These blocks are very convenient in qualitative analysis, and in the preparation of substances. The filter-paper containing the wet precipitate, or substance to be dried, is placed on the smooth side of the block, and after a short time much of its moisture is absorbed. One or more filter-papers may be placed between the substance and the block if too intimate contact of the substance and the block be not desired.

CHEMICAL LABORATORY OF THE BROOKLYN
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THE VOLUMETRIC DETERMINATION OF ZINC AND A NEW INDICATOR FOR FERROCYANIDE.[1]

BY GEORGE C. STONE.

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BEFORE titrating with ferrocyanide it is necessary to separate all the metals of the iron group. Rapid and accurate methods are known for all but manganese; the methods commonly used in gravimetric analysis take too long; and I have been unable to get even passably accurate results on the New Jersey ores by the method of Messrs. von Schultz and Low,[2] or the modification of it proposed by Mr. Hinman.[3] Not finding any satisfactory method of separation I have tried titrating the two together, determining the manganese in a separate portion, by titration with permanganate, and taking the zinc by difference, and find the method easy, rapid, and sufficiently accurate for technical work.

Indicators.—Uranium salts are generally used as indicators for ferrocyanide and are fairly satisfactory when titrating zinc alone, though the sensitiveness of the test varies very much with the amount of free acid present. In titrating manganese, uranium cannot be used in the usual manner because it reacts on the precipitated manganese ferrocyanide; good results can be obtained by its use by putting drops of the solutions to be tested, on filter-paper and allowing them to run together so that the uranium does not touch the precipitate; the reaction develops very slowly making the titration very tedious. Ferric chloride, another

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[1] Read before the N. Y. Section, March 9, 1895.

[2] Colorado Scientific Society, June 11, 1892; *J. Anal. Appl. Chem.*, 6, 682.

[3] S. of M. 2, 14, No. 1; *J. Anal. Appl. Chem.*, 6, 682.

commonly used indicator, proved entirely unsuitable. Copper sulphate was found to be about as delicate as uranium, but open to the same objections. Cobalt nitrate was by far the best indicator tried; the delicacy of the reaction is not affected by as much as one part of concentrated hydrochloric acid in fourteen of water; the reaction shows instantly and cobalt does not react on the precipitates. The cobalt solution should be quite dilute; a drop of it is placed on a white porcelain plate, and a drop of the solution to be tested by it, so that the drops touch but do not mix; an immediately shown faint greenish line, at the junction of the two, marks the end reaction. If the drops mix it is impossible to see the reaction; if the color does not show at once the end is not reached. Often when near the end the color will show after standing a few seconds, but at the actual end-point it shows as soon as the drops touch.

Manganese must be titrated at the ordinary temperature of the laboratory; at higher temperatures the amount of ferrocyanide used varies with the temperature. The composition of the precipitate is not normal, but is Mn_3Cfy_2; that is, an amount of ferrocyanide that will precipitate four atoms of zinc will only precipitate three of manganese.

Ferrocyanide Solution.—The best strength was found to be about thirty grams to the liter. It is standardized by titrating solutions containing known amounts of zinc or manganese, using about one-tenth gram, making slightly acid with hydrochloric acid and keeping the solution at about the volume used in the analysis.

The amount of ferrocyanide necessary to give a reaction with cobalt in this volume of acidulated water must be determined, and the amount so found deducted for each titration; it is about seven-tenths cc. for a volume of 140 cc.

Permanganate Solution.—1.99 grams of crystallized potassium permanganate to the liter gives a solution, one cc. of which equals 0.001 gram of manganese. It is standardized in the usual manner by iron, and the strength obtained by multiplying the iron value by 0.294646 (ten iron equals three manganese).

Sulphide ores are best dissolved in hydrochloric acid and potassium chlorate, taking care to have sufficient acid present to keep all the manganese in solution. Oxides, carbonates, and silicates can be dissolved in hydrochloric acid and oxidized by boiling with potassium chlorate. Ores containing franklinite or rhodonite must be fused with sodium carbonate and evaporated to dryness with hydrochloric acid to decompose them thoroughly, then taken up with a slight excess of hydrochloric acid, and boiled with potassium chlorate to oxidize the iron.

Lead alone need not be separated; copper can be precipitated by lead; or lead and copper can both be precipitated by aluminum. Cadmium, if present, must be precipitated by hydrogen sulphide and the solution oxidized after filtering out the precipitate.

Iron and alumina are best separated by barium carbonate; the solution should, preferably, not contain a very large amount of free acid; the iron must all be ferric; the solution must not be warmed and, most important, the barium carbonate must be entirely free from alkaline carbonates and hydroxides, barium hydroxide, and ammonium salts. No barium carbonate in the market answers these requirements, but the ordinary chemically pure salt can easily be purified so that it answers perfectly. Select a salt that is free from ammonia (*e. g.*, Merck's), suspend it in water, and warm for several hours with two or three per cent. of its weight of barium chloride; this converts the alkaline carbonate present to chloride; the small excess of soluble barium salt does not interfere.

The thoroughly oxidized solution of the ore should be washed into a 500 cc. flask, cooled, and barium carbonate, suspended in water, added until the precipitate curdles; an excess of barium does no harm. The change in the appearance of the precipitate is very marked. Pour into a beaker, mix thoroughly, let it settle, decant the clear liquid through a dry filter, and take portions of 50, 100, or 200 cc. for each titration. The solution must be filtered from the iron at once and should be titrated as soon as filtered. If it be necessary to let the solution stand it must be made slightly acid or some zinc will precipitate. One portion, which should contain between 0.01 and 0.04 gram of manganese, is diluted to about 200 cc., heated nearly to boiling in a white porcelain dish, and titrated rapidly with permanganate with very vigorous stirring. The greater part of the permanganate necessary should be added as rapidly as possible or the manganese oxide is apt to stick to the sides of the dish, making it difficult to see the pink color of the solution at the end. To obtain satisfactory results, the titration must be performed rapidly, so that, if the percentage of manganese be not approximately known, it is better to make a preliminary titration, adding one or two cc. at a time.

In a second portion, made slightly acid[1] with hydrochloric acid, the zinc and manganese are titrated together cold by ferrocyanide; if the manganese be present in appreciable quantity the color of the precipitate will darken as the ferrocyanide is run in and quite suddenly change to a light greenish yellow shortly before the end is reached. It is not necessary to begin to test the solution with cobalt until one or two cc. after the lightening of the precipitate; it should then be tested after the addition of each few drops. If there be little or no manganese present and the percentage of zinc be not approximately known, it saves time to make a preliminary titration, adding one or two cc. at a time. If lead be present the solution must be made quite strongly acid[1] before titrating to prevent the lead from being precipitated as ferrocyanide; five cc. of hydrochloric acid in 100 cc. of solution is sufficient.

The calculation of the results is best shown by an example: One cc. of the ferrocyanide used equaled 0.00606 gram of zinc or 0.00384 gram of manganese; one cc. of the permanganate equaled 0.001 gram of manganese; two and one-half grams of the ore were dissolved and the iron precipitated and filtered out as described above; fifty cc. of the solution was diluted, heated, and titrated with permanganate, requiring 18.45 cc., equal to 7.38 per cent. of manganese. 100 cc. titrated with ferrocyanide required 27.85 cc. The previous titration had shown that there was 0.0369 gram of manganese present which would require 9.61 cc. of ferrocyanide; deducting this left 18.24 cc. for the zinc, equal to 0.11053 gram, or 22.11 per cent.

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[1] Manganese ferrocyanide is soluble in a large excess of hydrochloric acid, which should therefore be avoided; or the results will be low if much manganese be present. Five cc. of concentrated hydrochloric acid added to 100 cc. of a solution containing 0.03 gram of manganese did not cause any appreciable error. Ten cc., however, prevented the precipitation of any manganese.

This method has been used for some months in the laboratory of the New Jersey Zinc and Iron Co., with very satisfactory results. The following table shows how this compares with the ordinary gravimetric methods.

Material Analyzed.	Zinc		Manganese	
	Gravimetric.	Volumetric.	Gravimetric.	Volumetric.
N. J. ore	22.05	22.11	7.58	7.38
“ “	26.58	26.48	N. D.	11.98
Brass	5.06	5.12	O.	O.
N. J. ore	22.50	22.47	N. D.	11.55
“ “	30.75	30.82	“	7.54
Blende	38.28	38.18	“	0.14
Willemite	55.55	55.68	O.	O.
Residuum	4.60	4.79	12.23	12.30
“	4.29	4.44	N. D.	11.99
“	9.15	8.99	“	11.61
Tailings	2.12	2.05	6.04	6.00
Middles	15.15	15.24	9.24	9.14

In conclusion I wish to express my thanks to Mr. D. A. Van Ingen, who has done much of the experimental work necessary in testing the method.

SOME PHYSICAL ASPECTS OF THE NEW GAS, ARGON. THE IDEAL THERMOMETRICAL SUBSTANCE FOR HIGH TEMPERATURES.

BY W. R. QUINAN.

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THE discovery, by Lord Rayleigh and Professor Ramsay, of a new gaseous constituent of the atmosphere, has a many-sided bearing upon science and excites the interest of the whole world.

While there may be mooted questions yet to be decided in regard to the elementary constitution of argon, certain extraordinary conclusions seem to have been reached. In the sense of the kinetic theory, it is a monatomic gas; that is, if heat be applied to it, all or very nearly all of this heat will be expended in dynamic energy. The kinetic theory, whatever may be its shortcomings, is certainly the most intelligible hypothesis now at our command, both to explain and to expound the ideal behavior of matter in its simplest form—the gaseous. The behavior, it must be remembered, is independent of the theory. It is the fruit of experimental research.