The Evolution of Chemical Analysis*

Walter C. McCrone**

On the eighth day, chemical analysis began. Adam, recovering after cooperating with God in creating Eve, felt the first pangs of hunger. Looking around, he spied a pile of stones left over after creation of some nearby mountains. He rejected a soft friable sandstone and chose a hard granite rock, took careful aim at a rabbit, and hit it squarely between the eyes. This was the basis for the first real meal in the Garden of Eden. A day or two later, Eve took a whiff of the rabbit carcass, thought for a moment, then fed it to the dog.

Thus, the first chemical analytical instruments were Adam's eye and hand and Eve's nose. These, plus taste, sufficed by themselves for a long time thereafter but, eventually, refinements were necessary.

Much later, the earliest alchemists invented most of the separation methods so useful to the analytical chemist. For a while, they were satisfied to use techniques such as filtration, decantation, and distillation. However, the jubilation produced as a result of drinking the liquid product from the drying of some rain-soaked maize by distillation led to numerous advances in analytical procedures. Partial destruction by burning produced a useful product, charcoal. Mixing and heating this product with some green and blue rocks produced a yellow metal thought by some to be gold, but this yellow changed back to green and blue in time, and true gold did not.

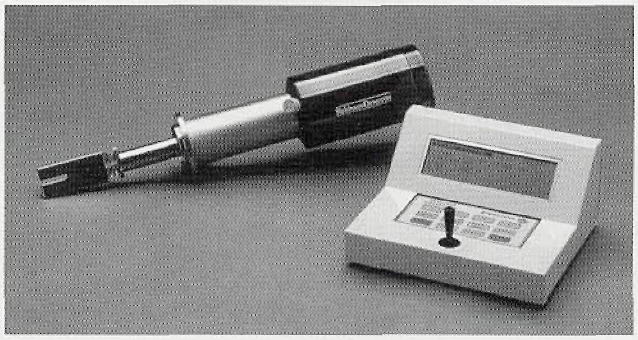
Observation followed observation until a large body of knowledge had to be named and "chemistry" was chosen. Those observations having to do with the production of substances were termed chemical synthesis and those related to determining what the substances were called chemical analysis. Most chemical analyses were now carried out in solution, but not all. No one talked about dry chemical methods per se, but many such methods existed, and these generally were based on four of the five senses, especially sight. (Those who had used taste had long since died.)

Color, for example, became very useful in chemical analysis, and chemists became highly proficient in associating color with chemical composition. A system developed for qualitative analysis was based on the colors of particles precipitated by specific reagents, e.g., H_2S. A chemist could identify almost any colored substance by sight and determine how the substance was generated. Black particles from an iron foundry would be Fe_3O_4 (especially if they were magnetic). A red earth would be Fe_2O_3 (hydrated, no doubt); a red rock, probably cinnabar; a green rock, probably malachite, etc.

There also evolved a group of microchemists, not small in stature but interested in making analyses on tinier and tinier samples. About that time (during the early 1800s) the quality of the light microscope became such that one could resolve and see the colors of very small samples, e.g., single particles less than one "thou" (0.001 in.). Henry Sorby was the most important of these analysts. He developed the study of rock thinsections as well as polished and etched metal sections. He used the polarized light microscope (PLM) and found he could observe many physical properties of small particles in a matrix or as individual particles. With that capability he could do two very important things: 1) identify small particles by their molecular composition, and 2) relate quality of a material (again, a particle if need be) to its microstructure. He could identify many microscopic particles by sight: minerals such as calcite, quartz, orthoclase, and mica: fibers such as cotton, rabbit hair or Kevlar®; metals such as brass, bronze, steel, and wrought-iron; one-celled plants and animals, such as diatoms, wheat starch, pollens, paramecia, and rotifers; and industrial dusts, such as china clay, coal boiler flyash, foundry fumes, and pigments. If Sorby had gathered together this information from his own diverse experience and published it, we would have had *The Particle Atlas*[1] one hundred years ago.

Sorby also was able to relate quality to microstructure, especially in metallurgy. He was often asked to look at polished sections of steel to answer the question of suitability of that ingot for rolling into railroad rails. He discovered the iron-carbon compound, cementite, and its eutectic with iron, pearlite,

He published more than 150 papers, most of them microscopical, in fields



from biology and medicine to metallurgy and mineralogy. It was apparent then, as now, that any change in chemical composition or physical treatment significantly changes the microscopical properties. With practice, a knowledge of these effects permits very rapid conclusions regarding both chemical composition and performance properties.

Mother Nature has used her building blocks in many ways to fashion different substances with a wide variety of applications and properties. Take $C_6H_{10}O_5$; as a monomer (plus H_2O), it is any of the monosaccharides (e.g., fructose); as a dimer, it could be any of the disaccharides (e.g., sucrose). As a higher polymer it may be starch (e.g., potato or rice) or cellulose (e.g., cotton, flax, or paper fibers from one of many species of tree). Silica (SiO_2), another bulding block, may be amorphous (diatoms, pumice, perlite, silica gel, silica flour, silica fibers, etc.). It may be any of numerous gems or any of numerous minerals. As sand grains, it may be changed by various processes such as lake beach action or by heat, grinding, dissolution, or reaction to a very wide variety of microscopical appearances, each with a unique set of properties observable and identifiable microscopically. There is, in fact, no other way to reasonably identify all of these substances expect the polarized light microscope; using DNA is unreasonable.

This ability to rapidly identify a very wide range of organic and inorganic substances, to rapidly relate quality to microscopical appearances, to rapidly determine why a given product is inferior or a process is faulty, is being rapidly lost. How can this be so? We can return to Henry Sorby for the beginning of an answer? In the 1860's, Sorby heard a lecture on spectroscopy given by G.G. Stokes and immediately built a spectroscope into his microscope. He then measured absorption spectra on a wide variety of minerals besides biological substances, including trace evidence in forensic cases. This was the beginning of a search for additional properties one could observe on small particles and use for characterization. Fluorescence was another such property.

Simultaneously, other developments began to appear, most of them developed by physicists. These included ultraviolet microscopes, interference microscopes, phase contrast, differential interference contrast, modulation contrast, automatic image analysis, pattern recognition, and (most important of all) the transmission and scanning electron microscopes (TEM and SEM). Furthermore, more and more physical analytical instruments were becoming more and more micro. These include diffraction methods such as X-ray diffraction (XRD) and selected area electron diffraction (SAED), X-ray fluorescence (measured by energy or wavelength dispersion), mass spectrometry; even nuclear magnetic resonance (NMR), infrared (IR), and electron scanning for chemical analysis (ESCA). (Many of these techniques required samples in the single particle range.

All of this, happening since World War II, has resulted in the near demise of polarized light microscopy. I feel that light microscopists have a tough problem they must face if they want to see the light microscopy we know and love return to the research laboratory and the university curriculum. I think I can see some light at the end of the tunnel (but I cannot yet be sure it is not an on-coming express).

Pressing buttons, examining a digital readout, or chart recording of data is not nearly as useful or satisfying as looking directly at the sample and interpreting, based on experience, its composition, how it was produced, how it will function in a process, or why it did not function.

Reading about the physical and chemical behavior of substances is one thing, but watching them behave as temperature, concentration, and pressure are changed is quite another. There is much more useful information in a microscopic field of view that can ever be digitized or plotted. ■

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1. McCrone, W.C. et al. Partricle Atlas, Vol.1-6, CD-ROM, MicroDataware, available from Hayward, CA; (510)582-6624; McCrone Accessories and Components: (800)MAC-8122 or McCrone Research Institurte: (312)842-7100.

* This paper is adapted from an earlier article in American Laboratory 10+ years ago.

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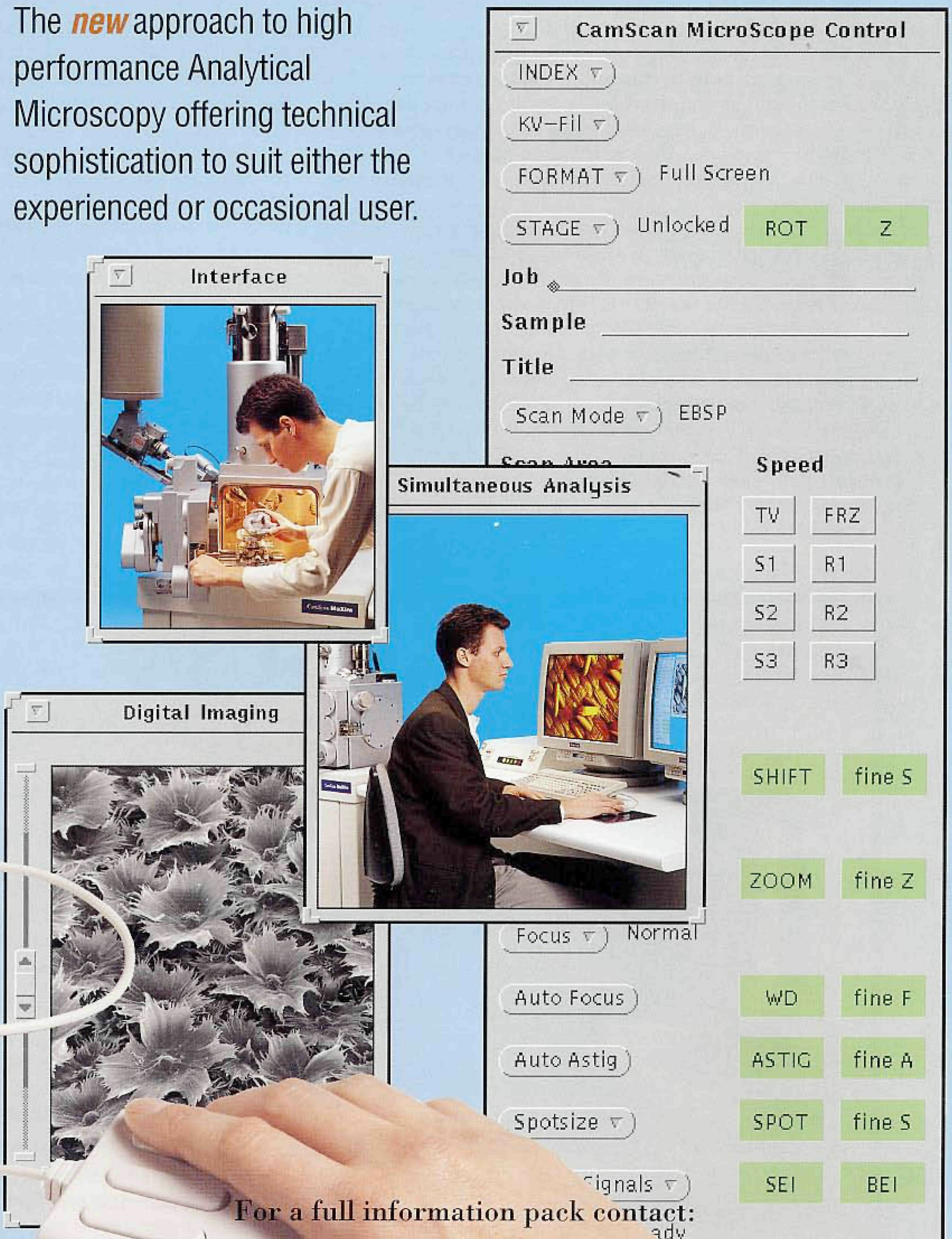

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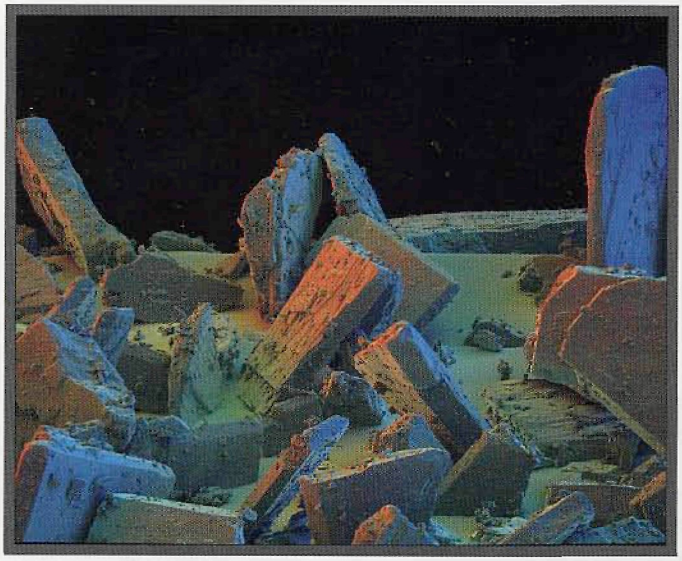

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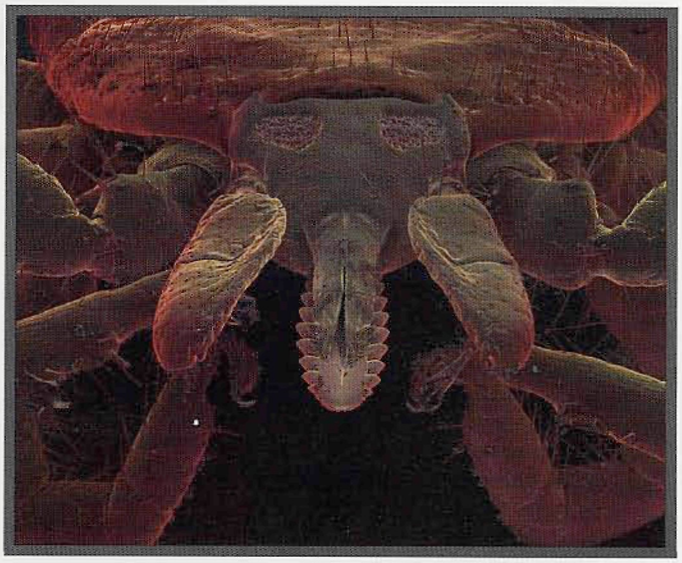

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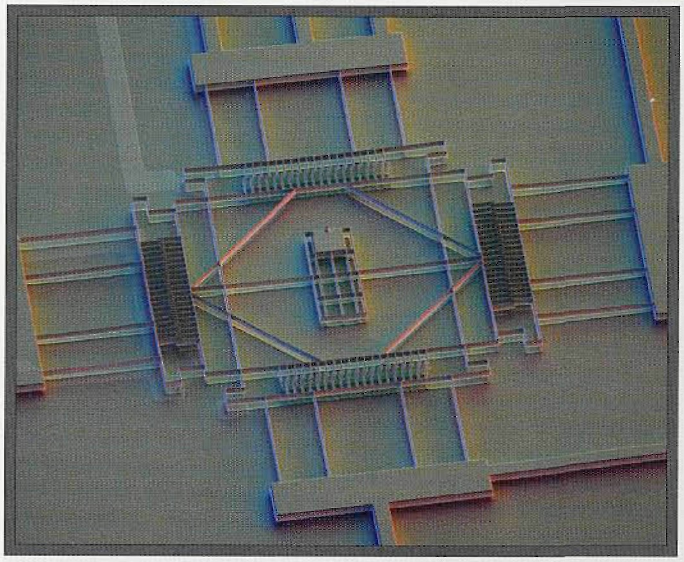

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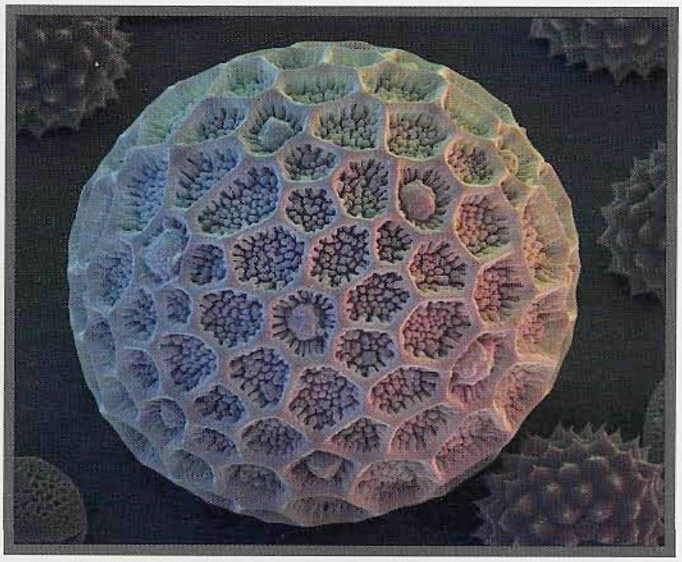

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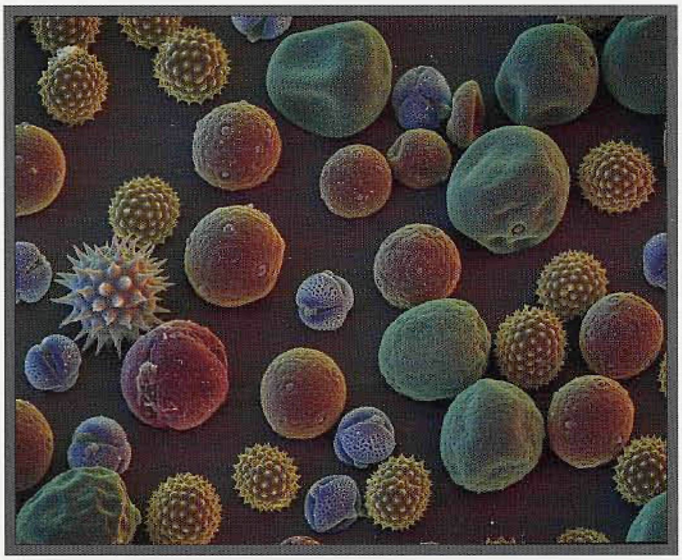

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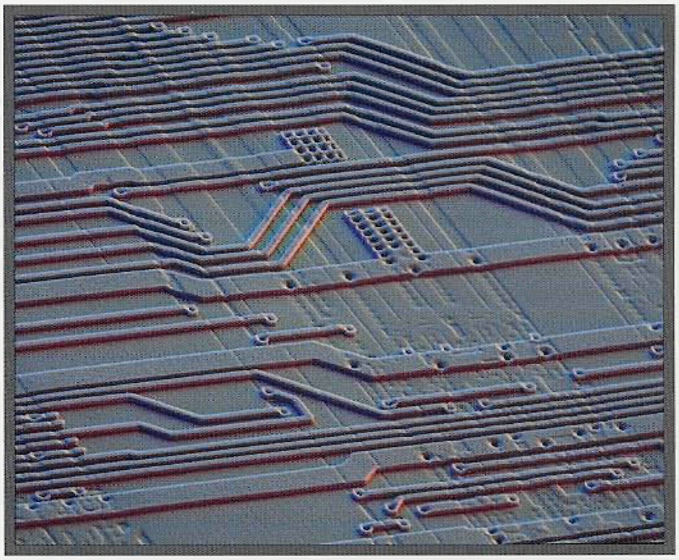

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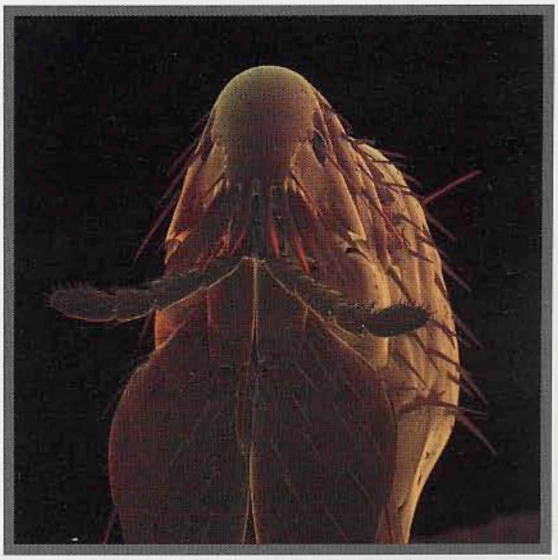

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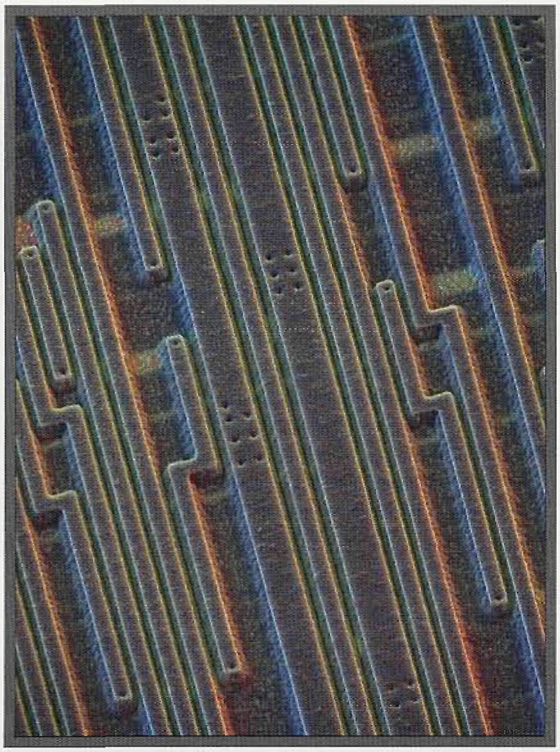

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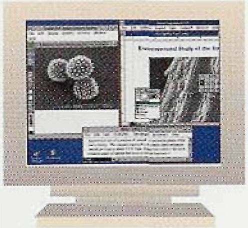

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