

III

**The
PARTICLE ATLAS
Edition Two**

McCRONE

DELLY

The PARTICLE ATLAS

Edition Two

An encyclopedia of techniques for small particle identification

Volume III

The Electron Microscopy Atlas

Walter C. McCrone
John Gustav Delly



ann arbor science PUBLISHERS INC.

POST OFFICE BOX 1425 • ANN ARBOR, MICHIGAN 48106

Type set by SSPA Typesetting, Inc., Carmel, Indiana
Printed by Thomson-Shore, Dexter, Michigan
Bound by John H. Dekker & Sons, Inc., Grand Rapids, Michigan

Sample preparation by Jacqui Smid
Scanning electron micrographs by John A. Brown
Transmission electron micrographs by Gene R. Grieger
EDXRA patterns by Ian M. Stewart
Editorial assistance by Sylvia Graft and Andrée Fé Coers

Copyright © 1973 by ANN ARBOR SCIENCE PUBLISHERS, INC.
P.O. Box 1425, Ann Arbor, Michigan 48106, USA

Library of Congress Catalog Card Number: 72-90881
International Standard Book Number: 0-250-40008-1

Manufactured in the United States of America

Contents

VOLUME III. THE ELECTRON MICROSCOPY ATLAS

FOREWORD	575
I. PROCEDURES FOR THE STUDY OF SAMPLES	577
A. <i>Scanning Electron Microscope (SEM)</i>	577
1. Mounting the Sample	577
2. Examination of Samples	577
3. Characterization of Particles	578
4. Use of the Atlas of Micrographs	582
B. <i>Transmission Electron Microscope (TEM)</i>	583
1. Mounting the Sample	583
2. Examination of Samples	583
3. Characterization of Particles	583
II. DESCRIPTIONS AND SCANNING ELECTRON MICROGRAPHS	587
INDEX	791

Foreword

The starting point for the identification of small particles is the polarizing microscope. With it, most substances, even single subnanogram particles, can be identified at sight or by observation of easily obtained optical properties. The investment in equipment (\$1,000 to \$2,000) and the speed with which even a diverse sample can be characterized are major advantages. The limitations of polarized light microscopy are two-fold. First, subpicogram particles, *e.g.*, foundry fumes, clays and pigments, cannot usually be identified. Second, the identification of any given substance depends on the analyst's being able to remember the identification characteristics for that substance or being able to refer to existing atlases or tables that include the identifying characteristics for that particular substance.

An experienced microscopist can identify, at sight, several thousand individual substances. He can identify many more by making quick measurements, but he is helpless if he can't remember that particular particle or measure some literature-tabulated characteristics for that particle. It is at this stage that the microscopist must go to another ultramicroanalytical tool, usually the scanning electron microscope (SEM; Volume I, pages 146–155).

The SEM is a logical second step for three good reasons. It shows the shape and surface of even large particles (1 to 100 μm) better than the polarizing microscope. This is due to superior depth of field (about 300 μm compared with about 1 μm for the polarizing microscope) and better contrast. The SEM image is best compared with that obtained using reflected light with a stereobinocular light microscope; however, resolution with the latter is unfortunately only about 2000 nm. One can also compare the SEM image with reflected light images in the polarizing microscope, but here, with increased resolution, the depth of field is very low and continuous focusing is necessary in order to visualize the entire particle.

This brings us to the second advantage of the SEM, *i.e.*, improved magnification and resolution over the

light microscope. The realistic or useful magnification for the SEM is about 30,000X compared with 1500X for the light microscope. This is very helpful in visualizing and identifying small particles.

A third advantage of the SEM is the ability to determine semiquantitatively the chemical composition of even tiny single particles. This is done by adding an energy dispersive x-ray analyzer (EDXRA, Volume I, page 160) capable of detecting any element in the periodic table above about oxygen. The lower atomic number limit depends principally on the thickness of a thin window on the detector. The low x-ray energies of the lowest atomic number elements preclude penetration of the detector window. We have, however, detected fluorine and oxygen with the EDXRA system on our SEM. Elemental analysis for a given particle is obviously more valuable than, say, refractive indices or a diffraction pattern since these identify substances only if the data have been previously measured and tabulated. Furthermore, it requires only seconds—or a minute or two—and minimal training to obtain an EDXRA analysis, whereas measurement of indices or diffraction patterns requires more training and much more time.

We have established the advantages of the SEM for particle identification, but, unfortunately, one should not expect to replace the light microscope and other physical analytical tools with the SEM. To put the SEM in its proper perspective, we need to consider its limitations. It does take longer to mount the sample for SEM than for light microscopy, and certainly most of the common particulate substances can be quickly identified by light microscopy. Without EDXRA, the SEM is little better than the light microscope. Most substances easily identified by SEM without EDXRA are also easily identified by light microscopy. Generally, this includes biological substances such as pollens and spores, natural and synthetic fibers or protozoa. Most other particles may show interesting shape and surface characteristics but not be sufficiently distinctive to effect identification. This is equally true for light

microscopy and SEM, but additional characterization data are quickly obtained by light microscopy (by crossing the polars, rotating the stage, focusing up and down and using transmitted or reflected light). This may or may not identify the particle, but no such flexibility is possible with the SEM. Only EDXRA makes generally possible the identification of particles not identifiable by polarized light microscopy. To be honest, some microscopists would argue that SEM without EDXRA would identify some pigments, foundry fumes and clays not identifiable by light microscopy. This, however, is only partly true. Most, if not all, pigments can be quickly identified by polarized light microscopy, and few clays or fumes can be identified by SEM alone. Shape and surface are simply not distinctive enough, and other data must be available.

What, now, about the TEM? Again, we have better

resolution (about 0.5 nm) and better depth of field (about 1 μm even at very high magnifications, say, 50,000X) than the light microscope. Unfortunately, it is also difficult to prepare the particle(s) for TEM, and, again, identification by shape alone is not likely. Fortunately, the TEM can be used to obtain selected area electron diffraction (SAED), and this parameter is nearly as useful as EDXRA. Incidentally, the installation of EDXRA on the TEM will certainly increase in the future in order to permit elemental analysis. The TEM and its application to particle identification are thoroughly discussed in Volume I, pages 129–146.

The advantages of the TEM are useful, if not necessary, for the identification of subfemtogram particles. The TEM is far more useful when fitted with SAED, and the combination of SAED with the EDXRA on the TEM is best of all.

I. Procedures for the Study of Samples

A. Scanning Electron Microscope (SEM)

1. Mounting the Sample

Mounting of particles for SEM is covered in detail in Volume I, pages 150–151 and 252–253. The particles must be fixed to a featureless, preferably conducting, substrate. Most particles are transferred to a highly polished plate in a drop of very dilute collodion or Formvar®. On evaporation of the solvent, the particle is covered with a very thin layer of polymer (thinner than the resolving power limit of the SEM) and is fixed to the substrate by the same polymer residue. Bombardment of the particle with an electron beam tends to build up a charge which must be conducted away to prevent image distortion. This is usually accomplished by evaporation of a very thin gold layer or a double film of gold and carbon. Some difficult samples were mounted on double-sided adhesive tape and metal coated.

Much has been written and will continue to be written about the desirability of fixing techniques such as critical-point drying for the examination of biological specimens. In preparing samples for the Atlas, this technique was not used, the philosophy being that the prime object of the Atlas was not the interpretation of biological structures but the identification of particulate contaminants such as might be encountered in a normal environmental dust. It is unlikely that most analysts would freeze-dry or critical-point dry every specimen; most would rather take a sample and insert it directly in the microscope. This will result in collapse of many of the biological structures, but we believe that, in general, the mode of collapse is itself typical of the sample: *e.g.*, spherical pollens will tend to collapse to polyhedrons; cylindrical fibers will tend to become ribbonlike.

In preparing the EDXRA spectra, special samples were mounted using a minimum of collodion on beryllium plates and no metal coating.

2. Examination of Samples

This Volume includes scanning electron micrographs and EDXRA spectra with descriptions of the material depicted. There are three substances to a page and three micrographs with each substance. The micrographs have been taken at magnifications of 100X, 1000X and 10,000X; in those cases where EDXRA spectra are included, the spectrum replaces one of the micrographs so that there will be two scanning electron micrographs and one EDXRA spectrum. The magnification of the micrographs in each column is indicated at the top by an ellipse. All of the micrographs were taken with the specimen tilted 45°. This naturally results in foreshortening of the image in the tilt direction. The ellipse reflects this; 1 μm at 10,000X (10 μm at 1000X and 100 μm at 100X) measures 1 cm parallel to the tilt axis but only 7.07 mm in the tilting plane. The major and minor axes of the three ellipses correspond to the magnifications in the two directions at 100X, 1000X and 10,000X (for the tilt axis). Note, however, that a sphere still appears to be a sphere in the SEM; only planes tilted 45° will be foreshortened to show a magnification of 70.7X, 707X or 7,070X respectively.

For the scanning electron micrographs, nearly all the samples were mounted on glass plates to give a smooth, featureless background. For the majority of specimens, the excitation voltage was 20 kV, although in some instances where charging problems were experienced voltages as low as 5 kV were used. X-ray detection was by an Ortec solid-state detector with an energy resolution of 190 eV as defined by the full width at half maximum peak height for the manganese 5.9 keV line. In

preparing the EDXRA spectra, the data were recorded until the height of the highest peak in the spectrum reached 1000 counts. As a result, the time of counting was variable, and thus the general background level of white radiation (Bremsstrahlung) is extremely high in many materials. A further corollary to this is that the presence of a major peak in such a long count background does not necessarily imply that there is a considerable amount of that element present. It may be present as a small contaminant which would not show significantly with the shorter times that most of the other spectra required.

A peak for iron appears in nearly all specimens; this originates from fluorescence from the bottom plate of the final lens of the microscope due to backscattered primary electrons. The magnitude of this peak will be a function of the count time, but the peak to background ratio should normally be fairly constant. We have endeavored, where possible, to differentiate between iron present in the specimen and iron originating from the instrument. Thus, in many EDXRA patterns iron will not be labeled although a peak is present.

In many of the mineral samples, it is impossible to decide whether Ba or Ti is responsible for the peak at approximately 4.5 keV. Ba has a family of about 4 peaks and Ti only 2, but in trace amounts of Ba not all the peaks will necessarily show. We have tried, where possible, to give our best guess as to which of these elements is present in small amounts, based on knowledge of the mineral assemblage, related elements and peak shape. When present in appreciable amounts, the problem does not arise, and the Ba family shows quite clearly.

The full width of the display shown in the EDXRA spectrum is 10 keV. This has been chosen to help differentiate the peaks and to display the resolution between adjacent peaks, *e.g.*, aluminum and silicon, to best advantage. Furthermore, with an SEM operating voltage at 20 kV, very few x-ray energy peaks are efficiently generated above 10 keV. It is important, however, to be aware of those peaks that lie above 10 keV which are frequently diagnostic where overlaps may occur between K radiation and M or L radiation of higher atomic number elements. In the spectrum for *cinnabar* (440), for example, mercury and sulfur occupy almost the same position in the spectrum (Hg, 2.20 keV; S, 2.31 keV), but the presence of mercury is confirmed by higher energy peaks at energies of 9.99

keV and 11.8 keV. In general, if excitation voltages above 20 kV are available, it would be desirable to use them if heavier elements are expected. For general purposes, even though 20 kV is normally adequate, we prefer to operate at 20 to 25 kV since this will give a satisfactory yield up to approximately the 15 keV level without adversely affecting the signal:noise ratio for elements such as sodium and magnesium.

In order to more clearly illustrate the peaks rather than present the more usual dotted outline CRT display, we have shown the spectrum as a solid white on a black background. This is obtained by exposing the film for the full period over which the data are being collected. Unfortunately, this is not the most stable display and apparent energy shifts may be noted. These are not true shifts; however, the static display "locks in" to the correct values. It is these latter values which have been used to identify and label the peaks, the energy for each having been verified with the multichannel analyzer energy calibrator.

We have included in Volume IV a series of CRT pictures showing the EDXRA spectra for elements with $Z > 10$. Although the peak positions represent specific energy levels for each element, the position of the peak can be varied depending on SEM and CRT conditions. These conditions were held constant and are defined in Volume IV. The conditions used for the CRT displays of EDXRA in this Volume are slightly different but as described above.

Tables I and II cover the x-ray energies of each of the elements with the intensities of each line in the EDXRA spectrum. They are given by element (Table I) and in order of increasing energy (Table II). These tables are adapted from more complete tables given in Volume IV but are included here because of their pertinence to particle identification by EDXRA.

3. Characterization of Particles

The identifying characteristics of particles by electron microscopy include shape and surface (SEM and, less effectively, TEM), EDXRA (SEM and sometimes TEM) and SAED (only TEM). Unfortunately, the morphological data are descriptive and hence, somewhat at least, subjective.

It is essential to have a set of generally understood descriptive terms by which shape and surface can be described. The British Standards Institute has published a list of ten terms used to describe particle shape, and these have been very useful and reasonably satis-

Table I

Energies of characteristic x-rays for the elements
(arranged by increasing Z number)

<i>Element</i>	<i>Line</i>	<i>Energy (keV)</i>	<i>Intensity*</i>
H	K α	0.014	—
He	K α	0.025	—
Li	K α	0.05	—
Be	K α	0.11	—
B	K α	0.19	150
C	K α	0.28	150
N	K α	0.39	150
O	K α	0.52	150
F	K α	0.68	150
Ne	K α	0.85	150
Na	K α	1.04	150
Mg	K α	1.25	150
Al	K α	1.49	150
Si	K α	1.74	150
P	K α	2.01	150
S	K α	2.31	150
Cl	K α	2.62	150
K	K α	3.31	150
	K β	3.59	30
Ca	K α	3.69	150
	K β	4.01	15
Sc	K α	4.09	150
	K β	4.46	15
Ti	K α	4.51	150
	K β	4.93	30
V	K α	4.92	150
	K β	5.43	30
Cr	K α	5.41	150
	K β	5.95	30
Mn	K α	5.90	150
	K β	6.49	15
Fe	K α	6.40	150
	K β	7.06	15
Co	K α	6.93	150
	K β	7.65	15
Ni	K α	7.48	150
	K β	8.26	15
Cu	K α	8.04	150
	K β	8.90	15
Zn	K α	8.64	150
	K β	9.57	15
	L α	1.01	110
Ga	K α	9.25	150
	K β	10.26	30
Ge	K α	9.88	150
	K β	10.98	30
As	K α	10.54	150
	K β	10.73	30
	L α	1.28	110
	L β	1.32	50

* Under normal conditions; relative intensities may vary widely with accelerating voltage and/or contaminating surface films.

<i>Element</i>	<i>Line</i>	<i>Energy (keV)</i>	<i>Intensity*</i>
Se	K α	11.22	150
	L α	1.38	110
	L β	1.43	50
Br	K α	11.92	150
	L α	1.48	110
	L β	1.53	50
Rb	L α	1.69	110
	L β	1.75	50
Sr	L α	1.81	110
	L β	1.87	50
Y	L α	1.92	100
	L β	2.00	50
Zr	L α	2.04	110
	L β	2.12	50
Nb	L α	2.17	110
	L β	2.26	50
Mo	L α	2.29	110
	L β	2.40	50
Ru	L α	2.56	110
	L β	2.68	50
Rh	L α	2.70	110
	L β	2.83	50
Pd	L α	2.84	100
	L β	2.99	50
Ag	L α	2.98	110
	L β	3.15	50
Cd	L α	3.13	110
	L β	3.32	50
In	L α	3.29	110
	L β	3.49	50
Sn	L α	3.44	110
	L β	3.66	50
Sb	L α	3.60	110
	L β	3.84	50
Te	L α	3.77	110
	L β	4.03	50
I	L α	3.94	110
	L β	4.22	50
Cs	L α	4.28	110
	L β	4.62	50
Ba	L α	4.47	100
	L β	4.83	50
La	L α	4.65	110
	L β	5.04	50
Ce	L α	4.84	100
	L β	5.26	50
Pr	L α	5.03	100
	L β	5.49	50
Nd	L α	5.23	100
	L β	5.72	54
Pm	L α	5.43	100
	L β	5.96	50
Sm	L α	5.64	100
	L β	6.21	50
	L γ	7.18	10
Eu	L α	5.85	100
	L β	6.46	50
	L γ	7.48	10

Table I—Continued

Element	Line	Energy (keV)	Intensity ^o
Gd	L α	6.06	100
	L β	6.71	50
	L γ	7.79	10
Tb	L α	6.28	100
	L β	6.98	50
	L γ	8.10	10
Dy	L α	6.50	100
	L β	7.25	50
	L γ	8.42	10
Ho	L α	6.72	100
	L β	7.53	50
	L γ	8.75	10
Er	L α	6.95	100
	L β	7.81	50
	L γ	9.09	10
Tm	L α	7.18	100
	L β	8.10	50
	L γ	9.42	10
Yb	L α	7.41	100
	L β	8.40	50
	L γ	9.78	10
Lu	L α	7.65	100
	L β	8.71	50
	L γ	10.14	10
Hf	M α	1.58	100
	L α	7.90	100
	L β	9.02	51
Ta	L γ	10.51	10
	M α	1.64	100
	L α	8.14	100
W	L β	9.34	50
	L γ	10.89	10
	M α	1.71	100
Re	L α	8.40	100
	L β	9.67	50
	L γ	11.28	10
Os	M α	1.78	100
	L α	8.65	100
	L β	10.01	50
Ir	L γ	11.68	10
	M α	1.84	100
	L α	8.91	100
Pt	L β	10.35	50
	L γ	12.09	10
	M α	1.91	100
Au	L α	9.17	100
	L β	10.70	50
	M α	1.98	100
Hg	L α	9.44	100
	L β	11.07	50
	M α	2.05	100
Tl	L α	9.71	100
	L β	11.44	50
	M α	2.12	100
	L α	9.99	100
	L β	11.82	50
	M α	2.20	100
	L α	10.27	100

Element	Line	Energy (keV)	Intensity ^o
Pb	L β	12.21	50
	M α	2.27	100
	L α	10.55	100
Bi	M α	2.35	100
	L α	10.84	100
	M α	2.42	100
Po	L α	11.13	100
At	L α	11.42	100
Rn	L α	11.72	100
Fr	L α	12.03	100
Ra	L α	12.34	100
Ac	L α	12.65	100
Th	L α	12.97	100
Pa	M α	3.00	100
	M α	3.08	100
	M α	3.17	100

Table II

Energies of characteristic x-rays for the elements
(arranged by increasing energy)

Energy (keV)	Element	Line	Intensity ^o
0.014	H	K α	—
0.025	He	K α	—
0.05	Li	K α	—
0.11	Be	K α	—
0.19	B	K α	150
0.28	C	K α	150
0.39	N	K α	150
0.52	O	K α	150
0.68	F	K α	150
0.85	Ne	K α	150
1.01	Zn	L α	110
1.04	Na	K α	150
1.25	Mg	K α	150
1.28	As	L α	110
1.32	As	L β	50
1.38	Se	L α	110
1.42	Se	L β	50
1.48	Br	L α	110
1.49	Al	K α	150
1.53	Br	L β	50
1.58	Lu	M α	100
1.64	Hf	M α	100
1.69	Rb	L α	110
1.71	Ta	M α	100
1.74	Si	K α	150
1.75	Rb	L β	50
1.78	W	M α	100
1.81	Sr	L α	110
1.84	Re	M α	100
1.87	Sr	L β	50
1.91	Os	M α	100
1.92	Y	L α	100

^o Under normal conditions; relative intensities may vary widely with accelerating voltage and/or contaminating surface films.

Table II—Continued

Energy (keV)	Element	Line	Intensity ^o	Energy (keV)	Element	Line	Intensity ^o
1.98	Ir	M α	100	5.26	Ce	L β	50
2.00	Y	L β	50	5.41	Cr	K α	150
2.01	P	K α	150	5.43	V	K β	30
2.04	Zr	L α	110	5.43	Pm	L α	100
2.05	Pt	M α	100	5.49	Pr	L β	50
2.12	Zr	L β	50	5.64	Sm	L α	100
2.12	Au	M α	100	5.72	Nd	L β	54
2.17	Nb	L α	110	5.85	Eu	L α	100
2.20	Hg	M α	100	5.90	Mn	K α	150
2.26	Nb	L β	50	5.95	Cr	K β	30
2.27	Tl	M α	100	5.96	Pm	L β	50
2.29	Mo	L α	110	6.06	Gd	L α	100
2.31	S	K α	150	6.21	Sm	L β	50
2.35	Pb	M α	100	6.28	Tb	L α	100
2.40	Mo	L β	50	6.40	Fe	K α	150
2.42	Bi	M α	100	6.46	Eu	L β	50
2.56	Ru	L α	110	6.49	Mn	K β	15
2.62	Cl	K α	150	6.50	Dy	L α	100
2.68	Ru	L β	50	6.71	Gd	L β	50
2.70	Rh	L α	100	6.72	Ho	L α	100
2.83	Rh	L β	50	6.93	Co	K α	150
2.84	Pd	L α	100	6.95	Er	L α	100
2.98	Ag	L α	110	6.98	Tb	L β	50
2.99	Pd	L β	50	7.06	Fe	K β	15
3.00	Th	M α	100	7.18	Tm	L α	100
3.08	Pa	M α	100	7.18	Sm	L γ	10
3.13	Cd	L α	110	7.25	Dy	L β	50
3.15	Ag	L β	50	7.41	Yb	L α	100
3.17	U	M α	100	7.48	Ni	K α	150
3.29	In	L α	110	7.48	Eu	L γ	10
3.31	K	K α	150	7.53	Ho	L β	50
3.32	Cd	L β	50	7.65	Co	K β	15
3.44	Sn	L α	110	7.65	Lu	L α	100
3.49	In	L β	50	7.79	Gd	L γ	10
3.59	K	K β	30	7.81	Er	L β	50
3.60	Sb	L α	110	7.90	Hf	L α	100
3.66	Sn	L β	50	8.04	Cu	K α	150
3.69	Ca	K α	150	8.10	Tm	L β	50
3.77	Te	L α	110	8.10	Tb	L γ	10
3.84	Sb	L β	50	8.14	Ta	L α	100
3.94	I	L α	110	8.26	Ni	K β	15
4.01	Ca	K β	15	8.40	W	L α	100
4.03	Te	L β	50	8.40	Yb	L β	50
4.09	Sc	K α	150	8.42	Dy	L γ	10
4.22	I	L β	50	8.64	Zn	K α	150
4.28	Cs	L α	110	8.65	Re	L α	100
4.46	Sc	K β	15	8.71	Lu	L β	50
4.47	Ba	L α	100	8.75	Ho	L γ	10
4.51	Ti	K α	150	8.90	Cu	K β	15
4.62	Cs	L β	50	8.91	Os	L α	100
4.65	La	L α	110	9.02	Hf	L β	51
4.83	Ba	L β	50	9.09	Er	L γ	10
4.84	Ce	L α	100	9.17	Ir	L α	100
4.92	V	K α	150	9.25	Ga	K α	150
4.93	Ti	K β	30	9.34	Ta	L β	50
5.03	Pr	L α	100	9.42	Tm	L γ	10
5.04	La	L β	50	9.44	Pt	L α	100
5.23	Nd	L α	100	9.57	Zn	K β	15
				9.67	W	L β	50

Table II—Continued

Energy (keV)	Element	Line	Intensity ^a
9.71	Au	L α	100
9.78	Yb	L γ	10
9.88	Ge	K α	150
9.99	Hg	L α	100
10.01	Re	L β	50
10.14	Lu	L γ	10
10.26	Ga	K β	30
10.27	Tl	L α	100
10.35	Os	L β	50
10.51	Hf	L γ	10
10.54	As	K α	150
10.55	Pb	L α	100
10.70	Ir	L β	50
10.73	As	K β	30
10.84	Bi	L α	100
10.89	Ta	L γ	10
10.98	Ge	K β	30
11.07	Pt	L β	50
11.13	Po	L α	100
11.22	Se	K α	150
11.28	W	L γ	10
11.42	At	L α	100
11.44	Au	L β	50
11.68	Re	L γ	10
11.72	Rn	L α	100
11.82	Hg	L β	50
11.92	Br	K α	150
12.03	Fr	L α	100
12.09	Os	L γ	10
12.21	Tl	L β	50
12.34	Ra	L α	100
12.65	Ac	L α	100
12.97	Th	L α	100

factory. We try to restrict our descriptions of single particles to this set of descriptors:

acicular	flake
angular	granular
crystalline	irregular
dendritic (or skeletal)	nodular
fibrous	spherical

A useful set of terms for describing particle surfaces, in use in our laboratory, is the following:

cemented	pitted
cracked	porous
cratered	reticulated
dimpled	smooth
orange peel	valleyed

Particles are tabulated by elemental analysis in Volume IV, *Particle Atlas Two*, and each is listed under the one, two or three major elements in that substance.

Substances containing only carbon, hydrogen and oxygen are not included in that tabulation. Fortunately, most of these are biological and easily identified by light microscopy.

4. Use of the Atlas of Micrographs

The basic purpose of the Atlas is twofold: first, to help identify unknown particles; second, to describe and depict frequently encountered particle types from particular sources.

a. Identification of an unknown particle

It is presumed that the analyst will already have examined the particle or particles by light microscopy and is utilizing the SEM to obtain additional data either on the morphology of extremely small particles for which the resolution of the light microscope has become a limiting factor or because he wishes to obtain some chemical information by, *e.g.*, EDXRA. Since he has already examined the prep by light microscopy, he will already have some indication of what to look for on the SEM and thus will be in a position to rapidly compare the unknown sample with the photographs in the Atlas. Morphology alone will not identify the particle for him but will give some indication of identification when other information is already available on the particle. It will not permit him to distinguish by morphology alone between, *e.g.*, *quartz* (183) and *glass dust* (510), both of which will give crushed particles sharply angular with conchoidal fracture, but he will be able to use EDXRA to determine which of these substances is present (quartz, only Si; ground glass, frequently Si, Ca, Al, Na). On the other hand, in dealing with a magnesium silicate mineral, EDXRA will not enable him to distinguish between, say, *talc* (198) and *chrysotile asbestos* (122), but the morphology of the particles will. Thus, the scanning electron microscope is just one more weapon in the particle analyst's armory.

b. Description for a known particle

Having identified his particle, the analyst generally needs to provide photographic and descriptive material to substantiate his identification. In such a case, it is always best, when possible, to obtain a known sample of the substance and compare it directly with the unknown. In this way, it is possible to make comparisons under identical instrument operating conditions.

On those occasions when a known sample cannot be obtained or it is desired to verify the authenticity of

the claimed known sample, the Atlas should be used. Consulting the index immediately refers one to electron micrograph, EDXRA spectrum and description. From this information, it should be possible to decide whether your unknown is identical with the substance depicted in the Atlas. The final step is to refer to the tables (Volume IV) to determine whether any other reasonable possibility exists or whether any confirmatory tests may be made to substantiate the identification.

B. Transmission Electron Microscope (TEM)

1. Mounting the Sample

Sample mounting for the TEM is described in detail in Volume I, pages 134–136 and 249–252.

Samples for the TEM are generally mounted on an electron transparent substrate in one of several ways. Powders may be ground until they are of the appropriate size for the electron microscope, generally $<1\ \mu\text{m}$ in size, or already small particles may simply be collected by various means described in Volume I, pages 204–210. The particles may be made into a suspension by adding an appropriate solvent and ultrasonerating the particles to disperse them, or the particles may be dusted onto the carbon substrate. The particles may also be mixed in a collodion slurry and prepared for TEM study by spreading a thin film on water and picking up a portion of the film on the TEM grid. This technique of dispersing pigments in collodion is widely used to get high degrees of dispersion for particle size counts.

Other techniques, such as replication, may also be used as described in Volume I, pages 135–136.

The electron diffraction patterns are taken using selected areas of many small particles for a powder pattern (Figure 3) or a single crystal for a single crystal pattern (Figures 2 and 7). Sometimes mixed patterns are obtained showing both spots due to a few large crystals and lines due to many fine particles (Figure

4). A few large crystals give spotty lines as in Figures 6 and 9, and noncrystalline particles give only broad rings (Figure 5).

In preparing the TEM micrographs, an accelerating voltage of 150 kV was used, although for some of the diffraction patterns 100 kV was used. Two instruments were used during preparation of the TEM micrographs, the RCA EMU IV and the JEOL, SEM 200.

2. Examination of Samples

The TEM micrographs in Figures 1 and 2, 4 and 5 and 7 and 8 were taken at 5000X and 25,000X. For individual particles, higher magnifications may be used, or, to get general features of an overall dispersion, lower magnifications may be used. The use of electron diffraction requires the stabilization of diffraction conditions outlined in Volume I, pages 136–140.

Accelerating voltages generally at 150 kV were used to give greater transmission through thicker particles. The selected area electron diffraction (SAED) patterns are well standardized so that instrument constants may be readily obtained, and identification of the materials is usually possible if data on the compounds present are available in the literature.

The identification of the patterns generally follows the ASTM card index, after indexing and measuring the patterns and converting the ring diameters to spacings as described in Volume I, pages 136–140.

3. Characterization of Particles

Particles can be characterized by TEM in terms of shape, size and surface as with the SEM, and similar descriptors should be used (I.A.3, above). Nearly all TEM instruments are fitted with SAED, and some are fitted with EDXRA. Without at least SAED, the TEM would be nearly useless for particle identification. In general, only biological particles could be reasonably identified, and, again, most of these can be identified by light microscopy.

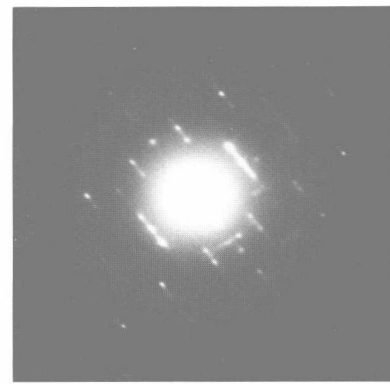
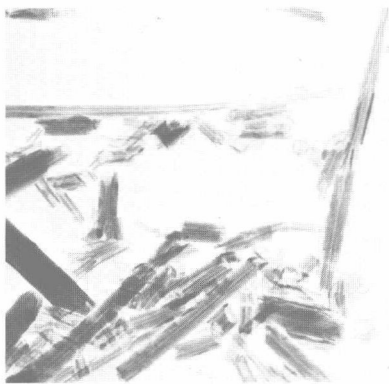
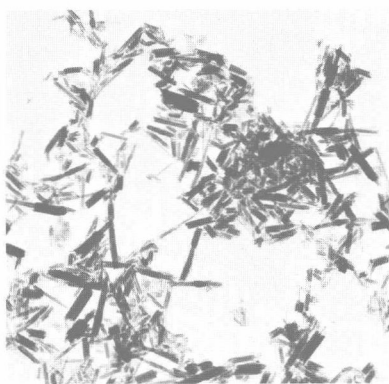


Figure 1. Halloysite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ —Well-formed but hollow rods usually less than $1\ \mu\text{m}$ in width. Often associated

with kaolin in clay beds and in altered areas in limestone associated with diaspore, alunite or gibbsite.

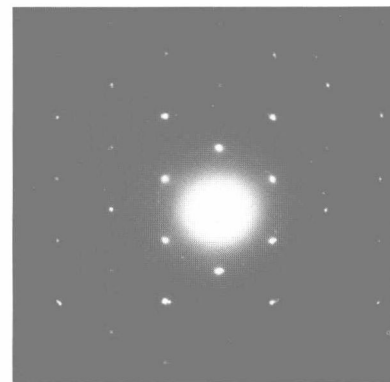
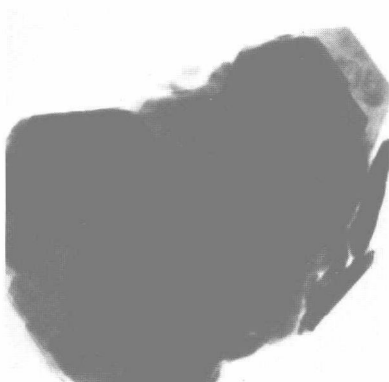
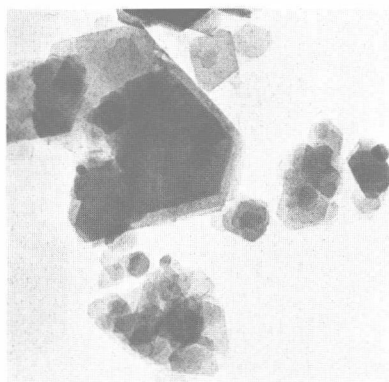


Figure 2. Kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ —Aggregates of pseudo-hexagonal monoclinic plates of submicrometer size; kaolin is used as a filler in rubber, paints, polymers and paper. It is

produced by decomposition of feldspars and occurs as a sedimentary clay mineral (*cf. kaolin, 155*).

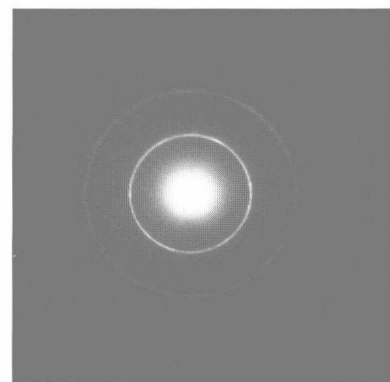
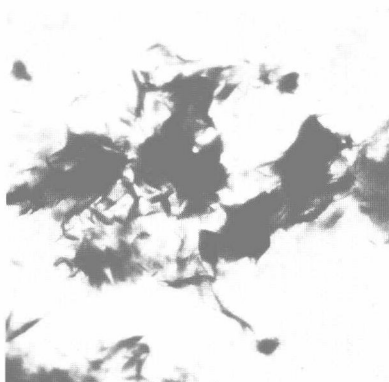


Figure 3. Montmorillonite, $(\text{Mg,Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ —Microcrystalline aggregates of fine scalelike crystals. Mono-

clinic, this clay is the chief constituent of bentonite and of Fuller's earth. It is an altered volcanic ash in origin.

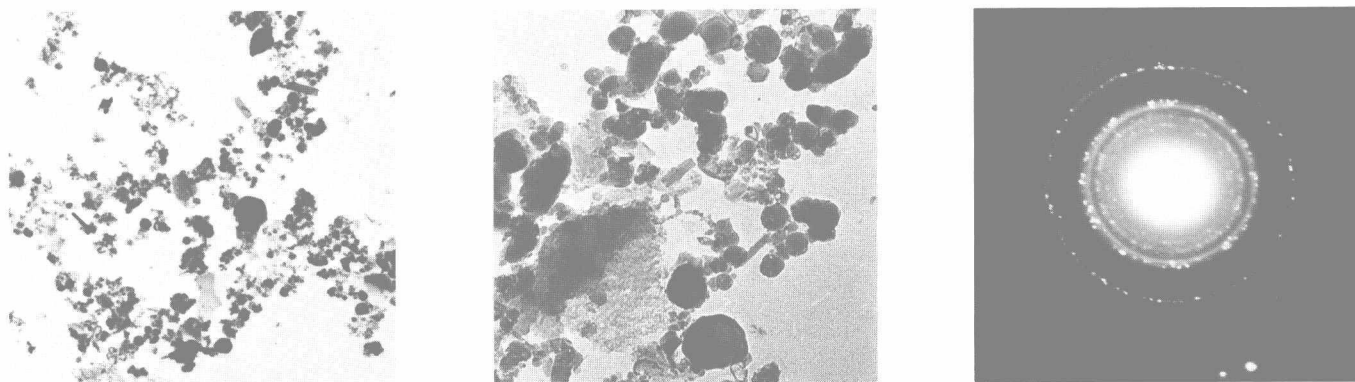


Figure 4. Alumina, Al_2O_3 —During the refining of aluminum, the hot metal oxidizes to form ultramicrocrystalline particles of alumina. Both thin rods and plates about $0.1\ \mu\text{m}$ long, and

spherical aggregates of very fine particles are apparent (*cf. activated alumina, 475*).

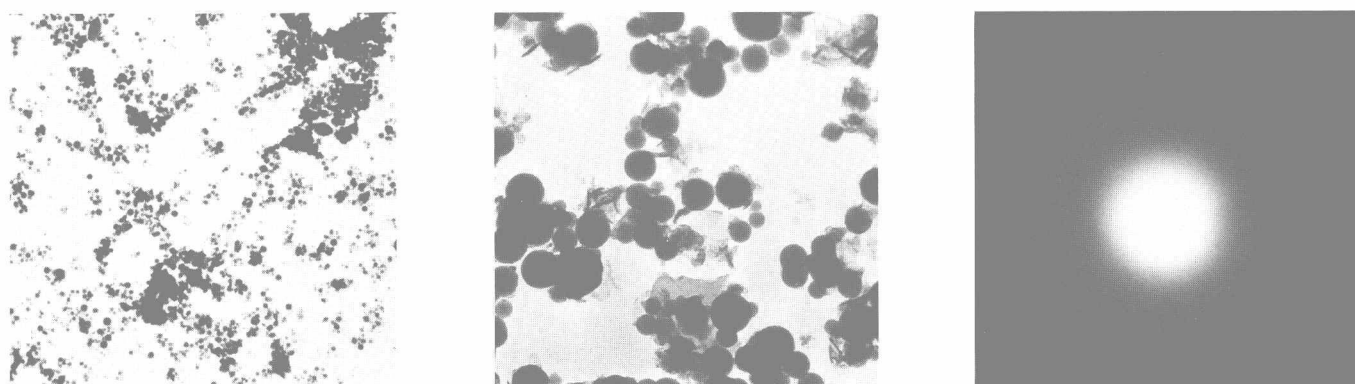


Figure 5. Ferric Oxide, Fe_2O_3 —This apparently amorphous foundry fume is made up of 0.1 to $0.5\ \mu\text{m}$ spheres. There are also a few platelike particles, many on edge, in the $25,000\times$

micrograph. The absence of spots in the SAED pattern indicates these also are noncrystalline (*cf. steel open hearth, 422 and 425*).



Figure 6. Zinc Oxide, ZnO —Zinc smelting and galvanizing operations yield a variety of forms. These consist of ZnO and

ZnS_2O_4 as shown by the spotty SAED pattern. Always very tiny, they make an excellent white paint pigment (*cf. 432*).

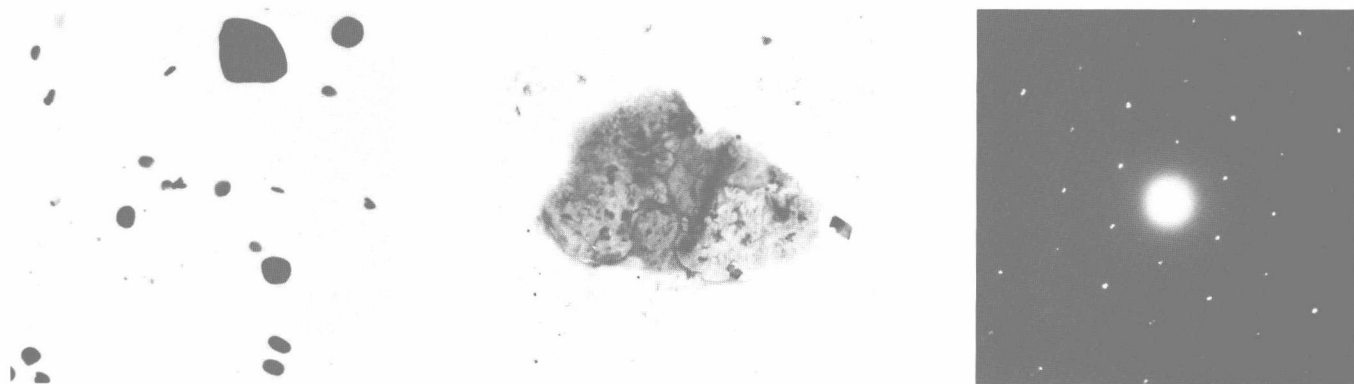


Figure 7. Auto Exhaust—A variety of compounds and crystal types are formed from leaded gasoline and engine wear. Many different lead compounds are formed including $\text{Pb}_3\text{C}_2\text{O}_7$, the

particle shown at 25,000X and in the SAED pattern (cf. 551 and 552).



Figure 8. Chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (cf. 122)—The most common asbestos forms hollow tubes like halloysite, but the fine chrysotile fibers are more uniform in size and show, of

course, a different SAED pattern and major amounts of Mg, whereas halloysite has no Mg.

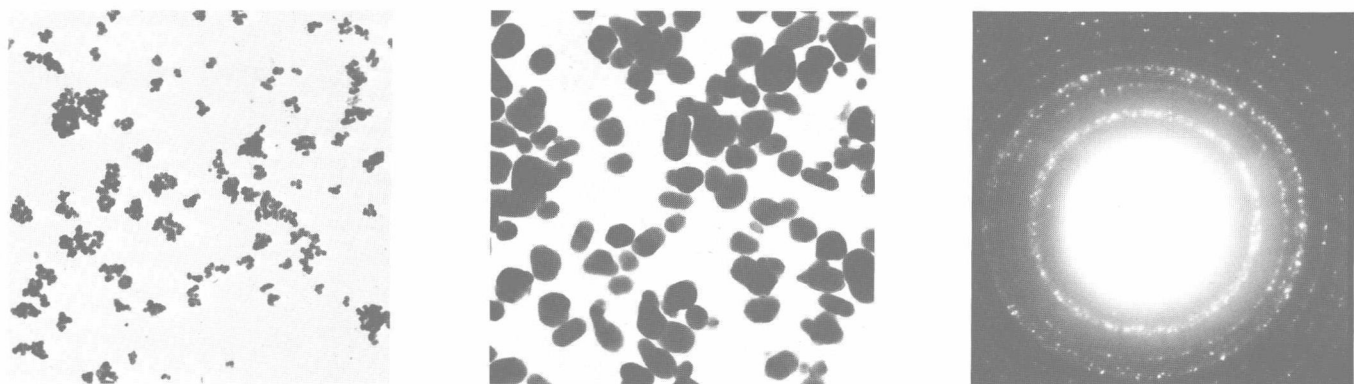


Figure 9. Titanium Dioxide, TiO_2 (cf. 448)—One of the most important white pigments, TiO_2 , prepared by calcination of ilmenite ore, is already very finely divided. Both forms, ru-

tile and anatase (and sometimes brookite), are used; this one is the tetragonal form, anatase.

II. Descriptions and Scanning Electron Micrographs