A Use of the Electron Microscope in Chemical Microscopy

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In this paper the possibilities that the electron microscope may offer in chemical microscopy are discussed, a technique for adapting the electron microscope to this study is presented, and typical pictures are shown of results obtained with the technique described. The technique for the controlled growth of crystals on thin plastic films is based on the diffusion of ions and molecules through the plastic film and subsequent precipitation on the film.

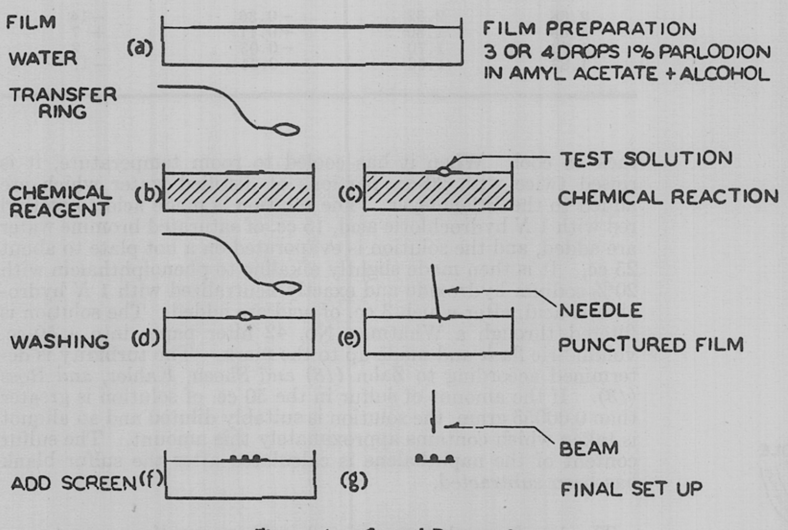


Figure 1. Crystal Preparation

THE light microscope has been used for many years to study the habit of crystals of insoluble precipitates as a means of chemically identifying the material. The first attempt at systematic microscopical qualitative analysis was proposed in 1877 by Boricky (*1*). Subsequent contributions by Behrens, Emich, Donau, and others developed the methods and techniques of chemical microscopical analyses. These methods are described in Chamot and Mason's (*3*) handbook.

In chemical microscopy, the light microscope is used to aid the eye in distinguishing the crystal habit of a substance. This habit is correlated with its chemical composition. The crystals studied are usually prepared by causing a reaction of a solution or crystal of the unknown with test reagents. For some reactions, if reproducible crystal habits are to be obtained, the concentration, pH, temperature, rate of growth, and other factors must be controlled. Additional information which may be helpful in identifying the material can be obtained from polarized light and refractive index studies on the crystal.

During the past decade the electron microscope has been developed to a point where it can be applied to a wide variety of problems. The purpose of this paper is (1) to investigate the possibilities that the electron microscope may offer in chemical microscopy, (2) to present one technique for adapting the electron microscope to this study, and (3) to show typical pictures of some results obtained with the technique described.

THE ELECTRON MICROSCOPE

Three factors in general limit the use of the light microscope: (1) the limited resolving power, (2) the limited depth of focus, and (3) the short working distance. Thus, the observation of detail is limited to an effective magnification of 1200 diameters. However, in order to obtain sufficient depth of focus, most light microscopic observations are made at magnifications of the order of 200 diameters. Therefore special precautions must be taken to grow crystals of the proper size for study.

The electron microscope has a useful magnification of about 50,000 diameters. At this magnification the instrument has a depth of focus of 10 microns and a limit of resolution of 0.004 micron. The light microscope at 200 diameters has a depth of focus of 4 microns and a resolution of 1 micron. These relationships have been described by Burton, Barnes, and Rochow (*2*).

These facts may favor a useful role for the electron microscope in chemical microscopy if technique can be developed for growing crystals which may be studied in the electron microscope.

With the present designs of electron microscopes, it is impossible to observe specimens unless they are exposed to a vacuum of 0.1 micron of mercury or better. This factor, as well

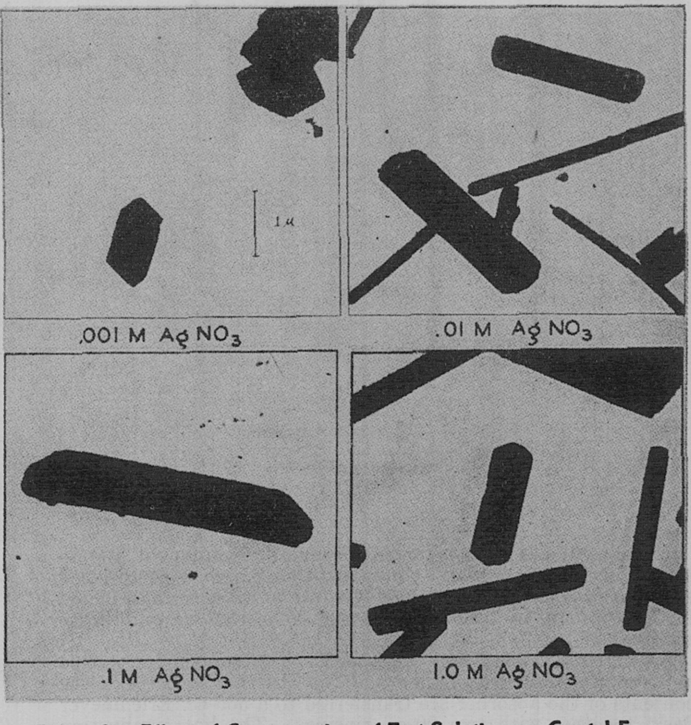


Figure 2. Effect of Concentration of Test Solution on Crystal Form

Reagent, 0.1 *M* K_2CrO_4. Precipitate, Ag_2CrO_4

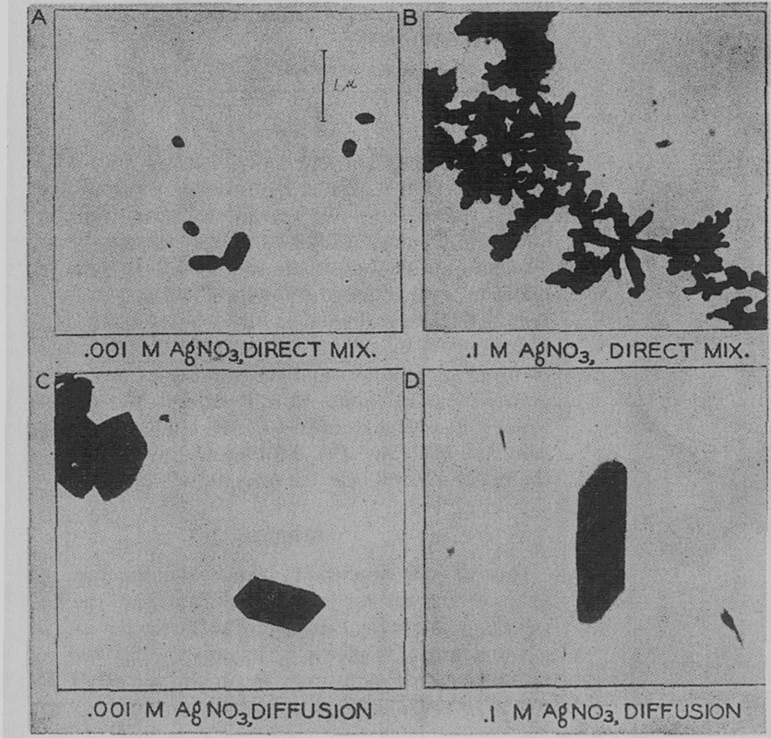


Figure 3. Effect of Method of Precipitation on Crystal Form

Reagent, 0.1 *M* K_2CrO_4. Precipitate, Ag_2CrO_4

as the absorption of energy of the electron beam by specimens of finite thickness, imposes limitations on the nature of the crystals which may be studied. Crystals containing water of crystallization or other volatile matter may decompose under the vacuum conditions in the electron microscope. The absorption of energy from the electron beam may be sufficient to melt the substance or to cause it to undergo decomposition or a transition of crystal phase.

The shadow technique is used for the study of small crystals, which are supported by a thin plastic film mounted on a fine-mesh metal screen. If the thin plastic film can be used for preparation of the crystals as well as for support in the microscope, the over-all technique will be simplified.

METHOD

The preparation of specimens for the electron microscope requires that the material be evaporated to dryness before being placed in the vacuum chamber. If the crystals are produced by the interaction of the two solutions, they must be collected in a dispersed manner on a thin plastic film and the mother liquor removed. This latter fact is an important difference in the manner of preparation of crystals for the electron microscope as contrasted with the light microscope. Crystals studied in the light microscope in chemical microscopy are usually observed in their mother liquor.

Many methods have been proposed for carrying out tests in chemical microscopy (*3*). Although a few of them could be adapted for use with the electron microscope, it is of considerable advantage to utilize the property of diffusion of ions and molecules through thin plastic films. The technique then is to collect, wash, and observe the crystals on the same piece of plastic film. The method is shown schematically in Figure 1.

A large section of Parlodion film is formed on clean distilled water, using 3 to 4 drops of a 1% solution of Parlodion in a 2 to 1 solvent mixture of amyl acetate and ethyl alcohol. The purpose of the alcohol is to increase the porosity of the film. Sections of the film, 1 cm. in diameter, are removed by raising a small ring under the Parlodion film; a small needle is used to cut the film away from the ring. The sections of film are now placed on the surface of the reagent in a small crystallizing dish. The concentration of the reagent is 0.1 molar. A small drop of the test solution is placed on the upper surface of the film by a small glass capillary tube. Diffusion of the ions through the film allows the formation of an insoluble crystalline precipitate in the drop where solubility factors permit and if test solutions which are known to produce crystalline precipitates are chosen for study. The time necessary to produce sufficient crystals for observation in the electron microscope is of the order of 1 to 2 minutes. A small hand lens is useful in observing the extent of crystallization.

The Parlodion film and crystals are removed from the reagent solution (Figure 1, *c*) by means of a second ring (with handle) slightly smaller in diameter than the one used in Figure 1, *a*. The film is now gently deposited on the surface of clean distilled water in a crystallizing dish. The water and ions will diffuse through the thin film and gradually eliminate the objectionable ions in the mother liquor. The washing process is allowed to proceed for 10 minutes. The film under the drop is punctured with a carefully sharpened needle and the residue liquor in the drop drains away. Blank tests indicate that the washing and subsequent drainage of the liquid by puncturing are sufficient to remove extraneous ions which would form crystals on the evaporation of the mother liquor. A metal screen is placed over the area of interest and the film plus screen removed to dry in a vacuum at room temperature.

Several modifications of the above technique for preparing crystals have been tried. The first modification is to add one reagent in the form of a crystal to the other reagent as a drop of solution resting on the plastic film over clean distilled water. After precipitation, the crystals are washed and the liquid drained away as described above. A second modification is to add a drop of test solution directly to a drop of reagent placed on the surface of the Parlodion film supported on clean distilled water. This is called the method of direct mixing to distinguish

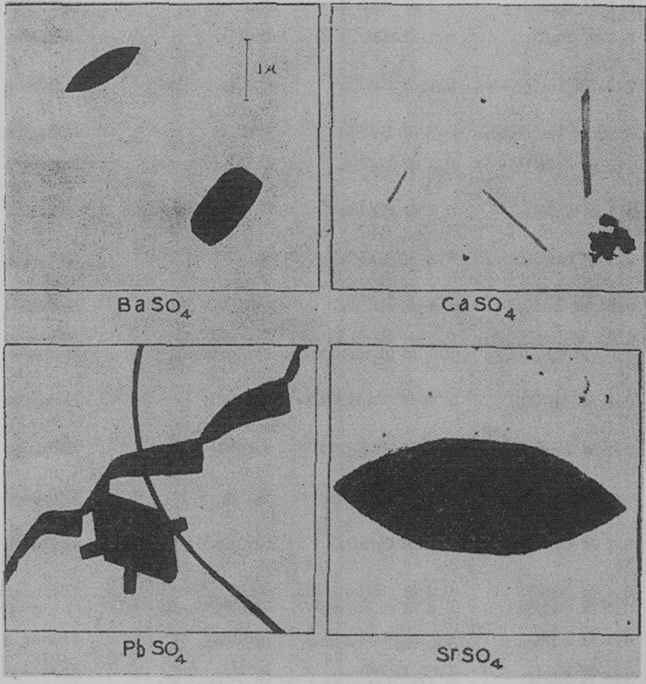


Figure 4. Sulfates of Barium, Calcium, Lead, and Strontium

Reagent, 0.1 *M* K_2SO_4

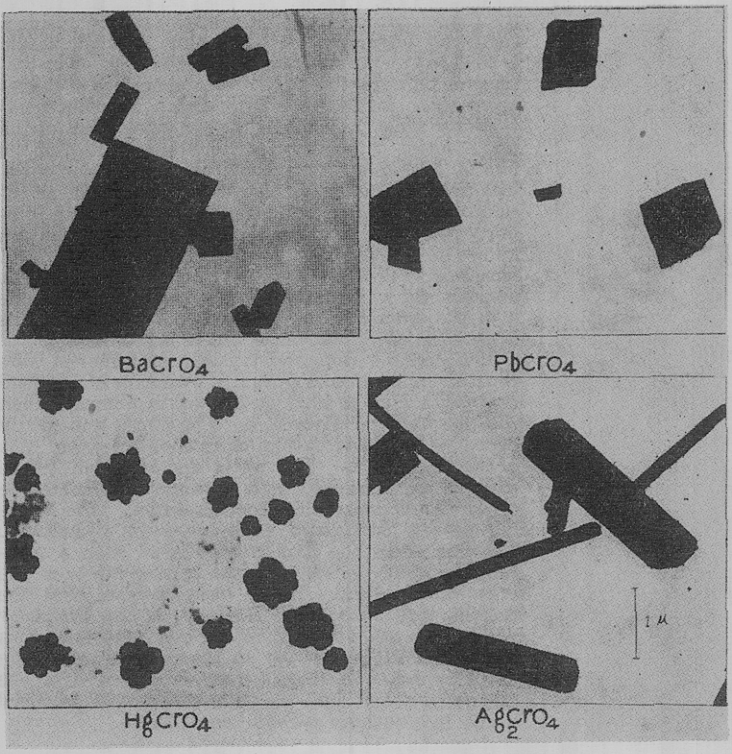


Figure 5. Chromates of Barium, Lead, Mercury, and Silver

Reagent, 0.1 *M* K_2CrO_4

it from precipitation and crystal formation by diffusion. The direct mixing methods are used for preparing the more soluble precipitates where considerable material must be diffused through the membrane. The diffusion method would require a long time for diffusion of the required amounts of ions for precipitation. A slight variation on these latter methods is to precipitate by mixing the two solutions on a spot plate or in a small capillary and then transfer the precipitate plus liquor to a Parlodion film on the water for washing. Most of the studies described here are made by the diffusion method because of the better control over the precipitation process.

RESULTS

One of the important factors determining the habit of the crystal is the concentration of the test solution. A study of this factor made for the case of silver chromate is shown in Figure 2. The test reagent is 0.1 *M* potassium chromate and 0.001 *M*, 0.01 *M*, 0.1 *M*, and 1.0 *M* test solutions of silver nitrate

Table I. Crystals Studied

Test Solution	Reagent	Precipitate	Method	Description of Crystals		
				Electron microscope	Light microscope	Macroscopic
0.1 *M* $BaCl_2$	0.1 *M* K_2SO_4	$BaSO_4$	Diffusion	Prismatic, tabular with pointed and square ends	Well-defined, tabular (*3*)	Prismatic (*5*)
$Ca(NO_3)_2$ crystal	0.1 *M* K_2SO_4	$CaSO_4.2H_2O$	Mixing	Acicular	Long, slender needles (*3*)	Prismatic to acicular (*5*)
0.01 *M* $Pb(NO_3)_2$	0.1 *M* K_2SO_4	$PbSO_4$	Diffusion	Prismatic, stalactitic	Granular, indistinct (*3*)	Stalactitic, tabular, conic (*5*)
0.1 *M* $Sr(NO_3)_2$	0.1 *M* K_2SO_4	$SrSO_4$	Diffusion	Prismatic, resembles $BaSO_4$	Granular, indistinct (*3*)	Prismatic (*5*)
0.1 *M* $BaCl_2$	0.1 *M* K_2CrO_4	$BaCrO_4$	Diffusion	Prismatic, large and small crystals	Minute grains; square or rectangular plates and tablets (*3*)	......
0.01 *M* $Pb(NO_3)_2$	0.1 *M* K_2CrO_4	$PbCrO_4$	Diffusion	Prismatic, tabular	Pulverulent (*3*)	Prismatic (*5*)
0.01 *M* $Hg(NO_3)_2$	0.1 *M* K_2CrO_4	$HgCrO_4$	Diffusion	Clusters of poorly developed crystals	No crystalline precipitate (*3*)	......
0.1 *M* $AgNO_3$	0.1 *M* K_2CrO_4	Ag_2CrO_4	Diffusion	Prismatic, columnar and acicular	Plates, rectangular, elongated (*3*)	......
0.1 *M* $BaCl_2$	0.1 *M* K_2CO_3	$BaCO_3$	Diffusion	Columnar, pointed, with poorly developed forms	Minute, needles, spider-like aggregates and tiny spherulites (*3*)	Columnar, crystals always repeated twins (*5*)
0.01 *M* $Ca(NO_3)_2$	0.1 *M* K_2CO_3	$CaCO_3$	Diffusion	Outlines suggest rhombohedrons; large crystals and small fibrous ones	Tiny disks and well-formed rhombohedra (*3*)	Variety of habits (*5*)
0.01 *M* $Pb(NO_3)_2$	0.1 *M* K_2CO_3	$PbCO_3$	Diffusion	Hexagonal and irregular outlines	Prismatic (*7*)	Tabular (*5*)
0.1 *M* $Sr(NO_3)_2$	0.1 *M* K_2CO_3	$SrCO_3$	Diffusion	Spear-shaped; poorly defined forms	Spherulites and dumbbell aggregates of tiny needles (*3*)	Spear-shaped, acicular (*5*)
0.1 *M* $CuSO_4$	0.1 *M* K_2CO_3	$Cu(OH)_2.CuCO_3{}^a$	Diffusion	Triangular, lamellar prisms grouped as rosettes	......	Slender, acicular prisms grouped as rosettes (*5*)
0.1 *M* $MnSO_4$	0.1 *M* K_2CO_3	$MnCO_3$	Diffusion	Rounded, irregular, globular	......	No distinct crystals (*5*)
0.1 *M* $AgNO_3$	0.1 *M* K_2CO_3	Ag_2CO_3	Diffusion	Hexagonal outlines	......	
0.01 *M* $ZnCl_2$	0.1 *M* K_2CO_3	$ZnCO_3$	Diffusion	Clusters of irregular and fibrous crystals	......	Rarely well crystallized (*5*)
0.01 *M* $Pb(NO_3)_2$	0.1 *M* Na_2HAsO_4	$Pb_3(AsO_4)_2{}^a$	Diffusion	Acicular	Gelatinous precipitate (*3*)	......
0.01 *M* $Pb(NO_3)_2$	0.1 *M* $(NH_4)_2HPO_4$	$Pb_3(PO_4)_2$	Diffusion	Regular and irregular hexagonal outlines	Curdy precipitate changing to minute rods and needles (*3*)	......
0.1 *M* $AgNO_3$	0.1 *M* Na_2HAsO_4	Ag_3AsO_4	Diffusion	Hexagonal outlines	Granular precipitate changing to irregular grains and platelets (*3*)	......
0.1 *M* $AgNO_3$	0.1 *M* $(NH_4)_2HPO_4$	Ag_3PO	Diffusion	Square and rectangular outlines	Granular; tiny dendritic stars, crosses, and radiates (*3*)	......
.05 *M* $SnCl$	0.1 *M* $Na_2C_2O_4$	SnC_2O_4	Diffusion	Irregular square and parallelogram outlines	Great variety of prismatic or imperfectly developed crystals (*3*)	......
0.1 *M* $CdSO_4$	0.1 *M* $CdSO_4$	$CdCO_3$	Diffusion	Prismatic, columnar; poorly developed crystals	......	
0.1 *M* $NiSO_4$	0.1 *M* $(NH_4)_2HPO_4$	$Ni_3(PO_4)_2$	Diffusion	Prismatic and equant	......	
0.1 *M* $CuSO_4$	0.1 *M* $(NH_4)_2HPO_4$	$Cu_3(PO_4)_2.Cu(OH)_2{}^a$	Diffusion	Compacts of irregular pointed crystals	......	Small prismatic; united in druses (*5*)
0.1 *M* K_2SO_4	5% $H_2PtCl_6.6H_2O$	K_2PtCl_6	Mixing	Hexagonal outlines	Well-formed octahedra (*3*)	Octahedral and cubic forms; well-formed (*7*)
0.1 *M* K_2SO_4	10% $HClO_4$	$KClO_4$	Diffusion	Prismatic, acicular	Prismatic, skeletal (*3*)	......
0.1 *M* $NiSO_4$	0.5% $C_4H_8N_2O_2$	$Ni(C_4H_7N_2O_2)_2$	Mixing	Long, slender needles	Acicular (*3*)	......
0.1 *M* $AgNO_3$	0.1 *M* KCNS	AgCNS	Diffusion	Prismatic, columnar	......	

[a] Composition uncertain.

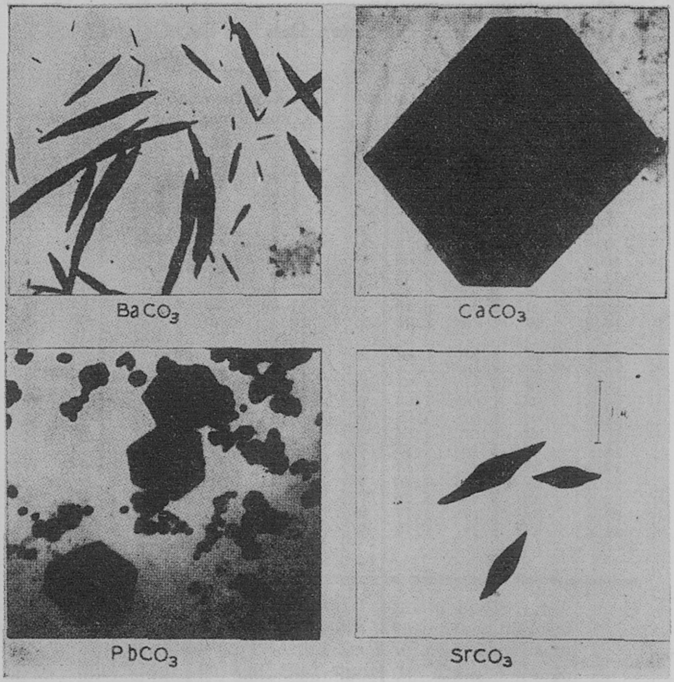


Figure 6. Carbonates of Barium, Calcium, Lead, and Strontium
Reagent, 0.1 *M* K_2CO_3

are used. The formation and growth of the crystal are carried out by the diffusion technique. As the concentration of silver nitrate is increased, both the number and size of the crystal increase. However, for the 1.0 *M* solution, the crystal size decreases. Although a statistical study was not made on the crystal size as affected by the concentration, observations of different portions of the specimen on the fluorescent screen indicated the tendencies noted. The habit of the crystal is similar for the various concentrations, although the prismatic form of the crystal is enhanced in the case of silver chromate by increasing the concentration. This is seen in the longer crystals which are formed.

Figure 3 shows a comparison of typical crystals obtained by the diffusion technique with those obtained by direct mixing. The effect of concentration of test solution on crystal habit is shown for both cases. For equal concentration of test solution the diffusion method produces the larger crystals; it also produces superior crystals having fewer intergrowths. Increasing the concentration produces smaller crystals by direct mixing while larger crystals are produced by the diffusion method.

A complete study of chemical crystallography would involve: (1) space lattice, (2) habit, (3) number of nuclei, (4) rate of growth, (5) solid solution, and (6) degree of supersaturation. This analysis is difficult and will not be attempted in this paper. However, certain correlations can be made of the chemical composition and the habit of the crystal based on the micro- and macroscopic crystals.

Figure 4 shows the crystal habits obtained for the sulfates of barium, calcium, lead, and strontium, all formed by diffusion precipitation except for calcium sulfate which was formed by the interaction of the test reagent with a crystal. Although the calcium sulfate is probably precipitated as calcium sulfate dihydrate, it is found to be stable to the vacuum and the electron beam in the electron microscope. Table I shows a list of the precipitates obtained in this study; their crystal habits are shown in Figures 4 to 10. The test reagent, test solution, and method of formation are also included.

Figure 5 shows the results obtained with the chromates of barium, lead, mercury, and silver. The carbonates of barium, calcium, lead, and strontium are shown in Figure 6, while Figure 7 shows the carbonates of copper, manganese, silver, and zinc. The arsenates and phosphates of lead and silver are shown in Figure 8, while Figure 9 shows the crystals of stannous oxalate, cadmium carbonate, and nickel and copper phosphate. Figure 10 shows the crystals of potassium perchlorate and chloroplatinate, nickel dimethylglyoxime, and silver thiocyanate.

The crystal habits of the various precipitates are found to be reproducible and, in general, simple habits are obtained. The experimentally observed habits of the crystals are compared in Table I with those given by Chamot and Mason (*3*) and Winchell (*7*) for the light microscope and those given by Dana (*4*, *5*) for macroscopic crystals. Fair agreement is obtained. For gelatinous and granular precipitates the advantage of the high resolving power of the electron microscope is evident. Strontium sulfate, for example, is granular and indistinct in the light microscope but is shown in Figure 4 to have a distinct prismatic habit. The electron micrographs or pictures were taken at 6,700 diameters and then enlarged optically to 16,750 diameters. The size of the crystals can be estimated by comparing the dimensions with the value of 1 micron drawn on each series of prints.

In addition to the experiments described above, the insoluble iodides and oxalates were studied. The iodides were found to melt or decompose in the electron beam. This process could be followed visually on the fluorescent screen. The oxalates decomposed in the microscope or else the crystal forms were not distinctive.

CALCULATIONS

Three calculations will be made: (1) the amount of silver ions precipitated in the experimen tshown in Figure 3, *C*, (2) the distribution of crystals in the specimen and in the photograph, and (3) the theoretical limit to the precipitation of silver ion by the chromate ion.

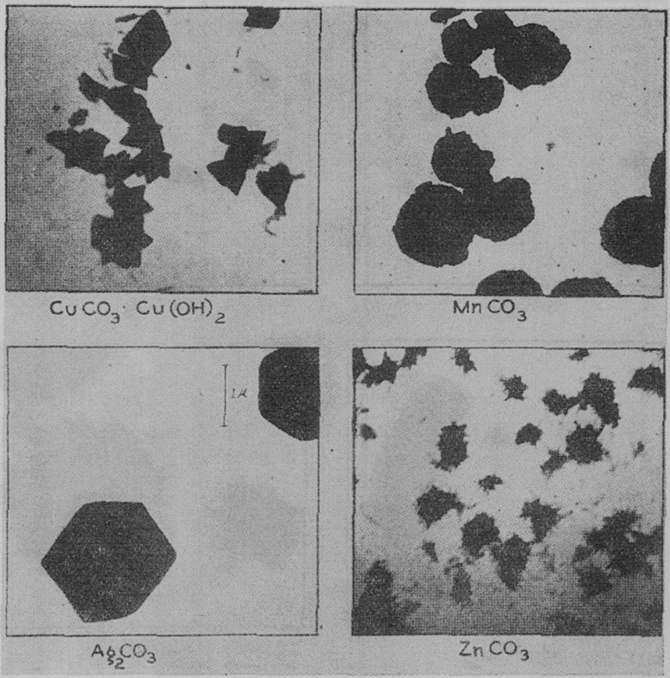
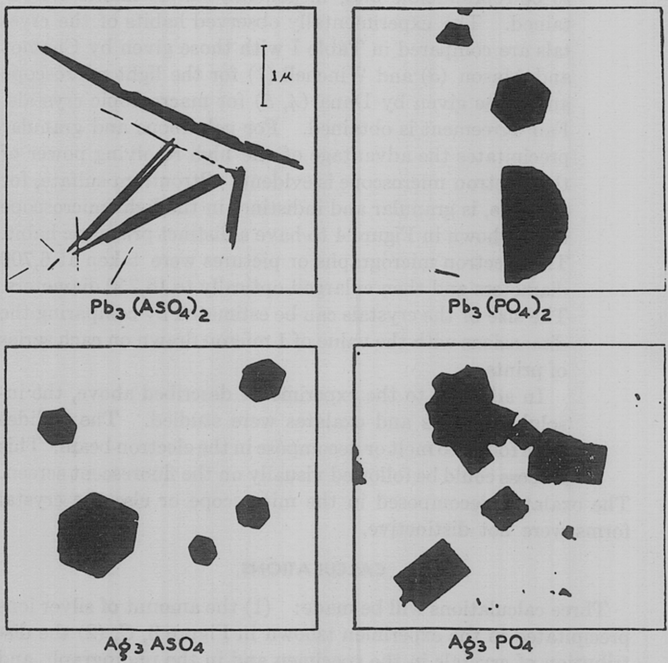


Figure 7. Carbonates of Copper, Manganese, Silver, and Zinc
Reagent, 0.1 *M* K_2CO_3

Table II. Gold Calibration

D, Mm.	I/I_0	d_{hkl}	$D \times d_{hkl}$
11.7	S	2.35	27.5
13.5	M	2.03	27.4
19.1	M	1.439	27.5
22.3	M	1.227	27.4
23.3	W	1.173	27.4
29.3	M	0.935	27.4
30.1	M	0.910	27.4
32.9	W	0.832	27.4
34.9	W	0.784	27.4
		Av.	27.4

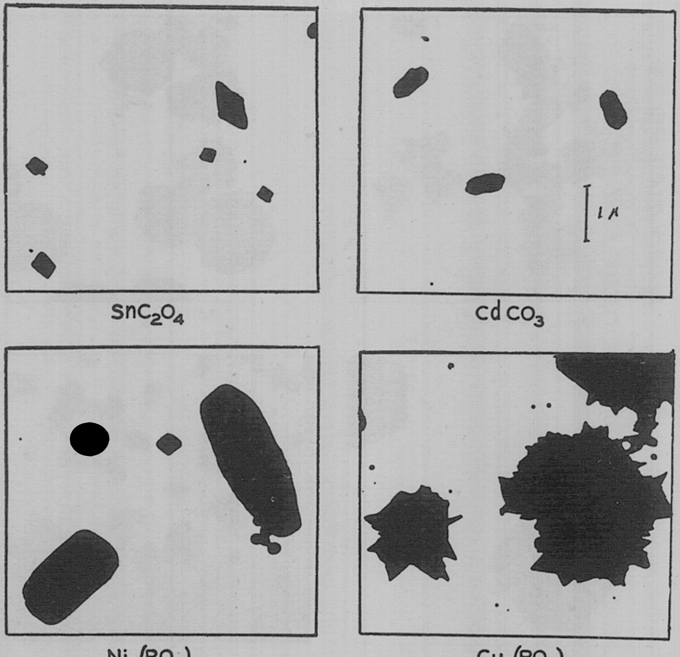


$Pb_3(AsO_4)_2$ $Pb_3(PO_4)_2$

Ag_3AsO_4 Ag_3PO_4

Figure 8. Arsenates and Phosphates of Lead and Silver

Reagents, 0.1 *M* $(NH_4)_2HPO_4$ and 0.1 *M* Na_2HAsO_4



SnC_2O_4 $CdCO_3$

$Ni_3(PO_4)_2$ $Cu_3(PO_4)_2$

Figure 9. Stannous Oxalate, Cadmium Carbonate, and Nickelous and Cupric Phosphates

Reagents, 0.1 *M* $Na_2C_2O_4$, 0.1 *M* K_2CO_3, and 0.1 *M* $(NH_4)_2HPO_4$

Table III. Electron Diffraction Data on $BaCrO_4$ and $BaSO_4$

$BaCrO_4$					$BaSO_4$				
Experimental			X-Ray tables		Experimental			X-Ray tables	
D, mm.	I/I_0	d_{hkl}	d_{hkl}	I/I_0	D, mm.	I/I_0	d_{hkl}	d_{hkl}	I/I_0
6.9	M	3.97	4.00	M	6.35	W	4.30	4.35	M
7.5	M	3.65	..	..	7.0	M	3.90	3.89	M
7.8	S	3.52	3.54	S	7.65	W	3.57	3.57	W
8.1	M	3.38	..	..	7.95	S	3.43	3.44	S
8.7	S	3.15	3.19	S	8.3	W	3.29	3.31	M
9.5	S	2.89	2.90	S	8.8	S	3.10	3.10	S
9.9	W	2.77	2.78	M	9.65	M	2.83	2.83	M
10.7	W	2.56	2.53	W	10.1	M	2.71	2.72	M
11.6	W	2.37	2.37	W	10.6	M	2.57	..	..
12.2	W	2.25	2.25	W	11.15	W	2.45	2.47	W
12.7	S	2.16	2.16	S	11.85	W	2.30	2.31	W
14.5	W	1.89	1.91	M	12.4	M	2.20	2.20	W
					13.0	S	2.10	2.10	S
14.9	W	1.84	1.80	W	13.3	W	2.05	2.04	W
15.2	W	1.80	..	..	14.2	W	1.92	1.92	W
16.0	M	1.71	1.71	M	14.9	W	1.83	1.85	W
16.5	W	1.66	1.66	W	15.9	W	1.72	1.74	W
16.9	W	1.62	1.62	W	16.85	W	1.62	1.63	W
17.5	W	1.57	1.56	W	17.2	W	1.59	1.58	W
18.9	W	1.45	1.45	W	17.85	W	1.53	1.52	M
19.4	W	1.41	1.41	W	19.2	W	1.42	1.42	W
21.2	W	1.29	1.29	W	19.4	W	1.41	..	..
22.2	W	1.24	1.25	W	21.6	W	1.26	1.26	W
23.4	W	1.17	1.17	W	24.9	W	1.10	1.09	W
24.4	W	1.12	1.12	W	27.7	W	0.987	..	..
					30.3	W	0.902	..	..

1. Silver nitrate, 0.001 *M*, is reacted with 0.1 *M* potassium chromate by diffusion. Sample volume is approximately 10^{-3} cc. or 1 cu. mm. This volume contains 1.08×10^{-7} gram of silver ions per cu. mm. This silver produces crystals upon diffusion of chromate into the sample volume—some are shown in Figure 3, *C*. The method in this case has detected 1.08×10^{-7} gram of silver.

2. The specimen area is 1 sq. mm. and 1 cu. mm. is used for the sample. Assume uniform distribution of crystals over the specimen area and also that the resulting silver chromate crystal is about 1 micron long, 0.5 micron wide and deep. This follows from analysis of crystal shown in Figure 3, *C*, and from the assumption that the crystal is as deep as it is wide. Weight of crystal is 1.41×10^{-12} gram and it contains about 0.91×10^{-12} gram of silver. If the silver ions are precipitated as silver chromate crystals of a uniform size, a total of about 118,000 crystals would be formed over the 1 sq. mm. area.

The area of specimen from which the micrograph was photographed (6700×) represents about 1/18,000 sq. mm. Therefore the average number of crystals found in the electron microscope on any 4 square inch area (2 × 2) is 6.5. This is ample. Specimens having one tenth or one hundredth of this number may be used, since the specimen can be moved on the stage in the electron microscope.

3. The theoretical limit to the detection of silver ion by the chromate ion can be estimated. The formation of crystals by the diffusion method is limited by the solubility product and by the time for the crystal to grow. The diffusion of the potassium and chromate ions into the drop is nearly independent of the silver and nitrate ion concentrations at low silver nitrate concentrations. However, the crystal nuclei must be formed and grow before the silver nitrate diffuses out of the drop and into the chromate solution. The solubility product of silver chromate is 9×10^{-12} at 25° C. If a 1 *M* potassium chromate solution is used as a reagent, the limiting concentration on the silver ion is 3×10^{-6} mole per liter or 3.24×10^{-10} gram per cu. mm. Therefore the method may detect one tenth or one hundredth the amount of silver specified in part 1 or 10^{-8} or 10^{-9} gram of silver. Below these figures solubility product considerations enter and difficulties may be encountered in finding crystals for study.

Similar calculations can be made for the other systems studied.

ELECTRON DIFFRACTION

An additional feature of the electron microscope, which is of considerable value in identifying the nature of the crystal, is the use of the electron diffraction adapter. For this purpose a heavier concentration of crystals is necessary, and the growth of well-formed crystals is not important. The technique of using the electron diffraction adapter has been described by Picard (*6*).

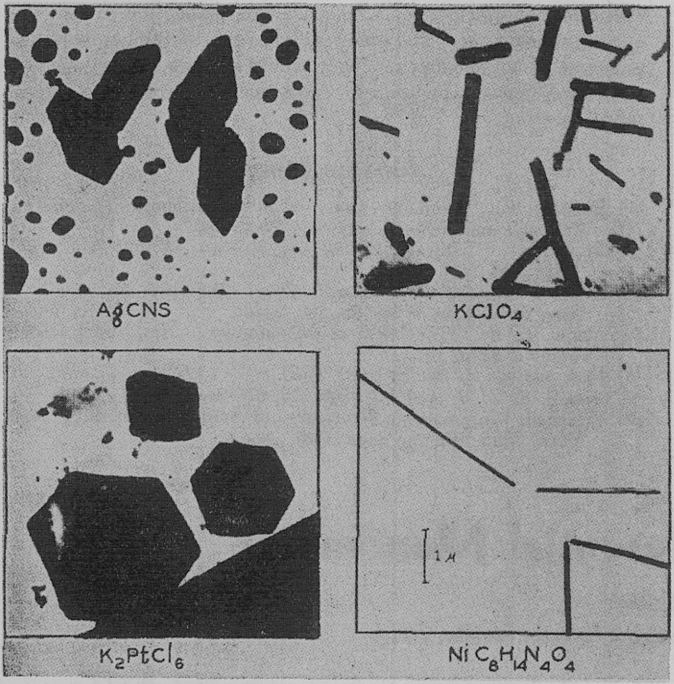


Figure 10. Silver Thiocyanate, Potassium Perchlorate and Chloroplatinate, and Nickel Dimethylglyoxime

Figure 11 shows typical diffraction pictures of barium chromate, barium sulfate, gold, and a Parlodion film. The barium chromate and barium sulfate are prepared by the diffusion technique, while the gold is formed by evaporation on to a Parlodion film. The gold picture is included for calibration purposes and is taken at the same time as the other pictures in the group. This calibration procedure is necessary because of the change in the absolute value of the accelerating voltage and also the change of the current in the diffraction focusing lens.

Table II shows the data obtained from the gold calibration. *D* refers to the diameter of the particular diffraction ring. The ratio I/I_0 is an estimate of the relative intensities of the several lines. S refers to strong, M to medium, and W to weak. The lattice spacings d_{hkl} are taken from x-ray diffraction tables. The calibration constant ($D \times d_{hkl}$) is found to be 27.4.

Table III shows the electron diffraction data obtained from barium chromate and barium sulfate crystals. The data obtained from x-ray tables are included for comparison; the agreement is good. The value of these data is apparent from the table.

CONCLUSIONS

A technique for the controlled growth of crystals on thin plastic films is based on the diffusion of ions and molecules through the plastic film and subsequent precipitation on the film.

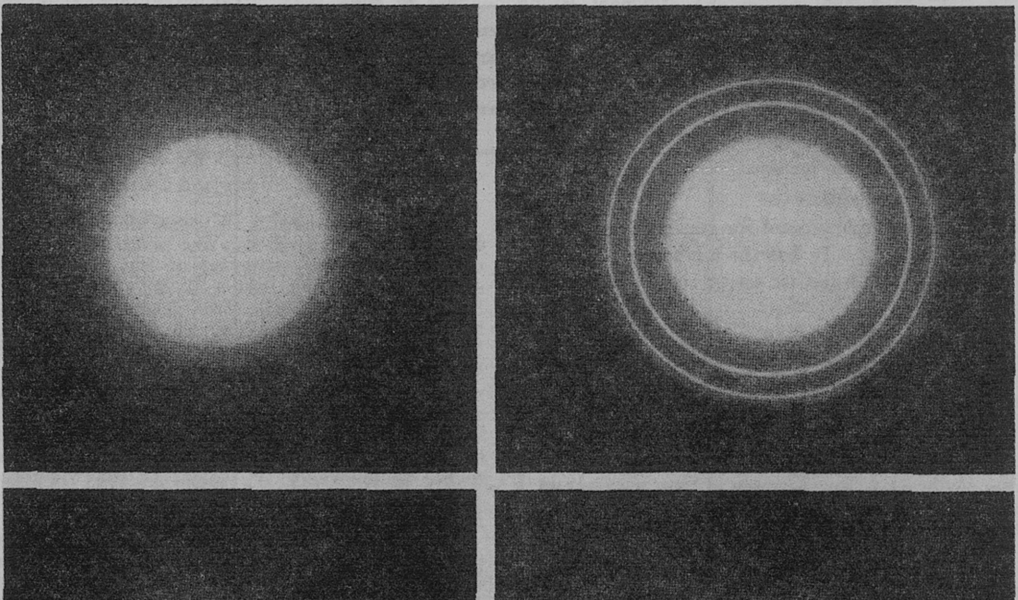


Figure 11. Diffraction Patterns of Parlodion, Evaporated Gold, Barium Sulfate, and Barium Chromate

The diffusion method offers better control of the crystal size and shape than preparing crystals by direct mixing.

Although the crystal size depends upon the concentration, the habit is only slightly affected.

A considerable number of crystals were prepared and electron micrographs taken. When the habit of the crystals was compared with that observed for micro- and macroscopic crystals, good agreement was observed.

Calculations for a typical reaction indicate that quantities of the order of 10^{-7} gram of silver ion can be detected in reaction with a 0.1 M potassium chromate solution. The theoretical limitation is approximately 10^{-8} or 10^{-9} gram of silver ion in the same reaction.

Electron diffraction analysis is utilized to help in identification of the crystal.

The application of the electron microscope to chemical microscopy is suggested. A useful role may be expected, especially in the study of precipitates which are not perceptible under the optical microscope. The practical details of individual reactions have yet to be developed. They would include a study of concentration limits, interferences, trials in the identification of real unknowns, etc.

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An Automatic Differential Manometer

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The author describes a gage for measuring pressure changes with an accuracy of 0.01 mm. when the total pressure is 50 mm. or more. The sensitivity of the instrument is independent of the total pressure and mercury is used as the confining liquid. Pressure changes are read directly off a scale graduated in millimeters.

THE problem of measuring small pressure changes in gaseous reactions has always presented considerable difficulty to the physical chemist. The McLeod gage has probably been used more than any other instrument for this purpose but it can be used only at relatively small total pressures. Bourdon and spoon gages have been used in many cases but they are of necessity very fragile if pressure changes of the order of 0.01 mm. are to be detected. In the opinion of the author the most satisfactory differential manometer for general laboratory use is that due to Pearson (*4*). It has the advantage of using mercury as the confining liquid and its sensitivity is independent of the total pressure.

The principle on which the gage operates is simple. Consider three vertical glass tubes, T_1, T_2, and T_3, joined together at the bottom and containing mercury. If T_1 is evacuated and T_2 is connected to the system whose pressure changes are to be measured, and if h_1, h_2, and h_3 are the corresponding heights of the mercury above a fixed horizontal plane, then the pressure in the system is obviously $h_1 - h_2$. Furthermore if, by some method, we are to maintain level h_1 constant, any change in pressure in the system must be compensated by a pressure change in tube T_3. Since there is a fixed amount of mercury in the gage, $\Delta h_3 / - \Delta h_2$ must be equal to $(d_2/d_3)^2$, where d_2 and d_3 are the internal diameters of tubes T_2 and T_3, respectively; or $\Delta p = (d_3/d_2)^2 \times \Delta h_3$, where p is the gas pressure in T_2. In practice d_2 may be 20 to 25 mm. and d_3 1 to 2 mm. The pressure change in T_2 can thus be magnified several hundred times. The two limiting factors are the method of indicating a constant level in T_1 and the method of controlling the pressure in T_3.

Blacet and his associates (*1*, *2*) have used this type of gage successfully in their work on photochemical gas reactions. The correct height of the mercury in T_1 was indicated by the making and breaking of an electrical contact between the mercury surface and a fine tungsten wire, the circuit being completed through a second tungsten wire sealed through the tube below the mercury surface. The pressure in T_3 was controlled manually by turning a three-way stopcock, either evacuating or admitting air to a large ballast volume at the top of T_3. In the author's experience this method of control was unsatisfactory for three reasons: (1) the turning of the stopcock communicated unde sirable vibrations to the mercury surfaces; (2) it was difficult to adjust the pressure in T_3 to the correct value manually; and (3) it would be a great advantage to be able to read the pressure at any time without having to manipulate the controls.

The gage in its present form is illustrated in Figure 1. It is similar in construction to that of Blacet *et al.* (*1*, *2*) with the exception of the automatic feature and a few minor changes.

The tungsten needle, W, was made from a piece of 1-mm diameter wire shaped to a fine point by treatment with sodium nitrite. Accurate centering of the needle was facilitated by sealing it as shown into a 10/30 ground joint lubricated with Apiezon N grease. The two electrical contacts were connected to a vacuum tube relay of the type described by Serfass (*5*). No time delay was used. The relay operated a fixed solenoid, S. When the solenoid is actuated the glass-enclosed iron plunger is raised and air enters the 500-cc. bulb, B, through the thin Alundum disk, D, sealed to the bottom of the 6-mm. diameter Pyrex tube. When the relay current is cut off the plunger falls, shutting off the air supply. The success of the instrument is largely due to the needle valve, N, which controls the rate of evacuation. After some investigation Hoke high-vacuum valve No. 318 was found to be most satisfactory.

For a porous disk, D, of fixed dimensions and with continuous pumping through N (a Hyvac pump was used) there is an equilibrium pressure for B where the rate at which air enters through D is equal to the rate at which it is pumped out through N. If this equilibrium pressure happens to be in the range where the gage is supposed to operate, control will be impossible. Consequently, it is necessary to adjust N so that the rate at which air is pumped away will be somewhat less than the rate at which it can enter (with D open) over the whole range of pressures to be encountered. If the pressure change during an experiment is large, an occasional slight adjustment of the needle valve will assure control at all times. In most of the author's experiments no readjustment was necessary.

In one model T_2 was approximately 22 mm. and T_3 2.0 mm. in inside diameter. T_2 was calibrated over a range of 100 mm. before sealing it into the apparatus. Since the pressure change in the system during a run was only of the order of 1 mm., the value of d_2 would remain practically constant. T_3 was calibrated over a range of about 300 mm., corresponding to a pressure in B of from 250 to 550 mm. For a nonuniform bore the expression for the pressure change becomes $\Delta p = \frac{\int d_3^2 \times dh_3}{d_2^2}$ where the