protective Colloids

Another approach in preparing and stabilizing metal colloids is by adsorption of macromolecules on their surfaces. A wide variety of materials have been used including gummy gelatinous liquids,[10] albumin,[27] Icelandic moss,[28] latex,[22] polyvinylpyrrolidone,[29] antibodies,[30] carbowax 20M,[31] polyvinylpyridine,[31] and various polymer-water/oil-water mixtures.[32] These

studies clearly indicate that "steric stabilization" of metal colloids is also important (along with electronic stabilization).[33]
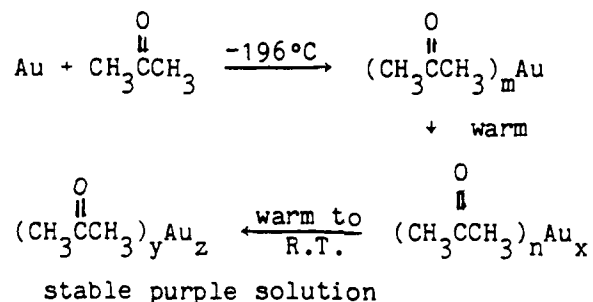
Results and Discussion

More direct and successful methods for the preparation of non-aqueous metal sols are desirable. Especially valuable would be a method that avoids the metal salt reduction step (and thus avoids contamination by other reagents), avoids electrical discharge methods which decompose organic solvents, and avoids macromolecule stabilization. Such a method would provide pure, non-aqueous metal colloids and should make efficient use of precious metals employed. Such colloids would be valuable technologically in many ways. They would also be valuable to study so that more could be learned about particle stabilization mechanisms in non-aqueous media, of which little is known at the present time.

We have reported numerous studies of the clustering of metal atoms in non-aqueous (organic) media.[34] And very recently our preliminary report of stable non-aqueous gold sols appeared.[35] The approach has been to disperse metal atoms in excess cold organic solvent thus forming solvated metal atoms. Upon warming atoms clustering takes place moderated by solvation. Particle (cluster) growth is eventually inhibited and stopped by strongly bound solvent molecules. As mentioned above, there is some precedent for this approach found in earlier work on the preparation of active metal slurries,[36] dispersed catalysts,[37] and metal atom clustering in polymer oils.[38] However, our initial report[35] was the first describing the preparation of stable metal sols by the solvated metal atom method.

The experimental apparatus used consisted of a stationary metal atom-vapor reactor which has been detailed in the literature earlier.[39] Metal was evaporated (-0.1 to 0.5 g) and codeposited at -196°C with excess organic

solvent vapor (~ 40-150 mL). The frozen matrix was allowed to warm under
controlled conditions, and upon melting stirring was commenced. after
warming to room temperature stable colloidal solutions were obtained and
syphoned out under N_2.

A variety of metals have now been investigated in our laboratory
including Fe, Co, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, In, Ge, Sn, and Pb.
Solvents employed have been acetone, ethanol, THF, diethylether,
dimethylsulfoxide, dimethylformamide, pyridine, triethylamine, ispropanol,
isopropanol-acetone, toluene, pentane, and water. Acetone-Au will be
discussed in detail herein, along with Ag.

$$Au + CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{-196°C} (CH_3\overset{O}{\overset{\|}{C}}CH_3)_m Au$$

$$\downarrow \quad warm$$

$$(CH_3\overset{O}{\overset{\|}{C}}CH_3)_y Au_z \xleftarrow[R.T.]{warm\ to} (CH_3\overset{O}{\overset{\|}{C}}CH_3)_n Au_x$$

36

stable purple solution

Formation and Stabilization of Colloidal Solutions

Concentration Effects:

In order to determine if particle size and distribution could be
controlled, we prepared a series of colloidal Au-acetone solutions of
varying concentrations. A drop of each solution was placed on a carbon
coated copper grid, and after acetone evaporation analyzed by transmission
electron microscopy (TEM). Lower concentrations of Au in acetone (0.002 M)
yielded smaller particles, and at very low concentrations quite good
selectivity to a certain size was possible (1-3 nm). Higher concentrations
of gold yielded larger particles with a broader distribution (4-7 nm), and
still higher concentration (0.04 M) gave particles 6-9 nm with some as large

as 20 nm (see Figures 1-3). Figure 4, a TEM micrograph of Au particles from acetone, shows that the particles appear spherical or oblong in shape and do not show crystalline faces or certain geometrical structures. The non-crystalline nature of these particles is not surprising since, as shown later, they do contain substantial portions of organic material. Their tendency to chain together might also be explained by the presence of organic residues.

The control of particle size by concentration indicates that particle growth is a kinetic phenomenon. It is unlikely that particle growth is reversible; once a Au-Au bond is formed it would not break under these experimental conditions. In a dilute solution of atoms, the frequency of encounters would be lower. As the gold atom-solvent matrix warms, the atoms and subsequent metal particles become mobile. It is the number of encounters that occur before particle stabilization that is important. If metal concentration is high the frequency of encounters is higher and the particles become bigger.

Interestingly, Tunekevich and coworkers[16,40] report the _reverse_ _effect_ for gold particle growth in aqueous media. Low concentrations of $HAuCl_3$ were reduced in solution and comparatively large gold particles with a broad distribution resulted. At higher concentrations of $HAuCl_3$ the mean particle size decreased and the size distribution narrowed. Evidently a certain critical concentration of reduced auric ions was necessary in order that they would agglomerate into a stable particle. Due to the statistical nature of physical events (encounters) this required local concentration would be achieved more readily in a concentrated solution, leading therefore predominantly to rapid nucleation rather than particle growth, which is slower.

Concentration effects for Ag-acetone were also studied in our laboratory. These colloidal solutions were black as compared with purple for Au-acetone. They were also sensitive to light (see later). According to TEM the Ag particles from acetone were much larger ($\sim$ 30 nm) compared with Au (2-9 nm). The Ag particles appeared to be denser and perhaps more crystalline. They contained much less organic residue than the Au particles. Particle size for Ag was also dependent on Ag-acetone concentration in the same way as for Au, and the Ag particles were more polyᵈsperse ranging from 20-40 nm.

Matrix Warmup:

Earlier we reported that Ni-pentane matrices upon warming from -196°C yielded tiny Ni particles that incorporated substantial organic material from fragmented pentane.[34] The amount of organic material (mainly C_1 fragments) could be increased and the Ni particle sizes decreased by allowing the Ni-pentane matrix to warm slowly.

Somewhat analogous behavior has been observed with these Au-acetone matrices. The most striking finding is that slow warmup (2h from -196°C to 25°C) was necessary to achieve a stable purple colloidal solution. Rapid warmup invariably caused excessive particle growth and flocculation/ precipitation of the Au particles. However, incorporation of organic residues does not appear to be the reason for this behavior since the resultant dry Au films (after acetone stripping) did not show significant or systematic changes with initial Au solvent ratio. In the case of Au-acetone and Pd-acetone[41] we suspect two reasons for this behavior: (1) solvent reordering and displacement during particle growth may be a slow process and (2) Au and Pd particles acquire negative charge, which helps stabilize their

colloidal nature, and this is probably a slow process (discussed next under the electrophoresis section).

Electrophoresis:

Electrophoresis, the movement of charged particles in response to an electric potential, has become very important in biochemistry and colloid chemistry. In the present study an apparatus similar to that described by Burton[42-45] was used. A U-tube with an inlet at the bottom and removable electrodes at the two upper ends was half filled with acetone. The a Au-acetone colloidal solution was carefully introduced from the bottom so that a sharp boundary was maintained between the clear acetone and the dark purple colloid solution. Next, platinum electrodes were placed in the top ends of the U-tube, and a DC potential applied. The movement of the boundary toward the positive pole was measured with time. Several Au-acetone colloids were studied, and electrophoretic velocities determined as 0.76-1.40 cm/h averaging 1.08 cm/h. Calculation of electrophoretic mobility μ takes the potential into account:

$$\text{electrophoretic velocity} = \frac{1.08}{3600 \text{ s}} = 30 \times 10^{-5} \text{ cm/s}$$

$$\text{electrophoretic mobility} = \mu = 30 \times 10^{-5} \text{ cm s}^{-1} / 12.67 \text{ V}$$

$$\mu = 2.36 \times 10^{-5} \text{ cm/V} \cdot \text{s}$$

This value can be compared with those reported for a variety of aqueous colloidal particles, eg colloidal gold = 30-40 $\times 10^{-5}$ (< 100 nm particle diameter), colloidal platinum = 20 $\times 10^{-5}$ (< 100 nm), colloidal lead = 12 $\times 10^{-5}$ (< 100 nm), and oil droplets = 32 $\times 10^{-5}$ (2000 nm).[43,44] The similarities of these numbers regardless of particle size suggests that the larger the particle is, the more negative charge it acquires.

The relation between electrophoretic mobility μ and the surface properties of the particle (usually modeled as an ionic double layer for aqueous systems) is a classical problem in colloid science.

The Helmholtz-Smolochowski equation is probably the oldest solution to

$$\mu = \frac{\varepsilon\xi}{4\pi\eta}$$

μ = electrophoretic mobility

ξ = electrokinetic potential (zeta potential)

ε = dielectric constant of the medium

η = viscosity of the medium (Stokes)[46]

the problem, but is known to be rather restricted. Huckel[47,48] considered electrophoretic retardation forces , well and proposed:

$$\mu = \frac{\varepsilon\xi}{6\pi\eta}$$

Henry[49] took into account the deformation of the applied D.C. field and proposed:

$$\mu = \frac{\varepsilon\xi}{6\pi\eta} \, f_{,}(\kappa a)$$

The dimentionaless κa is a measure of the ratio between the particle radius and the thickness of the ionic double layer. In the limit $\kappa a = \infty$ (the double layer is very thin compared with particle radius $f_{,}(\kappa a) = 3/2$ and the result is the Helmholtz-Smoluchowski equation. In the limit $\kappa a \to 0$, $f_{,}(\kappa a) = 1$ and Huckel's result is obtained.

Application of any of these expressions to our Au-acetone colloid system poses some problems. First, according to these theories the charge on the particle is supposed to result from the tight adsorption of negative ions and an outer more loosely attracted layer of counterions stabilizes the similarly charged outer layers of other particles, preventing coagulation.[50] Although our Au-acetone system must contain some kinds of positively charge species to preserve electrical neutrality, the nature of this species is

unknown. Also, all the equations derived have been worked out for aqueous systems.

The Huckel equation where $\kappa a \to 0$ is the one most likely to be applicable to electrophoresis in non-aqueous media:[44]

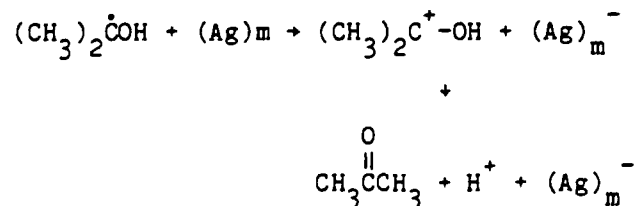$$\mu = \frac{\varepsilon \xi}{6\pi\eta}$$

Solving for ξ:

$$\xi = \frac{\mu 6\pi\eta}{\varepsilon}$$

Substituting the appropriate values:[41,51]

$$\xi = 768 \text{ mV}$$

This value is considerably larger than those reported earlier for aqueous metal sols:[43] colloidal gold = 58 mv, 32 mv; platinum = 44 mv, 30 mv; lead = 18 mv. However, such large values might be expected for a low dielectric medium such as acetone.

Although comparison of these values with those determined in aqueous systems is tenuous, it is clear that the Au particles do possess considerable negative charge. Where this charge comes from is puzzling. It is possible that organic free radicals formed by pyrolysis or by homolylic bond breaking on Au atoms could transfer electrons to Au particles. A number of radiolysis studies of metal colloids in water-acetone solutions indicate that organic radicals do transfer electrons, and the particles act as electron reservoirs (and can behave as catalysts for water reduction).[52,53]

$$(CH_3)_2\overset{\bullet}{C}OH + (Ag)m \to (CH_3)_2\overset{+}{C}-OH + (Ag)_m^-$$

$$\downarrow$$

$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + H^+ + (Ag)_m^-$$

If such a process was involved in our system, the generation of H^+ in solution would be expected. We have found no evidence for this (pH measurements, conductivities).

A second possibility is that the Au particles scavange electrons from the reaction electrodes, walls and solvent. This is the explanation we favor at the present time since we have been able to effect changes in electrophoretic mobilities by supplying electrical potential to the colloid solution as the particles form,[41] and the fact that such charging has been reported before, for example with oil droplets in water.[43]

Spectroscopic Studies:

UV-visible spectra of the Au-acetone sols showed absorptions at 706 and 572 nm, the latter being attributed to plasmon absorption.[54] We have found that the plazmon absorption was not a good indicator of true particle size (obtained by TEM) since the 572 band did not shift significantly with particle size.[35] However, in aqueous solution this band has been used successfully to roughly determine particle size.[55]

NMR studies of acetone stripped from colloidal solutions showed no reaction products.

Conductance Studies:

The conductance of several Au-acetone colloids was measured and compared to pure acetone, and NaI-acetone solutions. As expected the NaI-acetone solutions (0.00075 M up to 1.5 M) showed greatly increased conductivities (130 to >20,000 μohm s^{-1} cm^{-1}). However, the Au-acetone colloid solutions showed approximately the same conductivities (2.5 to 7.4 μohm s^{-1} cm^{-1}) as acetone itself (4.5 μohm s^{-1} cm^{-1}). We conclude that very little "electrolyte" (ion pairs) was present in the purple Au-acetone colloidal solutions.

Temperature Sensitivity:

Samples of Au-acetone colloid were subjected to boiling and freezing. Upon returning to room temperature the colloids remained stable and no flocculation had occurred. These results indicate that steric stabilization[33,43] (solvation) is a very important mechanism. Charge-stabilized colloids generally flocculate when subjected to such extremes of temperature.[56]

Light Sensitivity:

The initially purple-black Ag-acetone colloid solutions turned grey and the Ag precipitated as a spongy grey mass upon exposure to room light for 3-4 days. However, in the dark the colloid solutions remained stable indefinitely.

Particle Formation and Stabilization-Preliminary Conclusions:

Gold atoms dispersed in excess acetone (or other solvents) begin to cluster upon warming form -196°C. Particle (cluster) growth is moderated by two stabilizing mechanisms: (1) strong solvation which is a form of steric stabilization, and (2) electron scavanging to form negatively charged partirles, which is a form of charge stabilization. Ultimate particle size is also affected by initial metal concentration and by warmup time, which suggests that the rates for these processes (stabilization vs growth) are competitive and can be controlled somewhat by time and temperature. Thus, purely kinetic phenomena appear to be involved.

Film Formation

A novel feature of these Au-organic solvent colloids is their film forming properties that can be induced simply by solvent stripping. In this sense they are "living" colloidal particles. Films formed in this way are conductive, but less so than pure metals.[41] The higher resistance of the

films is due to the incorporation of substantial portions of the organic solvent, which can partially be removed by heating, and resistivity then decreases.[41]

Elemental Analyses:

After solvent (acetone) stripping at room temperature (10^{-3} Torr for 1 h) Au films were scraped out and elemental analyses obtained. Variable results were obtained where Au ranged from 63-83% by weight, C from 6-17%, H form 0.8-1.1, and oxygen (by difference) from 6-17%. A heated sample yielded much lower C and H (0.62 C and < 0.01 H). Silver films showed much lower values for C and H.

Pyrolyses:

A film from Au-acetone was pyrolyzed in stages up to 300°C. At intervals mass spectra were recorded, which showed the evolution of acetone (mainly) as well as other products. A similar experiment, where GC-MS was employed allowed identification of several of these minor products as CO_2, H_2O, C_2H_4, C_3H_6, C_3H_8, C_4H_8, C_4H_8O, and C_4H_2 (probably butadiyne). Pyrolysis of adsorbed acetone may be the source of these materials.

Similar treatment of a Ag film from acetone only evolved some CO_2.

Infrared Studies:

A gold residue from acetone was mixed with KBr and compressed to a pellet. Numerous IR scans were accumulated, and the spectrum indicated the presence of adsorbed acetone (mainly, 2960 and 1750 cm^{-1}). However, weaker bands at 2580, 1635, and 570 were also observed which perhaps indicate strongly chemisorbed acetone as Weinberg[57] has recently reported on a Ru surface. The 570 cm^{-1} band is probably due to v_{Au-C}.[58]

Resistivity:

A film was prepared by dripping a colloidal Au-acetone solution on a glass plate edged with silicon rubber adhesive resin. The acetone was allowed to evaporate, and resistivitiy was measured by trimming the film to a rectangular shape. It was connected to electrodes on each end by vapor depositing an opaque film of copper, and resistance measured with a Digital Multimeter KEITHLEY 178 Model, with the following results: Thickness of film = 4.5 μm, resistance = 46 Ω/cm^2, resistivity $\rho(\Omega \cdot cm)$ = 1.8 x 10^{-2}. This can be compared with bulk gold where ρ = 2.4 x 10^{-6}.[51] Thus, the gold film from Au-acetone is more than 7000 times less conductive due to the incorporation of organic material.

Film Formation-Preliminary Conclusions:

Removal of solvent allows the colloidal particles to grow to a film. However, strongly adsorbed acetone, and perhaps small amounts of acetone fragments or telomers as well, remain in the film affecting its electrical properties.

Experimental Section

Preparation of a Typical Au-Acetone Colloid

The metal atom reactor has been described previously.[39,59,60] As a typical example, a W-Al_2O_3 crucible was charged with 0.50g Au metal (one piece). Acetone (300 mL, dried over K_2CO_3) was placed in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 1 x 10^{-4} Torr while the crucible was warmed to red heat. A liquid N_2 filled Dewar was placed around the vessel and Au (0.2g) and acetone (80g) were codeposited over a 1.0 hr period. The matrix was a dark purple color at the end of the deposition. The matrix was allowed to warm

slowly under vacuum by removal of the liquid N_2 from the Dewar and placing the cold Dewar around the reactor.

Upon meltdown a purple solution was obtained. After addition of nitrogen the solution was allowed to warm for another 0.5 hr to room temperature. The solution was syphoned out under N_2 into Schlenk ware. Based on Au evaporated and acetone inlet the solution molarity could be calculated.

Electrophoresis Experiments

The elctrophoresis experiments were carried out by using a glass U-tube of 11.0 cm each with a stopcock on the base to connect a perpendicular glass tube 13 cm long and 35 cm high.[43,45] Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the pole of a 12V battery. The acetone was placed in the U-tube and then the colloid solution added slowly through the lower tube. The migration rate was determined based upon the average of the displacement in each side of the U-tube. A typical experiment was carried out for a period of 3 hr. at 25 °C.

GC-MS Experiments

GC-MS pyrolysis was carried out using a Porapak Q column 6-ft (flow rate 35 mL/min) attached to a Finnigan 4000 quadrupole GC-MS. The sample was placed in a stainless steel tube 10 cm long connected to a 4 way valve. One of the outlets was attached to a Porapak Q column interfaced with the M.S. The stainless steel tube containing a portion of Au colloid film was placed in a furnace connected to a Variac provided with a digitial quartz pyrometer to measure the temperature. Three pyrolysis were performed at 100, 200 and 350 °C with the Au-acetone film.

TEM Studies

Electron micrographs were obtained on JEOL, TEMSCAN -- 100 CX11 combined electron microscope and a HITACHI HV-11B (TEM) operated at 2×10^5 magnification. The specimens for TEM were obtained by placing a drop of the colloid solution on a copper grid coated by a carbon film.

Infrared Red Studies

Infrared spectra were recorded in a Perkin Elmer PE-1330 infrared spectrometer. IR studies of the metal films using either KBr pellets or Fluorolube yielded bands at 2960(s), 2580(m), 1750(s), 1635(m), and 570(w) cm^{-1}.

Acknowledgements

The support of the Office of Naval Research (Contract N0014-4-85-K-821) is acknowledged with gratitude. We thank Galo Cardenas-Trevino for helpful discussions, and Larry L. Seib for assistance with the TEM experiments. Also we want to thank Dr. Ileana Nieves for her assistance in obtaining spectra and Thomas J. Groshens for assistance with the mass spectrometer.

References

(1) Graham, T.; J. Chem. Soc. (London), 1864, 17, 325.

(2) Leicester, H. M., "The Historical Background of Chemistry," Dover Pub., New York, 1956, p 57. Davis, T. L., Isis, 1936, 25, 334.

(3) Higby, G. J.; Gold Bull., 1982, 15(4), 130.

(4) Hauser, E. A.; J. Chem. Ed., 1952, 29, 456; Antoni, F.; "Panacea Aurea: Auro Potabile," Bibliopolio Frobeniano, Hamburg, 1618

(5) Helcher, H. H.; "Aurum Potabile oder Gold Tincture," J. Herbord Klossen, Breslau and Leipzing, 1718; Juncker, J.; "Conspectus Chemiae Theroeticopracticae," Magdelburg, 1730, 1, 882; Macquer, P. J.; "Dictionnarie de Chymie, Paris, 1778.

(6) Ostwald, W.; Z. Chem. Ind. Kolloide, 1908, 4, 5-14 reviews Richter's work.

(7) Fulhame, M.; "An Essay on Combustion with a View to the Art of Dying [Dycing] and Painting," J. Cooper, London, 1794.

(8) Cassius, A.; "De Auro," Leiden, 1685.

(9) Glauber, J. R.; "Teutschlands Wohlfahrt," Amsterdam, 1659.

(10) Faraday, M.; Phil. Trans.," 1857, 147, 145.

(11) Mindel, J.; King, C. V.; J. Am. Chem. Soc., 1943, 65, 2112 and references therein.

(12) Franklin, M. T.; M. S. Thesis, Kansas State University, 1986 gives a complete historical review.

(13) Svedberg, T.; Ann. Phys., 1906, 18, 590; Svedberg, T.; Ber., 1905, 38, 3616.

(14) Zigmondy, Z.; Z. Physikal. Chem.; 1908, 56, 65.

(15) Kohlschutter, H. W.; "New Synthetic Methods, Vol. 3," Verlag Chemie, Weinheim, 1975, pg. 1.

(16) Turkevich, J.; Stevenson, P. C.; Hillier, J.; Faraday Diss., 1951, 55; Turkevich, J.; Hillier, J.; J. Phys. Chem., 1953, 57, 670; Chiang, Y. S.; Turkevich, J.; J. Colloid. Sci., 1963, 18, 772.

(17) Reitstotter, J.; Kolloidchem. Beichefte, 1917, 9, 221.

(18) Zakowski, J.; Kolloidchem. Beihefte, 1926, 23, 117.

(19) Mayer, W. M.; Ger. Pat. 1,133,345, July 1962.

(20) Kimura, K.; Bandow, S.; J. Chem. Soc. Japan, 1983, 56, 3578.

(21) Svedberg, T.; Koll. Zeit., 1907, 1, 229, 257; Svedberg, T.; Koll. Zeit., 1908, 2, 29.

(22) Natanson, E. M.; Kolloid. Zhur., 1949, 11, 84.

(23) Janek, A.; Schmidt, A.; Kolloid. Zhur., 1930, 52, 280.

(24) Marineseu, N.; Bull. Soc. Roumaine Phys., 1934, 36, 181.

(25) Yamakita, I.; Repts. Inst. Chem. Res., Kyoto Univ., 1947, 14, 12.

(26) Ledwith, A.; Chem. Ind., 1956, 1310.

(27) Mayer, E.; Lottermoser, A.; "Uber Anorganische Colloid," Stuttgart,
      1901.

(28) Guther, A.; Huber, J.; Kuhn, E.; Kolloid Zhur., 1916, 18, 57.

(29) Jirgensons, B.; Makromol. Chem., 1951, 6, 30.

(30) Falk, W. P., Taylor, G. M.; Immunochemistry, 1971, 8, 1081.

(31) Lee, P. C.; Meisel, D.; Chem. Phys. Lett., 1983, 99, 262.

(32) Kurihara, K.; Kizling, J.; Stenilus, P.; Fendler, J. H.; J. Am. Chem.
      Soc., 1983, 105, 2574; Ledwith, A.; Chem. Ind. (Lon), 1956, 1310.

(33) Hirtzel, C. s.; Rajogpalum, R.; "Colloidal Phenomena: Advanced
      Topics," Noyes Pubs., New Jersey, 1985, pp 88-97.

(34) Davis, S. C.; Severson, S.; Klabunde, K. J.; J. Am. Chem. Soc., 1981,
      103, 3024 and references therein.

(35) Lin, S. T.; Franklin, M. T.; Klabunde, K. J.; Langmuir, 1986, 2, 259.

(36) Klabunde, K. J.; Murdock, T. O.; J. Org. Chem., 1979, 44, 3901.

(37) Klabunde, K. J.; Tanaka, Y.; J. Mol. Catal., 1983, 21, 57; Imizu, Y.;
      Klabunde, K. J.; J. Am. Chem. Soc., 1984, 106, 2721; Matsuo, K.;
      Klabunde, K. J.; J. Org. Chem., 1982, 47, 843.

(38) Andrews, M. P.; Ozin, G. A.; J. Phys. Chem., 1986, 90, 2922, 2929,
      2938.

(39) Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S., Inorg. Syn.,
      Shriver, D., editor, 1979, 19, 59-86.

(40) Turkevich, J.; Hillier, J.; Anal. Chem., 1949, 21, 475; Turkevich, J.;
      Garton, G.; Stevenson, P. C.; J. Colloid Sci., 1954, Suppl. 1, 26.

(41) Cardenas, G.; Klabunde, K. J.; Dale, B.; Langmuir, submitted.

(42) Burton, E. F.; Phil. Mag., 1909, 17, 587.

(43) Jirgensons, B.; Stramanis, M. E.; "A Short Textbook of Colloid Chemistry," Macmillan, New York, 1962, pp. 132-133, 343.

(44) Shaw, D. J., "Introduction to Colloid and Surface Chemistry," Butterworth, 2nd Ed., London, 1970, pp 157-159.

(45) Shaw, D. J.; "Electrophoresis," Academic Press, New York, 1969.

(46) Overbeek, J. T.; Wiersema, P. H.; "Electrophoresis," Vol. II, M. Bier, Academic Press, New York, 1967, p. 2; Smoluchowski, M.; Bull. Acad. Sci. Cracovic, 1903, 182.

(47) Huckel, E.; Physik. Z., 1924, 25, 204.

(48) Hiemenz, P. C., "Principles of Colloid and Surface Chemistry," Lagowski, J. J., editor, Marcel Dekker, New York, 1977, 453-466.

(49) Overbeek, J. T. G.; Kolloidchem Beihefte, 1943, 54, 287 dicusses Henry's work.

(50) Verwey, E. J. W.; Overbeek, '. T. G.; "Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.

(51) CRC Handbook of Chemistry and Physics, 65th Ed., CRC Press, Boca Raton, Florida, 1984-85, pp F38 and E51.

(52) Hengelein, A.; J. Am. Chem. Soc., 1979, 83, 2209.

(53) Henglein, A.; Lillie, J.; J. Am. Chem. Soc., 1981, 103, 1059.

(54) Mie, G.; Ann. Phys., 1908, 25, 377; Doyle, W. T.; Phys. Rev., 1958, 111, 1067; Ferrell, T. L.; Calcott, T. A.; Warmack, R. J.; Am. Scientist, 1985, 75, 345.

(55) Sadler, P. J.; "Structure and Bonding 29," Dunity, J. D., et al., editors, Springer Verlag, Berlin, 1976, 178; Caro, R. A.; Nicolini, J. O.; Radicella, R.; Int. J. Appl. Radiol-Isotopes, 1967, 18, 327; Jeppeson, M. A.; Barlow, R. B.; J. Opt. Soc. Am., 1962, 52, 99.

(56) Vickery, J. R.; Dept. Sci. Ind. Res. Report Food Investigation Board,
     1929 (1930), 24; Also see Chem. Abs., 1931, 25, 5820.

(57) Templeton, M. K.; Weinberg, W. H.; J. Am. Chem. Soc., 1985, 107, 77⁴.

(58) Puddephatt, R. J.; "The Chemistry of Gold," Elsevier, Amsterdam, 1978,
     p. 220; Nakamoto, K.; "Infrared and Raman Spectra of Inorganic and
     Coordination Compounds," 3rd Ed., Wiley, New York, 1978; Scovell, W.
     M.; Tobias, R. S.; Inorg. Chem., 1970, 9, 945; Scovell, W. M.,;
     Stocco, G. C.; Tobias, R. S.; Inorg. Chem., 1970, 9, 2682.

(59) Klabunde, K. J.; "Chemistry of Free Atoms and Particles," Academic
     Press, New York, 1980.

(60) Timms, P. L. in "Cryochemistry," Moskovits, M.; Ozin, G. A., editors,
     Wiley, New York, 1976.

Figure 1.   Particle Size Distribution (Low Au:Acetone Ratio)

Figure 2.   Particle Size Distribution (Medium Au:Acetone Ratio)

Figure 3.   Particle Size Distribution (High Au:Acetone Ratio)

Figure 4.   TEM Micrograph of Au Particles From Acetone

(Individual particles about 8 nm
   that chain together)

MEAN 20Å
MEDIAN 20Å
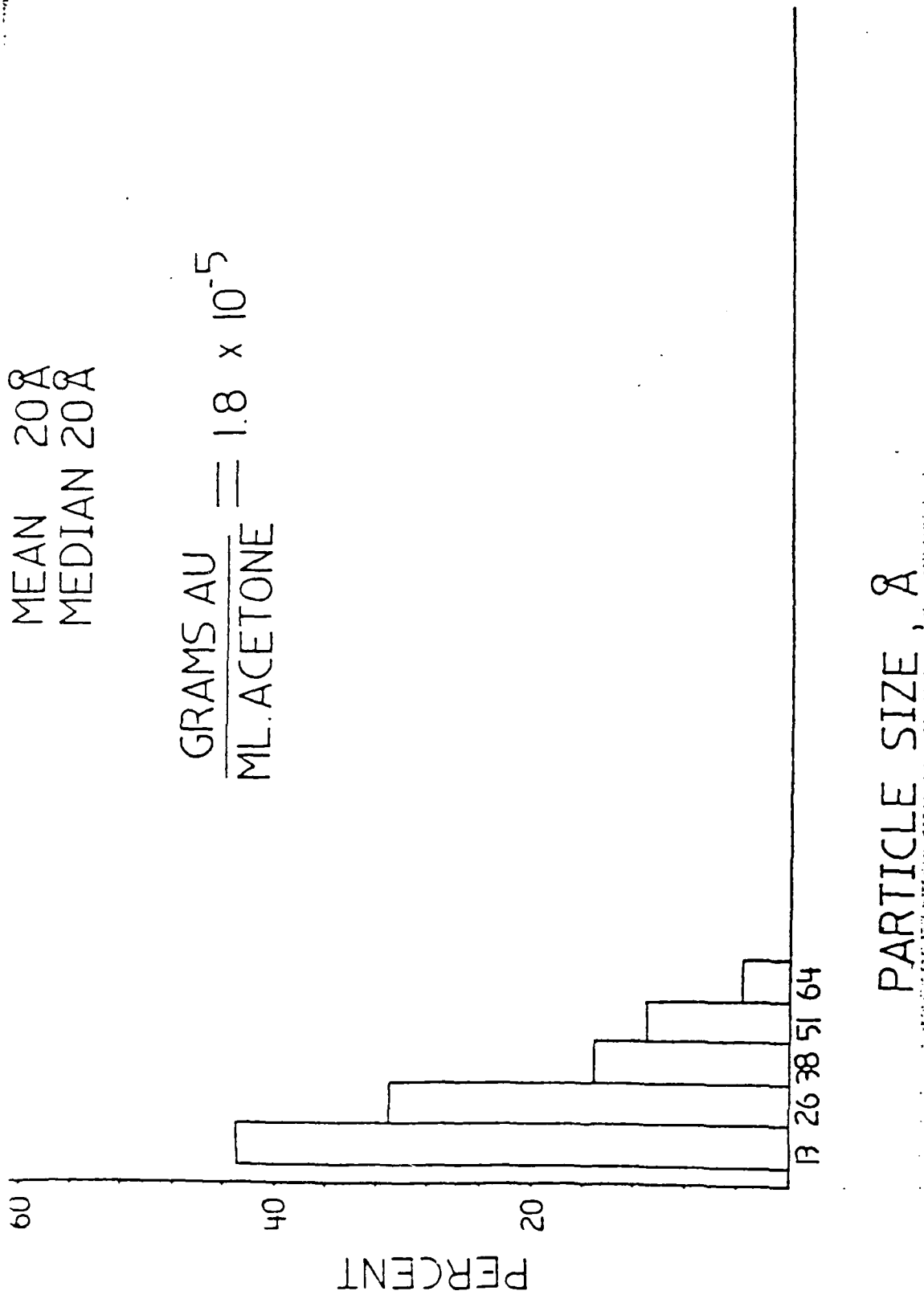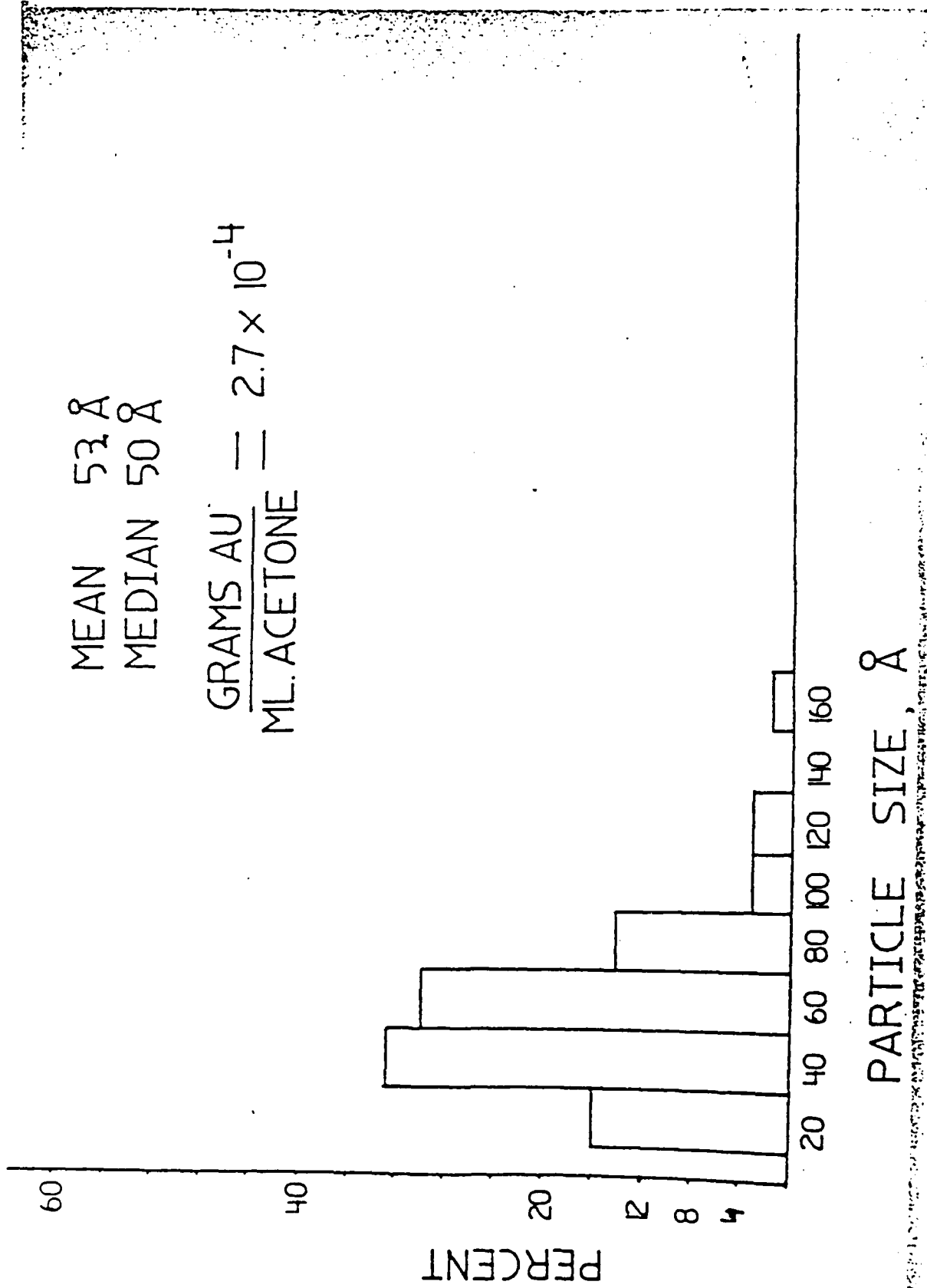
$$\frac{GRAMS\ AU}{ML.\ ACETONE} = 1.8 \times 10^{-5}$$

PARTICLE SIZE, Å

PERCENT

Fig 1

MEAN 53 Å
MEDIAN 50 Å

$$\frac{GRAMS\ AU}{ML.\ ACETONE} = 2.7 \times 10^{-4}$$

PARTICLE SIZE, Å

PERCENT

Fig 2
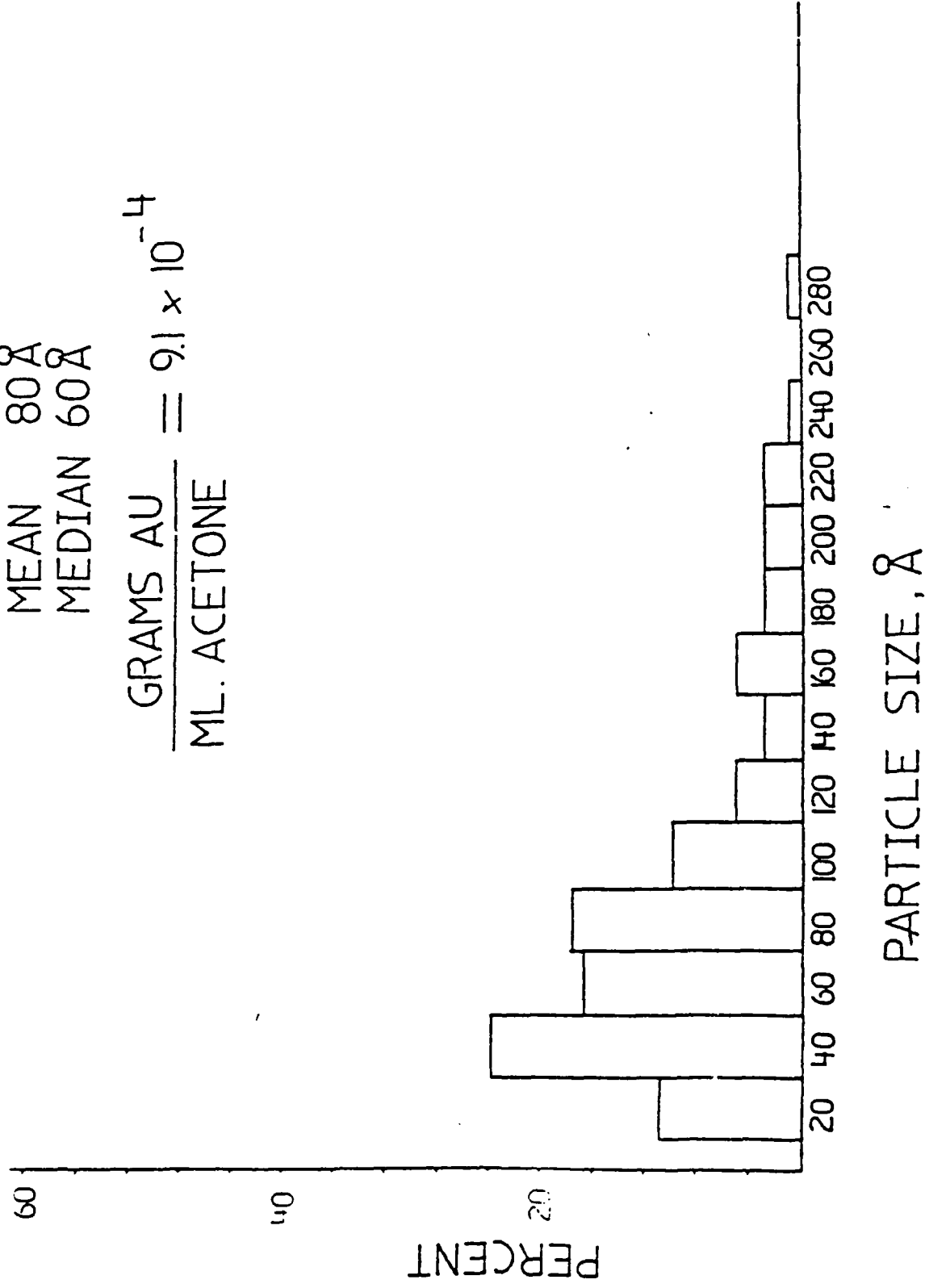
MEAN 80Å
MEDIAN 60Å

$$\frac{GRAMS\ AU}{ML.\ ACETONE} = 9.1 \times 10^{-4}$$

PARTICLE SIZE, Å

PERCENT

Fig 3

Fig. 4

DATE
ILMED
8