

## ON THE COLORIMETRIC DETERMINATION OF IRON WITH SPECIAL REFERENCE TO CHEMICAL REAGENTS.

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The literature of the colorimetric determination of iron is quite extensive.<sup>1</sup> Methods based on the color of the sulphocyanate, ferrocyanide, salicylate, tannate, sulphide, and acetylacetonate have been published. None of these has met with much consideration with the exception of the sulphocyanate methods, and the difficulties in the way of these have hitherto prevented their general adoption. It is hardly to be expected that a colorimetric method can be devised which will equal in accuracy the permanganate titration when moderately large quantities of iron are concerned. This, however, soon reaches its limit, and it is here that a satisfactory colorimetric method would find application.

The intensity of the color of ferric sulphocyanate, while very great, is extremely dependent upon the composition of the solution, and is by no means proportional to the concentration. The red color is due to the undissociated salt and to its double compounds, the ionized salt being colorless. The salt is further very prone to hydrolysis. Many substances interfere markedly with the reaction, notably fluorides, phosphates, arsenates, oxalates, citrates, tartrates, iodates, and to a less but still marked degree acetates and sulphates, the action of some of these being so strong that it is impossible to get the color even with considerable quantities of iron. In short, the intensity of the color is so influenced by the nature and concentration of the sub-

<sup>1</sup>For a list of references up to June, 1904, see Pulsifer, *J. Am. Chem. Soc.*, **26**, p. 974. Later articles are by Mouneyrat, *Comptes Rendus*, **142**, p. 1049, 1572 (as sulphide); Leather, *J. Chem. Ind.*, **24**, p. 385 (as ferrocyanide or sulphocyanate, with Lovibond's tintometer); Marriott and Wolf, *J. Biol. Chem.*, **1**, p. 451 (as sulphocyanate in acetone solution).

stances present that, unless the test solution and the standard solution with which it is compared have identical composition and concentration, results varying many hundred or even thousand per cent from the truth may be obtained. The determination of iron in a given material would therefore presuppose the possession of a sufficient sample of the same substance either entirely iron free or of accurately known iron content; a requirement which could naturally seldom be realized. Moreover, the presence of retarding substances would often diminish greatly the sensitiveness of the reaction. The direct determination of the color of the aqueous solution, as first proposed by Thompson,<sup>2</sup> is therefore little used, and only when test and comparison solutions can be made identical. A great improvement was made by Tatlock<sup>3</sup> in extracting the ferric sulphocyanate by ether and comparing the color with ethereal layers of the same volume and thickness containing known amounts of iron and reaching the correct result by a series of approximations. The extraction by ether is a great advance over the older method, for as fast as the sulphocyanate is removed from the aqueous solution more is formed, the result being that the greater part of the iron is extracted, although the removal is never complete, and the less so, the more disturbing substances are present. Lunge and von Kéler<sup>4</sup> have improved Tatlock's method and given it a somewhat wider scope. There are certain features of their method which are not satisfactory. It can be applied to but a limited amount of material; the contents of the comparison cylinders can be given an identical concentration only by the use of iron-free material; the large amount of salt or acid used interferes somewhat with the sensitiveness, and in some cases may hinder the formation of ferric sulphocyanate almost entirely; the ether solution changes color gradually, so that comparison can be made only after several hours, while by longer waiting the color is likely to fade, and unevenly in the two cylinders; the method of approximations with standards of different strengths is cumbersome.

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<sup>2</sup>J. Chem. Soc., **47**, p. 493; 1885.

<sup>3</sup>J. Chem. Ind., **6**, p. 276, 352; 1887, based on the observation of Natanson, Ann., **130**, p. 246; 1864, that the reaction is more sensitive when ether is employed as solvent.

<sup>4</sup>Zs. angew. Chem., 1894, p. 670; 1896, p. 3; Lunge, Chem. techn. Untersuchungsmethoden, 5<sup>te</sup> Aufl., **1**, p. 385.

The abnormal behavior of the color of the ether solution, noted by Lunge, we attribute to the presence of peroxides.<sup>5</sup> The color of the solution in ether which has been freed from peroxides by shaking with ferrous sulphate solution is pure pink or rose from the start; if, however, a drop of hydrogen peroxide be added, the solution becomes of a dirty yellowish pink, which becomes pure after a time, with deposition of a yellowish solid between the two layers. This is probably pseudosulphocyanogen, which is formed by the action of the peroxide on the isodisulphocyanic acid which is present. Even the best grades of ether show this behavior unless especially purified. The presence of peroxide in ether is readily detected by shaking it with freshly reduced acidified ferrous sulphate solution to which a sulphocyanate has been added, when ferric sulphocyanate is generated and is taken up by the ether. This is a good test for traces of hydrogen peroxide which might be used to determine it colorimetrically.

The method of Marriott and Wolf<sup>6</sup>, which consists in bringing out the color of the aqueous solution by the addition of about one and a half volumes of acetone, does not appear to afford a sufficient guarantee against bleaching, or against the effects of mass action or of inhibiting substances, and could be applied only to limited amounts of material, and to such substances as are sufficiently soluble in the aqueous acetone.

The unpleasant property of ether of giving discolored solutions led us to try other solvents. Of these, amyl alcohol proved to be the most satisfactory, giving a perfectly pure color from the start, and being a decidedly better solvent than ether for ferric sulphocyanate. A rather crude experiment with an intensely colored aqueous solution of ferric sulphocyanate, with excess of ammonium sulphocyanate and hydrochloric acid showed that ether left 3.7 times as much iron as was left by an equal volume of amyl alcohol. The relative efficiency doubtless varies with the composition of the solution, but the above figures show the decided superiority of amyl alcohol. Although we later discovered a method of inhibiting the discoloring action of peroxides on sulphocyanates we have for this reason retained the use of amyl alcohol, mixing it, however, with a cer-

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<sup>5</sup> See paper on Sulphocyanic Acid (this Bulletin, 3, p. 157).

<sup>6</sup> J. Biol. Chem., 1, p. 451; 1905.

tain proportion of ether. Amyl alcohol is somewhat too viscous to allow rapid separation. When mercuric sulphocyanate reagent is used, ether is a relatively still poorer solvent for ferric sulphocyanate and under certain conditions has the unusual property of forming three layers, the iron being mostly concentrated in the middle layer. These objectional features are entirely obviated by using a mixture of 5 vols amyl alcohol with 2 vols ether, and it is this mixture which is meant whenever the amylic layer is spoken of below.

Having satisfied ourselves by numerous experiments that the determination of traces of iron could not be effected with sufficient accuracy in the presence of large quantities of salts, we have worked out methods whereby it can be concentrated into small bulk, practically free from interfering substances. These methods will be described below under the head of *Concentration*. We have further replaced ammonium sulphocyanate by free sulphocyanic acid, which may easily be prepared iron free in a few minutes, and which serves as a solvent for the concentrated iron. We thus obtain a solution of iron in a great excess of free sulphocyanic acid, practically free from all other substances, and so secure the most favorable conditions possible for the complete conversion of the iron into undissociated ferric sulphocyanate.

The gradual bleaching of the solution of ferric sulphocyanate has been noted by various observers and is referred to by Tatlock, by Lunge, and by Marriott and Wolf in the articles quoted. This is a very usual phenomenon even in ethereal or amylic solutions, and it is not uncommon for two identical tubes, at first matching, to show a very marked difference within less than an hour. This fading, while it may be aided by the action of light, is due to the reduction of the iron to the ferrous state by other substances than normal sulphocyanic acid. Chief among these is isodisulphocyanic acid, which is always formed when sulphocyanates are acidified, and which reduces ferric salts with great rapidity.<sup>7</sup> Hydrocyanic acid and hydrogen sulphide, both of which are decomposition products of sulphocyanic acid, may possibly also take part. Hydrocyanic acid reduces traces of ferric salts, which are reoxidized by persulphate. A weak solution of ferric sulphocyanate in water or amyl alcohol is decolorized on boiling for a few moments and hydrogen sulphide can be detected in the escaping vapors.

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<sup>7</sup> See this Bulletin, 3, p. 159, ff.; 1907.

In order to keep the iron in the peroxidized condition and to obviate the necessity of previously oxidizing ferrous iron we invariably add a few milligrams of pure potassium persulphate to each tube. This is able to keep the iron peroxidized even in the presence of small quantities of hydrogen sulphide or sulphurous acid. The use of persulphate has one striking disadvantage which it is necessary to note. Like hydrogen peroxide, but less rapidly, it oxidizes sulphocyanic acid, forming a yellow substance which is taken up by the amyl alcohol, often rendering even an approximate comparison impossible. It appears that this yellow body does not proceed from normal sulphocyanic acid itself, but from other substances, possibly the still unknown isosulphocyanic acid, which may accompany it in small quantity. Sulphocyanic acid freshly prepared by decomposition of its silver or mercury salt by hydrogen sulphide gives but little of the yellow body with persulphate. If, on the contrary, its 5-10 per cent solution which has been allowed to stand for some time, or a freshly acidified solution of a sulphocyanate be treated with persulphate, the amylic extract is always colored. Be the cause what it may, there is always enough of the yellow substance formed by persulphate to render an accurate comparison impossible. Even without persulphate a solution of sulphocyanic acid which has stood for a few days always contains enough yellow substance to make it useless.

Fortunately we have discovered that the addition to the sulphocyanic acid of a sufficient amount of mercuric sulphocyanate to form the double compound,  $\text{Hg}(\text{SCN})_2 \cdot 2\text{HSCN}$ , not only totally inhibits the action of persulphate but preserves the acid indefinitely against injurious changes, while it does not appreciably diminish the sensitiveness of the reaction with ferric salts. The amylic solution has a perfectly pure color from the start and in the presence of a trace of persulphate and occasional stirring retains its intensity of color absolutely unchanged for many hours. The addition of persulphate is necessary, as mercuric sulphocyanate does not prevent the fading of the ferric sulphocyanate. The employment of mercury introduces certain complications which will be treated of in their proper places under the separation of iron from the various metals.

#### REAGENTS USED IN THE COLORIMETRIC IRON DETERMINATION.

*Standard Iron Solution.*—0.863 g ferric ammonium alum and 5 cc concentrated sulphuric acid are dissolved to 1 liter. The solu-

tion, which contains 0.1 g iron per liter, may be kept indefinitely. For use, 5 cc are diluted to 100 cc, giving a solution of which 1 cc contains 0.005 mg iron. As the dilute solution hydrolyzes and deposits iron on the glass it should be prepared fresh every day, and it is important that the measuring flask and burettes should be washed out with hydrochloric acid before using. Since persulphate is used in the cylinders the standard solution may equally well be made with the equivalent amount of ferrous ammonium sulphate, 0.702 g per liter.

*Sulphocyanic Acid Reagent.*—Seven per cent aqueous sulphocyanic acid, freshly prepared as directed in the following paper, is at once saturated with mercuric sulphocyanate, somewhat more of the latter than is required to form the compound  $\text{Hg}(\text{SCN})_2$ ,  $2\text{HSCN}$  being used, and the excess being left in the bottle. If treated with a small quantity of potassium persulphate the reagent should not impart the least yellow color to amyl alcohol, even after several hours. A slight trace of iron is occasionally observed, which comes from an impure mercuric salt. Small amounts of this are of no significance in quantitative tests, as equal quantities of the reagent are used in each cylinder. The reagent appears to keep indefinitely, but in hot weather it is well to keep it in a cool, dark place when not constantly in use.

*Mercuric Sulphocyanate.*—The commercial article which is prepared from the nitrate and which comes as a white or yellowish powder is not to be depended upon. It is better to prepare it by pouring a hot solution of the purest mercuric chloride (1 mol) into a solution of the purest ammonium sulphocyanate (1 mol). On cooling the sulphocyanate separates out in the form of needles, which are washed with cold water. In this case it is necessary to use twice the theoretical amount of mercuric chloride, otherwise no crystals are obtained. The excess of mercury is easily recovered by precipitation with aluminium scraps. The product is not entirely free from the double chlorine compound, but this exerts no prejudicial effect. While the yield from the nitrate is better it contains some nitrate which is undesirable because of its oxidizing action on sulphocyanic acid, and, moreover, the nitrate is not as easily obtained free from iron.

*Potassium Persulphate.*—This is easily obtained free from iron by

a single recrystallization, the hot concentrated solution being filtered and the crystals washed with a little cold water and carefully protected from dust.

*Amyl Alcohol and Ether.*—A good grade of isoamyl alcohol, such as that sold by Kahlbaum, is sufficiently pure; it need not be free from pyridine; 5 vols are mixed with 2 vols of good ether (such as Kahlbaum's 0.720). Since the discoloring action of the peroxides on sulphocyanic acid is entirely prevented by the use of mercuric sulphocyanate, no special purification is necessary.

#### THE COLORIMETER.

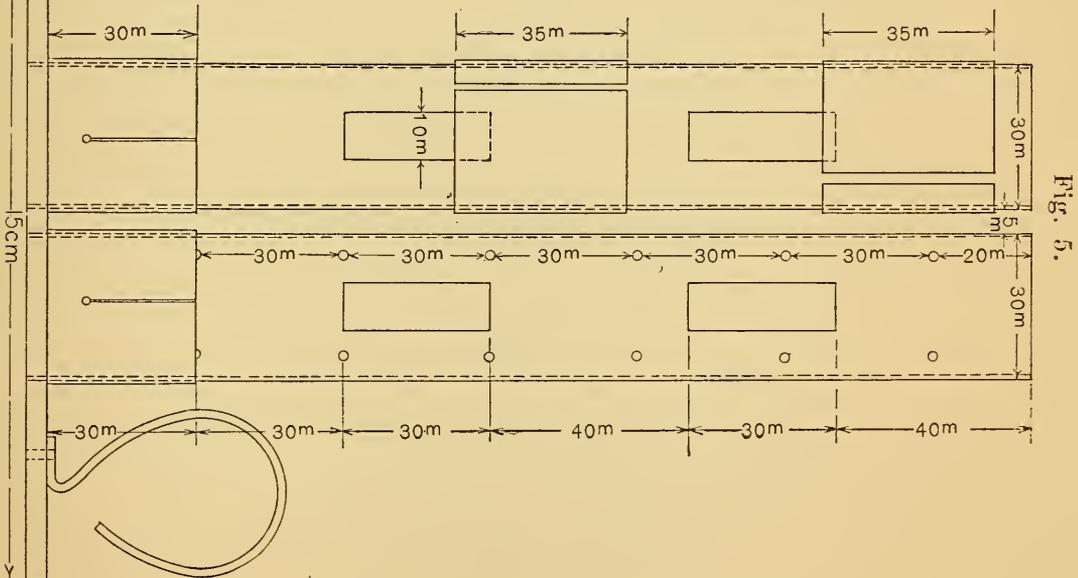
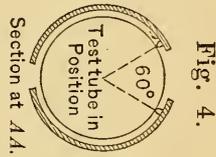
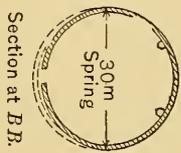
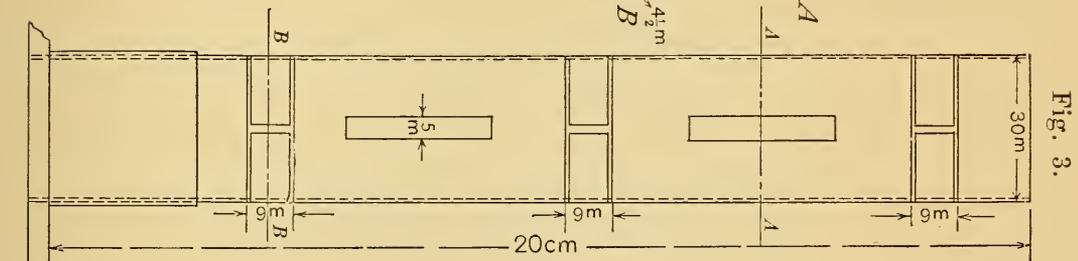
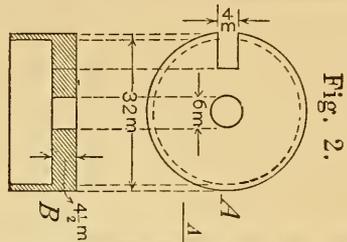
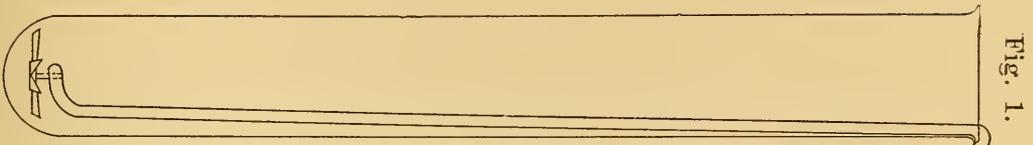
The use of the more elaborate and costly colorimeters, with lenses and prisms, is unnecessary, as the accuracy attained by the apparatus described below is quite sufficient, considering the minute amounts dealt with and the unavoidable errors involved in the methods of concentration and in working with traces of a substance so universally distributed as iron. Moreover, none of the instruments commonly in use enables one to employ an extracting liquid, as is done in our method.

Instead of graduated cylinders of equal diameters, provided with stoppers for the purpose of shaking, we use ordinary test tubes about 20 cm long and 24–25 mm diameter. These are carefully selected in pairs, with the aid of calipers. The cross sections must be as nearly circular as possible and the diameters of both tubes in a pair should not differ by more than 0.1 mm at corresponding heights, which would give a difference of 0.4 per cent in their readings. Each pair should be carefully numbered, and for ordinary purposes one or two pairs are sufficient. The mixing of the liquids is very effectively accomplished by stirrers, one of which is provided for each tube. The stirrer consists of a thin glass rod, bent as shown in Fig. 1, into the lower end of which is fused a short platinum wire, attached to a circular disk of platinum, slit radially and bent into the form of a propeller. When not in use the stirrer hangs from the edge of the test tube. It is essential to its proper functioning that the rod, when not in use, shall hang close to the side of the tube, so as not to interfere with vision; that the platinum disk shall almost, but not quite, touch the bottom, and that it shall work up and down easily. To exclude dust and prevent evaporation, it is well to provide each tube with a heavy, loosely-fitting brass cap, perforated to admit the tip

of the burette and provided with a radial slit through which the stirrer may pass (Fig. 2, a and b).

In comparing the colors in the two cylinders it is necessary to look through them horizontally, and in order to avoid the effect of the curvature of the glass and of reflection from the inside of the tubes they are surrounded by black mantles through which vertical slits are cut on exactly opposite sides. The slits have a height of about 1.5 cm and a width of 0.5 cm in the side toward the observer and 1 cm on the opposite side. Notwithstanding the curvature of the glass, slits of this width give a field of practically equal intensity, owing to the refractive action of the liquid. The mantle may be made by rolling thick black paper around the tube and pasting the edges so that the mantle may slip easily over the glass and yet retain its position through friction. Care must be taken that the centers of the slits are exactly opposite, which can be determined by marking the position with the calipers. The two cylinders are mounted in vertical position, as near together as possible, in some form of dark box such as is used in colorimetric work. Two 10-cc glass cock burettes, carrying the standard iron solution, are so mounted that their tips project into the cylinders. In reading we look against a uniformly illuminated vertical sheet of white paper, placed at an angle of about  $45^\circ$  with a window, the degree of the illumination being regulated by the angle. As there is generally a marked difference in the color sensitiveness of the two eyes, it is necessary, in comparing, to shield or close one eye, the other being opposite the center of the instrument. We have observed that in the great majority of persons the left eye is more sensitive to red, unless wearied. When much work involving the use of an extracting liquid is to be done it is convenient to have the mantles made of brass instead of paper and to provide them with springs which will easily hold the cylinders in place, and to mount them side by side in a permanent base. We give here a drawing and description of the instrument which we have employed in the greater part of this work.

*Mantles.*—The two mantles are identical in every respect. They are made of 30-mm brass tubing, of about  $3/4$  mm thickness, giving an internal diameter of about 28.5 mm. The total height is 20 cm (Figs. 3 and 5, and sections Fig. 4, a and b).



*Slits.*—Two pairs of slits are provided, for greater convenience in reading with varying volumes of liquid. Their length is 30 mm. The width on one side is 5 mm, on the other 10 mm; the opposite slits must exactly correspond in position, and especial care should be taken that their centers are exactly opposite with respect to the axis of the tube; the edges are cut parallel and sharp, not rounded or beveled.

*Collars.*—Each mantle has two thin brass sliding collars, of slit tubing, 35 mm high, the object of which is to close or vary the height of the slits. They are lined inside with black paper and must slide easily.

*Guide Points.*—Each mantle has 6 pairs of these, at equal distances, as indicated. Their object is to hold the cylinder exactly parallel to the axis of the mantle; it is therefore essential that they shall be exactly in line, parallel to the axis of the mantle; that they shall project into the tube exactly to the same distance, viz, about 1.5 mm, and that they shall have sharp edges or points, not rounded or flat heads. They are made by inserting brass pins or pegs through the wall of the mantle.

*Springs.*—These are intended to hold the cylinder in place against the guide points, and therefore parallel to the axis of the mantle. They are made in pairs, as indicated in the drawing, by cutting and bending in a portion of the tube, and should hold a 25-mm test tube filled with water firmly enough to stay in place, yet so that it can easily be shoved up or down with one hand.

*Mounting.*—Each mantle is supported in a socket, such as is used for microscope eyepieces, which is mounted on a brass plate 15 cm  $\times$  10 cm and not less than 4 mm thick, provided at one end with a handle for lifting. The mantles must turn easily in the sockets with one hand, and when mounted must be parallel and 5 mm apart.

*Finish.*—The whole instrument, except the inside of the sockets and the portion of the mantles inside them, is coated dull black, within and without.

In using the instrument, the narrow slit is turned toward the observer. In order to prevent reflection from the surface of the glass, the mantles are shielded by surrounding them with a box, made of thick, black paper open at top and bottom, 20 cm high, 10 cm deep, and 7.5 cm wide. In the front of this are cut two

openings 4 cm square, at heights corresponding to the slits; in the back at the same height are two pairs of openings 4 cm high and 1.5 cm wide, exactly coinciding with the slits in the mantles. When the box is in place, the rear openings should be invisible from the front. It is also desirable to have the two burettes mounted on a small clamp so that both can be raised or lowered at the same time. A convenient clamp is made by sawing two short pieces of brass tubing across, near the ends, and bending in the pieces so as to form springs. These tubes are soldered to a small vertical brass plate which is attached to a screw muff which supports it on a retort stand. The dimension of the clamp is such that the burette tips coincide with the centers of the cylinders. It is scarcely necessary to add that no iron is permissible, and that the apparatus should be kept free from dust.

#### METHOD AND ACCURACY OF COMPARISON.

The cylinders, which may be conveniently designated as the "test" and "standard," after charging in the manner described below, contain equal volumes ether-amyl alcohol mixture and equal volumes of sulphocyanic reagent diluted with equal volumes of water and a few mg potassium persulphate, and are therefore of identical composition and concentration, except that the "test" contains the iron and 2 or 3 mg manganese and oxidation products of sulphocyanic acid, an amount entirely too small to have any influence on the determination.<sup>8</sup> They are placed in the colorimeter and the colors are brought to equal intensity by carefully adding to the "standard" a sufficient amount of standard iron solution from the corresponding burette.<sup>9</sup>

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<sup>8</sup> To one of two carefully matched cylinders was added the manganese dioxide from 0.6 cc 1 per cent permanganate, about the quantity used in a concentration. Not the least change could be detected. After adding 40 mg sulphuric acid to one of the matched cylinders, 0.14 cc standard iron solution had to be added to the same cylinder to restore equality. It therefore appears that as little as 40 mg sulphuric acid may produce an error of  $-0.0007$  mg Fe. Since the sulphuric acid generated by the above amount of manganese does not exceed 1.2 mg its influence is clearly too small to be detected, amounting to only perhaps 0.004 cc standard solution.

<sup>9</sup> When the amount of standard added equals 1 cc, it is well to add an approximately equal volume of water to the "test" cylinder, so as to keep the volumes equal and counteract the unequal solvent action on the ether-amyl alcohol layer. If the concentration of the iron has been properly performed, the quality of the colors will be identical. A yellowish cast in the "test" is due to faulty concentration, and an accurate comparison can not then be made. As we read by looking

The difference of the two burettes is then noted, and the process is repeated three or four or more times by adding a few drops to one cylinder and bringing the other to match it. The average of the differences observed is the amount of standard iron equivalent to the iron sought: 1 cc = .005 mg Fe.

It is well known that extremely faint colors can not be matched as well as those of somewhat greater intensity. With this method it is possible to determine to within a few per cent an amount of iron so small that it scarcely gives a visible color to the amylic layer. The amylic mixture is used in multiples of 5 cc and the most favorable conditions appear to be when the volume used is roughly ten times the volume of the standard iron solution equivalent to the iron sought. Under these conditions the extreme differences between the readings should not exceed 5-6 per cent of the total iron present, a result which is much diminished by taking the mean of a series of readings.

The following experiments show the degree of accuracy attained.

1. Each cylinder was charged with 5 cc amylic mixture, 5 cc sulphocyanic reagent, and 5 cc water. The burettes were not read until the match was obtained.

Cc standard iron solution added		
Tube 1	Tube 2	Difference
0.19	0.19	0.00
.33	.33	.00
.45	.46	— .01
.64	.61	+ .03
.81	.77	+ .04
		Mean + .012
		= .00006 mg Fe.

through the amylic layer it is essential that this shall be perfectly clear and free from suspended water drops; the turbidity of the aqueous layer through suspended amyl alcohol is of no significance. If the stirring is properly performed the amylic layer becomes rapidly clear and the aqueous layer remains turbid. Whether or not this will be realized can be instantly told by observing the manner in which the separation occurs. If the churning be thorough large globules will be seen on the upper surface, which will be seen to coalesce rapidly, after the manner of bubbles, leaving a perfectly clear amylic layer, while below the mixture contains innumerable small drops which do not run together, but gradually rise, leaving a turbid aqueous layer. If, however, the churning has been imperfect the large globules are at the bottom and run together rapidly, leaving a sharply defined surface and a clear aqueous solution, while above are seen small globules, which gradually fall, leaving the amylic layer turbid. In general the former effect takes place; if it does not, even with sufficient churning, it can be brought about by adding more water to each cylinder.

2. 200 cc redistilled ammonia were evaporated to dryness in platinum in a dust-free atmosphere, and the residue taken up with sulphocyanic reagent.

Test	Standard	Difference
0.65	0.61	-0.04
.93	.95	+ .02
<b>Mean</b>		- .010
		= - .00005 mg Fe.

3. 200 cc distilled water treated as above.

Test	Standard	Difference
0.40	0.39	-0.01
.58	.53	- .05
.95	.96	+ .01
<b>Mean</b>		- .017
		= - .00008 mg Fe.

Lunge<sup>10</sup> estimates that the permanganate method can not be depended on to give results nearer than  $\pm 0.14$  mg Fe. This would mean an error of  $\pm 1$  per cent on 14 mg or of  $\pm 5$  per cent on 2.8 mg. It appears from the above that the colorimetric method gives an error of less than  $\pm 0.0001$  mg Fe, or  $\pm 1$  per cent of .01 mg, the amount which is conveniently employed in the colorimeter. Since larger quantities of iron can be diluted to any desired extent without introducing an error of this magnitude, it follows that the colorimetric method can be used to advantage up to about .014 g in the absence of interfering substances; above this limit the permanganate method is more accurate. Where a special concentration of the iron is necessary, the error may be estimated on the basis of our results at  $\pm 0.0005$  mg in the more unfavorable cases, or  $\pm 5$  per cent of .01 mg. In such cases the colorimetric method would be applicable, with suitable dilution, up to about .0028 g Fe.

#### CONCENTRATION METHODS.

The problem of separating a few ten-thousandths of a milligram of iron from several grams of material in a form suitable for determination in the colorimeter is one which must necessarily vary with the nature of the material under examination. We have worked out the conditions which will be found applicable in most cases. In

<sup>10</sup> Zs. angew. Chem., 1896, p. 3.

a few we have met with no success whatever, and must await the result of the future experiments. The details will be given below.

In all work with traces of iron it is necessary to exclude dust most carefully, especially where operations which consume considerable time are carried on. All utensils should be carefully rinsed with strong hydrochloric acid just before using; it is well to keep them under hydrochloric acid when not in use as far as practicable; all funnels and dishes should be kept covered with watch glasses, which, when removed, should never be placed on the table, but set concave side up, on small glass supports having three projecting glass points; reagent bottles should be kept covered with caps and the contents removed by pipetting rather than by pouring.

#### CONCENTRATION BY EVAPORATION.

When the material is volatile at a sufficiently low temperature and does not attack the vessels the iron may be concentrated by evaporation. This method is applicable to hydrochloric, nitric, sulphuric and acetic acids, ammonia, and other substances of a similar order of volatility. Substances like ammonium sulphate or oxalate and oxalic acid can not be so treated, as they attack the vessels appreciably. Concentration by evaporation alone is seldom sufficient for bringing the iron into a suitable form for colorimetric determination. Even the purest acids and ammonia are likely to contain traces of colored substances which pass over into the amyl layer, and so prevent accurate comparison. In general, after driving off the greatest part of the volatile material, or bringing to dryness and redissolving the residue in a few drops of hydrochloric acid, the iron must be precipitated by one of the methods given below.

The vessels used for evaporation may be of platinum, porcelain, or Jena glass. Except for ammonia and hydrofluoric acid, for which platinum should be used, this metal is unsatisfactory. All platinum contains a small amount of iron, either present as an original impurity or derived from the tools used for working the metal or from materials which have been previously contained in the vessels. This is quite sufficient to cause an appreciable error when acids or ammonium sulphide are evaporated. Berlin porcelain is better than platinum, and Jena glass superior to porcelain. The following data will show the relative values of the different materials:

100 cc of concentrated c. p. hydrochloric acid (*a* and *b*), nitric acid (*a* and *b*), and sulphuric acid were used in each case, the figures being the mean of the number of determinations indicated.

	HCl <i>a</i> mg Fe	HCl <i>b</i> mg Fe	HNO <sub>3</sub> <i>a</i> mg Fe	HNO <sub>3</sub> <i>b</i> mg Fe	H <sub>2</sub> SO <sub>4</sub> mg Fe
Evaporation in platinum . . . . .	.0102 (4 det.)	.0084 (3 det.)	.0095 (2 det.)	.0034 (2 det.)	.0226 (3 det.)
Evaporation in Berlin porcelain . . . . .		.0084 (3 det.)	.0083 (10 det.)	.0034 (3 det.)	.0162 (4 det.)
Evaporation in Jena glass . . . . .		.0074 (4 det.)		.0022 (5 det.)	.0130 (4 det.)
Direct neutralization and precip. of Fe	.0070 (8 det.)	.0068 (4 det.)	.0088 (6 det.)	.0026 (3 det.)	.0130 (4 det.)

Assuming, as we must, that higher results indicate contamination by iron contained in the material of the vessels, it will be seen that platinum is markedly superior to Jena glass in the case of sulphuric acid and, in a less degree in the case of nitric acid and hydrochloric acid, Berlin porcelain is more resistant than platinum and inferior to Jena glass. The results obtained by evaporation in Jena glass are close to those obtained by direct neutralization with redistilled ammonia and subsequent concentration of the iron by precipitation.

The individual data, which we can not quote here, show that the results obtained in Jena glass are much more uniform than those given by porcelain and platinum. We have used several platinum dishes, partly new ones which were reserved exclusively for this work, with the same result. Considering that platinum utensils are likely to be used for all sorts of purposes, and are therefore extremely subject to contamination, we must unqualifiedly recommend the use of Jena glass for evaporation in testing acids for iron. We have tried nonsol glass with unsatisfactory results, as the dishes are liable to crack with the high temperature and sudden changes involved in rapid evaporation. Doubtless vessels of fused quartz would give still better results, but unless extreme accuracy is desired their costliness renders their employment unnecessary. Probably crucibles or dishes of fused quartz might be used with advantage in driving off the more volatile salts. Evaporations should be made as rapidly as possible, in order to diminish the time of action upon the vessel, and entirely out of contact with the external air, so as to avoid dust. It is inadmissible to use any form of apparatus in which the condensed liquid can run or drop back into the vessel.

We have found the following form of apparatus entirely satisfactory: A circular disk of asbestos is placed upon a Chaddock's porcelain burner, and upon it is placed an inverted set of porcelain water-bath rings. Upon these rests a nine-inch funnel, the stem of which is drawn out and bent down. Through the stem is forced a current of air which has been filtered by passing through a long tube or series of tubes filled with cotton. A bent calcium chloride tube filled with cotton is directly connected with the stem of the funnel. The speed of the air current should be such as to prevent condensation in the stem of the funnel. The porcelain rings are slightly inclined so that the condensed liquid running down the sides of the funnel drops off at one point into a beaker. The whole rests on a glass plate. By this means it is possible to evaporate 100–200 cc concentrated sulphuric acid quietly and rapidly without danger of contamination from dust; 200 cc distilled water and 200 cc redistilled ammonia evaporated in this apparatus gave no trace of iron. (See page 127.)

The ordinary hemispherical Jena glass evaporating dishes with flat bottoms do not well bear the strain of this treatment. A suitable dish 9.5 cm wide by 4.5 cm high is conveniently made by cutting off the lower part of an 800 cc Jena-Griffin beaker, and making a lip in it. The dish rests on the porcelain rings, leaving an air space between it and the asbestos. In some cases it is desirable to finish the evaporation on a steam bath. For this purpose a Berlin porcelain steam bath is used, with the same funnel. If the steam, as is likely, carries over water containing iron in suspension, it should be passed through a separator, which is conveniently made of a large calcium chloride tube, half filled with beads and provided with an overflow for the water. Combustible liquids like acetic acid can not be evaporated over the free flame and are evaporated either on the steam bath or on a small electric hot plate fitted up as above.

#### CONCENTRATION BY PRECIPITATION.

In by far the greater number of cases it is necessary to concentrate the iron by precipitation. An almost indefinitely small quantity of iron may thus be determined in an indefinitely large amount of material, the only limit being the solubility of the iron precipitate in the solution. It is obviously impossible to collect on a filter

traces—say a thousandth of a milligram of ferric hydroxide or sulphide distributed through a considerable volume of an otherwise clear liquid. We therefore employ the method which has been occasionally used successfully in other cases, of mechanically carrying down the precipitate by a relatively large amount of another precipitate, which, when practicable, is generated simultaneously with the iron precipitate. We may designate this secondary precipitate as the “collector.” Various substances suggest themselves as collectors; their number is limited by the following considerations. A collector must be sufficiently insoluble, so that but a small amount of possibly impure foreign substance need be introduced; it must be of such physical consistency as to enable it to carry down all suspended precipitates, and must therefore be amorphous and flocculent, not granular or crystalline; it should not be gelatinous or otherwise difficult to wash out in the filter, neither should it be of such consistency as to run through the filter on washing; it must be easily soluble in 7 per cent sulphocyanic acid and must neither interfere with the ferric sulphocyanate reaction nor in the presence of mercuric sulphocyanate impart a color to any alcohol, or, if it does not meet these requirements, it must be capable of easy separation from the iron. Aluminium hydroxide would be the ideal collector were it not for the fact that it dissolves slowly and imperfectly in sulphocyanic acid, and thus frequently prevents complete solution of the accompanying ferric hydroxide. Repeated experiments have satisfied us that it is not to be depended on, and we have therefore employed it only in special cases where it was removed before final treatment of the precipitate with sulphocyanic acid. We precipitate the iron either as sulphide or as ferric hydroxide. The hydroxide precipitation is employed in the absence of materials which have a solvent action, such as citrates, tartrates, sugar, and many other organic substances, pyrophosphates, arsenites, arsenates, antimonates, etc. The usual collector for ferric hydroxide is hydrated manganese peroxide. The sulphide precipitation is used when from the presence of any of the just mentioned substances, hydroxide would remain in solution. It is also used when other sulphides insoluble in ammonium or sodium sulphide are practically absent. The best collector for iron sulphide is cadmium sulphide. In this case the cadmium sulphide is redissolved and the iron reprecipitated as hydroxide with manganese dioxide as collector.

In many cases the choice between the methods is optional. When there is reason to fear the presence of traces of organic matter, as in the case of materials which have been treated in wooden vessels in the process of manufacture, or when arsenic or other prejudicial substances may be present, as in the cruder reagents, the sulphide method is more accurate. For example, pure sodium chloride gave identical results by either method, while a sample of the best commercial chloride gave decidedly too low results with the hydroxide method.

Special care is necessary in sampling the substance, and wherever practicable duplicate determinations should be made on portions of the same solution, as it frequently happens that different samples, especially of crystallized substances, taken from the same bottle show widely varying results, owing to the irregular distribution of the iron.

#### APPARATUS AND REAGENTS USED IN CONCENTRATING.

The apparatus used for evaporations has been described above. Only the best ashless filters, Schleicher and Schüll's No. 590, should be used, and as even these contain very appreciable quantities of iron they must be moistened in the funnel with 1-1 hydrochloric acid, allowed to stand at least fifteen minutes, and then washed with water to which a few drops of ammonia are finally added. Only Jena or nonsol beakers or dishes, or platinum dishes, should be used, Jena glass dishes for evaporating strong acids, and these, or Jena beakers, for cadmium sulphide concentration, and for manganese dioxide precipitations when the time of heating is brief. For longer heating, or when sodium hydroxide is used, platinum is employed. Small pipettes are used for transferring the reagents from the bottles, and pouring should never be resorted to, as the lips of bottles are almost invariably dirty.

Reagents which are used in large amounts must be specially freed from iron; we have therefore limited these to the smallest possible number and to those most easily purified. Reagents which are used in very small amounts need not be specially purified, provided the amount of iron present is insufficient to affect the results.

*Ammonia.*—As even the best c. p. ammonia contains notable amounts of iron, it must always be redistilled. The washed ammonia gas is conducted into a cooled ceresine-lined bottle containing

water, in which it is kept. Only the best white ceresine should be used and care taken to coat the bottle uniformly up to but not into the neck.

*Hydrochloric Acid.*—The best c. p. hydrochloric acid invariably contains iron. We therefore always use carefully washed hydrochloric acid gas, prepared by dropping pure concentrated sulphuric acid upon pure ammonium chloride or concentrated hydrochloric acid. Rubber tubing should be avoided as much as possible, and that which is necessary should be washed out with acid. When practicable the gas is conducted directly into the solution; when aqueous acid is required, it should be freshly prepared.

*Hydrogen Sulphide.*—The use of hydrogen sulphide directly made from iron sulphide is inadmissible and may lead to gross errors. The gas is prepared by dropping acid into a sodium sulphhydrate solution. A stock solution of this is made by saturating 33 per cent sodium hydroxide with hydrogen sulphide and diluting four or five times before using.

*Ammonium Sulphide.*—In general the sulphhydrate is used and is always freshly prepared by saturating redistilled ammonia with hydrogen sulphide prepared as above.

*Bromine Water* is used to oxidize arsenious and antimonious oxides and to dissolve metals. As iron-free bromine and bromine water, kept in glass vessels, rapidly become contaminated with iron, the bromine water should be prepared as needed by drawing out a clean test tube so as to form a small retort, sucking in two or three cc bromine by alternate warming and cooling, and distilling it over into water.

*Nitric Acid.*—When more than one or two cc is required it should be redistilled from a small test-tube retort into a test tube placed in a beaker of water.

*Potassium Permanganate.*—A 1 per cent solution of the best c. p. grade is used. It furnishes the manganese dioxide used as collector for ferric hydroxide, and at the same time serves to oxidize traces of organic matter which might hold it in solution. If not sufficiently free from iron it may be purified by a manganese concentration.

*Cadmium Sulphate and Chloride* are used to supply the cadmium sulphide which serves as collector for iron sulphide, the chloride being used when barium, strontium, or calcium salts are present.

A one-fourth molecular stock solution is made, and freed from iron by making a manganese precipitation as described below. The presence of a slight excess of permanganate in the solution has no prejudicial influence.

*Sulphurous Acid, Ammonium Sulphite, Sodium or Ammonium Formate in 1 per cent solution and Alcohol* are used in small quantities to reduce permanganate to manganese dioxide. They need not be specially purified.

*Sodium Potassium Tartrate* is used to hold up alumina or chromic oxide in concentrating iron from their salts. A 20 per cent stock solution is made and freed from iron by a cadmium sulphide precipitation, as described below under tartrates. The alkaline solution should be neutralized to prevent its action on the glass.

*Sodium Hydroxide* is used in special cases, and its 5 per cent solution must be freed from iron by a manganese concentration. It should be freshly purified unless kept in platinum bottles.

#### CONCENTRATION BY MANGANESE DIOXIDE.

This is applicable in nearly all cases where substances which have a solvent action on ferric hydroxide, or more than traces of alumina and chromic oxide, are absent. There are certain special modifications of the method which will be given below, and we here give only the procedure in the simpler cases. The amount and concentration of the substance operated on seem to be immaterial; we often operate with as much as 50 g and in solutions as strong as 20 per cent. If the solution is not precipitated by ammonia and contains no substances capable of reducing permanganate to manganese dioxide, it is made weakly alkaline with ammonia, about 10 drops of permanganate are added, and then one to three drops of a reducer, such as 1 per cent formate, sulphurous acid, or occasionally alcohol, and the solution is then heated a few minutes until the manganese dioxide has separated in flocculent form. It is well to have a slight excess of permanganate. If the substance is one which is precipitated by ammonia, such as zinc, lead, or cadmium, just enough of this is added to form a slight permanent precipitate, and the manganese precipitation is made as above. The precipitate is collected on a 5.5 or 7 cm washed filter, and washed a few times with water. 2.5 cc of the sulphocyanic reagent are placed in the beaker to dissolve the pre-

precipitate adhering to the sides, and then dropped carefully around the top of the filter so as to dissolve the manganese dioxide and accompanying ferric hydroxide, the filtrate being run directly into the test cylinder. From 5 to 20 cc ether-amyl alcohol are added<sup>11</sup> according to the amount of iron present. The beaker is washed out with exactly 10 cc water, which is poured carefully through the filter. The standard cylinder is charged with 2.5 cc sulphocyanic reagent, 10 cc water, and as much ether-amyl alcohol as was used for the test. Finally a few mg potassium persulphate are added to each cylinder, and they are transferred to the colorimeter.

*Solubility of Ferric Hydroxide.*—The accuracy of the above method depends upon the degree of insolubility of ferric hydroxide in the weekly ammoniacal solutions of the various salts. In general this could be determined only by operating with solutions either iron free or containing an accurately known quantity of iron. In most cases this was impracticable owing to the lack of any method other than the one in question of accurately determining iron and to the difficulty of obtaining absolutely iron-free material. In the case of ammonium salts of volatile acids, however, the amount of iron can be accurately checked by evaporating the acid and using redistilled ammonia. The following are some of the results:

	Found	
	Fe	Fe <sub>2</sub> O <sub>3</sub>
	mg	mg
100 cc c.p. HCl, sp gr 1.19, evaporated in Jena glass (4 dets.) . . . . .	.0074	= .0106
The same neutralized with NH <sub>4</sub> OH and concentrated by Mn(4 dets.) . . . . .	.0068	= .0097
100 cc c.p. HNO <sub>3</sub> a, sp gr 1.42, evaporated in porcelain (10 dets.) . . . . .	.0083	= .0119
The same neutralized with NH <sub>4</sub> OH and concentrated by Mn(2 dets.) . . . . .	.0071	= .0102
100cc c.p. HNO <sub>3</sub> b, sp gr 1.42, evaporated in Jena glass (5 dets.) . . . . .	.0022	= .0031
The same neutralized with NH <sub>4</sub> OH and concentrated by Mn (3 dets.) . . . . .	.0026	= .0037
100 cc c.p. H <sub>2</sub> SO <sub>4</sub> , sp gr 1.84, evaporated in Jena glass (4 dets.) . . . . .	.0130	= .0187
The same neutralized with NH <sub>4</sub> OH and concentrated by Mn(4 dets.) . . . . .	.0130	= .0187
50 cc redistilled glacial acetic acid + .0100 mg Fe evaporated in Jena glass . . . . .	.0107	= .0153
The same neutralized with NH <sub>4</sub> OH and concentrated by Mn . . . . .	.0108	= .0154

<sup>11</sup> The ether-amyl alcohol should be added before adding the water, as otherwise there is likely to be a separation of mercuric sulphocyanate. The amount to be added can be judged by the color; it is better to add too little than too much, as more can be added later, if desired. If the amount of iron is very considerable, so as to require more than 5 cc standard iron solution, the filtrate can be diluted in a measuring flask and an aliquot portion taken, a fresh portion of sulphocyanic reagent being used.

Whence, in strong hot weakly ammoniacal solution,

		Fe	Fe <sub>2</sub> O <sub>3</sub>
100 g	NH <sub>4</sub> Cl dissolved	.0009 mg	.0013 mg
100 "	NH <sub>4</sub> NO <sub>3</sub>	.0009	.0013
100 "	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	none	none
100 "	NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	none	none

These figures, which are possibly high, if anything, owing to the solvent action of the evaporating acid on the vessel, can lay no claim to accuracy; but they at least show that the loss through solubility will not affect the percentage result of a determination nearer than the seventh decimal place, and may therefore be set off against the slight sources of contamination through dust, solvent action of the reagents on the vessels, etc.

#### CONCENTRATION BY CADMIUM SULPHIDE.

Cadmium sulphide is used as a collector for iron in the form of sulphide and is applicable in nearly all cases in which the substance under the examination either gives little or no precipitate with ammonium sulphide, or one soluble in an excess. Its chief use is to remove the iron as sulphide from solutions which exert a solvent action on ferric hydroxide, and from aluminium and chromium salts. The following is the method of procedure in the simpler cases.

To the cold solution contained in a Jena beaker, and which should not contain much free acid, are added 2 cc cadmium solution and then a slight excess of fresh ammonium sulphhydrate, or in case of sulphides soluble in an excess, enough to dissolve these. The liquid is allowed to stand in the cold for about half an hour, with frequent stirring, and the cadmium sulphide, which carries the iron, is then collected on a washed filter and washed a few times with water containing a little ammonium sulphhydrate. The precipitate can not be directly treated with sulphocyanic acid reagent, as much iron would be retained and much mercuric sulphide formed; neither can it, as we have found, be dissolved in bromine water with satisfactory results. It is therefore dissolved by carefully dropping hot 1-1 hydrochloric acid around the top of the filter, the solution and wash water being run back into the original beaker. The solution, which contains some free hydrogen sulphide, is treated as in a man-

ganese concentration, somewhat more than enough permanganate being added first, to oxidize the hydrogen sulphide, and then ammonia, the manganous salt in alkaline solution acting as the reducer of the permanganate. In general, the manganese dioxide comes down at once in good form or on gentle heating. The precipitate is collected on the same filter, or if this contains a residue, on a fresh one, and is further treated as described under manganese concentration. In the case of tartrates, oxalates, and other organic substances interfering with the manganese concentration, traces of which remain in the cadmium sulphide precipitate, hot 1-1 nitric acid is used in place of hydrochloric acid, and the organic matter is destroyed in the filtrate by adding permanganate to the hot acid solution until the color is permanent, when the solution is made ammoniacal as before. Special precautions to be observed in particular cases will be given below.

*Solubility of Iron Sulphide.*—In the absence of the disturbing factors above referred to, determinations made by both methods give practically identical results, from which it may be concluded that the solubility of iron sulphide, like that of the hydroxide, is negligible. There are certain exceptions to this, especially in the case of stannic salts, which will be noted below.

In the following we give the details of the determinations for a considerable number of reagents. It was obviously impossible to cover the whole field and we have chosen those cases which seemed of most importance as being typical or as most likely to cause difficulty. A few of the cases have presented difficulties which we have not yet been able to solve, and a few of the important types are omitted as it seemed undesirable to longer postpone publication. Some of the determinations were made before the details of the method were fully worked out and the results are therefore less accurate and less complete than would be the case now. In general the data for each substance were obtained from the same solution or liquid unless otherwise stated.

*Hydrochloric Acid, c. p.*—100 cc or 200 cc are evaporated down to a few cc in a Jena glass dish (page 130). In the residue the iron is concentrated by manganese. Finishing the evaporation on the steam bath and taking up the residue with sulphocyanic acid gives a somewhat discolored anylic solution which can not be sharply compared.

Instead of evaporating, 50 cc may be diluted with an equal volume of water, neutralized with redistilled ammonia, and treated with manganese. Results are identical in either case and identical with those obtained by the cadmium method. Hence it would appear that there is no appreciable loss of ferric chloride on evaporation.

Hydrochloric acid, c. p., sp gr 1.19. Two lots, *a* and *b*, the analysis labels of which indicated 0.0002 per cent Fe, gave:

Cc acid	Fe	per cent Fe	Method
50	<i>a</i> 0.0024 mg	0.0000040	} evaporation in porcelain
"	" 0.0021	0.0000035	
"	" 0.0024	0.0000040	
	Mean	0.0000038	
50	" 0.0022	0.0000037	} Mn conc. after neutralizing
"	" 0.0024	0.0000040	
	Mean	0.0000038	
50	" 0.0023	0.0000039	} Cd conc. after neutralizing
"	" 0.0021	0.0000035	
"	" 0.0020	0.0000034	
	Mean	0.0000036	
100	<i>b</i> 0.0074	0.0000062	} evaporation in Jena glass
"	" 0.0075	0.0000063	
"	" 0.0071	0.0000060	
"	" 0.0077	0.0000065	
	Mean	0.0000062	
50	" 0.0031	0.0000052	} Mn conc. after neutralizing
"	" 0.0044	0.0000074	
"	" 0.0028	0.0000048	
"	" 0.0039	0.0000066	
	Mean	0.0000060	

*Nitric Acid, c. p.*—The treatment of nitric acid is identical with that of hydrochloric acid. The results with evaporation, manganese, and cadmium concentrations coincide.

Nitric Acid, c. p., sp gr 1.42, the analysis label of which indicated 0.0002 per cent Fe, gave:

Cc acid	Fe	per cent Fe	Method
100	0.0022 mg	0.0000016	} evaporation in Jena glass
"	0.0022	0.0000016	
"	0.0024	0.0000017	
"	0.0022	0.0000016	
"	0.0022	0.0000016	
	Mean	0.0000016	
50	0.0013	0.0000018	} Mn conc. after neutralizing
"	0.0012	0.0000018	
"	0.0015	0.0000021	
	Mean	0.0000019	

*Sulphuric Acid, c. p.*—100 cc may be rapidly evaporated in Jena glass (page 130) and a manganese concentration made on the residue, or 25–50 cc may be diluted with 2–3 vols water, neutralized with redistilled ammonia, and the iron concentrated by manganese or cadmium.

Sulphuric acid, c. p., sp gr 1.84, gave :

Cc acid	Fe	per cent Fe	Method
100	0.0134 mg.	0.0000073	} evaporation in Jena glass
"	0.0122	0.0000066	
"	0.0137	0.0000074	
"	0.0129	0.0000070	
	Mean	0.0000071	
25	0.0029	0.0000063	} Mn conc. after neutralizing
"	0.0035	0.0000077	
"	0.0035	0.0000077	
"	0.0031	0.0000077	
	Mean	0.0000071	

*Acetic Acid.*—The iron may be determined in acetic acid either by evaporating to small volume in Jena glass on the steam bath or electric stove and precipitating in the residue with manganese, or by directly neutralizing with redistilled ammonia and concentrating with manganese or cadmium. It is essential to wash out the acetate thoroughly from the manganese precipitate as even small quantities interfere seriously with the sulphocyanate reaction.

100 cc glacial acetic acid "Kahlbaum" gave on evaporation 0.0075 mg Fe=0.0000071 per cent.

50 cc redistilled glacial acetic acid gave on evaporation 0.0015 mg Fe.

50 cc of the same to which 0.0200 mg Fe had been added gave by manganese concentration 0.0216 mg Fe.

*Ammonia.*—This is best evaporated in platinum, but may also be directly neutralized with gaseous hydrochloric acid. The evaporation residue usually contains something which discolors amylic solutions; it is therefore taken up with a few drops of hydrochloric acid and precipitated by manganese.

200 cc redistilled ammonia which had been kept in a ceresine lined bottle gave no iron on evaporation.

C. p. pyridine-free ammonia, sp gr 0.90, lots *a*, *b*, *c*, taken directly from the shipping bottle, gave on evaporation:

Cc ammonia		Fe	per cent Fe	Mean per cent Fe
200	<i>a</i>	0.0035 mg	.....	0.000020
200	<i>b</i>	0.0169	0.000094	0.000092
"	"	0.0160	0.000089	
"	"	0.0168	0.000094	
200	<i>c</i>	0.0171	0.000095	0.000093
"	"	0.0155	0.000086	
"	"	0.0178	0.000099	

All samples were free from sediment. It appears that the best c. p. ammonia after keeping in glass is likely to contain as much iron as the best grades of acids.

*Sodium and Potassium Hydroxides.*—These hydroxides frequently contain a little iron which gradually separates from the solution on standing, or as sulphide, on saturating with hydrogen sulphide. To determine this it may be concentrated directly by adding 2 drops sulphurous acid and 10 drops permanganate and heating in a platinum dish until the manganese dioxide has separated. This method is, however, likely to give somewhat too low results, and the precipitates occasionally give discolored amylic solutions; it must, however, be resorted to in certain cases where an iron-free caustic alkali is required. Better is it to neutralize with gaseous hydrochloric acid or carefully distilled acetic acid and to make a cadmium or manganese concentration. As shown by the following data, a 10 per cent sodium hydroxide solution gradually becomes weaker in iron apart from that which may be deposited as sediment, probably because a portion is taken up by, or at least firmly attached to, the glass of the bottle.

Two 10 per cent solutions of ordinary "pure" stick sodium hydroxide, lots *a* and *b*, were prepared and filtered; *a* was kept in a Jena glass bottle and tested at intervals, the bottle being shaken before each determination to disseminate any sediment.

100 cc *a* gave:

	Fe
fresh; direct Mn concentration.....	}0.0217 mg
	}0.0216
after 7 days; direct Mn concentration.....	0.0103
after 3 days; Cd conc. in acetate.....	0.0111
after 4 days; Cd conc. in acetate.....	0.0103
after 7 days; Cd conc. in acetate.....	0.0078

100 cc *b* fresh gave:

direct manganese concentration.....	}0.0231
	}0.0236
manganese concentration in acetate.....	}0.0264
	}0.0260
cadmium concentration in acetate.....	}0.0278
	}0.0257

*Sodium and Potassium Carbonates.*—The 10 per cent solution may either be treated directly with permanganate or neutralized with hydrochloric acid gas and treated by the manganese or cadmium methods, the results being practically the same.

Kahlbaum's potassium carbonate gave:

K <sub>2</sub> CO <sub>3</sub>	Fe	per cent Fe	Method
2.5 g	0.0085 mg	0.000340	direct Mn concentration
5.0	0.0179	0.000358	Mn concentration in chloride
2.5	0.0085	0.000340	Mn concentration in chloride
5.0	0.0173	0.000346	Cd concentration in acetate
	Mean	0.000346	

*Insoluble Carbonates.*—The substance is covered with water and decomposed by leading in hydrochloric acid gas, or if this is excluded, by iron free acetic or nitric acid; the iron is concentrated from the solution by the usual methods with due reference to the nature of the base.

Calcium carbonate "Kahlbaum" gave:

CaCO <sub>3</sub>	Fe	per cent Fe	Method
5.0 g	0.0201 mg	0.000402	Mn concentration in chloride
5.0	0.0206	0.000412	Cd concentration in chloride
	Mean	0.000407	

*Sulphides.*—Soluble sulphides are decomposed by leading in hydrochloric acid gas and making a cadmium or manganese concentration in the chloride solution. Or we may add the cadmium solution directly to the sulphide solution as it carries down the iron sulphide completely on sufficient stirring. Insoluble sulphides are either decomposed by iron-free acid or when practicable directly dissolved in ammonium sulphide.

Sodium sulphide from Kahlbaum, in 10 per cent solution gave:

Cryst. sulphide	Fe	per cent Fe	Method
10.0 g	0.0044 mg	0.000044	direct concentration by Cd
"	0.0035	0.000035	
"	0.0039	0.000039	
	Mean	0.000039	
10.0	0.0034	0.000034	Cd concentration in chloride
"	0.0038	0.000038	
	Mean	0.000036	

*Tartrates, citrates, and other organic substances which hold up ferric hydroxide*<sup>12</sup> must be treated by the cadmium method, which gives entirely satisfactory results as far as tested. Substances of this class containing metals whose sulphides are insoluble in ammonium sulphide or whose salts precipitate in ammoniacal solution in the cold have not been examined, and special methods would have to be devised for each. In some cases the organic matter might be destroyed with iron-free permanganate or other oxidizers, in others the metal might be removed by hydrogen sulphide. In considering the latter, it is important to bear in mind that sulphides frequently carry down iron from acid solution; we have occasionally found that over half the iron is precipitated in this way. Some substances, as calcium tartrate, are sufficiently soluble in the cold in ammonium salts to admit of the concentration being made. In any event, when such organic substances are present the cadmium sulphide precipitate must be washed as thoroughly as practicable, dissolved in nitric acid, and the trace of organic substance destroyed by heating with permanganate as described under the cadmium concentration (p. 136).

<sup>12</sup> For a list of such substances see Roszkowski, Z. anorg. Chem., **14**, p. 1; 1897. The statements in his article apply to larger quantities of iron and must not be unqualifiedly accepted with regard to traces.

The cadmium precipitate should stand at least a half hour, with frequent stirring, as otherwise very gross errors may result.

Sodium potassium tartrate in 10 per cent solution gave:

KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·4H <sub>2</sub> O	Fe	per cent Fe	Method
5.0 g	0.0105 mg	0.000210	Cadmium concentration
5.0	0.0104	0.000208	
5.0	0.0116	0.000232	
5.0	0.0106	0.000212	
	Mean	0.000215	

*Oxalic Acid.*—Oxalic acid does not rank as a substance capable of holding up ferric hydroxide in alkaline solution; as a matter of fact, however, it does do this to a slight extent and it has been found impossible to recover a trace of iron by the manganese method from solutions of ammonium oxalate to which small quantities of iron had been added. The cadmium method gives satisfactory results, but it is necessary to bear in mind that even traces of oxalate interfere seriously with the sulphocyanate reaction. The last traces remaining in the cadmium sulphide precipitate must therefore be destroyed by dissolving in nitric acid and oxidizing with permanganate. Insoluble oxalates may be decomposed by careful heating and subsequent treatment as under carbonates, care being taken to oxidize any remaining traces of oxalate with permanganate.

C. p. ammonium oxalate gave:

(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Fe	per cent Fe	Method
3.33 g	0.0056 mg	0.000168	Cadmium concentration
3.33	0.0050	0.000150	
5.00	0.0082	0.000164	
5.00	0.0075	0.000150	
	Mean	0.000156	
10.00	0.0001	0.000001	effect of not destroying last traces of oxalate

*Salts of the Alkali Metals.*—A very large class of salts of the alkali metals may be equally well treated by either the cadmium or manganese methods without special precautions, provided interfering substances are absent. Such are the chlorides, bromides, nitrates, nitrites, sulphates, sulphites, phosphates, sulphocyanates, acetates, and many others. Especially excluded are chromates and permanganates, which must be treated by the manganese method, and pyrophosphates, arsenites and arsenates, oxalates, salts of organic

acids containing alcoholic hydroxyl or mixtures containing these or carbohydrates, which require a cadmium precipitation. We give below a few cases which may be considered typical of this group.

*Sodium Chloride.*—C. p. sodium chloride from Kahlbaum, lots *a* and *b*, in 25 per cent solution gave:

NaCl	Fe	Per cent Fe	Method
lot <i>a</i>			
25 g	0.0019 mg	0.0000076	Manganese concentration
"	0.0020	0.0000080	
"	0.0023	0.0000092	
	Mean	0.0000083	
"	0.0023	0.0000092	Cadmium concentration
"	0.0024	0.0000096	
"	0.0022	0.0000088	
"	0.0023	0.0000092	
	Mean	0.0000092	
lot <i>b</i>			
25	0.0030	0.0000120	Manganese concentration
"	0.0031	0.0000124	
"	0.0030	0.0000120	
	Mean	0.0000122	
"	0.0031	0.0000124	Cadmium concentration
"	0.0030	0.0000120	
"	0.0028	0.0000112	
"	0.0030	0.0000120	
	Mean	0.0000119	

A 25 per cent solution of the best commercial sodium chloride gave the following, in which the different results by the two methods indicate a possible contamination interfering with the precipitation of iron as hydroxide:

NaCl	Fe	Per cent Fe	Method
25 g	0.0118 mg	0.0000472	Manganese concentration
"	0.0100	0.0000400	
"	0.0085	0.0000340	
"	0.0106	0.0000424	
"	0.0099	0.0000396	
	Mean	0.0000406	
"	0.0174	0.0000696	Cadmium concentration
"	0.0163	0.0000652	
	Mean	0.0000674	

*Orthophosphates.*—Alkali orthophosphates give equally good results by either the manganese or cadmium methods, provided pyrophosphate is absent. All trace of phosphate should be thoroughly washed out.

Sodium phosphate from Kahlbaum gave:

$\text{Na}_2\text{HPO}_4, 12 \text{ H}_2\text{O}$	Fe	Per cent Fe	Method
10 g	0.0094 mg	0.000094	Manganese concentration
"	0.0096	0.000096	
	Mean	0.000095	
"	0.0093	0.000093	Cadmium concentration
"	0.0096	0.000096	
	Mean	0.000094	

Insoluble phosphates which are soluble in ammonia may be concentrated by manganese; aluminium phosphate may be dissolved in acid, a tartrate or citrate (iron free) and ammonia added, and a cadmium concentration made. Calcium phosphate is best treated according to Glaser,<sup>13</sup> being dissolved in hydrochloric acid, the calcium precipitated by sulphuric acid and alcohol, and the iron removed from the filtrate by cadmium. One g tricalcium phosphate gave 0.0167 mg Fe (0.00167 per cent) and 0.0148 mg Fe (0.00148 per cent), and the precipitated calcium sulphate was free from iron.

*Pyrophosphates.*—Ferric pyrophosphate dissolves readily in ammonia in presence of an excess of alkali pyrophosphate; the manganese method is therefore inapplicable, and the cadmium precipitation must be employed.

Ten g Kahlbaum's sodium pyrophosphate gave 0.0114 mg Fe or 0.000114 per cent.

*Sulphocyanates.*—Sulphocyanic acid being the reagent *par excellence* for iron, the detection and determination of iron in its salts and their complete purification from it become points of considerable importance. All specimens of sulphocyanates which we have examined contain traces of iron. It is present even when the salt appears to be absolutely colorless, and such colorless salts not infrequently contain more iron than those which are slightly pinkish. Sulphocyanic acid is a reducer of ferric salts, as may be seen by

<sup>13</sup> Zs. angew. Chem., 1889, 636.

boiling a pink solution, when the color rapidly disappears. The same bleaching may be observed in the cold, and is due to the formation of colorless ferrous sulphocyanate. Moreover, the presence of a trace of free alkali or ammonia suffices to prevent the iron from betraying its presence. Whether a sample of sulphocyanate carrying iron changes from pink to colorless or *vice versa* depends on whether the reducing action of the salt or the oxidizing action of the air gets the upper hand. A convenient test for iron in sulphocyanate is to pour on a gram or two of the solid salt, contained in a test tube, an amount of redistilled ethyl alcohol insufficient to cover it; the alcohol at once becomes more or less pink even if the salt be absolutely colorless.

We have attempted to obtain iron-free ammonium and potassium sulphocyanate by careful recrystallization from water or alcohol, but without success; the point is soon reached where the contamination from dust, filter papers, and apparatus counteracts the effect of recrystallizing. Fortunately, purification by this means is unnecessary, and the chemist would do well to remove the last traces of iron himself rather than demand it of the manufacturer. For all but the roughest sort of qualitative work the solution should be purified after making up by adding a few milligrams of alum, making faintly ammoniacal and filtering off the alumina, which acts as collector for the iron. In the alkaline solution any ferrous hydroxide is at once oxidized by the dissolved air and carried down. That the iron is completely precipitated as hydroxide is shown by the following, in which an alumina concentration was made and a cadmium concentration in the filtrate.

50 cc of a 10 per cent ammonium sulphocyanate solution, lot *a*, the analysis label of which gave 0.004 per cent Fe, were used:

NH <sub>4</sub> SCN	Fe	Per cent Fe	Fe in filtrate	Method
5g	0.0034 mg	0.000068	.....	Mn concentration
"	0.0035	0.000070	.....	
"	0.0035	0.000072	0.0002 mg	Al concentration
"	0.0034	0.000068	0.0002	
"	0.0032	0.000064	0.0002	
	Mean	0.000068		

From these data it appears that the iron is entirely removed by the alumina method, the slight amount found in the filtrate being

within the limit of error of the method. It is also noteworthy that the amount of iron present was not more than one-sixtieth of that stated on the analysis label. If it is essential that no foreign substance be introduced a few drops of a solution of aluminium hydroxide in aqueous sulphocyanic acid may be used, and after purifying the solution may be neutralized with sulphocyanic acid. The removal of the iron by the manganese method is also practicable, though in this case oxidation products are introduced. Purification by extracting the iron as sulphocyanate with amyl alcohol is impracticable, as this solvent does not remove ferric sulphocyanate from very strong solutions of alkali sulphocyanate.

In the quantitative determination of iron in sulphocyanates the alumina method is not to be recommended, the precipitate being far too slowly soluble in sulphocyanic acid. We use either the manganese or the cadmium methods. The manganese concentration is carried out in the usual manner, except that as sulphocyanate in alkaline solution at once reduces permanganate to manganese dioxide no reducer is necessary, the solution must be made ammoniacal before adding permanganate and then gently heated to promote precipitation.

Ammonium sulphocyanate, lot *b*, an ordinary c.p. grade, gave the following:

NH <sub>4</sub> SCN	Fe	Per cent Fe	Method
5 g	0.0039 mg	0.000078	Manganese concentration
"	0.0044	0.000088	
	Mean	0.000083	
"	0.0046	0.000092	Cadmium concentration
"	0.0042	0.000084	
"	0.0036	0.000072	
	Mean	0.000083	

*Iodides.*—Soluble iodides give somewhat too low results by the manganese method, but this may be used when the cadmium method is inapplicable. No reducer is necessary, as permanganate at once gives a precipitate in the ammoniacal solution.

Potassium iodide from Kahlbaum gave:

KI	Fe	Per cent Fe	Method
10 g	0.0013 mg	0.000013	Manganese concentration
5	0.0001	0.000002	
5	0.0006	0.000012	
10	0.0030	0.000030	Cadmium concentration
5	0.0012	0.000024	
Average		0.000027	

*Calcium, Strontium, Barium.*—The soluble salts are treated like sodium chloride, the carbonates as described under insoluble carbonates, while the sulphates are heated to dull redness for some time in a porcelain crucible in a current of hydrogen, the resulting sulphides being dissolved in hydrochloric acid and treated as described under sulphides.

*Magnesium.*—The manganese and cadmium methods are applicable in most cases. In the manganese concentration enough ammonia is first added to give a faint precipitate, or at least to make the solution alkaline; for the cadmium precipitation enough ammonium salt should be present to prevent the separation of magnesia.

Magnesium sulphate from Kahlbaum gave:

MgSO <sub>4</sub> ·7H <sub>2</sub> O	Fe	Per cent Fe	Method
10 g	0.0208 mg	0.000208	Manganese concentration
"	0.0214	0.000214	
"	0.0210	0.000210	Cadmium concentration
Mean		0.000211	

*Zinc.*—The cadmium method is naturally inapplicable, and we employ the manganese method, adding enough ammonia to produce a slight permanent precipitate, or, at least, an alkaline reaction; the solution is then treated in the usual manner with permanganate and a reducer. Enough ammonia to redissolve the zinc hydroxide may be added, but in this way we get somewhat too low results.

Zinc sulphate from Kahlbaum gave:

ZnSO <sub>4</sub> ·7H <sub>2</sub> O	Fe	Per cent Fe	Method
10 g	0.0363 mg	0.000363	Supersaturation with ammonia
10	0.0397	0.000397	Neutralization with ammonia
5	0.0191	0.000382	
Mean		0.000389	

*Manganese.*—A little hydrochloric acid is added and then ammonia to alkaline reaction and the solution heated with addition

of either permanganate or a few drops of bromine water. In this case the manganous hydroxide itself serves as a reducer.

Manganese sulphate from Kahlbaum gave:

MnSO <sub>4</sub> .7H <sub>2</sub> O	Fe	Per cent Fe
5 g	0.0121 mg	0.000242
"	0.0133	0.000266
"	0.0131	0.000262
	Mean	0.000257

The salt gave no iron reaction when treated directly with sulphocyanate.

*Permanganates.*—Iron may be separated from permanganates by causing a manganese dioxide precipitate to form in the neutral or alkaline solution.

*Nickel.*—This metal presents a peculiar difficulty. Nickel sulphocyanate is insoluble in amyl alcohol; nickel mercuric sulphocyanate on the contrary is readily extracted from its aqueous solution by amyl alcohol, giving a green solution, the color of which, even in small amounts, partially neutralizes the pink of ferric sulphocyanate, and moreover imparts to it an impure tint. As the sulphocyanic reagent contains mercury it is absolutely essential to remove every trace of nickel from the manganese precipitate. One or two drops of ammonia are added to the nickel solution, enough to produce a slight permanent precipitate, or at least to make the solution alkaline; permanganate and a reducer are then added and the solution boiled. The precipitate is well washed, finally with strong ammonia, dissolved in hydrochloric acid and reprecipitated by permanganate, the second precipitation being also well washed with ammonia. The effect of the double precipitation is shown in the following figures:

Cobalt-free nickel sulphate from Kahlbaum gave:

NiSO <sub>4</sub> .7H <sub>2</sub> O	Fe	Per cent Fe	Method
1 g	0.0303 mg	0.00303	Single precipitation; color impure
"	0.0325	0.00325	
"	0.0334	0.00334	Double precipitation; color pure

*Cobalt.*—The behavior of cobalt with sulphocyanic acid is the exact reverse of that of nickel. Cobalt salts give with strong sulphocyanic acid or sulphocyanates a blue salt which is dissolved by

amyl alcohol, giving a deep blue solution (Vogel's reaction). Mercuric sulphocyanate reagent gives a beautiful blue crystalline double salt, practically insoluble in water and insoluble in amyl alcohol. When this reagent is used not a trace of cobalt passes over into the amylic layer. To the cobalt solution one or two drops of ammonia are added to produce a slight permanent precipitate, and then permanganate, after which the liquid is heated. A reducer is not needed, as the permanganate generates cobaltic oxide, the dark precipitate consisting of a mixture of this with manganese dioxide. This must be washed with ammonia, redissolved in hydrochloric acid, and reprecipitated. The object of the second precipitation is to get rid of most of the cobalt, which gives rise to the blue mercuric salt above referred to, which otherwise remains in the filter and holds back not a little of the iron, as the following figures show.

Cobalt sulphate from Kahlbaum gave:

CoSO <sub>4</sub> .7H <sub>2</sub> O	Fe	Per cent Fe	Method
0.25 g	0.0093 mg	0.00372	Single precipitation
"	0.0089	0.00356	
"	0.0208	0.00832	Double precipitation
"	0.0211	0.00844	
	Mean	0.00838	

*Copper.*—Cupric mercuric sulphocyanate dissolves in amyl alcohol with a yellow color, and even traces of copper in the manganese precipitate suffice to make the color of the amylic solution so impure that no accurate comparison can be made; such traces can be removed neither by washing with ammonia nor by double precipitation. The following method is effective. Enough ammonia is added to give a slight permanent precipitate, and the solution is heated after adding permanganate and a reducer. The washed precipitate is dissolved in hydrochloric acid, run back into the same beaker, the trace of copper precipitated by hydrogen sulphide, and the liquid filtered through the same filter. The iron is thrown out of the filtrate in the usual manner by permanganate, the hydrogen sulphide serving as reducer. The colors obtained in this way are perfectly pure. If necessary, the copper salt may be dissolved in ammonia.

Copper sulphate (Kahlbaum's I) gave:

CuSO <sub>4</sub> .5H <sub>2</sub> O	Fe	Per cent Fe
1.0 g	0.0075 mg	0.000750
2.5	0.0176	0.000704
	Mean	0.000727

*Lead.*—The manganese precipitation is made in a solution of lead salt in the usual manner, after adding enough ammonia to produce a slight permanent precipitate, or to make the solution alkaline. On treating the precipitate, which contains lead dioxide and manganese dioxide, on the filter with sulphocyanic reagent, the small amount of lead sulphocyanate remains behind.

*Cadmium.*—One or two drops of ammonia are added to produce a slight permanent precipitate, and then permanganate and a reducer, and the solution is heated. The addition of ammonia in excess, to redissolve the cadmium hydroxide, presents no advantages.

1.6 g 3CdSO<sub>4</sub>.8H<sub>2</sub>O gave 0.0058 mg Fe or 0.00036 per cent.

*Bismuth.*—We have been unable to devise a method of satisfactorily concentrating iron from bismuth salts. On account of the tendency to give basic salts a neutral or slightly alkaline solution in which a manganese precipitation may be made can not be obtained. Attempts to separate the bismuth as basic salt by dilution failed, because a large part of the iron, often as much as one-half, is carried down with the precipitate. On precipitating as sulphide from acid solution as much as two-thirds of the iron was carried down with the sulphide and could only be extracted by repeated precipitations.

*Mercury.*—Preliminary experiments indicate that iron may be removed from mercuric chloride solution by adding enough ammonia to give a slight precipitate, and then concentrating with manganese. Difficultly soluble or insoluble salts are dissolved in an iron-free sodium sulphide solution and the iron concentrated by cadmium. The results obtained were approximate only and much mercury was carried down with the cadmium sulphide.

*Aluminium.*—Iron is separated from aluminium salts by adding an equal weight of sodium potassium tartrate, which has been freed from iron, and making a cadmium concentration. The well-washed precipitate must be dissolved in nitric acid and the trace of tartrate destroyed by permanganate as described under cadmium sulphide concentration. Other methods, which appear to give less satisfactory results, are to dissolve in an excess of purified sodium hydroxide and concentrate with manganese, or to add an excess of purified sodium

pyrophosphate, make ammoniacal, and concentrate with cadmium. Ammonia alum from Kahlbaum gave:

$\text{NH}_4\text{Al}(\text{SO}_4)_2, 12\text{H}_2\text{O}$	Fe	Per cent Fe	Method
5 g	0.0217 mg	0.000434	Cd conc. in tartrate solution
"	0.0223	0.000446	
	Mean	0.000440	
"	0.0172	0.000344	Mn conc. in sodium hydrate solution
"	0.0153	0.000306	
"	0.0200	0.000400	
"	0.0163	0.000326	Cd conc. in pyrophosphate solution

*Chromium.*—Ammonia precipitates chromic hydroxide from chrome alum even in the presence of a large excess of tartrate; the precipitate does not redissolve on boiling. The same occurs if the chrome-alum solution be first boiled and then cooled before adding tartrate. If, however, the chromic salt and tartrate be boiled together for a moment, ammonia gives no precipitate. In order to separate iron from chromium we add an equal weight of purified sodium potassium tartrate, boil for a moment, cool and concentrate the iron with cadmium, taking care to destroy every trace of tartrate in the washed precipitate by dissolving in nitric acid and oxidizing with permanganate as directed.

Chrome alum from Kahlbaum gave:

$\text{KCr}(\text{SO}_4)_2, 12\text{H}_2\text{O}$	Fe	Per cent Fe
0.25 g	0.0223 mg	0.00892
"	0.0224	0.00896
	Mean	0.00894

*Chromates.*—Iron may be separated from chromates soluble in ammonia by the manganese method.

*Arsenic.*—As ferric hydroxide is readily soluble in ammonia in the presence of either arsenites or arsenates in excess, the manganese precipitation is inapplicable. Cadmium sulphide dissolves to a considerable extent in a solution of an arsenite in ammonium sulphhydrate, as does also iron sulphide. In order to remove the iron completely as sulphide the arsenic must be in the form of an arsenic compound. This is best effected by oxidizing the solution of arsenious acid or acidified arsenite with a slight excess of bromine water and making the cadmium precipitation in the usual manner. The pre-

caution of adding bromine water should be observed even in the case of arsenates. Arsenious sulphide may be dissolved in yellow ammonium sulphide containing enough polysulphide to convert it into the sulpharsenate. The presence of arsenic in the solution in which the second or manganese precipitation is made must be carefully avoided. The cadmium sulphide precipitate is dissolved on the filter in 1-1 hydrochloric acid as usual and any arsenic sulphide running through must be carefully filtered off.

*Solubility of iron sulphide in sulpharsenites.*—To a solution of 1 g carefully resublimed arsenious oxide was added 0.0100 mg Fe, and a cadmium precipitation made in the usual way. Only 0.0010 mg Fe was recovered.

Resublimed arsenious oxide, to which a definite amount of iron was added, gave the following results on oxidizing with bromine water and concentrating with cadmium:

As <sub>2</sub> O <sub>3</sub>	Fe added	Fe recovered
2 g	0.0150 mg	0.0167 mg
1	0.0100	0.0093
1	0.0200	0.0210
1	0.0200	0.0210

Sodium arsenate from Kahlbaum, without addition of bromine water, gave:

Sodium arsenate	Fe	Per cent Fe
5 g	0.0082 mg	0.000164
"	0.0070	0.000140
"	0.0066	0.000132
	Mean	0.000145

*Antimony.*—An ammoniacal solution of antimony trioxide dissolves small but appreciable amounts of ferric hydroxide. An ammoniacal solution of common potassium antimonate to which iron has been added dissolves traces only, but if it has been previously oxidized with bromine water to remove traces of the lower oxide no iron can be detected in the solution. This fact can not be made use of, however, for a manganese concentration, as the oxide must be dissolved in tartaric acid. Ammoniacal sulphantimonite solution dissolves notable amounts of iron sulphide,<sup>14</sup> and the solution has not the green color characteristic of colloidal iron sulphide; it also dissolves cadmium sulphide. Ammoniacal sulphantimonate, on the

<sup>14</sup> See Storch, Ber., 16, p. 2015; 1883.

contrary, is colored green by a trace of iron sulphide, and this is easily extracted by agitating with cadmium sulphide. On diluting an acid solution of antimonious acid or precipitating by hydrogen sulphide, the greater part of the iron is carried down with the precipitate.

These facts indicate the method to be followed in extracting traces of iron. The antimony compound is dissolved in iron free sodium potassium tartrate, oxidized with bromine and cadmium solution added, followed by ammonium sulphhydrate. Antimony trisulphide is dissolved in yellow, antimony pentasulphide in colorless ammonium sulphide, and cadmium solution added. The mixture is allowed to stand half an hour with frequent stirring. The cadmium precipitate is washed with water containing ammonium sulphide, dissolved in nitric acid, and precipitated by manganese, care being taken to destroy in the acid solution any remaining traces of tartaric acid.

We have been unable to obtain absolutely iron-free antimonious chloride, as some iron passes over on distillation, and we have therefore used the ordinary article, dissolved in sodium potassium tartrate.

SbCl <sub>3</sub>	Fe	Per cent Fe
2.5 g	0.0079 mg	0.000316
"	0.0074	0.000296
"	0.0070	0.000280
	Mean	<u>0.000297</u>

*Tin.*—We have been unable thus far to discover a satisfactory method of separating traces of iron from tin. The manganese concentration is impossible, as ammonia precipitates the hydroxide before neutrality is reached. A solution of stannic hydroxide in potassium hydroxide readily dissolves ferric hydroxide which is not precipitated on boiling. If stannic chloride be added to an excess of ammonia, a clear colloidal solution is obtained, but it appears to be impossible to produce a manganese precipitate in this. The sulphide concentration also offers difficulties, as a solution of stannic sulphide in ammonium sulphide dissolves both cadmium and iron sulphides readily under certain conditions.

*Platinum.*—The concentration of iron from platinum solution as sulphide is impracticable, owing to the difficult solubility of platinum sulphide in ammonium sulphide. We are therefore limited to concentration as hydroxide. The manganese method is unsatisfactory,

because manganese dioxide carries down a considerable amount of platinum from which it is very difficult to free it completely, either by reprecipitation, by hydrogen sulphide, or by reduction with formic acid. Traces of platinum exercise an extremely prejudicial effect on the colorimetric determination as they invariably pass over into the amyl layer and impart a yellowish color to the ferric sulphocyanate. We have found the following method to be rapid and to give satisfactory results. To the hot platinic chloride solution, which should be sufficiently dilute not to deposit ammonium chloroplatinate, are added a few milligrams alum and ammonia in excess. The washed alumina precipitate is dissolved in hydrochloric acid, enough sodium hydroxide is added to redissolve the alumina, and the iron is carried down by manganese dioxide. The color obtained from this precipitate is entirely pure.

0.2 g platinic chloride (10 per cent solution from Kahlbaum) gave 0.0205 mg Fe or 0.01025 per cent Fe.

20 cc 10 per cent platinic chloride solution was freed from iron by alumina, a definite amount of iron was added to the filtrate and concentrated as before.

Fe added	Fe found
0.0150 mg	0.0161 mg
0.0150	0.0150

#### SUMMARY.

1. The ferric sulphocyanate is extracted from its aqueous solution with a mixture of amyl alcohol and ether, using two cylinders, one of which contains the iron to be determined; standard iron solution is then added to both cylinders from two burettes, the difference of the readings indicating the amount of iron sought. The final result is reached by averaging a series of readings.

2. A form of colorimeter is described, adapted to the use of extracting liquids.

3. The iron is concentrated and freed from all interfering substances by evaporation or by precipitation as hydroxide or sulphide, using a suitable substance to collect and carry down the trace of precipitate; it is then dissolved in free sulphocyanic acid.

4. The fading out of the color of the ferric sulphocyanate is prevented by the use of persulphate, and the formation of discolored

amylic solutions is prevented by saturating the sulphocyanic acid with mercuric sulphocyanate.

5. Special directions are given for concentrating traces of iron from various substances, with analytical data.