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## THE EXAMINATION OF PAINT WITH THE ELECTRON MICROPROBE

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The electron microprobe is an instrument for the elemental analysis of micron size areas. An electron gun operated at a potential of five to fifty kilovolts produces a stream of electrons. These electrons are focused by two electromagnetic lenses to a spot of approximately one micron in diameter.

When this beam of electrons impinges upon a sample, it generates x-rays characteristic of the elements present. This radiation is analyzed by an x-ray spectrometer and detected by a flow proportional counter. Standard counting circuits<sup>1</sup> allow quantitative data to be collected. All elements from boron (5) to uranium in the periodic table can be detected, but the light elements from boron to sodium present some special problems.<sup>2</sup> The theoretical limit of detectability for a given element is in the 30 parts per million range, but in practice 50 to 100 ppm represents the lower limit for metallic samples.<sup>3</sup> Figure 1 depicts the basic components of the electron microprobe.

The focused beam can be swept back and forth across the sample in raster fashion. If the spectrometer is set to receive the radiation from one particular element, the distribution of this element can be observed on a synchronously scanned oscilloscope screen. In this mode the x-ray intensity readout from the spectrometer is used to modulate the intensity of the spot on the oscilloscope face. A photograph of such a distribution is shown in figure 2.

Alternatively, the sample can be driven slowly under a fixed beam, and in this way a line profile

of elemental distribution can be obtained. Several such line profiles representing the concentrations of several different elements along the same line are shown in figure 3 also.

Since the analysis is in large part non-destructive, the potential usefulness of this instrument in the examination of evidence materials, so often limited in size, is obvious.

### PAINT AS A SAMPLE

A prime example of this type of evidence material is paint. Samples are often small and in the case of multilayer paints, it would be ideal to be able to analyze each layer as a separate entity.

The examination of paint is complicated by three major problems which stem from basic characteristics of paint. The first problem is the poor electrical conductivity of paint. Since the sample is being bombarded by electrons, a static charge tends to build up at the point of beam impact. Unless this charge is dissipated, it will deflect the beam and cause it to jump erratically about the specimen surface. This condition not only makes it impossible to know the exact area being analyzed, but transient bursts associated with the deflection of the beam make quantitative readout meaningless.

The second problem associated with microprobe examination of paint is due to the sample's poor heat conductivity. This causes temperature rises at the point of beam impact with resultant charring of vehicle material. This condition also increases the deposition of carbon on the sample surface as a result of the polymerization of diffusion pump<sup>4</sup> oil in the evacuated column. This temperature rise could cause the volatilization of certain materials in paint and also causes changes in the observed fluorescence colors.

<sup>1</sup> BIRKS, L. S., *ELECTRON PROBE MICROANALYSIS* (Interscience Publishers, New York, 1963) Chap. 7.

<sup>2</sup> Poen Sing Ong, *Microprobe Analysis of the Elements Fluorine through Boron in THE ELECTRON MICROPROBE*, T. D. MCKINLEY, K. F. J. HEINRICH and D. B. WITTRY (eds.) (John Wiley & Sons, Inc., New York, 1966) p. 43.

<sup>3</sup> The instrument used in our laboratory is a Phillips Electronics AMR-3 electron micro analyzer.

<sup>4</sup> Poen Sing Ong, op. cit. p. 56.

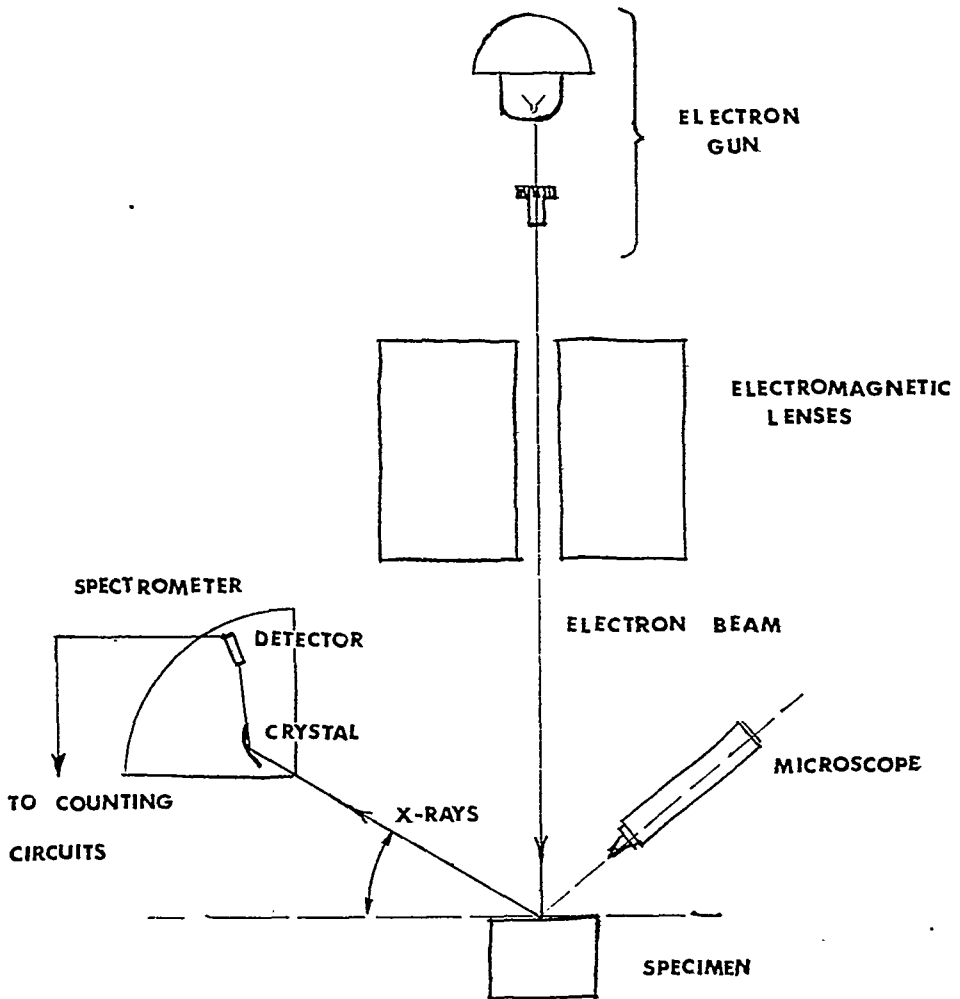


FIGURE 1  
Basic components of probe

The third troublesome characteristic of paint is its soft surface. It is impossible to polish a paint sample the way an ore or a metal sample can be polished. In order that quantitative data may be reliable, the sample surface must be as smooth and flat as possible. Our present solutions to these problems can best be demonstrated by describing our mounting and sample preparation technique. (See fig. 4.)

#### SAMPLE PREPARATION

Paint chips are placed face down on doubly adhesive Scotch tape, which has been fixed to a glass slide. The adhesive allows the chip to be placed in any desired position, including on edge. In some cases the Scotch tape has been used to

pick up particulate matter, and the other side of the tape is then spread against a glass slide. Silver loaded epoxy resin<sup>5</sup> is then mixed, and a little xylene is added to reduce the mixture's viscosity. The resin is then puddled over the paint chip or particles as the case may be, reasonable care being taken to avoid entrapping air bubbles. If the particles to be examined are very small, special techniques may be required.<sup>6</sup>

When the epoxy has hardened, the mass can be slipped off of the tape easily. The surface containing the paint chip is rinsed in methanol and the resin cured longer at about 80°C. This

<sup>5</sup> Obtainable from Dynaloy, Newark, New Jersey.

<sup>6</sup> Reichard, T. E. and Coakley, W. S., *Preparation of Non-Metallurgical Specimens for Electron Probe Microanalysis*, 37 *ANA. CHEM.* 317 (1965).

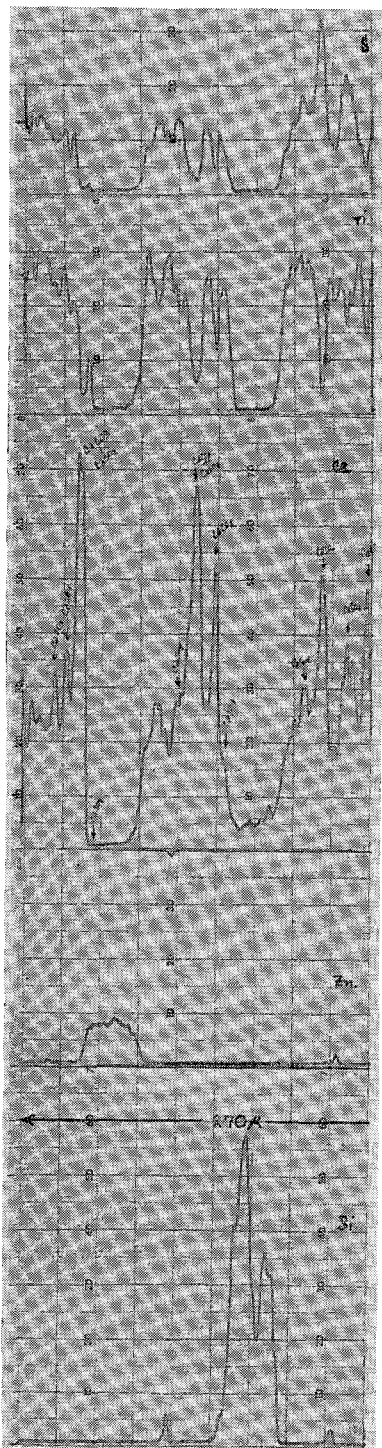


FIGURE 2

Line scans across the face of a white paint chip showing the linear concentrations of various elements along the same line in the sample.

extra hour of curing seems to add greatly to the epoxy hardness even after it has been allowed to harden over night at room temperature. The epoxy mass is now mounted in a standard one inch mount with a cold mount plastic that cures at room temperature.<sup>7</sup>

The surface of the mount is then washed with methanol to remove any tape adhesive that may remain. If the paint chips are flat and exposed, they are left in that state. If, however, the chip is not flat, or some epoxy has covered a good portion of the chip, the mount must be ground down to reveal the paint. Tests run at our laboratory indicate that grinding particles are not readily picked up by the paint, and a 20 second washing in a detergent solution in the ultrasonic cleaner seems to remove all foreign material from the paint. Grinding is usually started with a coarse emery paper and gradually finer grades are used, ending up the process with 4/0 emery. Hand grinding techniques are used for paint although grinding and polishing wheels are available for harder materials. This is due to the fact that generally little grinding is necessary, and the process must be very carefully controlled. This is best accomplished using hand methods.

When a flat smooth surface has been exposed, the sample is washed with detergent solution in an ultrasonic cleaner for 20 seconds then rinsed in methanol. The sample surface is then dried in a blast of warm air for about five minutes. At this time the surface should be clean and dry. The mount is then placed in a vacuum evaporator where a thin coat of amorphous carbon is laid down on the surface. The film is put down in a vacuum of at least  $5 \times 10^{-5}$  mm Hg. The thickness of the carbon film necessary to give good conductive properties to the paint is estimated from the shadow made on strips of filter paper placed under the sample during the evaporation. (See fig. 2 and 3.)

Thus the paint chip has been encased in material which has good electrical and thermal conductivity. The surface preparation technique described is the best one found to date although it is not perfect and the resulting surface is not perfectly smooth. If further polishing is attempted, the sample tends to wear away much faster than the embedding material thus creating a crater effect across the chip. This condition cannot be tolerated since it causes the take off angle at which

<sup>7</sup> Cold mount available from Buhler, Evanston, Illinois.

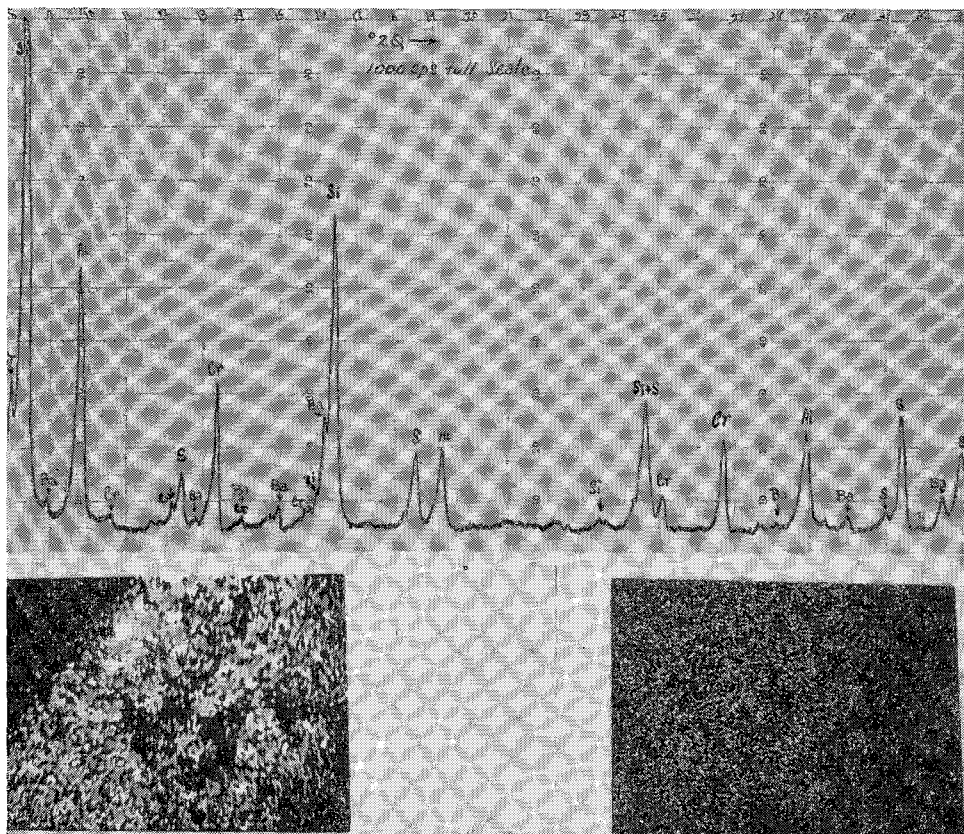


FIGURE 3

Wave length scan of a green paint chip showing the presence of Cr, Si, Al, Ba, Ti, and S and two oscilloscope face photographs showing the surface distribution of two elements in two paint chips.

x-rays are viewed to change in moving across the sample surface. Since the observed x-ray intensity for a given element is a function of take off angle as well as of the elements concentration, this type of sample would yield unreliable quantitative data.

In cases where multilayer paints are to be examined, there are several mounting procedures available. The chip can be set on end in the adhesive of the Scotch tape as mentioned earlier or the chip can be pierced with a hypodermic needle.<sup>8</sup> The needle is then mounted and the mount ground down to section the needle and expose the paint layers. Each layer is then examined for its elemental composition separately. There is no other instrument that can match the microprobe in this respect. All other techniques simply average the elemental composition of the sample. If there are only two layers present in a paint,

as is often the case, they are mounted one chip face up and another chip face down.

#### METHOD OF ANALYSIS

The practical limit in size for paint chips to be amenable to quantitative analysis is approximately  $1 \mu$  gm. of sample. This represents a cube of paint about  $100 \mu$  on a side. However, qualitative data on at least major constituents can be obtained from samples as small as  $10^{-11}$  gm.

After the mounted sample has been coated with carbon, it is placed in the sample cup and inserted into the column of the probe. Because paint is a rather delicate sample to work with, care must be taken to use proper instrument parameters. Generally a 20 KV accelerating potential and a specimen current of about  $.030 \mu$  amp. are used. In addition a larger beam size is used than the  $1 \mu$  limit which can be obtained with best focus. This tends to spread the imping-

<sup>8</sup> BIRKS, L. S., op. cit. p. 144.

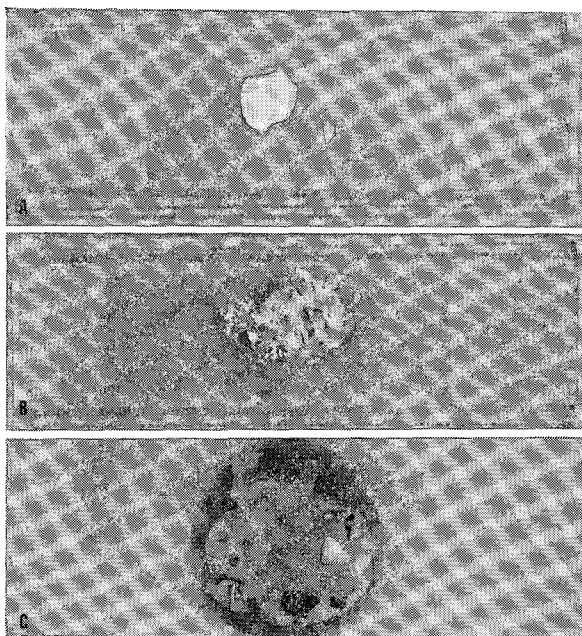


FIGURE 4

- A. Paint chip embedded in Scotch tape  
 B. Silver loaded epoxy puddled over chip  
 C. Finished mount ready for examination

ing energy over a wider area making it easier to dissipate heat and charge.

After the samples are placed in the probe they are examined according to a regular program. The known material, which is usually not limited in size, is examined first. Of course both the known paint and the sample being compared to it are placed in the same mount so that they receive the same polishing and coating.

First the paints are given a general visual examination under the microprobe's microscope ( $\approx 300\times$ ). Then a qualitative scan is made to determine what elements are present. (See fig. 2) Following this the beam is expanded to fill the field of view, and the microscope illumination is turned off. An examination of the fluorescence colors excited by the beam will give an indication of what type extender pigments have been used. These colors are noted and their positions marked. Then the beam is focused again and semi quantitative scans are run on each of the different colored areas. In this way the presence of materials in concentrations as low as .05% on an average basis can be clearly established. Several points can be noted with respect to the extender materials present. For example, if the scan shows that  $\text{CaCO}_3$  is present, this could be as precipitated  $\text{CaCO}_3$

or as calcite which has been ground. Both materials are used in paint as extenders. Ordinary precipitated  $\text{CaCO}_3$  yields a pale blue color with occasional pale orange hints, while calcite yields a bright melon-orange color that persists very well.

Another example is  $\text{CaSO}_4$  which is used as an extender in paints also. Anhydrite, the mineral form of  $\text{CaSO}_4$  fluoresces with a pale blue and shows fairly frequent red inclusions whereas the hydrated product  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  also used as an extender exhibits colors from pale blue to pale violet.

Very small particles of pure  $\text{SiO}_2$  glow an intense bright blue, whereas ground kaolin which is an aluminum silicate often used as an extender yields a green-blue color not nearly as bright. These observations must always be double checked by focusing the beam and obtaining an x-ray analysis of the colored particle of course, but many useful suggestions can be made by the sample itself when viewed in this manner.

The next step is to make a quantitative analysis on an average basis. In order to do this the beam can be expanded to about  $300\ \mu$  or a scan can be made over the sample surface in a raster about  $300\ \mu$  on a side. One spectrometer is set for titanium radiation, and the other to receive some other

radiation of interest. The number of counts accumulated in a given amount of time is noted, and a series of three measurements of the same radiation at different spots on the sample are made. Naturally modifications are made for smaller sample sizes. It may be possible in some case to obtain only two or even one quantitative read-out. Normally in small samples the size of the raster on the sample surface is reduced. Since the two spectrometers were accepting data at the same time, ratios can be used to reduce any instrumental drift that may be present. This process is repeated for all the elements of interest. Again the known sample is examined first to determine what count rates can be obtained, what counting times will be necessary to produce statistical accuracy, etc. The actual quantitative comparison is carried out by measuring a ratio on the known and then going directly to the unknown to measure the same ratio, then a new element ratio is chosen and the process repeated. This is done to further reduce the influence of any instrumental drift that may be present.

Normally obtaining accurate quantitative data with the probe is a rather involved procedure due to various absorption and secondary fluorescence corrections which must be made in order to convert observed x-ray intensity to weight percent. Under these conditions, one normally uses pure elements as standards. It is generally agreed, however, that the best results are obtained when standards of known composition are made up and are very close in composition to the sample being examined. Forensic science is fortunate in this one respect. We are not actually interested in absolute quantitative data but rather in relative quantitative data. That is, we are not concerned with the exact titanium percentage in a sample, rather the question is whether these two samples contain exactly the same concentration of titanium. Thus when we place the known paint and the unknown for comparison in the same mount, we are using an exact standard, provided that they match in reality of course. So quantitative comparison on the microprobe is much easier than absolute quantitative analysis. Thus the most important characteristics of the analysis are sensitivity and reproducibility.

In order to obtain an idea of sensitivity, some previously analyzed paint was ground up and additional material was added to one portion of it. Then the powders were pressed back into chips

and re-examined. It was found that at the major constituent level, which was taken to be 30 percent, it was possible to detect changes down to .25% of the amount present. At low levels of concentration, sensitivity is limited by standard deviation, that is, essentially by reproducibility.

At relatively high concentrations, standard deviation is usually less than two percent since counting times can be kept relatively short and a good number of counts collected. However, at the low concentration level, standard deviation runs up to approximately 15%. This is due to the fact that short counting times cause large statistical variations and long counting times cause sample contamination by the beam. The contamination, which consists of the deposition of polymerized diffusion pump oil, coupled with sample charring, change the absorption and configuration of the sample surface during the counting process.<sup>9</sup>

One further consideration that had to be made was the completeness of the analysis. It was necessary to know the practical limit of detection for elements in a paint matrix. Investigations of pre-analyzed paints<sup>10</sup> indicated that concentrations as low as 100 ppm. or the .01% level were detected. Samples were obtained which had been analyzed to very low levels by neutron activation techniques. That analysis had indicated that some elements were present in most ranges. They were: Ti 12%, Zn 1.5%, Al .09%, Na .01%, Co .01%, Mn .001%, La .001%, Sm .0002%, and In .00003%. We were able to detect Na and Co, but could not detect Mn or below even with very high take off angles. These high take off angles, as high as 80°, were obtained with special mounting techniques. The normal take off angle in the Phillips probe is 15°.

Having obtained some knowledge of the instrument's capabilities and developed methods of sample preparation, we addressed ourselves to what we felt was the most critical problem in the forensic analysis of paint samples. That is, the attempt to differentiate between batches of paint of the same color made by the same manufacturer at the same plant.

<sup>9</sup> At the writing of this paper we are investigating the possible use of a cold stage to reduce these effects and possibly reduce the standard deviation.

<sup>10</sup> BRYAN, D. E., GUINN, V. P. AND SETTLE, D. M., *Applications of Neutron Activation Analysis in Scientific Crime Detection*, GENERAL ATOMIC REPORT GA-7041 (San Diego, California) p. 23.

## DEGREE OF PARTICULARIZATION

Arrangements were made with Sherwin Williams paint manufacturers to hold out samples on a batch to batch basis. The paint was a white exterior trim paint. Approximately twenty batches of this paint were tested. In this paint Ti, Ca, S, Ba, O, C, Si, and Al were detected.

The set of pre-analyzed paints mentioned above also contained eight different batches of the same color paint made by the same manufacturer. In this paint Ti, Zn, O, S, Ca, Al, Na, Co, and Si were detected. The two paints, made by different manufacturers could be distinguished with ease, but no regular batch to batch differences could be detected in either of them. While one element in a given batch might significantly differ from the others in rare cases, this did not happen as a general rule.

In Table I are presented some typical results. This data was gathered using a 20 KV beam and a specimen current of .030  $\mu$  amp. A scanning technique was used to average the amount present. The approximate concentrations of these ele-

ments are: Ti 12.5%, Al .10%, Ca 23.5%, S 14.0%, Zn 1.5%, Na .01%, and Co .01%.

Neutron activation analysis indicates that significant differences begin to occur at the .10% to .01% level. Unfortunately, at this time standard deviation at these levels is too large to let these differences show through. But it does indicate that with refinements in technique it may soon be possible to see batch to batch differences.

## COMPATIBILITY WITH OTHER METHODS OF ANALYSIS

Microprobe analysis is compatible with x-ray diffraction techniques, and many samples have been run after they had been examined in the x-ray powder camera. The probe is not compatible with infrared analysis with present mounting techniques. It is all but impossible to remove a mounted sample from the probe without destroying it. This is unfortunate since the probe is of almost no aid in organic analysis, and so resins and organic pigments go in effect undetected. Where enough sample is present, however, it can be shared with infrared, and one must keep in mind that in many cases the sample is not severely limited compared to how little is actually needed by the probe.

The time necessary for analysis is from two to three days including mounting and coating time. However, samples may be batched and gains made in efficiency in this way.

## CONCLUSION

In conclusion it may be said that at present some fairly detailed characteristics of paint can be examined with the microprobe, and layer by layer analysis can be accomplished on multilayer paints. It would also seem that there is reason to hope to see batch to batch differences in the future although we cannot make that claim at this time. The results obtained so far are encouraging enough to cause us to continue research and refinement of technique in this field.

Our laboratory as a whole is engaged in the study of paint and the electron probe is but one link in a chain of instruments used in an effort to push back the boundaries in the particularization of paint.

TABLE I  
COUNT RATIOS OBTAINED ON WHITE PAINT

Batch	Ca/Ti	S/Ti	Zn/Ti	Al/Ti $\times$ 100	Na/Ti $\times$ 1000	Co/Ti $\times$ 1000
1	.454	.842	.0157	.147	.046	.362
2	.450	.838	.0151	.126	.051	.320
3	.451	.845	.0160	.120	.039	.351
4	.457	.844	.0148	.149	.048	.338
5	.450	.839	.0145	.113	.040	.361
6	.460	.844	.0155	.129	.055	.341
7	.453	.843	.0141	.156	.035	.345
8	.448	.848	.0150	.122	.045	.352

## % Standard Deviation

	Ca/Ti	S/Ti	Zn/Ti	Al/Ti $\times$ 100	Na/Ti $\times$ 1000	Co/Ti $\times$ 1000
1	1.57	1.46	5.46	15.2	15.3	15.3
2	1.31	1.52	4.21	15.0	14.9	15.2
3	1.72	1.58	5.21	15.2	14.4	14.9
4	1.58	1.41	4.85	14.8	15.0	14.9
5	1.55	1.53	4.93	15.0	14.9	15.2
6	1.49	1.40	5.25	15.2	15.2	15.4
7	1.62	1.50	5.21	14.9	15.3	15.1
8	1.56	1.43	4.98	15.1	14.8	15.1