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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

ANALYSIS OF IRON BLUE PIGMENTS

Period Covered: January 1945 to December 1945.

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Period Covered: January 1945 to December 1945.

SUBMITTED BY: A. R. Manke DATE SUBMITTED: March 23, 1946

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ANALYSIS OF IRON BLUE PIGMENTS

INTRODUCTION

Although iron blue pigments represent a substantial percentage of our total pigment manufacture, there has been no comprehensive analytical work done on such pigments. Analytical data, although not standing alone, are quite necessary for a good understanding of the properties of iron blue pigments. Improvements in methods of manufacture and properties can be indicated by a critical examination of such analytical data.

This work was originally started with the primary purpose of providing data for a comparison of the ferrocyanide content of our pigments with that of our compitators. The work however extended to the complete analysis of iron blue pigments.

The report is divided into two sections. The first part deals with the development of the various methods. The second part deals with a brief statistical treatment of the data. It had originally been intended to include a third part covering an interpretation of the data. Since certain ideas concerned with this interpretation are still in the formative stage, it was thought advisable to intoduce the interpretation of the data in another report.

In developing the methods of analysis, the literature was freely drawn upon. The references found to be of value are listed in the bibliography. As a rule, considetable modification was made of methods obtained from the literature. The development of each method is treated separately, giving such information thought to be of value or interest even though some of the information was not incorporated in the finally chosen method. A statistical treatment of the data is included to provide a means of comparing methods as well as assessing the precision of the various methods. It also serves to illustrate the application of statistical methods to problems of this kind. No attempt is made to develop any theory of statistics and some knowledge of such is presupposed. For a simple discussion of the application of statistical methods see, "Analysis of Variation", ICI (Dyestuffs) Technical Report March 16, 1941, File No. H5824.

SUMMARY

This report describes methods for determining the following constituents. The methods in detail are found in the appendix as indicated:

Appendix	(1)	Ferrocyanide by ceric sulfate tetration.
"	(2)	Total Nitrogen
"	(3)	Ammonia nitrogen
"	(4)	Total iron
"	(5)	Total alkali metals
"	(6)	Chromium
"	(7)	Sulfate
"	(8)	Total water
"	(9)	Iron outside of the iron blue molecule
"	(10)	Organic treating agent.

The described methods were applied to a series of Iron Blue pigments, the results of which are tabulated in Table 1.

SUGGESTIONS FOR FURTHER RESEARCH

(1) Investigate the possibility that some of the cationic iron in commercial iron blue pigments is there as ferrous iron such as

$$\underset{\text{white precipitate}}{Fe(NH_4)_2\ FE(CN)_6}$$

or $Fe^{+2}\ Fe^{+3}\ Fe^{+2}\ (CN)_6$

which may be considered as the ferrous salt of the acid

$$H\ Fe^{+3}\ Fe^{+2}\ (CN)_6$$

(2) Develop a method which would distinguish between the alkali metal incorporated in the iron blue molecule and the alkali metal simply adsorbed on the pigment.

(3) Further investigate methods for determining total water. The total hydrogen minus ammonia hydrogen method gives results higher than the loss in weight method. Why? If it were possible to have compounds of the species

$$Fe\ H\ Fe^{+3}\ Fe^{+2}\ (CN)_6$$

the total hydrogen method would give high results.

TABLE I

ANALYTICAL DATA ON IRON BLUE PIGMENTS

Sample	Total Iron as % Fe	Total Nitrogen as % N	Ammonia Nitrogen as % NH_3	Cationic (CN) Iron as % Fe	(CN) Nitrogen as % $Fe(CN)_6$	Chromium as % Cr_2O_3	Sodium as % Na_2O	Sulfur as % SO_3	Loss in Weight on Heating as % H_2O	Total hydrogen minus ammonia hydrogen as % H_2O	% Treating agent	Iron Oxide of the Iron Blue Molecule as % Fe_2O_3
Calco 50-A750												
C-47418	36.98	30.11	4.84	19.47	66.43	0.42	1.15	0.32	4.65	5.00		0.29
Calco 50-4070												
C-48030	26.18	29.43	4.46	18.92	65.47	none	0.96	1.23	5.50		0.86	
Imperial A-4406												
C-48031	37.19	30.81	4.97	19.28	67.94	none	1.32	0.30	3.45	5.09		
B-197-D												
SD-48249	36.72	30.11	4.56	19.06	66.98	0.19	1.08	0.85	4.35	6.34		
B-216-D												
SD-48321	35.96	28.42	4.21	19.25	63.40	0.39	0.74	1.28	4.80		2.52	
B-66-D												
SD-47988	35.81	28.40	3.88	18.94	64.01	0.82	1.22	1.69	6.45	9.47		
1105-38												
Untreated B-216-D	36.68	30.19	4.61	19.00	67.08	0.27	0.82	1.51	4.83	5.45		0.20
B-1661-D												
Lot T303	35.44	29.21	4.55	18.38	64.74	0.32	0.86	1.08	4.40		3.27	
*1105-38 Heated at												
160°C. for 412 hrs.	44.10	17.14	3.40	34.46	36.56	0.35	1.00	1.99	5.66	8.22		36.73
TONING BLUES												
Imperial X-712												
C-47592	33.52	27.14	6.45	18.77	55.94	2.29	0.74	0.62	10.60	11.17		
Standard Ultra-marine #450												
C-48249	33.87	27.18	6.48	19.20	56.04	1.42	0.58	0.27	11.00	12.60		0.92
B-152-D												
Lot 8238	33.95	27.80	6.56	18.87	57.23	none	0.34	0.16	8.25		3.77	

*After heating, the sample was allowed to pick up as much moisture as it would at room temperature before storing in an air tight container.

EXPERIMENTAL

I Development of Methods

A Determination of the Complex Iron Cyanide Iron

There are quite a few methods available for determining the complex iron cyanide iron. Of these methods, four were chosen for investigation. These methods were:-

(1) Destruction of blue pigment with caustic and titration of the ferrocyanide produced with a standard oxidying agent.
(2) Detruction of blue pigment with caustic and titration of the ferrocyanide produced with a standard solution of zinc sulfate.
(3) Determination of the (CN) nitrogen and expressing it as $Fe(CN)_6$.
(4) Determination of total carbon acid expressing it as $Fe(CN)_6$

In working with the first two methods certain difficulties became apparent and as a result, these methods were finally discarded. In the first place it was found quite difficult to completely separate the ferrocyanide from the ferric hydroxide after alkali destruction of the blue pigment. When an iron blue pigment is treated with a caustic solution, ferric hydroxide and a soluble ferrocyanide are produced according to the equation,

$$Fe\,NH_4\,Fe(CN)_6 + 4\bar{O}H \rightarrow \underline{Fe(OH)_3} + Fe(\bar{C}\bar{N})_6^{\bar{}\bar{}} + NH_3\uparrow + H_2O$$

It is impossible to wash this ferric hydroxide precipitate free of ferrocyanide when using the customary wash solution of 1% ammonium chloride. This phenomenon is very pronounced. No ferrocyanide at all is found in the wash filtrate until distilled water is used. Using distilled water, it becomes possible to wash out all of the ferrocyanide but the ferric hydroxide is peptized and runs through the filter before the ferrocyanide is completely removed. Using a wash solution of sodium hydroxide in place of ammonium chloride also did not work. The ferric hydroxide still ran through the filter. A technique was worked out whereby the peptized ferric hydroxide plus the remaining ferrocyanide was caught in a separate beaker. The ferric hydroxide was coagulated by the addition of ammonium chloride and refiltered. Since this amount of ferric hydroxide was always small, the amount of ferrocyanide adsorbed on it was considered too small to affect the results. This technique was found to be superior to the customary reprecipitation technique since several reprecipitations were necessary bringing the salt concentration up quite high.

Acidifying a solution in which reactions like the above have taken place would result in the formation of some iron blue.

$$Fe^{+++} + NH_4^{+} + Fe(\overline{CN})_6 \rightarrow \underbrace{Fe\,NH_4\,Fe(CN)_6}_{\text{Iron blue}}$$

or

$$\underbrace{4\,Fe(NH_4)_2\,Fe(CN)_6}_{\text{White precipitate}} + O_2\ (\text{from air}) \rightarrow \underbrace{4FeNH_4Fe(CN)_6}_{\text{Iron blue}} + 4NH_4^{+} + 2H_2O$$

Reaction (3) which produces formate will cause high results if allowed to go to any appreciable extent. Formate is capable of oxidation by ceric sulfate as follows:-

$$2Ce(SO_4)_2 + H\,COOH \rightarrow Ce_2(SO_4)_3 + CO_2\uparrow + H_2SO_4$$

An inspection of the equations shows that one ferrocyanide iron produces 6 formate irons which means that one reduction equivalent produces 12 reduction equivalents or a net increase of 11 reduction equivalents for every ferrocyanide iron converted to formate. This will give high results as indeed, high results were sometimes obtained.

Since it seemed evident that some reactions were taking place that affected the results, and since some iron blue pigments contain organic treating agents whose effect on ceric sulfate might not be predictable, the direct titration of ferrocyanide produced from iron blue pigments was abandoned. The method may be applicable in certain cases and it may be possible to get the variables under control by doing further work on it. Some of the comparisons with other methods were quite good as can be seen in table 2. The method employing the titration with ceric sulfate is given in detail in appendix 1. It is given becuase it embodies certain useful techniques and ideas that can serve as a starting point if it is found desirable to do any further work along the line of the direct determination of ferrocyanide in iron blue pigments.

A small amount of work was done on the zinc sulfate titration method in conjunction with the ceric sulfate method. Here again, the precision was very poor and since the method is admittedly empirical, the position of the endpoint being dependent on the kind and concentration of salts in the solution, the method was discarded.

The third method investigated was the determination of (CN) nitrogen, expressing it as $Fe(\overline{CN})_6^{-}$. This was accomplished by first determining the total nitrogen following the standard Kjeldahl technique and then determining the ammonia nitrogen by a simple alkaline distillation. The difference was (CN) nitrogen. Here again the observation was made that some of the ferrocyanide decomposed to give ammonia presumably accoding to the equations,

$$Fe(\overline{CN})_6 \rightleftharpoons Fe^{++} + 6\,\overline{CN}$$

$$\overline{CN} + 2H_2O \rightarrow [\overline{COOH}] + NH_3\uparrow$$

Repeated alkaline distillations of the ferrocyanide from the blue pigment always yielded a small amount of something alkaline, presumably ammonia. This did not occur during a blank determination. Such a reaction would not cause as large an error in this case as in the titration with ceric sulfate. One ferrocyanide iron would produce six equivalents of ammonia whereas in the ceric sulfate titration method, one ferrocyanide iron lost would create 12 equivalents of formate. The production of ammonia in this manner was small and sufficiently constant so a correction could be applied. Employing such a correction changed the percent $Fe(CN)_6$ by only 0.1% absolute which is hardly worth considering and serves to indicate that the method is not subjected to serious error because of this reaction.

A fourth method was considered primarly to serve as a check on the (CN) nitrogen method. This determined the total carbon by microcombustion and calculated it to ferrocyanide. Strangely enough the method gave results which as a rule were 2.2% relative high. The precision of both methods was about the same. No good explanation is offered for this difference. Other sources of carbon such as carbonates, organic treating agents, or small amounts of organic impurities picked up during manufacture would give high results although the blue pigments run for total carbon were supposed to contain no treating agent. Table 2 compares the values for ferrocyanide obtained using the (CN) nitrogen method, $Ce(SO_4)_2$ method, and the total carbon method. It should be noted that in those of the five samples tested the (CN) nitrogen and the $Ce(SO_4)_2$ method are in good agreement. It should be further noted that in every case the total carbon method is higher than the other methods. It ranges from a high of 5.4% relative to 0.4% relative higher than the (CN) nitrogen method. In

spite of the fact that the reason for this difference is not clearly understood, in view of the fact that treating agents are frequently found in iron blue pigments, the most reliable method studied is the method determining the (CN) nitrogen. This is given in detail in appendices 2 & 3. The standard deviation for 14 degrees of freedom is ±0.324% Fe $(CN)_6$.

TABLE F

Comparison of Methods for Fe $(CN)_6$ Determination

SAMPLE	Percent Fe $(CN)_6$ (CN) Nitrogen Method	Ce $(SO_4)_2$ Method	Total Carbon by Microcombustion	Relative Percent Difference between $Ce(SO_4)_2$ Method & (CN) Nitrogen Method	Total Carbon Method & (CN) Nitrogen Method
Calco 50-1750 C-47418	66.43	67.58	68.77	+1.7	+3.5
Imperial A-4406 C-48031	67.94	68.30	69.19	+0.5	+1.8
B-197-D SD-48249	66.98	68.12	68.37	+1.7	+2.1
B-66-D SD-47988	64.01	63.79	65.14	-0.3	+1.7
1105-38 Untreated B-216-D	67.08	66.78	67.33	-0.4	+0.4
Imperial X-712 C-47592	55.94	-	57.13	-	+2.1
Stand-Ultramarine #450 C-48249	56.04	-	57.21	-	+2.1
1105-38(Untreated B-216-D) Heated for 412 hrs. at 160°C.	36.56	-	38.5?	-	+5.4

B Determination of Total Iron and Cationic Iron

For the determination of total iron, the pigment must be opened in such a manner that the complete destruction of the complex iron is assured. Gentle ignition of the iron blue in an open beaker can do this but it has been our experience that sometimes a small amount of blue remains unchanged. Subsequent solution of the iron oxide formed is often incomplete expecially if the sample is strongly ignited to insure complete destruction of the blue. It has been postulated that small amounts of iron carbide form which will not easily dissolve in HCL. Unchanged iron blue will not dissolve in HCL and strongly ignited Fe_2O_3 or Fe_3O_4 will dissolve with difficulty. The presence of treating agents will also inhibit the destruction of iron blue. The use of perchloric acid has circumvented all these difficulties . The blue pigment is first gently ignited, no attempt being made to completely destroy the pigment. This is followed by a treatment with HCL and finally with 72% $HCLO_4$. All the reactions are carried out in a flask that can be equipped with an all glass trap. Such a trap will prevent loss of iron by volatilization of ferric chloride and also loss of iron by having it carried away in the $HCLO_4$ fumes.

The iron can now be determined by any of the standard methods for iron. The choice of method must take into account the possibility of having interfering ions present, particularly chromium and aluminum. Titration with standard titanous chloride was chosen as the most direct way for determining the total iron. Chromium, if present, will be oxidized to chromate by the $HCLO_4$ but this is reduced with peroxide the iron remaining in the ferric state; aluminum will not interfere. The details of the method are to be found in appendix 4. The standard deviation for 13 degrees of freedom is ±0.042% total iron.

The cationic iron can be determined directly by first destroying the blue pigment with caustic and filtering off the ferric hydroxide, or it can be determined indirectly by subtracting the complex iron from the total iron. In view of the difficulties attendant with the complete separation of the cationic iron from the ferrocyanide mentioned in past A, the indirect method was chosen as most desirable. Sample 1105-38, a B-216-D type but without treating agent, was analyzed both ways. The cationic iron was precipitated three time to free it from ferrocyanide. It was then dried, ignited, and weighed. The weight was corrected for the chromium present as found by an independent determination. The two method agreed very well. The direct method gave 18.99% Fe and the indirect method gave 19.00% Fe. These figures are not meant to imply that the precision is as good as this. It simply indicates that in all probability, both methods are reliable. It was not considered sufficiently important to do the work on the direct method necessary for a statistical study of these two methods. The cationic iron as determined indirectly from the total iron and the complex iron has a standard deviation for 13 degrees of freedom of ±0.095% cation iron.

C Determination of Total Alkali Metals

The method consists of removing all other cations and weighing what is left as sulfates. The method is essentially that described by Jameson, (Ref. 3) wherein the pigment is gently ignited in an evaporating dish, the iron oxide remaining, dissolved in HCL, removed with NH_4OH and the solution evaporated to dryness with a little sulfuric acid. An important modification was the addition of bromine water as suggested in Gardner (Ref. 4). The bromine water helped to open up the pigment and oxidized any ferrous iron to the ferric state. It was also observed that in the absence of bromine water some sulfide was formed presumably by reduction of some of the sulfate in the blue. This caused the formation of a small amount of iron sulfide when the solution was made ammoniacal. This sulfide had a tendency to run through the filter paper and so complicated the removal of the iron. After the addition of bromine water a few drops of 30% H_2O_2 were added to reduce any chromium to the trivalent state that may have been oxidized by the bromine. The addition of ammonium hydroxide then took out the iron, and chromium in the pigment. Any aluminum in the pigment would also be removed.

It was observed that the solution, supposed to be iron free, almost invariably contained traces of iron. Although this iron could be removed as the sulfide, it was found simpler and quite effective to evaporate the solution, containing the trace of iron, to dryness, and gently ignite. The iron was rendered insoluble by this procedure and the soluble salts were leached from the residue. One such evaporation process was generally all that was required for the removal of this trace of iron. In all of the blue pigments encountered, no further treatment was necessary. If ions such as zinc, nickel, or the alkaline earths are present, hydrogen sulfide and ammonium carbonate can be used to take them out, but in their absence hydrogen sulfide is not necessary.

Flame tests served to distinguish between sodium and potassium. If potassium was to be determined in the presence of the sodium, it was conveniently precipitated as the potassium salt of 6 chloro-5 nitro toluene 3 sulfonic acid following the procedure of KCR-44. All of the commercial blue pigments examined contained no potassium hence this method did not receive much attention. The method for total alkali metals is described in detail in appendix 5. The standard deviation for 11 degrees of freedom is ± 0.048 $\%Na_2O$

D Determination of Total Chromium

Since perchloric acid conveniently opens up an iron blue pigment and oxidizes the chromium to chromate at the same time, this method was chosen. It is essentially the same as that used for determining total iron. An important modification is the rapid cooling of the perchloric acid solution. This is necessary to prevent the partial reduction of the chromate as explained by G. Frederick Smith (Ref.5). An attempt was made to titrate the chromate directly with a standard Mohr's salt solution using barium diphenylamine sulfonate as the indicator and phosphoric acid to complex the iron, but the concentration of ferric iron was so high that the endpoint was sluggish and ill defined. Using a calomel-platinum electrode system to detect the endpoint did not improve matters. The higher oxidation potential of potassium permanganate was used by adding a slight excess of Mohr's salt and titrating the excess with standard permanganate. This gave an endpoint, though not ideal, sufficiently good for accurate work. This method is described in detail in appendix 6. The standard deviation for 16 degrees of freedom is ±0.027% Cr_2O_3.

E Determination of Sulfate

Some of the methods suggested in the literature opened up the pigment by gentle ignition followed by solution in hydrochloric acid (Ref. 4). Such a method did not seem to be based on sound chemical principles because of the danger of loss of SO_3 during the ignition process. The identification of some sulfide iron using a similar procedure during the development of the method for total alkali metals also stamped this method as being unreliable. It is true that the addition of bromine water would oxidize any sulfide to sulfate, still some H_2S could be lost before oxidation to sulfate.

Kappelmeier (Ref. 6,7) suggested a method for the alkaline destruction of iron blue in which the ferrocyanide was destroyed by forming the more stable mercuric cyanide complex. He applied the method to chrome greens and we found it to work quite well for iron blue pigments. Kappelmeier used mercuric oxide as his source of mercury but we found that mercuric oxide added directly worked very poorly. It was necessary to use freshly precipitated mercuric oxide. Aged material was far less reactive . The method finally adapted is a modification of the original method of Kappelmeier and is described in detail in appendix 7. The standard deviation for 14 degrees of freedom is ±0.065 %SO_3. The ignition method and the alkaline mercuric oxide method were compared by running two samples both ways. As was predicted, the alkaline mercuric oxide method gave substantially higher results, 0.80% SO_3 as against 1.28% SO_3 for one sample and 0.42 as against 0.62 for another sample. The alkaline mercuric oxide method was checked by adding sulfate to a low sulfate blue and comparing the expected answer with that obtained. The expected answer was 58 mg $BaSO_4$ as against 62 mg $BaSO_4$ obtained. This seems to indicate that the method may give slightly high results but since the amount of sulfate in a blue pigment is never very large, such an error may be accepted. The method was further checked by having three

samples run by an independent laboratory, the plant analytical Laboratory. Table 3 shows the agreement between laboratories which is in keeping with the variations to be expected.

TABLE 3

Sample	% SO_3 Research Laboratory	Plant Analytical Laboratory
B-197-D SD48349	0.9	1.0
B-216-D SD48321	1.3	1.4
1105-38 (Untreated B-216-D)	1.5	1.5

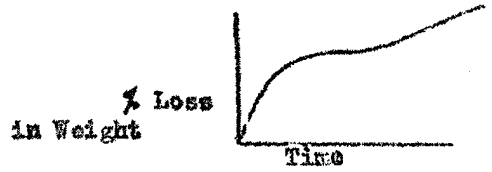
F. Determination of Total Water

This determination is very difficult. Moisture is strongly held by iron blue and attempting to drive it off by heating, caused some decomposition of the pigment before all of the water was driven off. Toluene distillation does not seem to get all of the moisture. It comes off very slowly and long distillation periods are required. Even after around 15 hrs. a small amount of additional moisture can be obtained for some blue pigments. Ignition of the sample to iron oxide and calculating the loss in weight other than that due to loss of $(CN)_2$ & NH_3 has been suggested (Ref. 3). This did not work because the natural errors in the dependent determinations made the precision of the moisture determination so poor as to be practically worthless. Furthermore, some of the iron was converted to Fe_3O_4 which could not easily be converted to Fe_2O_3, hence there was a mixture of Fe_2O_3 and Fe_3O_4 in unknown proportion.

A simple ignition in a combustion tube and an attempt to collect the gases evolved also failed. Cyanogen and polymers of cyanogen were produced which clogged the absorption train and gave results that could not be correlated with moisture.

A modification of the toluene distillation method was tried in which the blue pigment was first ignited while in the flask equipped with a condenser. Moisture could be seen along the inside of the condenser walk but when the ignited product was distilled with toluene, no moisture came over. Evidentally the iron oxide produced, was able to adsorb and hold the moisture even more strongly than iron blue.

In spite of the heat decomposition of iron blue pigments, the most promising method appeared to be the loss in weight on heating. For this purpose, a Brabender Moisture Tester was used. This instrument is essentially a drying oven with a balance attached in such fashion that the sample can be weighed without removing it from the oven. Drying curves were obtained at 160°C. It was observed that the curves all had the same general shape as follows:



The rate for normal drying is roughly proportional to the percent moisture remaining in the blue hence the slope in the curve should fall off and eventually become zero, i.e., a horizontal line, when the water is all gone. The fact that the slope never becomes zero even after 412 hrs. is strongly indicative that decomposition is taking place. Decomposition is also indicated when comparing the analytical results of the heated and unheated samples in table 1. The fact that this region of the curve is essentially linear suggests that it may be possible to correct for the loss in weight due to decomposition of the blue. To make this correction, one simply needs to extrapolate the linear portion of the curve back to zero time. The percent loss in weight as indicated by this extrapolated line is the percent loss in weight corrected for the loss due to decomposition.

Graphs 1 & 2 show typical curves. It should be observed that the decomposition rate is low and in no case should introduce a large positive error. The toning blues are in a class by themselves with a distinctly higher decomposition rate. C-48931 is Imperial's A-4496. C-47592 is Imperial's X-712. Both C-47592 and B-152-D are toning Blue. Graph 2 shows that the decomposition rate remains essentially the same, with possibly a slight increase, even up to 412 hrs.

This method was found to give results that compared within experimental error with the loss in weight after drying for one hr. at 160°F. Possible exceptions are toning blues where the decomposition rate is abnormally high. This method implies that the decomposition rate is the same in the presence and absence of water. It is at best empirical and there is some evidence to show that the method gives low results. In spite of its shortcomings, it is still a good control method and is considered superior to the toluene distillation method. The method is described in detail in appendix 8. The standard deviation for 19 degrees of freedom is $\pm 0.164\% H_2O$.

Drying over sulfuric acid at room temperature in a vacuum was also considered. Here the shape of the curve was much the same as when drying at elevated temperatures in that there was a rapid initial loss in weight followed by a leveling off of the curve. Graph 3 shows a typical curve. The attempt was made to show that it was simply a question of time, and vacuum drying would give the same answer as drying at elevated temperatures. This was not shown because as seen by referring to Graph 3, even at 1600 hrs. the loss in weight had only reached 5.6%. Referring to the curve for B-152-D, Graph 1, the percent moisture by the extrapolation method is about 8.2%. It should also be observed however, that the vacuum drying curve is still rising, and all that can be concluded is that no essential difference has been observed in the type of moisture driven off during vacuum drying as against that driven

off during drying at elevated temperatures. The depression in the curve at around 300 hrs. was brought about by the inadvertent breaking of the vacuum allowing moisture laden air to enter the desiccator. It clearly illustrates the extreme care necessary in keeping these dried samples away from moisture.

Another method considered was the microcombustion method for total hydrogen. This method after correction for the hydrogen from the NH_4 would give that due to water. Unfortunately the precision of this method was poorer than that of the loss in weight method but it is significient that in all cases the total hydrogen method gave higher results. Table 4 compares these methods.

TABLE 4

Comparison of Methods for Total Water

Sample	%H_2O by Total H- Ammonia H	%H_2O by Loss in Weight	Diff.	Ratio	Relative Percent Difference
1105-38 Untreated B-216-D	5.45	4.90	.55	1.112	10.8
Calco 50-1750 C-47418	5.00	4.65	.35	1.075	7.3
Imperial A-4406 C-48031	5.09	3.45	1.64	1.475	38.4
B-197-D SD-48249	6.34	4.35	1.99	1.457	37.2
B-66-D SD-47988	9.47	6.45	3.02	1.468	38.9
1105-58 Heated	8.22	5.66	2.56	1.452	36.9
Imperial X-712 C-47592	11.17	10.60	.57	1.054	5.2
Std. Ultramarine #450 C-48249	12.60	11.00	1.60	1.145	13.6

The standard deviation for the total hydrogen method of determining H_2O is $\pm$ 0.688% H_2O for 8 degrees of freedom which means one could expect differences no greater than about 2.0 around 1% of an infinite number of trials. The fact that the total hydrogen method is consistently higher than the loss in weight method is significient but there is insufficient data to tell much about the magnitude of the difference. This is because the total hydrogen method has such poor precision. One can conclude however that the total hydrogen method gives higher results.

G. Determination of Iron Outside of the Iron Blue Molecule

It is conceivable that some of the cationic iron in a commercial pigment is there simply as a basic ferric salt such as the sulfate, or simply as a hydrated oxide. The problem of its detection is made difficult by the fact that iron blue is a strong adsorber and may strongly hold on to such cationic iron. Boiling with hydrochloric acid caused some destruction of the blue, liberating iron from the pigment molecule, hence that method of extraction could not be used.

The method developed involved the shaking of the pigment in an automatic shaking device with 20% by volume hydrochloric acid (80 ml H_2O + 20 ml Conc. HCL). An overnight period of shaking was chosen simply for the sake of convenience. The method probably gives low results but in view of the fact that the amount of iron outside of the blue was found to be quite small, a large relative error could be tolerated without seriously affecting the results.

A sample that had been deliberately heated to cause some decomposition was completely analysised and the amount of cationic iron outside of the iron blue molecule deduced from a consideration of the equivalence balance gave a figure of 35.9% Fe_2O_3. The direct determination by shaking with hydrochloric acid gave 34.7% Fe_2O_3 so the method probably gives results no lower than 3% relative. For normal samples, the iron found outside of the blue amounted to only several tenths of a percent Fe_2O_3 hence the method was considered suitable for this work. For the complete analysis of the heated and unheated sample see Table 1 Page 3 .

Some attention was given to the possibility that some of this iron might be in the ferrous state. No definite evidence could be found for soluble ferrous iron and if any was present, it was present in very small amounts. No ferrous iron outside of the iron blue molecule was found in a toning blue studied. Since there is fairly good evidence that incomplete oxidation of the ferrous ammonium ferrocyanide takes place in the manufacture of toning blues, we can conclude that this method does not measure the ferrous iron in ferrous ammonium ferrocyanide but is a true measure of the iron unassociated with the ferrocyanide.

The method is described in detail in appendix 9.

H. Determination of Treating Agent

Work had been done back in 1942 in developing a method for the determination of treating agents such as naphthenic acid in iron blue pigments. This method, (KCR-119) destroyed the blue with caustic and extracted the treating agent from the acidified filtrate with petroleum ether. A straight extraction of the pigment with petroleum ether in a Soxhlet extractor did not work, presumably because the iron blue so strongly adsorbed the treating agent that the solvent could not remove it. The method was cumbersome and consumed a great deal of the operators time. Treating agents have since been added to iron blue pigments

that are alkali insoluble hence simply extracting the acidified filtrate would lose the treating agent in the ferric hydroxide precipitate. This required a modification of the method to include the [illegible] treating agent that might be present in the precipitate hence the method became still more cumbersome and time consuming.

Work was done in the attempt to find a mixed solvent which could strip most any kind of organic treating agent directly from the blue pigment. A 5% by volume mixture of acetic acid in chloroform (5 ml HOAC + 95 ml $CHCl_3$) was found to be suitable. Such a mixture was superior to chloroform alone or to a 5% by volume mixture of acetic acid in diethyl ether. The acid medium produced by the acetic acid would convert any salt form of the treating agent to the more chloroform soluble acid form, hence increase the efficiency of the extraction. A 24 hr. extraction period was sufficient to remove practically all of the treating agent.

One sample studied, bled quite severely in the mixed solvent. It did not bleed in an acetic-acid-ether mixture, but then the treating agent could not be completely extracted. To get around this difficulty the sample was allowed to bleed in the acetic-acid -chloroform mixture. The chloroform was then evaporated and ether substituted. This caused flocculation of the blue making it possible to filter. The clean filtrate then contained the treating agent. The method however, gave somewhat low results. The flocculated blue pigment still contained some treating agent. In one sample tested, this amounted to 9mg of treating agent or to 0.3% treating agent in the pigment. This brought the amount of treating agent up from 3.47% to 3.77%.

The overall time required for the Soxhlet extraction method is longer than for the KCR-119 method but it requires less of the operators time.

The following description of the brief experiments performed serve to justify the claims made for the method.

Experiment 1
Solvent - 5% by Vol. HOAc in $CHCl_3$
3 grams B-216-D extracted 16 hrs. yielded 3.52% extracted.
Additional 8 hrs. yielded 0.22% extracted.
Repeat for a straight run of 24 hrs. yielded 3.67% extracted.

Experiment 2
Solvent - $CHCl_3$ alone
3 grams B-216-D extracted 24 hrs. yielded 3.38% extracted.
Note:- This is lower than the results of experiment 1.

Experiment 3
Method according to KCR-119.
Sample B-216-D 2.9% extracted
Note:- This is much lower than the results of experiment 1.

Experiment 4
Solvent - 5% by Vol. HOAc in $CHCl_3$
3 grams sample B-1661-D extracted 24 hrs. yielded 2.97% extracted.
The extracted pigment was examined for remaining treating agent by decomposition with caustic and extraction of both the acidified filtrate and the acidified precipitate. The amount found was 0.09% treating agent.
Note:- This indicates that for all practical purposes all of the treating agent is removed.

Some evidence has been accumulated which indicates that it is difficult to extract the treating agent from iron blue pigments, that are high in moisture, (10%). Better results are obtained if the moisture content is brought down to ar ound 5%. This point will bear more investigating. The drying cannot be accomplished by heating the pigment because some of the treating agent will be driven off. Drying over sulfuric acid in a vacuum must be done and since this is a slow process, the total time required for a determination is increased by several days. The total time required is then around 9 days but a good deal of that time is simply extracting and drying and does not take up the time of the operator.

The method in detail is given in appendix 10.

II Application of Statistical Methods to the Analytical Data
Introduction

For a simple discussion of the use of statistical methods see Ref. 8. No attempt will be made here to discuss the complete significience of the statistical terms used and reference should be made to the above mentioned reference or to some standard text on statistical methods. The following discussion simply defines the terms and indicates their application to the data of this report.

The "Standard Deviation", designated by the symbol s is a measure of the precision of a method. A large s means poor precision. The square of the "Standard Deviation", s^2 is called the "Variance", V. The best estimate of V is obtained by the formula,

$$V = \frac{\text{Sum of Squares}}{\text{Degrees of Freedom}}$$

The "Degrees of Freedom" (n-1) is defined as one less the number of independent measurements n.

The "Sum of Squares" is an abbreviation for "the sum of the squares of the deviation of the measurements from their arithmetic mean",

$$\sum_{i=1}^{n} (w_i - \bar{w})^2 = \text{Sum of Squares}$$

where w_i = The individual values of the n measurements.
n = Number of measurements.
$\bar{w}$ = Arithmetic mean of the n measurements

The formula for "V" then becomes,

$$V = \frac{\sum_{i=1}^{n} (w_i - \bar{w})^2}{n-1}$$

Another formula for V which is mathematically identical with the one just given is,

$$V = \frac{\sum_{i=1}^{n} w_i^2 - \frac{\left(\sum_{i=1}^{n} w_i\right)^2}{n}}{n-1}$$

This equation is simpler for large amounts of data because it does not involve an average but simply the square of the sum and the sum of the squares.

$$s = \pm \sqrt{V}$$

The data of this report consists of relatively few measurements made on a number of different samples. In this case the best estimate of V is given by the equation,

$$V = \frac{\sum_{i=1}^{n_1} (w_i - \bar{w})^2 + \sum_{i=1}^{n_2} (x_i - \bar{x})^2 + \sum_{i=1}^{n_3} (y_i - \bar{y})^2 + \sum_{i=1}^{n_4} (z_i - \bar{z}) + \cdots}{[n_1 - 1] + [n_2 - 1] + [n_3 - 1] + [n_4 - 1] + \cdots}$$

where n_1, n_2, n_3, n_4 ⋯ = The number of determinations for different samples designated, 1, 2, 3, 4.

w_i, x_i, y_i, z_i = The individual measurements of the 1, 2, 3, 4 samples respectively.

$\bar{w}$, $\bar{x}$, $\bar{y}$, $\bar{z}$ = Arithmetic means of the values represented by w_i, x_i, y_i, z_i

Since the standard deviation is not dimensionless but carries the same dimensions as the terms from which it is derived, changing the units of the terms will proportionately change the value of the standard deviation. For example, "s", for the ml. of $Ce(SO_4)_2$ solution required to titrate the ferrocyanide derived from an iron blue pigment is ± 0.2669 ml. If it is desired to express the results in terms of precent $Fe(CN)_6$ instead of ml $Ce(SO_4)_2$, the standard deviation must also be changed to the new unit basis. The average ml of $Ce(SO_4)_2$ is 30.67 ml and this converted to $Fe(CN)_6$ is 65.66%. The standard deviation will be changed according to the formula

$$s_{65.66} = s_{30.65} \times \frac{65.66}{30.65}$$

or

$$V_{65.66} = V_{30.65} \times \frac{(65.66)^2}{(30.65)^2}$$

This method of treating the variance and standard deviation becomes necessary when the variances from two independent methods are combined to give a third variance for the combination of the two methods or when the variances of two methods are to be compared. The use of average figures in this manner will introduce some error in the standard deviation and variance particularly if the individual measurements vary considerably from sample to sample.

The variance of a determination which is in turn dependent on other determinations will change as the magnitude of each of the dependent determinations change. It is sufficient to use an average, recognizing its limitations and realizing that the variation between samples is not enough to invalidate any conclusions drawn from the data. When a single sample is considered, it becomes possible to use the magnitude of the determination of that particular sample in determining the proper basis for the variance. This should then be done and the average not use. It is to be understood that whenever the term standard deviation or variance is used, what is really meant is the best estimate of the standard deviation and the best estimate of the variance. The true standard deviation and the true variance can never be obtained because then imply and ifinite amount of data. The fact that a relatively small number of measurements are made is properly taken into consideration in the statistical tables consulted.

Other statistical relationships used are that the variance of the sum or diff. of two numbers A & B is equal to the sum of the variances.

$$V_{A \pm B} = V_A + V_B$$

The variance of the average of n determinations is $\frac{1}{n}$ times the variance of a single determination. This means that for a determination in duplicate,

$$V = \frac{V\ (\text{single determination})}{2}$$

or

$$s = \frac{s\ (\text{single Determination})}{\sqrt{2}}$$

It is an interesting observation that the variance of the difference between two sets of duplicate determinations is the same as the variance of a single determination.

Let V_1 = Variance of a single determination.
Let V_2 = Variance of the average of two determinations.
Let V_3 = Variance of the difference between duplicate sets of determinations.

then

$$V_2 = \frac{V_1}{2}$$

since

$$V_{A-B} = V_A + V_B$$

$$V_3 = \frac{V_1}{2} + \frac{V_1}{2}$$

or $$V_3 = V_1$$

This relationship is useful in cross check work where it is desirable to have some measure of the expected deviation between duplicate sets of determinations.

A Standard Deviation for Ferrocyanide as Determined by the Ceric Sulfate Method

TABLE 5

DATA FOR CALCULATION OF STANDARD DEVIATION

Sample	No. of Measurements n	Ml of Ceric Sulfate Required for Each Determination	Mean	Sum of Squares	Degrees of Freedom
1105-38 Untreated B-216-D	3	30.40, 30.41, 30.45	30.42	0.0014	2
B-66-D SD 47988	3	29.05, 29.03, 29.10	29.06	0.0026	2
B-197-D SD 48249	7	31.30, 31.31, 31.70, 31.08, 31.15, 30.86, 31.03	31.20	0.4335	6
Galco-50-1750 C-47418	4	30.81, 31.00 31.03, 30.30	30.79	0.3422	3
Imperial A-4406 C-48031	3	31.35, 31.40, 30.70	31.15	0.3050	2
TOTALS	20	613.46	152.62	1.0847	15

$$\text{Sample mean} = \frac{152.62}{5} = 30.52$$

$$V = \frac{1.0847}{15} = 0.07231$$

$$s = \sqrt{0.07231} = \pm 0.2689 \text{ ml Ce } (SO_4)_2$$

An average percent ferrocyanide is 62.05%. The variance should then be changed to this basis:

$$V_{62.05} = 0.07231 \times \frac{(62.05)^2}{(30.52)^2}$$

$$V_{62.05} = 0.2989$$

$$s_{62.05} = \sqrt{0.2989} = \pm 0.5468\% \text{ Fe } (CN)_6$$

B Standard Deviation for Total Nitrogen Method

TABLE 6

DATA FOR CALCULATION OF STANDARD DEVIATION

Sample	No. of Measurements n	ml Na OH, equivalent to NH3 distilled	Mean	Sum of Squares	Degrees of Freedom
Calco 50-1950 C-47438	2	28.88, 28.54	28.71	.0578	1
Calco 50-4070 C-48030	2	28.07, 28.04	28.06	.0005	1
Imperial A-4406 C-48031	2	29.43, 29.30	29.37	.0085	1
B-197-D SD-48249	2	28.72, 28.67	28.70	.0013	1
B-66-D SD-47988	2	26.99, 27.16	27.08	.0145	1
1105-38 Untreated B-216-D	4	28.82, 28.80, 28.69, 28.82	28.78	.0117	3
B-1661-D Lot 7303	2	27.69, 27.64	27.67	.0013	1
B-216-D SD-48321	2	27.22, 26.98	27.10	.0286	1
Stand. Ultramarine #450 C-48249	4	29.24, 28.85, 28.95, 28.97	29.00	.0835	3
Imperial X-712 C-47592	2	25.65, 25.60	25.63	.0013	1
TOTALS	24	675.72	280.10	.2092	14

$$\text{Sample mean} = \frac{280.10}{10} = 28.01 \text{ ml}$$

$$V = \frac{0.2092}{14} = 0.01494$$

$$s_{28.01} = \sqrt{0.01494} = \pm 0.1222 \text{ ml Na OH}$$

Since this variance will be used later in connection with the ferrocyanide determination, it will be useful to express it in percent ferrocyanide units. The total nitrogen average is 29.10% N. This when expressed as ferrocyanide becomes 73.36% Fe $(CN)_6$

$$V_{73.36} = 0.01494 \times \frac{(73.36)^2}{(28.01)^2}$$

$$V_{73.36} = 0.1025$$

$$s_{73.36} = \sqrt{0.1025} = \pm 0.3202\% \text{ Fe } (CN)_6$$

Expressing the results in terms of total nitrogen,

$$V_{29.10} = 0.01494 \times \frac{(29.10)^2}{(28.01)^2}$$

$$V_{29.10} = 0.01613$$

$$s_{29.10} = \sqrt{0.01613} = \pm 0.1270\ \%\ N$$

C Standard Deviation for Ammonia Nitrogen Method

TABLE I

DATA FOR CALCULATION OF STANDARD DEVIATION

Sample	No. of Measurements n	ml Na OH Equivalent to NH3 Distilled	Mean	Sum of Squares	Degrees of Freedom
Calco 50-1750 C-47418	2	14.52, 14.55	14.53	0.0005	1
Calco 50-4070 C-48030	2	13.47, 13.36	13.42	0.0061	1
Imperial A-4406 C-48031	2	14.93, 14.91	14.92	0.0002	1
B-197-D SD-48249	2	13.68, 13.70	13.69	0.0002	1
B-66D SD-47988	2	13.70, 13.66	13.68	0.0008	1
1105-38 Untreated B-216-D	2	13.82, 13.79	13.81	0.0005	1
B-1661-D Lot 7303	2	13.67, 13.56	13.59	0.0013	1
B-216-D SD 48321	3	12.44, 12.70, 12.62	12.59	0.0355	2
Stand. Ultramarine #450 C-48249	2	19.14, 19.12	19.13	0.0002	1
Imperial X-712 C-47592	2	19.03, 19.05	19.04	0.0002	1
TOTAL	21	309.36	148.40	0.0455	11

$$\text{Sample Mean} = \frac{148.40}{10} = 14.84 \text{ ml}$$

$$V_{14.84} = \frac{0.0455}{11} = 0.004136$$

$$s_{14.84} = \sqrt{0.004136} = \pm 0.06431 \text{ ml Na OH}$$

Since this variance will be used later to calculate the variance of the ferrocyanide as determined by total nitrogen minus ammonia nitrogen, it will be useful to express it in percent ferrocyanide units. Expressing the average ammonia nitrogen as ferrocyanide gives 11.31% $Fe(CN)_6$

$$V_{11.31} = 0.004136 \times \frac{(11.31)^2}{(14.84)^2} =$$

$$V_{11.31} = 0.002402$$

$$s_{11.31} = \sqrt{0.002402} = \pm 0.04901 \%Fe(CN)_6$$

Expressing the results in terms of percent NH_4^+, where the average value is 5.78 $\%NH_4$

$$V_{5.78} = 0.004136 \times \frac{(5.78)^2}{(14.84)^2}$$

$$V_{5.78} = 0.0006274$$

$$s_{5.78} = \sqrt{0.0006274} = \pm 0.02505\% NH_4$$

Expressing the results in terms of H_2O which will be used in the total hydrogen method for H_2O,

$$V_{11.54} = 0.004136 \times \frac{(11.54)^2}{(14.84)^2}$$

$$V_{11.54} = 0.002501$$

$$s_{11.54} = \sqrt{0.002501} = \pm 0.05001 \% H_2O$$

D Standard Deviation for Ferrocyanide as Determined by Total Nitrogen Minus Ammonia Nitrogen Method

The variance of the sum or difference of two measurements is given by the equation,

$$V_{A \pm B} = V_A + V_B$$

Applying this equation

From II, B, $V_{73.36}$ for total nitrogen = 0.1025

From II, C, $V_{11.31}$ for ammonia nitrogen = 0.0024

Therefore $V_{73.36} - 11.31 = 0.1025 + 0.0024$

$V_{62.05} = 0.1049$ for (CN) nitrogen method

$s_{62.05} = \sqrt{0.1049} = \pm 0.3239 \% Fe(CN)_6$

It will also be desirable to express the results in terms of % Fe because this method is used to determine the cationic iron. The value 62.05% Fe $(CN)_6$ is equivalent to 16.36% Fe.

$$V_{16.36} = 0.1049 \times \frac{(16.36)^2}{(62.05)^2}$$

$$V_{16.36} = 0.007292$$

$$s_{16.36} = \sqrt{0.007292} = \pm 0.08539 \text{ \% Fe}$$

E Comparison of Precision of the Ce $(SO_4)_2$ Method and (CN) Nitrogen Method for Ferrocyanide

The statistical approach to the problem is to compare the variances and then through the use of the "F" tables (Ref. 3) ascertain whether the observed difference can be considered significient. Obviously for a small number of determinations, the variance difference must be larger before it can be stated that the difference is significient and not due to the normal variations expected with small amounts of data. Hence the decision as to whether a difference is significient or not depends not only on the magnitude of the difference but also on the degrees of freedom.

From II, A, V_1 for Ce $(SO_4)_2$ Method = 0.2989 for 15 degrees of freedom.

From II, D, V_2 for (CN) Nitrogen Method = 0.1042 for 14 degrees of freedom.

$$\frac{V_1 \text{(15 degrees of freedom)}}{V_2 \text{(14 degrees of freedom)}} \quad \frac{0.2989}{0.1049} = 2.85$$

Consulting the "F" tables for the 5% probability point gives a limiting ratio for 12 & 14 degrees of freedom of 2.53. The table does not give the 15 & 14 degrees of freedom as requested by the data but it would give a limiting ration of even less than 2.53. We can conclude then that the ratio 2.85 is significient and therefore the (CN) nitrogen method is more precise than the Ce $(SO_4)_2$ method. The significience of the 5% probability point is that we still run the risk of being wrong to the extent of 5 times out of every 100 such decisions made. In other words, 5% of an infinite number of ration observed would be equal to or in excess of 2.53 even though the true ratio was 1. The statistician must set his risk. If we had wanted to be wrong only 1 in 100 times we would have used the 1% probability point and the limiting ratio would then be 3.80. This is in excess of the observed 3.85, hence, the difference could not be considered significient. As a rule, the 5% probability point is not considered too much risk in such tests of significience.

F Standard Deviation for Total Iron Method

TABLE 8

DATA FOR CALCULATION OF STANDARD DEVIATION

Sample	No. of Measurements	ml Ti Cl3 Equivalent to Total Iron	Mean	Sum of Squares	Degrees of Freedom
Calco 50-1750 C-47418	2	40.48, 40.48	40.48	0	1
Calco 50-4070 C-48030	2	39.70, 39.80	39.75	.0050	1
Imperial A-4406 C-48031	2	40.85, 40.86	40.85	.0001	1
B-197-D SD 48249	4	40.20 40.25, 40.30, 40.22,	40.19	.0127	3
B-66-D SD 47988	2	39.19, 39.20	39.20	.0001	1
1105-38 Untreated B-216-D	2	40.15, 40.17	40.16	.0002	1
B-1161-D Lot 7303	2	38.89, 39.02	38.91	.0005	1
B-216-D SD 48321	2	39.38, 39.42	39.36	.0072	1
Stand. Ultramarine #450 C-48249	2	37.30, 37.36	37.33	.0018	1
B-152-D Lot 8238	2	37.30, 37.30	37.30	0	1
Imperial X-712 C-47592	2	36.84, 36.82	36.83	.0002	1
TOTALS	24	941.20	430.36	.0278	13

$$\text{Sample Mean} = \frac{430.36}{11} = 39.12$$

$$V = \frac{.0278}{13} = 0.002138$$

or $\overset{s}{39.12} = \sqrt{0.002138} = \pm 0.0462$ ml Ti Cl3

Converting to the basis of the average percent total iron of 35.67%,

$$V_{35.67} = 0.002138 \times \frac{(35.67)^2}{(39.22)^2}$$

$$V_{35.67} = 0.001768$$

$$\sigma_{35.67} = \sqrt{0.001768} = \pm 0.04205\% \text{ total iron}$$

G Standard Deviation for Cationic Iron Method Determined by Total Iron minus Ferrocyanide

The variance of the sum or difference of two measurements is given by the equation,

$$V_{A \pm B} = V_A + V_B$$

Applying this equation,

From II, F $V_{35.67}$ for total iron = 0.001768

From II, D $V_{16.36}$ for ferrocyanide iron = 0.007292

Therfore $V_{35.67} - V_{16.36} = 0.001768 + 0.007292$

$$V_{19.31} = 0.009060$$

$$\sigma_{19.31} = \sqrt{0.009060} = \pm 0.09520\% \ Fe^{+++}$$

H Standard Deviation for Total Alkali Metals Method

TABLE 9

DATA FOR STANDARD DEVIATION

Sample	No. of Measurements n	Milligrams of Alkali Metal Sulfate	Mean	Sum of Squares	Degrees of Freedom
Calco 50-1750 C-47418	2	27.2, 25.1	26.1	2.21	1
Calco 50-4070 C-4 8030	2	20.8, 22.9	21.9	2.21	1
Imperial A-4406 C-48031	2	29.7, 30.7	30.2	0.50	1
B-197-D SD-48249	2	25.1, 24.6	24.9	0.13	1
B-66-D SD 47988	2	28.5, 27.2	27.9	0.85	1
1105-38 Untreated B-216-D	3	18.9, 18.4, 18.8	16.7	0.14	2
B-1661-D Lot 7303	2	19.9, 19.4	19.7	0.13	1
B-216-D SD 48321	2	18.4, 16.2	17.3	2.42	1
Stand. Ultramarine #450 C-48249	2	12.1, 14.3	13.2	2.42	1
Imperial X-712 C-47592	2	18.1, 16.0	17.0	2.21	1
TOTALS	21	452.3	216.9	13.22	11

Mean per sample = $\frac{216.9}{10} = 21.69$

$$V_{21.69} = \frac{13.22}{11} = 1.202$$

Milligrams of alkali metal sulfate are converted to % Na_2O by the formula,

$$\text{mg alk. sulfate} \times 0.04364 = \%\ Na_2O$$

To convert the variance to a % Na_2O basis it must be multiplied by $(0.04364)^2$

$$V_{\%Na_2O} = 1.202 \times (0.04364)^2 = 0.002289$$

$$s_{\%Na_2O} = \sqrt{0.002289} = \pm 0.04784\%\ Na_2O$$

I Standard Deviation for Total Chromium Method

TABLE 10

DATA FOR STANDARD DEVIATION

Sample	No. of Measurements n	Precent Chromium as Cr_2O_3	Mean	Sum of Squares	Degrees of Freedom
Calco 50-1750 C-47418	2	0.277, 0.299	0.288	0.000242	1
B-197-D SD-48249	6	0.143, 0.085, 0.155 0.122, 0.123, 0.145	0.129	0.003169	5
B-66-D SD 47988	2	0.264, 0.319	0.292	0.001513	1
B-1661-D Lot 7303	2	0.217, 0.222	0.220	0.000073	1
B-216-D SD-48321	4	0.275 0.205, 0.275, 0.264,	0.255	0.003581	3
Stand. Ultramarine #450 C-48249	3	1.009, 0.933, 0.981	0.974	0.002955	2
Imperial X-712 C-47592	3	1.571, 1.571, 1.566	1.569	0.000017	2
1105-38 Heated	2	0.250, 0.250	0.250	0	1
TOTALS	24		3.977	0.011270	16

$$\text{Sample Mean} = \frac{11.521}{24} = 0.497$$

$$V = \frac{0.011270}{16} = 0.0007044$$

$$s = \sqrt{0.0007044} = \pm 0.02655\%\ Cr_2O_3$$

J Standard Deviation for Total Sulfate Method

TABLE II

DATA FOR STANDARD DEVIATION

Sample	No. of Determinations n	mg. of Ba SO_4	Mean	Sum of Squares	Degrees of Freedom	
Calco 50-1750 C-47418	2	9.9, 8.9	9.4	0.50	1	
Calco 50-4070 C-48030	2	36.3, 36.2, 35.2	35.9	0.74	1	
Imperial A-4406 C-48031	2	8.3, 8.9	8.6	0.18	1	
B-197-D SD-48249	2	25.4, 24.4	24.9	0.50	1	
B-46-D SD-47988	2	49.2, 48.9	49.0	0.05	1	
1105-38 Untreated B-2166D	2	43.6, 44.5	44.0	0.41	1	
B-1661-D Lot 7303	2	32.5, 30.2	31.3	2.65	1	
B-216-D SD-48321	2	36.4, 38.3	37.4	1.81	1	
Stand. Ultramarine #450 C-48249	2	7.5, 8.1	7.8	0.18	1	
B-152-D Lot 8238	3	3.1, 6.4, 2.6	4.7	20.66	2	
Imperial X-712 C-47592	4	20.0 14.7, 20.6, 17.4	18.2	21.89	3	
TOTALS	25	619.5	271.2	49.57	14	

$$\text{Sample Mean} = \frac{271.2}{11} = 24.7$$

$$V = \frac{49.57}{14} = 3.541$$

$$s = \sqrt{3.541} = \pm 1.88 \text{ mg Ba } SO_4$$

Milligrams of barium sulfate are converted to percent SO_3 by the formula,

$$\text{mg Ba } SO_4 \times 0.03430 = \%SO_3$$

To convert the variance to a % SO_3 basis, it must be multiplied by $(0.03430)^2$

$$V_{\%SO_3} = 3.541 \times (0.03430)^2$$

$$V_{\%SO_3} = 0.004166$$

$$s_{\%SO_3} = \sqrt{0.004166} = \pm 0.064\% SO_3$$

K Standard Deviation for Total Water by Loss in Weight Method

TABLE 12

DATA FOR STANDARD DEVIATION

Sample	No. of Determinations n	Percent loss in Weight 1 hr. heating at 160°C.	Mean	Sum of Squares	Degrees of Freedom
Calco 50-1750 C-47418	4	4.65, 4.55, 4.50, 4.70	4.60	0.0150	3
Calco 50-4070 C-48030	2	5.60, 5.55, 5.50	5.55	0.0050	2
Imperial A-4406 C-48031	2	3.55, 3.60	3.58	0.0013	1
B-197-D SD-48249	2	4.40, 4.30	4.35	0.0050	1
B-66-D SD-47988	3	6.55, 6.65, 6.40	6.53	0.0317	2
1105-38 Untreated B-216-D	6	4.90, 5.15 4.70, 4.75, 4.45, 5.00,	4.83	0.3039	5
B-1661-D Lot 7303	2	4.40, 4.50	4.45	0.0050	1
B-216-D SD-48321	2	4.95, 4.90	4.92	0.0013	1
Std. Ultramarine #450 C-48249	2	11.00, 10.80	10.90	0.0200	1
B-152-D Lot 8238	2	8.00, 7.55	7.78	0.1013	1
Imperial X-712 C-47592	2	10.50, 10.70	10.60	0.0200	1
TOTALS	29		68.09	0.5095	19

$$\text{Mean per sample} = \frac{68.09}{11} = 6.19\%\ H_2O$$

$$V_{6.19} = \frac{0.5095}{19} = 0.02682$$

$$\sigma_{6.19} = \sqrt{0.02682} = \pm 0.1638\%\ H_2O$$

L Standard Deviation for Hydrogen Method

TABLE 13

DATA FOR STANDARD DEVIATION

Sample	No. of Determinations n	Percent Total Hydrogen	Mean	Sum of Squares	Degrees of Freedom
1105-38 Untreated B-216-D	2	1.67, 1.61	1.64	0.0018	1
1105-38 (Heated) Untreated B-216-D	2	1.78, 1.58	1.68	0.0200	1
Calco 50-1750 C-47418	2	1.74, 1.55	1.65	0.0180	1
Imperial A-4406 C-48031	2	1.70, 1.67	1.69	0.0005	1
B-197-D SD-48249	2	1.72, 1.74	1.73	0.0002	1
B-66-D SD-47988	2	1.97, 1.89	1.93	0.0032	1
Imperial X-712 C-47592	2	2.71, 2.67	2.69	0.0008	1
Std. Ultramarine #450 C-48249	2	2.90, 2.82	2.86	0.0032	1
TOTALS	16		15.87	0.0477	8

$$\text{Mean per Sample} = \frac{15.87}{8} = 1.984$$

$$V_{1.984} = \frac{0.0477}{8} = 0.005962$$

$$\sigma_{1.984} = \sqrt{0.005962} = \pm 0.07721\% \ H_2$$

Expressing the results as % H_2O

$$1.984 \times \frac{18.016}{2.016} = 17.73\% \ H_2O$$

$$V_{17.73} = 0.005962 \times \frac{(17.73)^2}{(1.984)^2}$$

$$V_{17.73} = 0.4761$$

$$\sigma_{17.73} = \sqrt{0.4761} = \pm 0.6901 \ \% \ H_2O$$

M Standard Deviation for Total Water Method Determined by Total Hydrogen minus Ammonia Hydrogen

The variance of the sum or difference of two measurements is given by the equation,

$$V_{A \pm B} = V_A + V_B$$

Applying this equation,

From II L, $V_{17.73} = 0.4761$

From II O, $V_{11.54} = 0.002501$

Therefore $V_{17.73 - 11.54} = 0.4761 + 0.0025$

$$V_{6.19} = 0.4736$$

$$s_{6.19} = \sqrt{0.4736} = \pm 0.6881 \% H_2O$$

N Comparison of Precisions of the Loss in Weight Method and the Total Hydrogen Method for Water

From II, M, V_1 for Total Hydrogen Method = 0.4761 for 8 degrees of freedom

From II, K, V_2 for Loss in Weight Method = 0.02682 for 14 degrees of freedom

$$\frac{V_1(8 \text{ degrees of freedom})}{V_2(14 \text{ degrees of freedom})} = \frac{.4736}{0.02682} = 17.66$$

Consulting the "s" tables (Ref. 3) for the 1% probability point gives a limiting ratio of 4.14 for 8 and 14 degrees of freedom hence we can conclude that the difference in observed variance is significiont. The loss in weight method is more precise than the total hydrogen method.

Reference for Experimental Work

A Complex Iron Cyanide Determination

NB-1144 pp67-68; 74-79; 140-156
NB-1166 p 27; 36; 170-171
NB-1132 p 188
Letter Tiedcke to Hanke 6/26/45
" " " " 12/15/45

B Total Iron and Cationic Iron

NB-1125 p 140; 143; P146-147
NB-1144 p 36-37; 54-56
NB-1166 p 6-7; 20-27; 72-75; 173

C Total Alkali Metals

NB-1144 pp 29-33; 52-53;
NB-1166 p93; 190

D Total Chromium

NB-1166 pp 31; 38; 172.
NBp1132 p115

E Total Sulfate

NB-1144 pp 16-25
NB-1166 pp68-69; 92; 147; 191-192
NB-1132 p190

F Total Water

NB-1144 pp 6-28; 57-59; 82-85
NB-1166 p36
Letter Tiedcke to Hanke 6/26/45
" " " " 12/15/45

G Iron Outside of Iron Blue Molecule

NB-1166 pp60-61
NB-1182 p25
NB-1132 pp113-114; 187-188

H Organic Treating Agent

NB-1182 pp12-19
NB-1132 p 132

LITERATURE REFERENCES

(1) Die Industrie der Cyanverbindungen. H. Kohler

(2) Handbuck der Anorganischen Chemie Vol. 4 Sec. 3, Part B Edition 2 (1942)

(3) The Analysis of Blue Pigments. F. L. Jamecon Paint Mfg. p. 167, Sept. 1942.

(4) Physical and Chemical Examination of Paints, Varnishes, Lacquers, Colors. Gardner p. 1002. Eighth edition (1937)

(5) Mixed Perchloric, Sulfuric and Phosphoric Acids and their application in Analysis p. 55. G. Frederick Smith Chemical Co. publication.

(6) Analysis of Chrome Green and Pigments of Similar Composition. C.P.A. Kappelmeier. Rec. Trav. chim, 50, 711-18 (1931)

(7) Analysis of Chromate Green. C. P. A. Kappelmeier. Verfkronick. 7, 12-14, 35-36 (1934)

(8) Analysis of Variation, I. C. I. (Dyestuffs) Technical Report, March 16, 1941. File No. H5824.

APPENDIX 1

I **Subject** - Iron Blue Pigments

II **Determination** - Ferrocyanide by Ceric Sulfate Titration

III **Principle** - The pigment is opened up with dilute caustic and the ferrocyanide produced titrated with a standard solution of ceric sulfate

IV **Reference** - NB -1144 p. 148-151
"Ceric Sulfate" Published by G. Fredrick Smith Chemical Co. Aug. 1935.

V **Reagents** - (1) Sodium Hydroxide solution - 20 grams/100 ml
(2) Hydrochloric acid - conc. C.P. & ±0.1N
(3) Standard ceric sulfate solution ±0.1N
(4) Arsenous oxide C. P. primary standard
(5) Iodine monochloride solution ±0.005M
To prepare dissolve 0.279g KI and 0.178g KIO_3 in 25° ml water. Add all at once 25° ml conc. HCl. This solution can be tested for equivalence potential by adding small amounts of KI & KIO_3 and observing the break in the potential when using a calomel - platinum electrode system. Such adjusting is usually not necessary.

VI **Special Equipment** - An electrometer employing a platinum - calomel electrode system such as the Fisher titrimeter.

VII **Procedure** - Weigh 2.5000 g pigment into a beaker. Add 10 ml of sodium hydroxide solution (20g/100 ml). Stir until the iron blue is completely destroyed and the precipitate consists only of ferric hydroxide. Warm gently if necessary to affect decomposition but avoid excessive heating. Transfer completely to a 250 ml volumetric flask and make to the mark. Filter through a dry filter paper (Whatmann #41), discarding the first ±10 ml of filtrate. After somewhat more than 100 ml have been filtered, pipette 100 ml of the clear filtrate into a beaker. Add 15 ml of concentrated hydrochloric acid and titrate immediately with standard ceric sulfate solution using a platinum - calomel electrode system to detect the endpoint. The endpoint will be indicated by a sharp rise in the potential. Run in duplicate starting with another 2.5g sample.

Repeat the determination using a 2.5g sample but make the volume to 500 ml instead of 250 ml. (Note)

NOTE: This enables a correction for the volume occupied by the precipitate. This correction is not great and for most work, can be neglected. After its magnitude is once established, the determinations at double dilution need not be repeated, but the same corrections applied to all determinations.

VIII Calculations -

A. Correcting for volume of precipitate

Let A = ml $Ce(SO_4)_2$ required at the 250 ml dilution.
Let B = ml $Ce(SO_4)_2$ required at the 500 ml dilution

A - 2B = Volume error for the 500 ml dilution

2 (A-2B) = Volume error for the 250 ml dilution
Call this volume error C.

A - C = Corrected ml $Ce(SO_4)_2$ required for $\frac{100}{250}$ of the sample weight.

It may also be obtained directly from the following:
4B - A = corr. ml $Ce(SO_4)_2$

B. Calculating Percent Ferrocyanide

$$\frac{\text{Ml } Ce(SO_4)_2 \text{ (corrected)} \times N \times 0.2119 \times 100}{\text{Sample Wt. in aliquot}} = \% \; Fe(CN)_6$$

IX Preparation of Ceric Sulfate Solution

The theoretical amount of $Ce(SO_4)_2$ required to give a 0.1N solution is 33.23g/liter. If the quality of the available $Ce(SO_4)_2$ is unknown, a trial portion should be prepared by pasting somewhat in excess of 8.3g in some conc. H_2SO_4, diluting with water, filtering, and making to a volume of 250 ml. This should be roughly standardized by the method outlined below and from this datum the proper amount of $Ce(SO_4)_2$ is calculated, and used to prepare a more nearly 0.1N solution. Some ceric sulfate purchased from the G. Frederick Smith Chemical Company required 110.8g in 2 liters to produce a 0.1036N solution.

Paste the required amount of $Ce(SO_4)_2$ in ± 56 ml of conc. H_2SO_4. Dilute to somewhat less than 2 liters and heat until no more will go into solution. Filter, preferably through sintered glass, and make to 2 liters.

X Standardization of Ceric Sulfate Solution using As_2O_3

Accurately weigh 4 g As_2O_3 primary standard previously dried at 110° - 120°C. Dissolve in ± 10 ml Na OH (20g/100ml) plus about 40 ml distilled water. After the As_2O_3 is completely in solution, dilute to 400-500 ml and neutralize with ±0.1N hydrochloric acid, using a small strip of indicator paper added to the solution. After the solution is slightly acid, remove the paper with a stirring rod. Rinse both rod and paper, and transfer the solution completely to a 1 liter volumetric flask. Dilute to volume. The normality, of the solution will be 0.2011N.

Pipette 50 ml of this solution into a beaker. Add ±50 ml water and ±10 ml conc. hydrochloric acid. Add 0.5 ml iodine monochloride (±0.005M).

Heat to 50°C and titrate with the ceric sulfate solution. The endpoint is detected potentiometrically using a platinum - calomel electrode system. A sharp rise in the potential indicates the endpoint.

The $Ce(SO_4)_2$ normality is calculated from the equation,

$$N \text{ of } Ce(SO_4)_2 = \frac{N \text{ of } As_2O_3 \times ml\ As_2O_3}{ml\ Ce(SO_4)_2}$$

or

$$N \text{ of } Ce(SO_4)_2 = \frac{5.055}{ml\ Ce(SO_4)_2}$$

XI Standardization of Ceric Sulfate Solution using Potassium Ferrocyanide

Dissolve 2g $K_4Fe(CN)_6 \cdot 3H_2O$ (NOTE) in 100 ml water. Add 10 ml conc. hydrochloric acid and titrate immediately with the ceric sulfate solution in a manner similar to that of a $Fe(CN)_6$ determination (sec. XI)

NOTE: Potassium ferrocyanide trihydrate can be considered a primary standard. The crystals should not be unduly exposed to dry air. If they have a white and powdery appearance, they may have lost some of their water of hydration and should not be used. The water vapor pressure of 30% H_2SO_4 will prevent the loss of water of crystallization and the crystals of $K_4Fe(CN)_6 \cdot 3H_2O$ may be kept in a desiccator over 30% H_2SO_4. Practically, simply keeping the CP. crystals in a well stoppered bottle will suffice.

The normality is calculated from the equation,

$$N \text{ of } Ce(SO_4)_2 = \frac{\text{grams of } K_4Fe(CN)_6 \cdot 3H_2O}{0.4224 \times ml\ Ce(SO_4)_2}$$

or

$$N \text{ of } Ce(SO_4)_2 = \frac{0.04734}{ml\ Ce(SO_4)_2}$$

APPENDIX 2

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Total Nitrogen

III. Principle - The conventional Kjeldahl method is used to convert the nitrogen in the sample to ammonia nitrogen and the ammonia is distilled into an excess of standard acid, the remaining acid back titrated with standard alkali. A control is run using reagent grade ammonium chloride to evaluate any loss of ammonia during the digestion and distillation procedure.

IV. REFERENCE - N. B. #1166 p.29

V. REAGENTS

1. Sulfuric acid - C. P. Conc.
2. Copper sulfate - C. P. Cryst.
3. Potassium Sulfate - C. P. Anhyd.
4. Mossy zinc or zinc shot
5. Paraffin
6. Standard sulfuric acid solution (±0.3N)
7. Standard sodium hydroxide solution (±0.3N)
8. Ammonium chloride - C. P. Gran.
9. Methyl Red indicator - 0.02% solution
10. Sodium hydroxide solution (40g/100ml).

VI. PROCEDURE

Accurately weigh a 0.5-g. sample and wrap in a piece of filter paper. A sheet of 12.5 cm #40 Whatman is suggested. Place the wrapped sample in an 800-ml. Kjeldahl flask. Add 10-grams of potassium sulfate, a small crystal of copper sulfate, and 25-ml. of Conc. H_2SO_4. Digest over a low flame turning the flask from time to time until a straw colored solution results. This usually takes about three hours. Allow the flask to cool but do not let it stand much longer than the time necessary to cool it. Add 350-ml. water and a few pieces of mossy zinc or zinc shot (Note 1). Carefully add, down the side of the flask to avoid mixing, 125-ml. of concentrated sodium hydroxide solution. Connect to a Kjeldahl still arranged to receive the distillate into 40-ml. of standard sulfuric acid (±0.3N) containing 3 drops Methyl Red indicator. After it is well-connected, shake the flask to thoroughly mix. Start the distillation and distill over about 3/4 of the solution. Back titrate the excess standard acid with a standard solution of sodium hydroxide (±0.3N).

Run a control in a manner similar to a determination but instead of a sample use an amount of C. P. ammonium chloride dried at 110°C comparable to the nitrogen present in the sample (Note 2). Calculate a factor "K" (see section VII Calculations).

Determine the alkali equivalent and the blank collectively by running through the regular procedure but without using a sample. Let the ml. sodium hydroxide required for 40-ml. of sulfuric acid under these conditions be called "E".

NOTES

1. If the sample contains a treating agent, it is liable to froth during the distillation. Usually the treating agent is destroyed during the digesting of the sample but occasionally enough remains to make trouble. Also the sample sometimes froths even without a treating agent. A small amount of paraffin added at this point will help cut down frothing. What is even more effective is an infra-red lamp held close to the neck of the flask. A coil of wire so fashioned as to spiral up inside the neck of the flask also aids in breaking the bubbles as they rise.

2. The control should give very nearly theoretical results so no great error is introduced if the amount of ammonium chloride used deviates from the equivalent in the sample. It is recommended that if there is interest in both ammonia nitrogen and total nitrogen, the amount of ammonium chloride used in the control come midway between that customarily found in an ammonium nitrogen and a total nitrogen. Using a 0.5-g. sample for total nitrogen, and a 2-g. sample for ammonia nitrogen, and assuming 29% N as typical for total nitrogen and 4% N as typical for ammonia nitrogen, an amount of ammonium chloride suitable for a control is 0.45-g. NH_4Cl.

VII. CALCULATIONS

A. Calculation of control constant "K"

$$K = \frac{\text{Weight of } NH_4Cl \text{ used}}{(E\text{-ml. NaOH for back titration}) \times \text{Normality of NaOH} \times 0.0535}$$

The value of "K" should not be much greater than 1.003
E = ml. of NaOH required to neutralize 40-ml. of standard H_2SO_4 while making a blank determination as outlined in the last paragraph of the procedure.

B. CAlculation of % total nitrogen

$$\frac{(E\text{-ml. NaOH back titrated}) \times \text{Normality of NaOH} \times 0.014 \times K \times 100}{\text{Sample Weight}} = \% \text{ total nitrogen}$$

C. Calculation of $(C\bar{N})$ nitrogen as $Fe(CN)_6$

(This calculation presupposes data for ammonia nitrogen)

$$\frac{(E\text{-ml NaOH for total nitrogen}) \times \text{Normality} \times K \times 100}{\text{Sample weight for total nitrogen}} = \% \text{ milliequivalence of total nitrogen} = A.$$

$$\frac{\text{(E-ml NaOH for ammonia nitrogen) x Normality x K x 100}}{\text{Sample weight for ammonia nitrogen}} = \% \text{ milliequivalence of ammonia nitrogen} = B$$

$$(A-B) \times 0.03533 = \%Fe(CN)_6$$

APPENDIX 3

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Ammonia Nitrogen

III. PRINCIPLE - The conventional Kjeldahl still is used to distill the ammonia, from a sample made alkaline, into an excess of standard acid and back titrating the excess with standard alkali. A correction is applied for the small amount of ammonia produced by the slight decomposition of the ferrocyanide.

IV. REFERENCE - N. B. #1166. p. 36 N. B. #1132 p. 188.

V. REAGENTS

1. Sulfuric acid - C. P. Conc.
2. Sodium hydroxide solution (40-g/100-ml.)
3. Mossy zinc or zinc shot.
4. Paraffin
5. Standard sulfuric acid solution (±0.3N)
6. " sodium hydroxide " "
7. Ammonium chloride - C. P. Gran.
8. Methyl Red indicator

VI. PROCEDURE

Accurately weigh a 2-gram sample into an 800-ml. Kjeldahl flask. Add 300-ml. of water. Add 5-ml. Conc. $HgSO_4$ and mix thoroughly. Add a few pieces of mossy zinc or zinc shot and carefully add, down the side of the flask to avoid mixing, 125-ml. of concentrated sodium hydroxide solution (Note 1). Connect to a Kjeldahl still arranged to receive the distillate into 40-ml. of standard sulfuric acid (±0.3N) containing 3 drops of Methyl Red indicator. After it is well-connected, shake the flask to thoroughly mix. Start the distillation and distill over about 3/4 of the solution. Back titrate the excess standard acid with standard sodium hydroxide solution (±0.3N).

Run a control in a manner similar to a determination but instead of a sample use an amount of C. P. ammonium chloride dried at 110°F. comparable to the nitrogen present in the sample (Note 2). Calculate a factor, "K" (see section VII Calculations).

Determine the alkali equivalent of the acid, the blank, and the ammonia formed because of the decomposition of the ferrocyanide (Note 3) by running a typical iron blue pigment for ammonia nitrogen, filling the distillation flask back to the original mark with distilled water, and redistilling into another position of standard acid. Repeat this procedure three more times and average the last three results. Let this quantity be called "E" and use it in the calculations as indicated in section VII.

NOTES

1. If the sample contains a treating agent, it is liable to froth during the distillation. A small amount of paraffin added at this point will help cut down frothing. What is even more effective is an infra-red lamp held close to the neck of the flask. A coil of wire so fashioned as to spiral up inside the neck of the flask also aids in breaking the bubbles as they rise.

2. The control should give very nearly theoretical results whether run as a total nitrogen method or an ammonium nitrogen method. If there is interest in both, it is permissable to run one control for both and use an amount of ammonium chloride midway from that which would be found as ammonia nitrogen and total nitrogen. Using a 0.5-g. sample for total nitrogen, and a 2-g. sample for ammonia nitrogen, and assuming 29% N as typical for total nitrogen and 4% N as typical for ammonia nitrogen, and amount of ammonium chloride suitable for a control is 0.5-g. NH_4Cl.

3. Prolonged alkali distillation of a ferrocyanide can produce some ammonia by decomposition of the ferrocyanide. This amounts to about 0.22 ml of 0.335N NaOH. This is quite constant and after it is once established, it can be considered the same for all samples and all determinations. Its constancy and amount are illustrated by the following data:

	Distilling $Fe(CN)_6$ from Iron Blue with caustic ml NaOH back titrated from 40 ml standard acid	Distilling a Blank ml NaOH back Titrated from 40 ml Stand. acid
1st distillation	-	31.10
2nd "	30.95	31.10
3rd "	30.90	31.11
4th "	30.88	31.10
5th "	30.83	31.10
6th "	30.91	31.11
7th "	30.90	
8th "	30.80	
9th "	30.88	
Ave.	30.88	31.10

31.10 ml
- 30.88 ml
.22 ml of 0.3353N NaOH

VII. CALCULATIONS

A. Calculation of Control Constant, "K"

$$\text{"K"} = \frac{\text{Weight of } NH_4Cl \text{ used}}{\left(\begin{array}{c}\text{E-ml NaOH for back titration} \\ \text{of control}\end{array}\right) \times \text{Normality of NaOH} \times 0.0535}$$

E-ml of NaOH required to neutralize 40-ml. of standard H_2SO_4 while making a blank determination.

B. Calculation of ammonia nitrogen

$$\frac{\text{(E-ml. NaOH back titration of sample)} \times \text{Normality of NaOH} \times 0.01804 \times K \times 100 = \%NH_4}{\text{Sample Weight}}$$

APPENDIX 4

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Total Iron.

III. PRINCIPLE - The sample is opened up by gentle ignition and treatment with hydrochloric acid and perchloric acid. The ferric iron is then titrated with a standard solution of titanous chloride.

IV. REFERENCE - N. B. #1166 pp. 6, 20

V. REAGENTS -

1. Hydrochloric acid - C. P. Conc.
2. Perchloric acid - C. P. 72%
3. Superoxol (30% H_2O_2)
4. Potassium permanganate ±0.1N
5. Titanous chloride - Standard solution ±0.1N
6. Potassium thiocyanate solution (15-g/100-ml)
7. Starch - potassium iodide paper.
8. Titration mixture. Dissolve 90g $MnSO_4.H_2O$ in 650 ml water; heat if necessary. Add 175 ml conc. H_3PO_4 and 175 ml conc. H_2SO_4. Dilute to 1 liter.

VI. PROCEDURE

Accurately weigh 0.4000-g. sample into a flask (500-ml. suggested size). Ignite over a free flame rolling the sample around in the flask during the ignition process. After most of the sample is decomposed (Note 1), add 10-ml. Conc. HCl and 15-ml. $HClO_4$. Place a trap on the flask to prevent excessive loss of required for $HClO_4$ fumes (Note 2). Use goggles. Continue the heating until the solution acquires a clear orange color. Allow the solution to cool and add 200-ml. water. Remove trap and heat to boiling until all of the free chlorine is boiled off as indicated by a negative test with starch-potassium iodide paper. Add 0.5-ml. superoxol to reduce chromium if any. Boil until the volume is ±100-ml. to destroy the excess superoxol. Add 5-ml. titration mixture and a drop of potassium permanganate solution. If the permanganate is reduced, add more until a faint pink color persists. It should not take more than 3 or 4 drops. Add a drop of titanous chloride solution to discharge the permanganate color. Do not count this drop in the titanous chloride titration. Add water to a volume of ±200-ml. Add 40-ml. of Conc. HCl and titrate slowly with standard titanous chloride solution (±0.1N). Near the end-point, add ±10-ml. of KCNS solution and slowly continue the titration to the disappearance of the red complex thiocyanate color (Note 3).

NOTES

1. It is not necessary to decompose all of the blue because

the subsequent treatment with $HClO_4$ will complete the destruction.

2. Perchloric acid is safe when properly used but to minimize its dangers when carelessly used, goggles should be worn at all times when working with this material.

A trap of some sort is necessary because $HClO_4$ fumes tend to carry off some of the constituents of the sample. Also the loss of iron, because of the volatility of ferric chloride, is prevented. The trap must be all glass. No rubber or cork connections are permissable because of the explosive nature of perchloric acid when brought into contact under certain conditions with organic materials.

A distilling head with a 24/40 standard taper in connection with a 24/40 standard taper flat bottom boiling flask makes a satisfactory combination.

3. The titration should be carried out slowly because the reaction is sluggish. This is particularly true near the endpoint. The presence of the phosphate from the titration mixture further tends to inhibit the reaction. It is good technique to add more potassium thiocyanate when at the endpoint. If a slight reddening of the solution occurs, the endpoint was not quite reached. If no reddening occurs, add a drop of ferric iron of about the same normality as the titanous chloride. There should now be a reddening of the solution. If none occurs, the endpoint was passed and the proper correction should be applied as indicated by the small back titration with the ferric iron.

VII. CALCULATIONS

$$\frac{\text{ml } Ti\ Cl_3 \text{ Solution} \times N \times 0.5585 \times 100}{\text{Sample Weight}} = \% \text{ Fe}$$

APPENDIX. 5

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Total Alkali Metals

III. PRINCIPLE - The sample is decomposed by gentle ignition followed by treatment with Bromine water and superoxol. The heavy metals are removed with ammonium hydroxide and the alkali metals weighed as sulfates.

IV. REFERENCE - N. B. #1166 P. 93.

V. REAGENTS -

1. Bromine
2. Superoxol - 30% H_2O_2
3. Ammonium hydroxide - CP Concentrated.
4. Ammonium chloride - 1% Sol'n.
5. Hydrochloric acid - CP Conc.
6. Nitric Acid - CP Conc.
7. Sulfuric acid - CP Conc.
8. Ammonium carbonate - CP.

VI. PROCEDURE

Accurately weigh 1-gram into a porcelain evaporating dish (3-3/4" dia. suggested). Gently ignite over a free flame until all of the blue has been oxidised and the residue has a brown iron oxide color. Avoid igniting much beyond this stage. Add 15-ml. conc. HCl and warm on a steam bath. Add cautiously a few drops of bromine and continue warming for a few minutes. Place a ribbed watch glass over the dish. Carefully add a few drops of superoxol to the dish maintaining the watch glass in such a position as to prevent loss by spattering, and continue heating until the soltuion is evaporated to a low volume. Wash down the sides of the dish with distilled water as necessary during these operations. Transfer to a beaker and dilute to ±200-ml. Heat to boiling and boil 10 minutes. Add Conc. Ammonium Hydroxide dropwise, with stirring, until all of the iron is precipitated and the pH is ±7. Boil the solution until the precipitated is well coagulated (±1 min). Filter through a #41 Whatman paper or its equivalent and wash with hot 1% NH_4Cl solution. Dissolve the ferric hydroxide precipitate in about 100-ml. of ±3N hydrochloric acid and reprecipitate with ammonium hydroxide as before. Filter and combine filtrates. Evaporate to a low volume and cautiously add ±50-ml. of Conc. HNO_3. After the evolution of oxides of nitrogen has subsided, continue the evaporation. Add another ±50-ml. portion of Conc. HNO_3 and treat as before washing down the sides of the beaker as necessary. Treat with a third ±50-ml. portion of Conc. HNO_3. By now most all of the ammonium salts should have been removed and the addition of HNO_3 should not give rise to further liberation of oxides of nitrogen. However, if the reaction is such as to suggest more ammonium salts, continue the treatments with HNO_3, washing down the sides of the beaker until the further

addition of HNO_3 causes no liberation of oxides of nitrogen. Evaporate to a low volume and add ±50-ml. Conc. HCl. Again evaporate to a low volume and add a second ±50-ml. portion of Conc. HCl and evaporate to a low volume. Add a third portion of Conc. HCl which, by now, should not give rise to the liberation of oxides of nitrogen, the nitrates being converted to chlorides. If oxides of nitrogen are produced, continue the addition of Conc. HCl, washing down the sides of the beaker until no oxides of nitrogen are liberated. Evaporate almost to dryness (avoid spattering) and transfer to a silica dish by repeated washings with water. A silica dish 4 1/2" dia. is recommended. Add 6 drops Conc. H_2SO_4. Place a ribbed watch glass over the dish and evaporated on a steam bath to as low a volume as possible. Remove to a hot plate and gradually increase the temperature. Finally, ignite over a free flame playing the flame over the entire dish until SO_3 fumes no longer are liberated. (Note 1). Leach with hot water and filter through small #40 Whatman paper or its equivalent into a tared silica dish. Wash residue thoroughly with hot water. Add 6 drops Conc. H_2SO_4 to the filtrate in the dish and repeat the evaporation and ignition. Add a small amount of solid ammonium carbonate to the residue in the dish and heat until the ammonium carbonate disappears Repeat this procedure about three times. This destroys any pyrosulfates that may have formed. Cool in a desiccator and weigh as alkali metal sulfates (Note 2). The identity of the alkali metal can be established by the conventional flame test.

NOTES

1. This ignition converts the remaining iron to the oxide making it insoluble and filterable and eliminates the need for H_2S. For the removal of certain metals, it may be necessary to saturate the solution at this point with H_2S and add a little ammonium carbonate before filtering. If this procedure is necessary, the addition of ±10-ml. of 0.02% solution of low ash gelatine will aid in the coagulation of the sulfide.

2. The residue will usually contain a trace of iron which may be neglected. If the amount is thought to be excessive, the residue should again be leached with hot water and the filtration and ignition processes repeated.

VII. CALCULATIONS

$$\frac{\text{Weight of residue}}{\text{Sample weight}} \times 100 \times 0.4364 = \%Na_2O$$

$$\frac{\text{Weight of residue}}{\text{Sample weight}} \times 100 \times 0.5406 = \%K_2O$$

APPENDIX 6

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Total Chromium

III. PRINCIPLE - The iron blue is destroyed by gentle ignition followed by treatment with hydrochloric acid and perchloric acid. The chromium is oxidized during the perchloric acid treatment and it is determined by adding an excess of a standard solution of Mohr's Salt, and back titrating with a standard solution of permanganate.

IV. REFERENCE - N. B. #1166 pp. 31, 38 KCR - #117

V. REAGENTS

1. Hydrochloric acid - CP conc.
2. Perchloric acid - CP 70-72%.
3. Standard solution of Mohr's Salt (±0.1N)
4. Standard solution of Potassium Permanganate ± (0.1N)
5. Titration mixture.
6. Starch - potassium iodide paper.

VI. PROCEDURE

Accurately weigh a 2-gram sample into a flask (500 ml suggested size) (Note 1). Ignite over a free flame rolling the sample around in the flask during the ignition process. After part of the sample is decomposed (Note 2), add 5-ml Conc. HCl down the side of the flask washing down any pigment adhering to the sides. Evaporate nearly to dryness but avoid spattering. Add 15-ml $HClO_4$. Attach a trap to the flask to prevent excessive loss of $HClO_4$ fumes and heat at a temperature somewhat in excess of that required for $HClO_4$ fumes. Use goggles (Note 3). Continue the heating until the solution acquires a clear orange color. Remove from the source of heat and allow to cool slightly (±10 sec) cautiously add a little cold water through the trap and then plunge the flask into ice water. Withdraw immediately and again plunge into the ice water while swirling the contents of the flask. Add 60-ml cold water (Note 4). Remove the flask from the ice water bath and wipe dry, add 140-ml water. Remove the trap and heat to boiling until all of the free chlorine is boiled off as indicated by a negative test on starch - potassium iodide paper. Cool and add 10-ml titration mixture. Add an excess of standard Mohr's salt solution (10-ml suggested) and titrate the excess with standard permanganate to the first color change. (Note 5).

NOTES

1. The amount of chromium has been known to yield very. The 2-gram sample weight suggested assumes around 0.5% Cr. For low amounts of chromium, the sample weight can be cut down but it should not be more than 2-grams because it is more difficult to open up a large sample and the high concentration of ferric iron makes the titration more difficult.

Notes (Cont'd).

2. It is not necessary to decompose all of the blue, in fact, it is quite difficult to do so because of an insufficient supply of oxygen inside the flask. The small amount of blue remaining will be completely destroyed by the perchloric acid.

3. Perchloric acid is safe when properly used but to minimize its dangers when carelessly used, goggles should be worn at all times when working with this material.

A trap of some sort is necessary because $HClO_4$ fumes tend to carry off some of the chromium. The trap must be all glass. No rubber or cork connections are permissable when using perchloric acid because of its explosive nature when brought into contact under certain conditions with organic materials.

4. The solution must be cooled rapidly because it has been observed that the reduction products or decomposition products of perchloric acid may reduce some of the chromium. If the solution is rapidly cooled, this occurs to a negligible extent.

5. For larger amounts of chromium, it may be necessary to add more than 10-ml. of Mohr's salt. An excess is indicated when the solution has a clear, greenish color. The endpoint is rather indistinct because of the high concentration of ferric iron. With a little experience, there is no trouble.

VII. CALCULATIONS

(ml Mohr's salt x Normality of Mohr's salt)-ml $KMnO_4$ x

$$\frac{\text{Normality of } KMnO_4 \times 0.01733 \times 100}{\text{Sample Weight}} \times G$$

APPENDIX I

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Total Sulfates

III. PRINCIPLE - The iron blue pigment is decomposed by boiling with sodium carbonate solution. The iron cyanide complex is converted to the mercury cyanide complex with freshly precipitated HgO. Sulfate is determined on the acidified filtrate by precipitation and weighing as barium sulfate.

IV. STATUS

This method has been used successfully on quite a number of iron blue samples. The sulfate recovery when sulfate has been added to a sample has been good.

V. REFERENCE - N. B. #1166 P.92, 147

VI. REAGENTS -

1. Sodium carbonate - C. P. Cryst.
2. " " - 10% solution
3. Hydrochloric acid - Conc. C. P.
4. Yellow mercuric oxide - C. P.
5. Ammonium chloride - C. P. Cryst.
6. Ammonium Hydroxide - C. P. Conc.
7. Barium chloride - 20% Ba Cl_2 .2 H_2O.

VII. PROCEDURE

Accurately weigh a 1-gram sample into a 400-ml. beaker. Add 15-ml. of 10% Na_2CO_3 solution and boil for at least 5 minutes. Prepare some freshly precipitated mercuric oxide by dissolving 3-grams of C. P. yellow mercuric oxide in a small amount of hydrochloric acid and then reprecipitating the oxide by adding first solid sodium carbonate and when precipitation starts, add a 10% solution of sodium carbonate until the mixture reacts basic to indicator paper. Add this mercuric oxide slurry to the decomposed iron blue slurry and boil for 15 minutes, washing down the sides of the beaker as necessary. To test for the complete destruction of the ferrocyanide, take out a small portion of the slurry (.5-ml.) and acidefy it with hydrochloric acid. Let stand a few minutes. No blue color should appear. Add sodium carbonate solution to this test portion until it is again alkaline and return to the bulk of the slurry. Continue according to one of the two following alternate procedures. At present, alternate procedure No. 2 is thought to be less troublesome (Note 1).

Alternate Procedure No. 1

If no blue color appeared, add 100-ml. of bromine water and boil the solution. Test for acidity and if acid, add more sodium carbonate solution. Filter through a #40 Whatman paper or its equivalent and wash with a hot 1% solution of ammonium chloride. If some of the precipitate appears to run through or if a slight precipitate forms in the filtrate, it may be neglected. Add hydrochloric acid to the filtrate (Caution - use a hood because hydrocyanic acid is liberated) until the solution tests strongly acid and start boiling to a low volume. Dissolve the precipitate in ±100-ml. of ±3M HCl (1:3) and reprecipitate with sodium carbonate adding it first as a solid and when near the neutral point, add it as a 10% solution. Add enough to make the solution distinctly basic, heat to boiling, boil for a few minutes and filter through a Whatman #40 or its equivalent. Wash the precipitate with a hot 1% NH_4Cl solution. Acidify the filtrate with hydrochloric acid and combine with the first filtrate.

Alternate Procedure No. 2

If no blue color appeared, add 5-ml. of ammonium hydroxide, boil a few minutes longer and filter through a #40 Whatman paper or its equivalent. Wash the precipitate with a room temperature 1% solution of ammonium chloride. A slight turbidity in the filtrate may be neglected. Add hydrochloric acid to the filtrate (Caution - use a hood because hydrocyanic acid is liberated) until the solution tests strongly acid, and start boiling to a low volume. Dissolve the precipitate in ±100-ml. of ±3-M hydrochloric acid (1:3). A certain amount of the precipitate will remain as a white residue. This need not be dissolved. Reprecipitate with sodium carbonate adding it first as a solid and when near the neutral point, add it as a 10% solution. Add enough to make the solution distinctly basic, and boil for a few minutes. Add 5-ml. of ammonium hydroxide and again boil for a few minutes. Filter through a Whatman #40 paper and wash with 1% ammonium chloride solution at room temperature. Neglect any slight precipitate in the filtrate. Acidify the filtrate with hydrochloric acid and combine with the first filtrate.

Continuation of Regular Procedure.

Evaporate the combined filtrates to a low volume (until crystals appear or until the volume is about 100-ml.). Test the acidity during the evaporation process and if the solution has turned neutral, add more hydrochloric acid. This evaporation insures the removal of all of the NH_4Cl. Make the volume to ±400-ml. Add ammonium hydroxide until the appearance of a precipitate. Add 4-ml. Conc. HCl, heat to boiling and add, dropwise with stirring, 10-ml. of 20% barium chloride solution. Heat for 1/2-hr. and let stand overnight. Filter through a weighed Gooch crucible containing an asbestos mat and an ashless filter paper disk (Whatman #40 or equivalent) (Note 2). Wash with hot water, ignite, cool and weigh as $BaSO_4$).

NOTES

1. Either alternate procedure tends to give a cloudy filtrate and the separation of the mercury is incomplete but the amount remaining seems to do but little harm. Alternate No. 2 removes more of the mercury giving a cleaner separation and it is for this reason that it is thought to be less troublesome.

2. The filter paper disk is optional. If many sulfate determinations are made, it is convenient to use a paper disk which permits the removal of the bulk of the $BaSO_4$ ash by simply blowing it out or brushing it out. The same asbestos mat may then be used many times.

VIII. CALCULATIONS

$$\frac{\text{Wt. of } BaSO_4 \text{ precipitate} \times 0.3430 \times 100}{\text{Sample Weight.}} = \% \ SO_3$$

APPENDIX 8

I. SUBJECT - Iron Blue Pigments.

II. DETERMINATION - Total moisture by loss in weight.

III. PRINCIPLE - The sample is dried at a constant temperature of 160°C. Compensation is made by loss in weight due to decomposition of the blue by an extrapolation technique.

IV. REFERENCE - N. B. #1166 P. 36.

V. SPECIAL EQUIPMENT

Brabender moisture tester. This is simply an oven with a balance so attached that the sample can be weighed without removing it from the oven. The weight scale reads directly, %loss in weight.

VI. STATUS

The method is admittedly empirical. It has been applied to a large number of iron blue pigments with results that are believed to be comparable.

VII. PROCEDURE

Weigh a 10-gram sample of pigment on the properly tared aluminum pan provided with the Brabender tester. Place in the Brabender oven which has been preheated to 160°C. Detailed directions for the use of the instrument are supplied by the manufacturer and should be considered. During the time of heating, no sample should be left in the space immediately in front of the oven door because experience has shown that the temperature is a little lower in this position. The position of the samples in the oven should not be changed except as is necessary when weighing the samples. After the samples are weighed, they should be returned to their original positions. This will minimize the effect of a temperature variation in the oven. The oven door should never be opened during the course of a determination and the oven should be kept away from drafts. Readings are taken every hour for the first 5 or 6 hours.

The data are plotted on rectilinear cross section paper; plotting time as abscissa and percent loss in weight as ordinate. It will be observed that after the first or second hour, the curve will be essentially a straight line and will be almost parallel with the abscissa. (Note 1). Laying a straight edge along the linear portion of the curve, draw a line which will intersect the ordinate. The percent loss in weight as indicated by the intersection of this line is taken as the percent moisture in the blue (Note 2).

NOTES

1. There will be a constant loss in weight due to the decomposition of the blue. This will give the linear portion of the curve a slight slope. The magnitude of this slope will depend on the nature of the blue, being quite large for toning blues such as B-152-[illegible].

2. This extrapolation to zero time eliminates the decomposition effect of the blue. It has been observed that the loss in weight, after drying for one hour, is reasonably close to this extrapolated figure, hence for routine analyses, it may suffice to use the percent loss in weight after one hour at 160°C. as the percent moisture in the sample.

APPENDIX 9

I. **SUBJECT** - Iron Blue Pigments

II. **DETERMINATION** - Iron outside of the Iron Blue molecule.

III. **PRINCIPLE** - A sample is shaken with 20% by volume hydrochloric acid and the iron in solution is titrated with a standard solution of Ti Cl3.

IV. **REFERENCE** - N. B. #1166 p. 60-61; N. B. #1132 p. 187

V. **REAGENTS**

(1) Hydrochloric Acid - 20% by volume. (80ml H_2O + 20 ml Conc. HCl)

(2) Potassium Thiocyanate solution - (15 g/100 ml)

(3) Titanous chloride standard solution ±0.1N.

VI. **PROCEDURE**

Weigh a 5 gram sample into a 125 ml glass stoppered flask. Pipette 100 ml of 20% by volume hydrochloric acid. Shake overnight (±16 hrs.) in an automatic shaking device. Let stand until some settling has taken place (±2 hrs.). Decant into a 100 ml centrifuge tube, stopper the tube and centrifuge until the supernatent liquid is clear (±45 min.). Filter through a dry #3 Whatman filter paper or its equivalent, discarding the first ±15 ml. of filtrate. Filter somewhat in excess of 50 ml. Pipettte 50 ml of the filtrate into a small flask. Add 5 ml of the KCNS solution and titrate slowly with ±0.1N Ti Cl_3 solution to the disappearance of the red ferric thiocyanate complex.

VII. **CALCULATIONS**

$$\frac{\text{ml Ti Cl}_3\text{ Sol'n} \times N \times 0.07985 \times 100}{\text{Sample Weight in aliquot}} = \% \text{ Fe}_2\text{O}_3$$

APPENDIX 10

I. SUBJECT - Iron Blue Pigments

II. DETERMINATION - Organic Treating Agent.

III. PRINCIPLE - The treating agent is extracted in a Soxhlet extrator using a 5% by volume solution of acetic acid in chloroform.

IV. REFERENCE - N. B. #1182 p. 12-19 N. B. #1132 p. 132

V. REAGENTS -

(1) Acetic Acid - Glacial C. P.
(2) Chloroform

VI. PROCEDURE -

Accurately weigh three grams of pigment and wrap in a piece of #40 Whatman filter paper or its equivalent. Place in an extraction thimble and extract in a Soxhlet extrator for 24 hrs. If the solution contains pigment particles or filter paper fibers etc. it should be filtered. Otherwise transfer to a beaker and evaporate to a low volume on a steam bath. Transfer to a weighed evaporating dish and evaporate to dryness.Avoid excessive heating because some treating agents have rather high vapor pressures. Place in a vacuum desiccator over sulfuric acid and dry to constant weight. This will usually take no longer than three days.

NOTE

Some samples bleed quite badly because of the nature of the treating agent. The effect of this bleed can be minimized by evaporating most of the chloroform and substituting diethyl ether. This often time flocculates the iron blue and it may now be filtered. If filtration is still difficult the ether suspension may be centrifuged and the practically clear supernatent liquid filtered through a #3 Whatman filter paper or its equivalent. The small amount of pigment separated in this manner will contain measurable amounts of treating agent. If greater accuracy is required, this pigment should be re-extracted in a manner similar to the first extraction.

VII. CALCULATIONS

$$\frac{\text{Wt. of extract} \times 100}{\text{Sample Weight}} = \% \text{ Organic Treating Agent.}$$