V.—*Observations on the Use of Permanganate of Potash in Volumetric Analysis, and on the Estimation of Iron in Iron Ores.*

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Of all chemical reagents applicable to volumetric analysis, probably the most delicate is permanganate of potash. Hence its extensive application not only for the estimation, directly, of a reducing material, but indirectly of an oxidising material, by first mixing that material with a known weight of a reducing agent, and determining the excess of the latter.

Various circumstances, however, vitiate the results thus obtained. One of these is the production, by the application of permanganate, of a coloured material which obscures the exact point of peroxidation.

An important case of this kind is iron, when present as ferrous chloride. The yellow colour of the resulting ferric chloride so hinders the determination of the exact point of peroxidation, that the use of permanganate in the analysis of iron ores has, I believe, been entirely superseded by that of bichromate of potash. If the iron is present as ferrous sulphate, of course no such difficulty exists; but in the analysis of almost every variety of iron ore, hydrochloric acid has to be employed as the solvent, rather than sulphuric acid.

This hindrance to the use of permanganate with ferrous chloride may, however, be overcome by a very simple expedient, namely, the use of artificial light instead of daylight. Viewed by the light of a candle, as radiated from a white background, the intensity of the yellow colour of ferric chloride is greatly reduced. A solution containing one part of metallic iron (or about three parts of ferric chloride) in 400 parts of water is almost colourless. In such a solution, when viewed by candle light, an exceedingly minute trace of permanganate produces a distinct coloration, but in daylight a much larger quantity is necessary to produce a decided effect.

By this method of manipulating, iron present as chloride may be estimated with even greater accuracy than by bichromate and ferricyanide. The operation may also be conducted with greater facility and dispatch; a circumstance of no small importance in the technical laboratory. Another advantage possessed by permanganate over bichromate, in the estimation of iron, is that it allows of the use of zinc instead of sulphurous acid as the preliminary reducing agent. As a solution of zinc produces a white precipitate with a very dilute solution of ferricyanide of potassium, the presence of a large quantity of zinc prevents the detection of a minute trace of ferrous oxide by that

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reagent. Hence sulphurous acid has to be employed when bichromate is used, although zinc is more effective, and provided titanous acid is not present, more convenient.

Various methods have been recommended for standardising the solution of permanganate. A recent experimenter, M. Berthelot, considers oxalic acid preferable to iron or any ferrous preparation. The slowness of the action, when approaching complete oxidation, is an important objection to the use of oxalic acid.

I have no hesitation in giving the preference to arsenious acid, as the standardising material. In respect of the facility with which it may be obtained in a state of absolute purity, and preserved without change, arsenious acid is certainly preferable to any preparation of iron. But a difficulty presents itself in the tardiness of the action when near completion, even although hydrochloric acid is present in considerable excess. The last traces of arsenious acid reduce permanganic acid, not to manganous oxide, but to a higher oxide, commonly known as manganic oxide, which gives a brownish tinge to the liquid. This difficulty, however, may be easily overcome. After adding enough permanganate to develop a faint pink colour (a proof that all arsenious acid is oxidised), I introduce a small quantity of standard solution of ferrous sulphate; this immediately reduces the manganic oxide, and causes the disappearance of the brownish colour. The excess of ferrous sulphate is then peroxidised by the permanganate. By this conjunction of arsenious acid with iron, we have the advantage of combining the best material as regards purity with the best material as regards delicacy for the finishing touch.

I may observe, that for the estimation of iron I employ a solution of permanganate containing 2.21 grams per litre, of which about 114 c.c. correspond with 0.5 gram metallic iron. For standardising I use a solution of arsenious acid containing 4.42 grams per half litre; the arsenious acid being first dissolved in caustic soda, and this supersaturated with hydrochloric acid: 50 c.c. of this solution correspond with 0.5 gram metallic iron.

If the quantity of iron ore operated on is not less than 1.0 gram, and the ore not of the worst quality, then to the reduced solution, filtered in an atmosphere of carbonic acid gas, 100 c.c. of the above permanganate solution may be freely introduced by means of a pipette, which is itself used as a stirrer, the remainder being applied from a burette in artificial light. The burette may also be used as a stirrer, its extremity being elongated for that purpose to a couple of inches below the glass stopper. With a moderate excess of hydrochloric acid, at ordinary temperature, not the slightest odour of peroxide of chlorine, or similar gas, is perceptible. If a brownish colour appears on the first addition of permanganate, more hydrochloric acid has to be

added. It is convenient to have at hand, for comparison, a beaker containing solution of ferric chloride of similar strength to that operated on; also another to retain a portion of the liquid in case the permanganate is added in excess. When the peroxidation is complete, half a drop of the permanganate produces, in artificial light, a decided change of colour.

Application of heat is not only unnecessary, but has to be avoided, owing to the greater intensity of colour of ferric chloride when hot than when cold, both in daylight and in artificial light. It may not be uninteresting to observe, that if a solution of ferric chloride containing 1 of iron in 100 of water is heated to near the boiling point, the intensity of its colour is so much increased, that 7 or 8 volumes of boiling water have to be added to reduce the colour to that of the cold liquid.