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INORGANIC ANALYSIS.

Quantitative Estimation of Arsenic by the Gutzeit Method. C. R. Sanger and O. F. Black. (*Journ. Soc. Chem. Ind.*, 1907, **26**, 1115-1123.)—If the arsenuretted hydrogen be made to act along the surface of the sensitised paper instead of against it, there is no difficulty in differentiating between the stains caused by various amounts of the gas. Cold-pressed Whatman drawing-paper gives better results than filter-paper. It should be cut into strips of 4 mm. in width, which are sensitised by being drawn repeatedly through a 5 per cent. solution of recrystallised mercuric chloride, then dried on a horizontal rack of glass rods, cut into lengths of 7 cm., and kept in the dark in a bottle containing calcium chloride, covered with a layer of cotton-wool until required for use. The apparatus consists of a 30-c.c. bottle, closed by a pure rubber cork, through which is passed a small thistle funnel, reaching nearly to the bottom, and also an outlet tube for the gas. This tube is bent first at a right angle and then back again in the form of a ⊏, and is connected by means of a rubber stopper with a bulb tube about 12 mm. in diameter, terminating in a longer tube with an internal diameter slightly over 4 mm. The bulb of the tube is loosely filled with dry cotton-wool, and a strip of the sensitised paper slipped into the open end of the tube to a definite distance. The bottle is charged with 3 grams of arsenic-free zinc, 15 c.c. of pure dilute hydrochloric acid (1 : 6) introduced through the funnel, and the hydrogen allowed to pass over the paper for at least ten minutes. The solution (not exceeding 15 c.c.) of the substance under examination is now introduced, and in the presence of arsenic the coloured deposit appears on the paper in a few minutes, and reaches its maximum intensity within thirty minutes. The amount of arsenic may then be found by comparison with standard bands prepared from known quantities of arsenic. A set of standards may be kept without much alteration for some months, if sealed up in glass tubes about 5 mm. in diameter, containing at the end a little phosphorus pentoxide covered with dry cotton-wool. If the colour bands be developed by treatment with hydrochloric acid (1 : 1), they are rendered somewhat more permanent, whilst development with N-ammonia solutions changes them into black stains, which are much more permanent than the originals. They should, however, be sealed up in glass tubes containing a little powdered fresh quicklime. After ten or twelve estimations, the atmosphere in the deposition tube becomes too moist, and it is necessary to replace the cotton-wool in the bulb tube ; otherwise the bands on the paper will be too short. Hydrogen sulphide may be eliminated by inserting a strip of lead acetate paper into the deposition tube. Small amounts of antimony do not prevent the detection of arsenic, but may interfere with its estimation. In the case of arsenates, the slower reduction to arsenuretted hydrogen causes the bands on the paper to be smaller than would result in the same time from an equivalent quantity of arsenious acid. An approximate valuation may be made in such cases by comparing the bands with standards prepared from known quantities of arsenic acid or by multiplying the readings of the ordinary standard bands by 2 or 2·5. For more accurate work, however, the solution containing an arsenate (or after oxidation with nitric acid) should be treated with sulphur dioxide solution in sufficient quantity to reduce the arsenate to arsenite, and the excess of sulphur

dioxide expelled by partial evaporation of the liquid, care being taken not to carry the evaporation so far as to cause loss of arsenic when chlorides are present. The method is said to be capable of detecting $\frac{1}{15000}$ mgm. to $\frac{1}{20000}$ mgm. of arsenic, but $\frac{1}{1000}$ mgm. is suggested as a working limit.   C. A. M.

Reduction of Arsenic Trisulphide and Pentasulphide to Arsenic Disulphide. R. Ehrenfeld. (*Ber. deut. Chem. Ges.*, 1907, **40**, 3962-3965.) — It sometimes happens that in following out the ordinary routine of qualitative analysis, antimony instead of arsenic is found when tin is also present in the mixture. When the sulphides of the tin group are digested with ammonium carbonate, and the filtrate is acidified, the arsenic appears in the form of an orange-red precipitate instead of a yellow one. It is now proved that this orange precipitate is arsenic disulphide (As_2S_2) which may readily be prepared by heating either the trisulphide or the pentasulphide with a solution of stannous chloride in hydrochloric acid.

                                                          J. F. B.

Note on the Volumetric Estimation of Bismuth. R. Ehrenfeld. (*Zeit. anal. Chem.*, 1907, **46**, 710-711.)—The author has endeavoured to render the phosphate method for the estimation of bismuth volumetric (*Cf.* ANALYST, 1906, **31**, 54); the bismuth solution, containing a slight excess of nitric acid, was precipitated with a measured excess of sodium phosphate solution, and the excess of the latter titrated back with uranium acetate after the addition of sodium acetate, but the difficulty of observing the end-point of the titration caused the results to be untrustworthy. The quantities found varied from -9 to $+25$ per cent. of the amounts of bismuth trioxide taken.   W. P. S.

The Constants and Variables of the Parr Calorimeter. S. W. Parr. (*Journ. Amer. Chem. Soc.*, 1907, **29**, 1606-1622.)—The author discusses the accuracy of the results given by his calorimeter (ANALYST, 1901, **26**, 52 ; 1907, **32**, 62). He shows that with proper care the results obtained are within 1, or at most 2 per cent. of those given by the Mahler-Attwater bomb. In cases where unburnt carbon is left, this should be filtered off, weighed, and taken into account. He finds that the empirical factor, 73 per cent., by which the results must be multiplied, to be correct for both carbon and hydrogen, and to agree well with the theoretical heat of formation of sodium peroxide. As accelerator, he prefers potassium chlorate ; if 0·5 gram of this is used, 0·040° C. must be deducted from the observed rise of temperature, whilst the correction is 0·108° for 1 gram of the reagent. A mixture of 2 parts of potassium persulphate with 1 of ammonium persulphate may also be used ; the correction amounts to 0·197° per 0·5 gram. Using 0·5 gram of the fuel, the other corrections which must be made are : 0·006° for every 1 per cent. of sulphur ; 0·001° for every 1 per cent. of silicious ash ; 0·0033° for every 1 per cent. of combined water, amounting to about 0·033° for bituminous coals, 0·066° for black lignites, and 0·111° for brown lignites ; and 0·008° for the ignition wire.

The author mentions that " pure " naphthalene generally contains appreciable quantities of sulphur.   A. G. L.

Estimation of Carbon Monoxide in Atmospheric Air. J. L. R. Morgan and J. E. McWhorter. (*Journ. Amer. Chem. Soc.*, 1907, **29**, 1589-1592.)—In the estimation of carbon monoxide by passing it over heated iodine pentoxide, the authors find that traces of animal fat, such as might be derived from the lubricant used with glass stoppers, react violently with the pentoxide at 100° C., or even less. Hence this reagent should be contained in glass tubes, the ends of which are drawn out after filling. The authors work at a temperature of 150° C., and pass the iodine and carbon dioxide, products of the reaction between iodine pentoxide and carbon monoxide, first through potassium iodide solution, and then through barium hydroxide solution. A check is obtained on the results by titrating both the iodine obtained and the residual barium hydroxide. Moreover, by passing the air through a barium hydroxide tube before it enters the purifying chain leading to the iodine pentoxide tube, the carbon dioxide in the air may be determined on the same sample. A. G. L.

Adsorption of Iodine by Carbon. Oliver C. M. Davis. (*Trans. Chem. Soc.*, 1907, **91**, 1666.)—The adsorption of iodine, dissolved in various organic solvents, by means of animal, sugar, and cocoa-nut charcoal, has been definitely proved to consist of a surface condensation and a diffusion into the interior of the carbon, since the adsorption is rapid at first until a " surface equilibrium " is produced, and then proceeds slowly for lengthened periods. The effect of temperature is small, but the time allowed has a marked influence on the adsorption. The adsorption values of animal- and sugar-carbon are approximately equal, and mainly due to surface condensation, while that of cocoa-nut carbon is much smaller, and due chiefly to diffusion into the interior. A. R. T.

Two Volumetric Methods for the Estimation of Chromium. A. W. Gregory and J. McCallum. (*Journ. Chem. Soc.*, 1907, **91**, 1846-1849.)—In the absence of manganese, 20 c.c. of a 1 per cent. solution of silver nitrate and 10 grams of ammonium persulphate are added to the nitric acid solution of chromium. The liquid is then boiled for five minutes, when a few c.c. of a dilute solution of manganese sulphate are added. If any persulphate remains undecomposed, a pink colour will be produced, which is just destroyed by the addition of hydrogen peroxide, drop by drop. After once more heating the liquid to boiling, it is cooled and titrated with ferrous sulphate and standard potassium bichromate in the usual manner.

If manganese is present, the nitric acid solution is boiled, as before, with silver nitrate and ammonium persulphate. A quantity of ammonium chloride is then added sufficient to precipitate nearly all the silver as chloride. On boiling again, the permanganic acid is decomposed with formation of the hydrated peroxide. After making the liquid up to a definite volume, this is filtered off on an asbestos filter, and chromium determined in half the filtrate as above. A. G. L.

Rapid Analysis by Electrolysis without Rotating Electrodes. F. C. Frary. (*Journ. Amer. Chem. Soc.*, 1907, **29**, 1592-1596.)—Electrolysis can be rapidly carried out with stationary electrodes by circulating the liquid. This is

effected by surrounding it by a magnetic field. The author describes two forms of apparatus, both of which can be obtained from the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin. In the first, 500 turns of 1·5 mm. copper wire are wound on a copper cylinder, 6 cm. in diameter and 11 cm. high, with sheet-iron flanges. A hollow iron cylinder, 4 cm. high, with walls 1 cm. thick, stands in the lower part of the copper cylinder. The solenoid is enclosed in an iron mantle 2 mm. thick. The beaker in which the electrolysis is carried out is placed inside the solenoid, on the top of the iron cylinder. A cylinder of platinum gauze is preferably used as cathode ; it should fit the beaker fairly closely. The anode may be a spiral wire in the centre of the beaker. The solenoid will take a current of up to 5 amperes, and is generally connected in series with the electrodes. As heat is developed, the beaker may be water-cooled if necessary.

The second form of apparatus is designed for use with a mercury cathode. The bottom of the beaker is given an annular form and rests on the solenoid, the iron core of which extends upwards into the central space. The beaker is surrounded by an iron ring acting as the other pole of the electro-magnet.   A. G. L.

The Ignition Temperatures of Gaseous Mixtures. K. G. Falk. (*Journ. Amer. Chem. Soc.*, 1907, **29**, 1536-1557.)—The ignition temperatures of a number of gaseous mixtures were determined by suddenly compressing the gases contained in steel cylinders until explosion occurred. The compression was effected by dropping a weight on a piston fitting the cylinder, and was so rapid as to be adiabatic ; consequently, the temperature reached could be calculated from the initial and final pressures. To eliminate various errors, four pieces of apparatus, holding different quantities of gas, were used, but the results obtained agreed very closely with each other. The effect of the pressure on the ignition temperature is disregarded, but should be small. The following table shows some of the results obtained :

Mixture.	Ignition Temperature.	Mixture.	Ignition Temperature.
$4H_2 + O_2$	878° C.	$6CO + O_2$	994° C.
$2H_2 + O_2$	813° C.	$4CO + O_2$	901° C.
$H_2 + O_2$	787° C.	$2CO + O_2$	874° C.
$H_2 + 2O_2$	803° C.	$CO + O_2$	904° C.
$H_2 + 4O_2$	844° C.	$H_2 + O_2 + CO$	812° C.

The ignition temperature of mixtures of hydrogen, oxygen, and nitrogen can be calculated from the (empirical) formula : $T = T_c + 30n$ (*a*), where T^c is the ignition temperature as given by the above table, and n equals the volume of inert gas divided by the volume of H_2 or of O_2, whichever is the smaller. The calculated results agree well with those observed. Similarly, the ignition temperature of mixtures of carbon monoxide, oxygen, and nitrogen can be found from the formula : $T = T_c + 80n'$ (*b*), where T_c is the ignition temperature as shown by the table, and n'

equals the volume of inert gas divided by the volume of carbon monoxide. For mixtures of hydrogen, carbon monoxide, and oxygen, the ignition temperatures should be calculated according to both the above equations, assuming in one case that hydrogen is an inert gas, in the other that carbon monoxide is inert. The lower of the two results found will approximate closely to the observed ignition temperature.

The author also shows the reaction between hydrogen and oxygen to be bi-molecular, hydrogen peroxide probably being the first product, and that between carbon monoxide and oxygen to be trimolecular. With excess of hydrogen or of carbon monoxide present, the reactions do not follow any simple law of chemical kinetics. The velocity coefficient per 10° C. rise in temperature is calculated to be 1·31 at 800° C. and 1·13 at 900° C. for the reaction between hydrogen and oxygen, and 1·24 at 900° C. and 1·14 at 1000° C. for that between carbon monoxide and oxygen.
A. G. L.

The Occurrence of Helium in Natural Gas and the Composition of Natural Gas. H. P. Cady and D. F. McFarland. (*Journ. Amer. Chem. Soc.*, 1907, **29**, 1523-1536.)—Analysis of forty-one samples of natural gas from various parts of the United States showed helium to be present in every case except one. Its quantity varied from a trace up to 1·84 per cent., and tends to increase, although not directly, with that of the nitrogen. It was found possible to trace lines of "iso-helium" and "iso-paraffin" content across the State of Kansas, these lines following approximately the lines of outcrop of the various geological strata. The helium was isolated by absorbing the other gases not liquefied by liquid air in cooled cocoanut charcoal, according to Dewar's method. The authors find that this absorbs hydrogen rather freely, neon much less than hydrogen, and helium practically not at all. Some typical analyses are given in the following table:

Locality.	Oxygen.	Carbon Dioxide.	Olefines, etc.	Carbon Monoxide.	Methane.	Ethane.	Hydrogen.	Helium.	Nitrogen.
Dexter, Kansas ...	0·20	—	—	—	14·85	0·41	trace	1·84	82·70
Garnett, Kansas...	trace	0 20	0·16	—	94·30	0·36	—	0·37	4·61
Arkansas City, Kansas ...	0·20	0·10	0·10	—	81·10	11·95	—	0·159	6·39
Blackwell, Okla....	—	—-	0·61	—	83·40	10·31	0·33	0·16	5·19
Sheffield, Mo. ...	0·20	0·83	0·50	0·10	92·90	—	—	0·041	5·43
Kansas City, Mo...	0·10	0·60	1·20	0·20	87·20	7·03	—	0·013	3·65
Butler, Ohio ...	0·05	—	0·40	—	70·00	16·75	0·27	0·15	12·38
Marion, Ind. ...	—	0·73	0·86	—	77·40	14·18	—	0·167	6·66
Morgantown, W. Va.	—	0·24	0·65	—	88·10	7·37	0·25	0·09	3·60
Jennings, La. ...	1·81	1·80	0·80	0·40	88·40	1·03	—	trace	5·76
Los Angeles, Cal.	2·86	6·68	0·20	0·25	83·70	—	—	—	6·31

The last two samples contained air. In a sample from Bartlesville, Ind. Terr., helium was found to be present, but its amount was not determined.   A. G. L.

Volumetric Estimation of Lead. H. Bollenbach. (*Zeit. anal. Chem.*, 1907, **46**, 582-588.)—In the method proposed the lead solution is titrated with potassium permanganate. The lead solution is first treated with sodium hydroxide until the precipitate which forms is redissolved, and the whole is then diluted to a known volume. Fifty c.c. of this solution are run slowly from a pipette into a measured volume (which must be an excess) of standard permanganate solution placed previously, together with about 400 c.c. of hot water and 5 c.c. of 8 per cent. sodium hydroxide solution, in a 500-c.c. flask. During the addition of the lead solution the mixture is well agitated. The excess of permanganate is then titrated back by means of $\frac{N}{10}$ lead nitrate solution. The titration is complete when the violet coloration disappears. The reaction proceeds according to the equation :

$$6Pb(NO_3)_2 + 2KMnO_4 + 12NaOH = 2MnO_2 + 3Pb_2O_3 + 2KOH + 12NaNO_3 + 5H_2O.$$
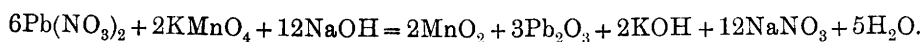
The permanganate solution is standardised on $\frac{N}{10}$ lead nitrate solution. The results are not influenced by the presence of chlorides, bromides, or sulphates, but iodides, sulphides, acetates, nitrites, arsenic and mercurous salts, and other substances which reduce permanganate, must not be present.   W. P. S.

Volumetric Estimation of Magnesium. L. Rosenthaler. (*Zeit. anal. Chem.*, 1907, **46**, 714-716.)—The magnesium is precipitated in ammoniacal solution by the addition of standard potassium hydrogen arsenate solution, and the excess of the latter is titrated after the removal of the magnesium ammonium arsenate by filtration. The magnesium solution is placed in a graduated flask, a measured excess of potassium hydrogen arsenate (KH_2AsO_4) solution is added, and the mixture is diluted to a known volume with 10 per cent. ammonia. After three hours, the solution is poured through a dry filter, and a definite quantity (as large as possible) of the filtrate is evaporated to dryness on the water-bath. The residue is taken up with the least possible quantity of water, the solution is poured into a stoppered flask, and the basin is rinsed with a cold mixture of equal parts of sulphuric acid and water, or with concentrated hydrochloric acid, the rinsings being also added to the flask. A concentrated potassium iodide solution is now added to the acid solution ; usually a precipitate forms (if not, a little more acid is added), and is dissolved by the addition of just sufficient water. After standing for fifteen minutes, the liberated iodine is titrated with thiosulphate solution (*cf.* ANALYST, 1906, **31**, 416). The potassium hydrogen arsenate solution should contain about 9 grams of the salt per litre, and it is standardised on the thiosulphate solution. The quantity of arsenate precipitated by the magnesium is thus found in terms of thiosulphate solution, and the magnesium is calculated from the latter. Each c.c. of $\frac{N}{10}$ thiosulphate solution is equivalent to 0·002018 gram of magnesia (MgO). The proportion of the quantity of filtrate taken to the total volume is, of course, taken into account in the calculation.   W. P. S.

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Modifications for Shortening Volhard's Method for the Estimation of Manganese. E. W. Mayer. (*Zeits. angew. Chem.*, 1907, **20**, 1980-1981.)—The

method originally described by Volhard for the estimation of manganese in iron and steel involves a considerable expenditure of time and labour, and various proposals have been made with a view to its simplification. The author has investigated the four modified methods described below, comparing the results obtained with those yielded by the original Volhard method.

1. One gram of ferro-manganese, 4 grams of pig-iron, or 8 grams of steel, are dissolved in strong hydrochloric acid and oxidised by cautiously adding potassium chlorate. The liquid is boiled until it no longer smells of chlorine, and is transferred with water into a litre measuring flask. The iron is precipitated by means of zinc oxide paste, water is added up to the mark, and the liquid is mixed and filtered through a dry filter. An aliquot portion of the filtrate is then titrated with permanganate without the addition of nitric acid.

2. The hydrochloric acid solution of the metal is oxidised with concentrated nitric acid instead of with potassium chlorate, and the procedure described under 1 is followed.

3. The metal is dissolved in nitric acid (specific gravity 1·2); the solution is concentrated to a small bulk, then diluted and treated as before.

4. The metal is dissolved in nitric acid (specific gravity 1·2), and a few drops of strong hydrochloric acid are added to increase the oxidising effect; further treatment as before.

The results showed that none of the above modifications is more accurate than the others, but that all are available for technical analyses. Noteworthy differences between these methods and the original Volhard's method only occur in the case of alloys rich in manganese. This is due to the incomplete oxidation of organic compounds by the wet methods, and the error may be allowed for by deducting 0·2 to 0·3 c.c. of $\frac{N}{10}$ permanganate from the quantity consumed. The author prefers to dissolve the metal in nitric acid because this acid is more rapid in its action than hydrochloric acid. The chlorate method is not so convenient because it is necessary to remove the excess of chlorine before proceeding with the analysis. J. F. B.

Estimation of Mercury by Reduction of Mercuric to Mercurous Chloride by Hydrogen Peroxide. A. Kolb and A. Feldhofen. (*Zeits. angew. Chem.*,

1907, **20**, 1977-1980.)—It was observed some years ago that mercuric salts under suitable conditions may be reduced by means of hydrogen peroxide to mercurous chloride or metallic mercury, and the authors have now worked out a method for the estimation of mercury by weighing the mercurous chloride produced, or preferably by titrating it with iodine. The reduction to mercurous chloride only takes place in neutral or slightly acid solutions; in alkaline solutions metallic mercury is formed. In the reduction of mercuric chloride hydrochloric acid is set free, and a salt of a weak organic acid must be added to remove it, for which purpose ammonium tartrate is most suitable. For the estimation, 25 c.c. of mercuric chloride solution (5 grams per litre) are mixed with 10 c.c. of 2N hydrochloric acid and 25 c.c. of a

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10 per cent. solution of tartaric acid. The liquid is then neutralised with strong ammonia (3·8 c.c.), and again made faintly acid with tartaric acid. The liquid is warmed, and 10 c.c. of 3 per cent. hydrogen peroxide are added. Further quantities of the peroxide are added, 5 c.c. at a time, at intervals until, after about forty-five minutes, 25 to 30 c.c. have been used. The liquid is then left for fifteen minutes on the water-bath, and diluted with an equal volume of water. After settling, the mercurous chloride is collected on a tared filter and weighed after drying, or else the moist filter and precipitate are placed in a bottle with excess of $\frac{N}{10}$ iodine and 10 c.c. of 10 per cent. potassium iodide, and the excess of iodine is titrated back with thiosulphate. Mercuric chloride may be estimated in the presence of arsenic, antimony, tin, cadmium, and bismuth, but not in presence of lead or copper. The presence of nitrates, as in the case of bismuth nitrate, exerts a retarding influence on the reduction; double the usual quantity of peroxide must be used, and the reduction is only complete after about three hours.

<div align="right">J. F. B.</div>

The Volumetric Estimation of Potassium as Cobaltinitrite. W. A. Drushel. (Zeit. anorg. Chem., 1907, **56**, 223-229.)—The solution of the potassium salt, which must not contain more than 0·2 gram of potassium oxide and must be free from ammonium salts, is treated with a fairly large excess of an acetic acid solution of sodium cobaltinitrite, and evaporated to a paste-like consistency on the water-bath. The residue is cooled, treated with 50 to 100 c.c. of cold water to dissolve the excess of sodium cobaltinitrite, allowed to stand, and the precipitate collected on an asbestos filter, and washed with cold water. It is then introduced, together with the asbestos, into a known quantity of nearly boiling $\frac{N}{10}$ potassium permanganate solution, and stirred for five or six minutes until oxidation is complete. From 5 to 25 c.c. of sulphuric acid (1 : 7) are then added, and the solution stirred and allowed to stand for some minutes, after which a measured excess of N-oxalic acid solution, containing 50 c.c. of concentrated sulphuric acid, is introduced, and the temperature maintained at a little below the boiling-point until the manganese hydroxide has completely separated. The liquid is then titrated back with permanganate solution, and the quantity of potassium calculated by multiplying by the factor 1·09, the oxygen value of the permanganate consumed by the original solution.

In applying the method to fertilisers, 10 grams of the sample are boiled for thirty minutes with 300 c.c. of water, and then made slightly alkaline with ammonia, and treated with sufficient ammonium oxalate to precipitate all the calcium. The contents of the flask are next made up to 500 c.c., thoroughly shaken and filtered, 50 c.c. of the filtrate evaporated to 25 c.c., and the evaporation completed after the addition of 1 c.c. of sulphuric acid (1 : 1). The residue is cautiously ignited, the potassium sulphate dissolved in hot water, and the potassium estimated as above described. The method is more rapid than the platinum chloride method, or the cobalti-nitrite method of Adie and Wood (Journ. Chem. Soc., **77**, 1076), and, unlike the latter, does not require the use of a potassium solution of definite concentration.

<div align="right">C. A. M.</div>