

## ANALYTICAL CHEMISTRY.

IN presenting this Report of the year's work in analytical chemistry, the writer wishes to emphasise the fact that, from the nature of the subject, it is scarcely possible to fulfil the object of the "Reports" as set forth in the "Introduction" to Vol. I. (1904). In the first place, the text must necessarily be somewhat disjointed, since, in the particular branch of chemistry under review, it is much more difficult than in others to construct a connected narrative, for prominence can seldom be given to any particular researches which tend to advance our knowledge of the subject as a whole. The broad reasons for this are not far to seek. Although there are some notable exceptions, it cannot be denied that the number of papers found in journals devoted to analysis in which new chemical principles are brought forward is but few, the greater part of the literary matter which has to be perused in writing a review on analytical chemistry dealing with what may at best be described as improvements rather than original discoveries. Moreover, among this majority are to be found some communications which are not only valueless but actually misleading. For these reasons, therefore, as well as from the fact that this report makes no attempt at being exhaustive, it is obvious that some selection must be made, and—apart from his own experience—the writer has based his selection on the internal evidence contained in each paper. In so voluminous and widely disseminated a literature, it is possible, indeed probable, that several deserving contributions to the subject may not have received notice, either from inadvertence or errors in judgment, but it is hoped that these omissions may amount to a minimum, and that a judicious selection has been made.

In connexion with research in analytical chemistry, it may be mentioned that an important step has been taken by the "Society of Public Analysts and Other Analytical Chemists" in inaugurating a scheme for the investigation of analytical processes and of problems in analytical chemistry, and also for the revision of published methods and their extended study when desirable. Under

this scheme it is suggested that the investigations might be undertaken by some of the senior students working in the larger colleges and teaching institutions, and a fund has been established by the above Society for defraying incumbent expenses. The only conditions are that accounts of the researches are to be published (subject to the approval of the Editorial Committee) in *The Analyst*, and, when possible, to be brought before the Society in the form of communications.<sup>1</sup>

### *Inorganic Chemistry.*

*Qualitative.*—The system of qualitative analysis, the first two papers on which were published last year by A. A. Noyes and W. C. Bray,<sup>2</sup> has been further developed by A. A. Noyes, W. C. Bray, and E. B. Spear.<sup>3</sup> This third communication deals with the metals of the ammonium sulphide group. It is impossible to review such a paper as a whole, covering as it does some eighty pages, but among other things the authors show that when the precipitate obtained with ammonia and ammonium sulphide is dissolved in acid, and the solution boiled with a mixture of sodium peroxide, hydroxide, and carbonate, the members of the iron group, including nickel, cobalt, thallium, manganese, titanium, and zirconium, are precipitated, whilst those of the aluminium group, including glucinum, zinc chromium, uranium, and vanadium, remain in solution as sodium salts. A somewhat similar scheme, involving the use of hydrogen peroxide and sodium hydroxide, is suggested by E. Ebler.<sup>4</sup> H. Caron and D. Raquet<sup>5</sup> suggest sodium peroxide as a reagent for the separation of the elements of group III in presence of phosphates. The same compound is recommended by D. F. Calhane<sup>6</sup> for the detection of chromium in presence of iron; the oxidation proceeds to the perchromate stage. For the rapid qualitative analysis of a mineral, W. B. Pollard's<sup>7</sup> process consists in fusing it with vaselin and sodium peroxide. The more positive elements remain in the melt as insoluble oxides and carbonates, whilst the others exist in the highest state of oxidation as soluble sodium salts; special tests must be made for mercury (on account of its volatility) and for sodium. J. H. Walton, jun., and H. A. Scholz<sup>8</sup> describe a method for decomposing certain slags and

<sup>1</sup> *Analyst*, 1908, **33**, 41.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1907, **29**, 137; *A.*, 1907, ii, 391.

<sup>3</sup> *Ibid.*, 1908, **30**, 481; *A.*, ii, 538.

<sup>4</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 665; *A.*, ii, 987.

<sup>5</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 622; *A.*, ii, 630.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 770; *A.*, ii, 630.

<sup>7</sup> *Chem. News*, 1908, **98**, 211; *A.*, ii, 1069.

<sup>8</sup> *Amer. Chem. J.*, 1908, **39**, 771; *A.*, ii, 732.

sulphide ores, which consists in fusing them with a mixture of sodium peroxide, zinc sulphide, and potassium persulphate.

In order to detect helium in minerals, F. Bordas<sup>9</sup> heats the substance, and passes the gas through a Dewar's charcoal tube; the helium is much less readily absorbed than other gases, and may be detected spectroscopically.

E. Selvatici<sup>10</sup> advocates the use of thioacetic acid instead of hydrogen sulphide for the precipitation of the metals of group II. He also gives a scheme of separation obviating the use of ammonium sulphide. H. Bollenbach<sup>11</sup> makes use of ammonium persulphate in separating the metals of group II. G. D. Lander and H. W. Winter<sup>12</sup> deal with the detection of poisonous metals.

L. Tschugaeff<sup>13</sup> has pointed out that Pozzi-Escot's molybdate method of detecting nickel<sup>14</sup> is less sensitive than his own dimethylglyoxime method.<sup>15</sup> Pozzi-Escot<sup>16</sup> has modified his molybdate method, and more recently<sup>17</sup> he has described conditions whereby cobalt may be detected in the presence of 1000 times its amount of nickel. H. Grossmann and B. Schück<sup>18</sup> state that this method had been previously described by Marckwald; they also state that as a test for nickel in the presence of cobalt it is less delicate than their own,<sup>19</sup> besides which there is a tendency for the precipitation of cobalt as the violet molybdate.<sup>20</sup> H. Grossmann and W. Heilborn<sup>21</sup> suggest the use of dicyanodiamidine for the simultaneous detection of nickel and cobalt. The former metal gives a crystalline precipitate,<sup>22</sup> and the latter an intense reddish-violet coloration.<sup>23</sup>

W. Neumann<sup>24</sup> describes an electrolytic method whereby 0.008 milligram of zinc in 0.1 c.c. of solution may be detected. L. W. McKay<sup>25</sup> draws attention to the danger of zinc sulphide re-dissolving when precipitated in presence of sodium hydroxide.

<sup>9</sup> *Compt. rend.*, 1908, **146**, 628; *A.*, ii, 430.

<sup>10</sup> *Boll. chim. farm.*, 1908, **47**, 73; *A.*, ii, 322.

<sup>11</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 690; *A.*, ii, 984.

<sup>12</sup> *Analyst*, 1908, **33**, 450; *A.*, 1909, ii, 95.

<sup>13</sup> *Compt. rend.*, 1907, **145**, 697; *A.*, 1907, ii, 989.

<sup>14</sup> *Ann. Report*, 1907, 200.

<sup>15</sup> *Ber.*, 1905, **38**, 2520; *A.*, 1905, ii, 613; Kraut, *Zeitsch. angew. Chem.*, 1906, **19**, 793; *A.*, 1906, ii, 858; Brunck, *Ann. Report*, 1907, 205.

<sup>16</sup> *Ann. Chim. anal.*, 1908, **13**, 16; *A.*, ii, 133.

<sup>17</sup> *Ibid.*, 390; *A.*, ii, 988.

<sup>18</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 14; *A.*, ii, 230.

<sup>19</sup> *Ber.*, 1906, **39**, 3356; *A.*, 1906, ii, 908.

<sup>20</sup> See, further, *Chem. Zeit.*, 1908, **32**, 804; *Bull. Soc. chim.*, 1908, [iv], **3**, 894; *A.*, ii, 899. <sup>21</sup> *Ber.*, 1908, **41**, 1878; *A.*, ii, 635. <sup>22</sup> *Ann. Report*, 1907, 205.

<sup>23</sup> See also H. Grossmann, *Chem. Zeit.*, 1908, **32**, 315; *A.*, ii, 434.

<sup>24</sup> *Zeitsch. Elektrochem.*, 1907, **13**, 751; *A.*, ii, 67.

<sup>25</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 376; *A.*, ii, 431.

W. Bettel<sup>26</sup> states that molybdic acid gives, with hydrogen peroxide and a trace of ammonia, a brownish-red coloration. A method for the detection of ruthenium in platinum alloys has been devised by N. A. Orloff.<sup>27</sup>

N. Schoorl<sup>28</sup> describes the appearance under the microscope of silver, lead, and mercurous chlorides, and later<sup>29</sup> that of arsenic, antimony, and tin compounds. Subsequently<sup>30</sup> he deals with the microchemical analysis of the sulphides of mercury, bismuth, lead, copper, and cadmium. In connexion with the well-known volatility of mercury compounds, K. Kof and H. Haehn<sup>31</sup> state that a moistened filter-paper placed over a 2 per cent. solution of mercuric chloride for sixty-five hours is rendered black on treatment with hydrogen sulphide; also that a distinct white patch is obtained on developing a photographic plate which has been kept for twenty-four hours at a distance of 2 to 3 mm. from a drop of a 0.01 per cent. solution of mercuric chloride.<sup>32</sup> J. Moir<sup>33</sup> gives two methods for the detection of mercuric chloride in nitrocellulose.

According to M. Delépine,<sup>34</sup> one part of copper in 1,000,000 can be detected by the brown coloration produced with a solution of a dialkyldithiocarbamate. Iron gives a pink colour with this reagent; nickel and cobalt also give colours. E. Knecht<sup>35</sup> shows that when titanous sulphate is added to a solution of a copper salt (limit one part of copper per 1,000,000), metallic copper separates. A. W. Gregory<sup>36</sup> states that 0.01 milligram of silver may be detected by the brown colour produced on addition of ammonium salicylate and persulphate. W. J. Karstake's method for the detection of manganese and chromium in mixtures<sup>37</sup> consists in boiling the solution in nitric or sulphuric acid with ammonium persulphate and silver nitrate, when permanganate and perchromate are formed. When shaken with hydrogen peroxide and ether, the former is decomposed, whilst the latter dissolves in the ether with the production of the well-known blue colour.

H. Caron and D. Raquet<sup>38</sup> point out that in the well-known method of detecting barium in presence of strontium and calcium,

<sup>26</sup> *Chem. News*, 1908, **97**, 40; *A.*, ii, 230.

<sup>27</sup> *Chem. Zeit.*, 1908, **32**, 77; *A.*, ii, 231.

<sup>28</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 209; *A.*, ii, 432.

<sup>29</sup> *Ibid.*, 367; *A.*, ii, 777.

<sup>30</sup> *Ibid.*, 729; *A.*, 1909, ii, 96.

<sup>31</sup> *Arch. Pharm.*, 1907, **245**, 529; *A.*, ii, 69.

<sup>32</sup> Compare *Zeitsch. physikal. Chem.*, 1907, **60**, 367; *A.*, 1907, ii, 732.

<sup>33</sup> *Chem. News*, 1908, **97**, 133.

<sup>34</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 652; *A.*, ii, 633.

<sup>35</sup> *Ber.*, 1908, **41**, 498; *A.*, ii, 270.

<sup>36</sup> *Proc.*, 1908, **24**, 125.

<sup>37</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 905; *A.*, ii, 635.

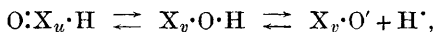
<sup>38</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 483; *A.*, ii, 496.

the addition of hydrofluosilicic acid sometimes leads to the deposition of gelatinous silica, which may be mistaken for barium silicofluoride. They show<sup>39</sup> that barium may be eliminated from strontium salts by fractional precipitation by alkali chromates.

J. Milbauer<sup>40</sup> states that neodymium gives a colourless borax bead in the oxidising, and a violet in the reducing, flame, whilst praseodymium gives a yellowish-green bead in the oxidising, and a green in the reducing, flame. O. Lutz<sup>41</sup> points out that borax beads are to be preferred for the detection of positive, and phosphate beads for negative, ions. J. Donau<sup>42</sup> describes a delicate method of detecting gold, platinum, and silver by means of the metaphosphate bead.

For the detection of phosphates in minerals, A. P. Lidoff<sup>43</sup> heats the finely-powdered mineral first alone, and then with magnesium or a mixture of it and aluminium; the fusion is gently warmed with 20 per cent. sodium hydroxide solution, the evolved gases being brought in contact with copper sulphate paper. The formation of copper phosphide (black coloration) indicates the presence of phosphorus. J. S. Jamieson<sup>44</sup> describes a test for bromides.

*Quantitative.*—An important contribution to the theory of indicators is that of J. T. Hewitt,<sup>45</sup> who points out the insufficiency of the ionic theory alone in explaining the colour changes of phenolphthalein, and concludes that the assumption of tautomeric change must also be made. In the light of A. G. Green's experiments,<sup>46</sup> Hewitt assumes that this and like indicators obey the following equilibrium in solution:



where  $\text{X}_u$  and  $\text{X}_v$  are isomeric radicles. These considerations led him to recommend *p*-nitrobenzeneazo- $\alpha$ -naphthol as an indicator. It yields results similar to phenolphthalein when used for the titration of alkali hydroxides with weak acids, the colour change being from purple to yellow. The view that phenolphthalein exhibits tautomerism was put forward by S. F. Acree in 1904, but was denied by J. Stieglitz. Acree's latest hypothesis<sup>47</sup> commends itself, however, to Stieglitz.<sup>48</sup> A. Hantzsch and F. Hilscher<sup>49</sup> bring

<sup>39</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 493; *A.*, ii, 496.

<sup>40</sup> *Zeitsch. anal. Chem.*, 1907, **46**, 657; *A.*, ii, 70.

<sup>41</sup> *Ibid.*, 1908, **47**, 1; *A.*, ii, 226.

<sup>42</sup> *Zeitsch. Chem. Ind. Kolloide*, 1908, **2**, 273; *A.*, ii, 434.

<sup>43</sup> *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 817; *A.*, ii, 894.

<sup>44</sup> *Proc.*, 1908, **24**, 144.

<sup>45</sup> *Analyst*, 1908, **33**, 85; *A.*, i, 269.

<sup>46</sup> *Ber.*, 1907, **40**, 3724; *J. Soc. Chem. Ind.*, 1908, **27**, 4; *A.*, 1907, i, 933.

<sup>47</sup> *Amer. Chem. J.*, 1908, **39**, 528, 649; *A.*, i, 422, 652.

<sup>48</sup> *Ibid.*, 651; *A.*, i, 652; compare *Ibid.*, 789; *A.*, i, 653.

<sup>49</sup> *Ber.*, 1908, **41**, 1187; *A.*, i, 469.

forward evidence that helianthin, in the solid state, has a quinonoid structure, but that in aqueous solution it exists as an aminoazo- and sulphonic acid-form in equilibrium, whilst its sodium salt (methyl-orange) is a sulphonate both in the solid state and in solution. J. H. Hildebrand<sup>50</sup> has applied the König spectrophotometer to the measurement of the dissociation constant of phenolphthalein dissolved in aqueous solutions of ammonia and ammonium chloride, in which the concentration of the hydrogen ions is known. It is found to be  $1.7 \times 10^{-10}$  for solutions in which 5 to 65 per cent. of the phenolphthalein is dissociated.<sup>51</sup> M. Barberio<sup>52</sup> has described a new indicator, "resorubin," obtained by the action of nitrous acid on resorcinol; the violet neutral solution becomes blue with alkalis or yellow with acids. It is said to resemble lacmoid, but to be more sensitive in presence of ammonium salts. E. Rupp and R. Loose<sup>53</sup> propose *p*-dimethylaminoazobenzene-*o*-carboxylic acid as an indicator which may be used for the titration of weak bases such as alkaloids; it can be used to titrate ammonia even in *N*/100-solution. To distinguish mineral from organic acids, E. Linder<sup>54</sup> employs metanil-yellow paper, which (with the former only) becomes violet. A. B. Lyons<sup>55</sup> recommends hæmatoxylin for titrating phosphoric acid. J. K. Wood<sup>56</sup> has carefully determined the basic and acidic constants of arsenious and aluminium hydroxide. V. H. Veley's paper on the affinity constants of bases, as determined by the aid of methyl-orange,<sup>57</sup> is of interest to analytical chemists. S. P. L. Sørensen and A. C. Andersen<sup>58</sup> give some useful hints on Winkler's method of estimating hydroxides in presence of carbonates.<sup>59</sup> L. Clarke and C. L. Jackson<sup>60</sup> show that rosocyanin, the substance which is produced in the test for boric acid with turmeric paper, is an isomeride of curcumin,  $C_{14}H_{14}O_2$ .

In connexion with halogen derivatives, P. Jannasch<sup>61</sup> has continued his studies on the separation of the halogens by means of hydrogen peroxide.<sup>62</sup> In its present form, his method is quantitative, good results being obtained for chlorine and iodine, whilst those for bromine are slightly low. H. Baubigny<sup>63</sup> has modified Hager's

<sup>50</sup> *Zeitsch. Elektrochem.*, 1908, **14**, 349; *A.*, ii, 646.

<sup>51</sup> Compare R. Wegscheider and A. Schugowitsch, *Ibid.*, 510; *A.*, ii, 806.

<sup>52</sup> *Gazzetta*, 1907, **37**, ii, 577; *A.*, i, 161.

<sup>53</sup> *Ber.*, 1908, **41**, 3905; *A.*, 1909, ii, 90.

<sup>54</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 485; *A.*, ii, 627.

<sup>55</sup> *Pharm. Rev.*, 1908, **26**, 97; *A.*, ii, 532.

<sup>56</sup> *Trans.*, 1908, **93**, 411.

<sup>57</sup> *Ibid.*, 652. <sup>58</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 279; *A.*, ii, 534.

<sup>59</sup> Compare also Andersen, *Tidskr. Kem. Farm. Terapi*, 1908, **11**, 161; *A.*, ii, 985.

<sup>60</sup> *Amer. Chem. J.*, 1908, **39**, 696; *A.*, i, 670.

<sup>61</sup> *J. pr. Chem.*, 1908, [ii], **78**, 28; *A.*, ii, 730.

<sup>62</sup> *Ann. Report*, 1906, 203. <sup>63</sup> *Compt. rend.* 1908, **146**, 335; *A.*, ii, 321.

method of separating silver halides.<sup>64</sup> When only the chloride and iodide are present, these may be separated quantitatively by treatment at 70—80° with a solution containing 10 grams of ammonium sesquicarbonate and 20 c.c. of 20 per cent. ammonia per litre; this dissolves the silver iodide only. B. H. Buttle and J. T. Hewitt<sup>65</sup> have studied the solubility of silver chloride in mercuric nitrate solution, and arrive at the same conclusion as Morse,<sup>66</sup> that when mercuric nitrate is present in large excess, chlorine only occurs as HgCl ions. For the determination of fluorine in rocks, etc., in quantities up to 3 per cent., G. Steiger<sup>67</sup> makes use of the fact that fluorides bleach the coloration produced by hydrogen peroxide and titanium. As this is not a linear function, reference is made to a curve. The presence of aluminium salts and phosphates influence the results, which, however, are in no case trustworthy when as much as 10 per cent. of fluorine is present. B. Carlson and J. Gelhaar<sup>68</sup> deal with the detection and estimation of chlorites and hypochlorites in chlorates. E. Knecht<sup>69</sup> has devised a volumetric method for the estimation of chlorates. D. Venditori<sup>70</sup> makes the interesting observation that, in presence of sulphuric acid, chlorates but not perchlorates are reduced by finely-divided aluminium. Grützner's method of determining chlorates and bromates by heating with formaldehyde, nitric acid, and silver nitrate<sup>71</sup> has been extended to iodates and periodates by H. Brunner and R. Mellet.<sup>72</sup> To prevent loss of free halogen, and to obviate working in a closed vessel, potassium persulphate is added to the reaction mixture. H. Baubigny<sup>73</sup> shows that an ammoniacal solution of silver chloride or bromide, when heated with iodic acid, only deposits silver iodide when a temperature of 200° is reached.

Use has been made of sodium peroxide by S. W. Parr<sup>74</sup> in the estimation of sulphur in pyrites, coal, and indiarubber. Pyrites is mixed with sodium peroxide, potassium chlorate, and benzoic acid, and the mixture ignited in a special bomb; the melt contains the sulphur as sulphate. A special mixture appears to be required

<sup>64</sup> *Zeitsch. anal. Chem.*, 1871, **10**, 341.

<sup>65</sup> *Trans.*, 1908, **93**, 1405.

<sup>66</sup> *Zeitsch. physikal. Chem.*, 1902, **41**, 709; *A.*, 1903, ii, 12.

<sup>67</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 219; *A.*, ii, 426.

<sup>68</sup> *Chem. Zeit.*, 1908, **32**, 604, 633; *A.*, ii, 731.

<sup>69</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 434; *A.*, ii, 627.

<sup>70</sup> *Gazzetta*, 1907, **37**, ii, 383; *A.*, ii, 63.

<sup>71</sup> *Arch. Pharm.*, 1896, **234**, 634; *A.*, 1897, ii, 166.

<sup>72</sup> *J. pr. Chem.*, 1908, [ii], **77**, 33; *A.*, ii, 222.

<sup>73</sup> *Compt. rend.*, 1908, **146**, 1097; *A.*, ii, 577.

<sup>74</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 764; *A.*, ii, 628.



for each substance. Carbon in carborundum may be estimated (as carbonate) by heating the sample in this way with sodium peroxide and "boro-magnesium" mixture.<sup>75</sup> The results quoted are satisfactory (see also under Organic Chemistry). E. Jaboulay<sup>76</sup> describes a volumetric method for estimating sulphur in steel. For a detailed study of the various methods for this purpose, M. Orthey's paper<sup>77</sup> may be consulted. According to H. Kiliani,<sup>78</sup> when alkali thiosulphate is titrated in alkaline solution with permanganate, as in Reinige's method of estimating iodides,<sup>79</sup> sulphate and not tetrathionate is formed, hence 8 mols. of permanganate require 3 mols. of thiosulphate for decomposition. V. Lenher<sup>80</sup> shows that in the method of estimating tellurium by precipitation with hydrazine,<sup>81</sup> it is an advantage if the solution contains sulphurous acid; the results are accurate.

As usual, a great many papers have appeared during the year dealing with the estimation of phosphorus and phosphates. F. W. Hinrichsen<sup>82</sup> has confirmed the accuracy of H. Lidholm's process<sup>83</sup> for the estimation of phosphorus in calcium carbide. An accurate method for the estimation of phosphorus in phosphor-tin has been devised by W. Gemmell and S. L. Archbutt.<sup>84</sup> F. Repiton<sup>85</sup> describes a modification of Malot's method of estimating phosphoric acid by titration with uranic solution, employing cochineal, *in situ*, as indicator; the results are shown to be satisfactory. For the estimation of phosphorus in iron, etc., G. Chesneau<sup>86</sup> weighs the ammonium phosphomolybdate precipitate, and states conditions whereby this compound may be precipitated in presence of ammonium nitrate containing constantly 1.6 per cent. of phosphorus. With reference to the estimation of phosphoric acid as ammonium phosphomolybdate,<sup>87</sup> G. von Knorre,<sup>88</sup> adverting to his previous statement that tungstic acid may be separated from phosphoric acid almost quantitatively by precipitation with benzidine hydrochloride, points out that the results are vitiated by the insol-

<sup>75</sup> *Loc. cit.* <sup>76</sup> *Rev. gen. chim. pure appl.*, 1907, **10**, 193; *A.*, ii, 223.

<sup>77</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 1359, 1393; *A.*, ii, 731.

<sup>78</sup> *Chem. Zeit.*, 1908, **32**, 1018; *A.*, ii, 982

<sup>79</sup> *Zeitsch. anal. Chem.*, 1870, **9**, 39.

<sup>80</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 388; *A.*, ii, 426.

<sup>81</sup> Gutbier, *Ber.*, 1901, **34**, 2724; *A.*, 1901, ii, 687.

<sup>82</sup> *Mitt. K. Materialprüfs-Amt. Gross. Lichterfelde West*, 1907, **25**, 110; *A.* 1908, ii, 131.

<sup>83</sup> *Zeitsch. angew. Chem.*, 1904, **17**, 1452; *A.*, 1904, ii, 776.

<sup>84</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 427; *A.*, ii, 629.

<sup>85</sup> *Mon. Sci.*, 1907, [iv], **21**, ii, 753, 815; *A.*, ii, 320, 428.

<sup>86</sup> *Compt. rend.*, 1908, **146**, 758; *A.*, ii, 427.

<sup>87</sup> Compare P. Christensen, *Zeitsch. anal. Chem.*, 1908, **47**, 529; *A.*, ii, 895; E. Raben, *ibid.*, 546; *A.*, ii, 896.

<sup>88</sup> *Ibid.*, 37; *A.*, ii, 231.



bility of benzidine phosphate in water, but he shows that the separation is quantitative when the homologous tolidine hydrochloride is employed.

In connexion with the estimation of carbon in iron and steel, M. Orthey<sup>89</sup> shows that the combustion method in a current of oxygen in presence of bismuth oxide gives good results. L. L. de Koninck and E. von Winiwarter<sup>90</sup> propose to burn the substance with lead borate in a current of oxygen. H. Isham and J. Aumer<sup>91</sup> show that when iron or steel is ignited in a current of oxygen alone, the carbon (but not the sulphur) is almost completely burnt. C. M. Johnson<sup>92</sup> describes an electric furnace for the estimation of carbon in iron, etc. New apparatus for the moist method have been devised by M. Widemann<sup>93</sup> and by T. Grzeschik.<sup>94</sup> E. P. Moore and J. W. Bain<sup>95</sup> show that during the solution of steel in potassium cupric chloride there may be a loss of 0.4—0.5 milligram of carbon per gram of steel. In titrating lead with sodium sulphide, H. Koch<sup>96</sup> adds carbon tetrachloride to cause the subsidence of the precipitate. Some useful data on the colorimetric estimation of lead as sulphide are given by H. W. Woudstra.<sup>97</sup> Several papers dealing with the assay of red lead have been published during the year.<sup>98</sup> The last-mentioned shows the limit of accuracy of the various methods in use. Some useful volumetric methods of estimating mercury are described by E. Rupp,<sup>99</sup> and by the same author in conjunction with W. F. Schirmer.<sup>1</sup> For the estimation of mercuric salts, S. G. Liversedge<sup>2</sup> suggests conversion into mercuric iodide and extraction of the latter with ether; the method is particularly adapted for the estimation of small quantities of mercury. In connexion with the estimation of mercury, the volatility of its salts (see p. 183) is, as a rule, ignored by authors. J. F. Spencer and Miss M. Le Pla<sup>3</sup> have devised a very accurate method of estimating silver and thallium

<sup>89</sup> *Chem. Zeit.*, 1908, **32**, 31; *A.*, ii, 131.

<sup>90</sup> *Bull. Soc. chim. Belg.*, 1908, **22**, 104; *A.*, ii, 320.

<sup>91</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1236; *A.*, ii, 898.

<sup>92</sup> *Ibid.*, 773; *A.*, ii, 630.

<sup>93</sup> *Zeitsch. chem. Apparatenkunde*, 1908, **3**, 296; *A.*, ii, 984.

<sup>94</sup> *Chem. Zeit.*, 1908, **32**, 1092; *A.*, ii, 1071.

<sup>95</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 845; *A.*, ii, 899.

<sup>96</sup> *Chem. Zeit.*, 1908, **32**, 124; *A.*, ii, 227.

<sup>97</sup> *Zeitsch. anorg. Chem.*, 1908, **58**, 168; *A.*, ii, 638.

<sup>98</sup> See for instance J. F. Sacher, *Chem. Zeit.*, 1908, **32**, 62; *A.*, ii, 228; E. Piesczek, *Pharm. Zeit.*, 1908, **53**, 87; *A.*, ii, 228; E. E. Dunlap, *J. Amer. Chem. Soc.*, 1908, **30**, 611; *A.*, ii, 537; P. Beck, *Zeitsch. anal. Chem.*, 1908, **47**, 465; *A.*, ii, 777.

<sup>99</sup> *Chem. Zeit.*, 1908, **32**, 1077; *A.*, ii, 1073.

<sup>1</sup> *Pharm. Zeit.*, 1908, **53**, 928; *A.*, ii, 1073.

<sup>2</sup> *Analyst*, 1908, **33**, 217; *A.*, ii, 634.

<sup>3</sup> *Trans.*, 1908, **93**, 858.

in mixtures. W. R. Lang and J. O. Woodhouse<sup>4</sup> describe a modification of Lang and Allen's apparatus<sup>5</sup> which may be employed for the estimation of silver by Gay-Lussac's method.

G. S. Jamieson, H. L. Levy, and H. L. Wells<sup>6</sup> propose a volumetric method for the estimation of copper, which, on their evidence, has an average limit of accuracy of one in 300. The copper is precipitated as cuprous thiocyanate, and the latter, after washing, dissolved in dilute hydrochloric acid and titrated with potassium iodate and chloroform. The writer can fully confirm H. Theodor's statements<sup>7</sup> regarding the accuracy of Volhard's titration method of estimating copper; more than twenty years ago he used the method of neutralising the solution with a slight excess of ammonia before reducing with sulphurous acid for the purpose of getting rid of the nitric acid, which is now suggested by O. Kuhn.<sup>8</sup> A. K. Huntington and C. H. Desch<sup>9</sup> deal with the planimetric analysis of alloys and the structure of phosphor-copper.

The fact that when titrated with permanganate in presence of hydrochloric acid ferrous salts require more of the standard solution than is necessary for their oxidation to the ferric state has long been known. T. W. Harrison and F. M. Perkin<sup>10</sup> find that addition of manganous sulphate retards the reducing action of hydrochloric acid, but that the colour interferes with the end point of the titration. In discussing their paper, O. Hehner<sup>11</sup> quoted Fresenius's directions, and cited a paper by Loewenthal and Lenssen.<sup>12</sup> In a lengthy paper by L. Brandt,<sup>13</sup> the necessity is urged of standardising the permanganate in presence of hydrochloric acid when that acid occurs in the assay liquid. Directions are given for the preparation of ferric oxide in a state of purity, which is recommended as the best compound to use in standardising the solution; the reduction is effected by stannous chloride. In other papers on the permanganate method, M. M. P. Muir<sup>14</sup> proposes to arrest the evolution of hydrogen, when the reduction of ferric salt is accomplished with zinc, by the addition of mercuric chloride; and H. D. Newton<sup>15</sup> employs titanous sulphate as reducing agent, destroying the excess with bismuth oxide. The results quoted are

<sup>4</sup> *Trans.*, 1908, **93**, 1037.      <sup>5</sup> *Ibid.*, 1907, **91**, 1370.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 760; *A.*, ii, 634.

<sup>7</sup> *Chem. Zeit.*, 1908, **32**, 889; *A.*, ii, 898.

<sup>8</sup> *Ibid.*, 1056; *A.*, ii, 1072.

<sup>9</sup> *Trans. Faraday Soc.*, 1908, **4**, 51; *A.*, ii, 846.

<sup>10</sup> *Analyst*, 1908, **33**, 43; *A.*, ii, 228.

<sup>11</sup> *Ibid.*

<sup>12</sup> *Zeitsch. anal. Chem.*, 1861, **1**, 329, 361.

<sup>13</sup> *Chem. Zeit.*, 1908, **32**, 812; *A.*, ii, 899.

<sup>14</sup> *Chem. News*, 1908, **97**, 57; *A.*, ii, 228.

<sup>15</sup> *Amer. J. Sci.*, 1908, [iv], **25**, 343; *A.*, ii, 538.

very accurate. G. Edgar<sup>16</sup> deals with the estimation of iron and vanadium in mixtures by titration with permanganate, and in another paper<sup>17</sup> he has elaborated conditions whereby vanadic and molybdc oxides may be estimated by permanganate. S. B. Jatar's method<sup>18</sup> for the estimation of iron and chromium by titration with titanous chloride appears useful and accurate. H. Bollenbach<sup>19</sup> proposed to titrate ferric salts with sodium hyposulphite ( $\text{Na}_2\text{SO}_2$ ).

For the decomposition of ferro-compounds, especially ferro-silicon, P. Nicolardot<sup>20</sup> heats with sulphur chloride. R. B. Moore and I. Miller<sup>21</sup> show that iron may be precipitated from a solution containing free hydrochloric acid by means of pyridine; aluminium, chromium, and zinc are partly precipitated, whereas manganese, nickel, and cobalt remain in solution. F. C. Mathers<sup>22</sup> shows that traces of iron may be removed from indium by precipitation from an acetic acid solution by nitroso- $\beta$ -naphthol.

According to A. W. Gregory,<sup>23</sup> one part of iron in 10,000 of copper may be detected by the red colour given by ferric salts with salicylic acid in presence of sodium acetate. He bases a colorimetric method on this reaction.

With reference to the dimethylglyoxime and dicyanodiamidine methods of estimating nickel,<sup>24</sup> O. Brunck<sup>25</sup> brings forward evidence showing the superior accuracy of the former, whilst Grossmann and Schück<sup>26</sup> uphold the dicyanodiamidine method on the ground that the nickel compound is insoluble in strong ammoniacal alkali hydroxide solutions. H. Cantoni and M. Rosenstein<sup>27</sup> propose for the volumetric estimation of nickel, titration with either ferro- or ferri-cyanide, using ferric (or uranium) or ferrous indicators respectively; the ferricyanide method with the liquid faintly acidified with acetic acid gives the better results.

In a series of papers M. E. Pozzi-Escot deals with the estimation of both nickel and cobalt by the molybdate method and the separation of these metals from others.<sup>28</sup>

<sup>16</sup> *Zeitsch. anorg. Chem.*, 1908, **59**, 74.

<sup>17</sup> *Amer. J. Sci.*, 1908, [iv], **25**, 232; *A.*, ii, 540.

<sup>18</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 673; *A.*, ii, 778.

<sup>19</sup> *Chem. Zeit.*, 1908, **32**, 146; *A.*, ii, 229.

<sup>20</sup> *Compt. rend.*, 1908, **147**, 676; *A.*, ii, 1074.

<sup>21</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 593; *A.*, ii, 434.

<sup>22</sup> *Ibid.*, 209; *A.*, ii, 434.

<sup>23</sup> *Trans.*, 1908, **93**, 93.

<sup>24</sup> *Ann. Report*, 1907, 205.

<sup>25</sup> *Zeitsch. angew. Chem.*, 1907, **20**, 1845; *A.*, 1907, ii, 989.

<sup>26</sup> *Ibid.*, 1981; *A.*, ii, 71.

<sup>27</sup> *Bull. Soc. chim.*, 1908, [iv], **1**, 1163; *A.*, ii, 230.

<sup>28</sup> *Ann. Chim. anal.*, 1908, **13**, 66; *Compt. rend.*, 1907, **145**, 1334; *A.*, ii, 229; *Ann. Chim. anal.*, 1908, **13**, 89; *A.*, ii, 324; *ibid.*, 85, 215, 217; *A.*, ii, 539, 540, 635.

E. D. Campbell and W. Arthur<sup>29</sup> describe a modification of Moore's volumetric method<sup>30</sup> for the estimation of nickel and chromium in steel. A. A. Blair<sup>31</sup> has worked out a scheme for the determination of vanadium, molybdenum, chromium, and nickel in steel; from the single example given, it appears to be very accurate. The estimation of vanadium in iron and steel is dealt with by E. D. Campbell and E. L. Woodhams.<sup>32</sup>

In connexion with the estimation of tin, D. B. Dott<sup>33</sup> draws attention to the solubility of metastannic acid in hydrochloric acid; he points out further that, in the analysis of ores, tin is volatilised when a solution in aqua regia is evaporated to dryness for the purpose of separating the silica.<sup>34</sup> H. Reynolds<sup>35</sup> titrates a stannous solution with dichromate, using azobenzenesulphonic acid as indicator; the restoration of the red colour of the indicator marks the end of the oxidation. E. Schürmann and W. Scharfenberg<sup>36</sup> describe a modification of Clarke's oxalic acid method for the analysis of white metal. A. Kolb and R. Formhals<sup>37</sup> show that the reaction  $\text{Sb}_2\text{O}_5 + 4\text{HI} \rightleftharpoons \text{Sb}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{I}_2$  is practically complete from left to right if sufficient excess of hydriodic acid be used.

L. Rosenthaler's observations<sup>38</sup> respecting the quantitative precipitation of arsenious and arsenic acids, the former by barium chloride and ammonia and the latter by barium chloride and sodium hydroxide, are worthy of attention. H. Reckleben and G. Lockemann<sup>39</sup> describe gravimetric, volumetric, and gasometric methods of estimating arsine in air.

P. Cazeneuve<sup>40</sup> utters a warning against the use of arseniferous dressings as insecticides in agriculture. The Gutzeit test for arsenic, antimony, and phosphorus has been rendered more conclusive by B. Sjollem.<sup>41</sup> In the case of arsenic, he states that he was able to obtain microscopical crystals with 0.005 milligram of arsenious oxide. C. H. Nieuwland,<sup>42</sup> on the other hand, was unable to

<sup>29</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1116; *A.*, ii, 779.

<sup>30</sup> *Chem. News*, 1895, **72**, 92; *A.*, 1895, ii, 534.

<sup>31</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1229; *A.*, ii, 900.

<sup>32</sup> *Ibid.*, 1233; *A.*, ii, 901.

<sup>33</sup> *Pharm. J.*, 1908, [iv], **27**, 486; *A.*, ii, 899.

<sup>34</sup> See further, *Ibid.*, 585; *A.*, ii, 1075.

<sup>35</sup> *Chem. News*, 1908, **97**, 13; *A.*, ii, 134.

<sup>36</sup> *Mitt. K. Materialprüfungs.-Amt.*, 1908, **25**, 270; *A.*, ii, 537.

<sup>37</sup> *Zeitsch. anorg. Chem.*, 1908, **58**, 189; *A.*, ii, 599.

<sup>38</sup> *Apoth. Zeit.*, 1907, **22**, 982; *A.*, ii, 322.

<sup>39</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 126; *A.*, ii, 224.

<sup>40</sup> *Rev. intern. Falsif.*, 1908, **21**, 11.

<sup>41</sup> *Chem. Weekblad.*, 1908, **5**, 11; *A.*, ii, 431.

<sup>42</sup> *Ibid.*, 558; *A.*, ii, 896.

detect less than 0.05 milligram of arsenious oxide in this way.<sup>43</sup> W. van Ryn<sup>44</sup> points out that sodium fluoride may prevent completely the formation of arsenical mirrors in the Marsh-Berzelius method, although it has no influence on the Gutzeit or Flückiger reaction. E. Salkowski<sup>45</sup> deals with the detection and estimation of arsenic in urine. To detect arsenic in sulphur, J. Brand<sup>46</sup> extracts the finely-powdered sulphur with ammonia.

M. Orthey<sup>47</sup> has made a careful study of certain volumetric methods of estimating manganese in ferro-manganese ores, and he shows that the Volhard-Wolff method<sup>48</sup> and those of von Knorre<sup>49</sup> and Blair<sup>50</sup> give results agreeing well with those yielded by the ordinary gravimetric method; the first two are specially recommended.<sup>51</sup> For the detection and colorimetric estimation of manganese, M. Duyk<sup>52</sup> makes use of the red coloration produced when a trace of manganese is heated with an alkaline solution of hypochlorite in presence of a trace of copper sulphate. H. W. Rowell<sup>53</sup> estimates small quantities of bismuth colorimetrically as iodide.

Miss Z. Kahan<sup>54</sup> has devised a method for the quantitative separation of barium and strontium. O. Hauser, in conjunction with F. Wirth, has published some important data on the solubility of the oxalates of the rare earths in dilute sulphuric and oxalic acids.<sup>55</sup> Later<sup>56</sup> he shows that the precipitation of these oxalates is incomplete in presence of uranyl salts. M. Dittrich<sup>57</sup> describes the separation of cerium from other metals and its estimation.

To separate lithium from other alkali metals, L. Kahlenberg and F. C. Krauskopf<sup>58</sup> take advantage of the solubility of lithium chloride in pyridine. The precipitation of potassium as cobalti-

<sup>43</sup> For microchemical reactions of arsenic, see also G. Denigès, *Compt. rend.*, 1908, **147**, 596, 744; *A.*, ii, 1070.

<sup>44</sup> *Pharm. Weekblad.*, 1908, **45**, 98; *A.*, ii, 224.

<sup>45</sup> *Zeitsch. physiol. Chem.*, 1908, **56**, 95; *A.*, ii, 734.

<sup>46</sup> *Zeitsch. ges. Brauwesen*, 1908, **31**, 33; *A.*, ii, 532.

<sup>47</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 547; *A.*, ii, 898.

<sup>48</sup> *Ibid.*, 1880, **20**, 271; compare Volhard, *A.*, 1880, 141.

<sup>49</sup> *Ibid.*, 1904, **43**, 643; compare *A.*, 1902, ii, 108.

<sup>50</sup> *Ibid.*, 1904, **43**, 647; compare *A.*, 1904, ii, 683.

<sup>51</sup> Compare E. W. Meyer, *Zeitsch. angew. Chem.*, 1907, **20**, 1980; *A.*, ii, 71; L. Sacerdoti, *L'Industria Chimica*, 1907, **7**, 258; *A.*, ii, 228.

<sup>52</sup> *Ann. Chim. anal.*, 1907, **12**, 465; *A.*, ii, 70.

<sup>53</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 102; *A.*, ii, 325.

<sup>54</sup> *Analyst*, 1908, **33**, 12; *A.*, ii, 133.

<sup>55</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 389; *A.*, ii, 778.

<sup>56</sup> *Ibid.*, 677; *A.*, ii, 987.

<sup>57</sup> *Ber.*, 1908, **41**, 4373.

<sup>58</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1104; *A.*, ii, 777.

nitrite<sup>59</sup> is dealt with by W. A. Drushel,<sup>60</sup> and by W. Autenrieth,<sup>61</sup> who shows that the precipitate obtained with de Koninck's cobalt reagent is not of constant composition.

For the estimation of tungsten and its separation from other substances, advantage may be taken of the fact that it is volatilised as oxychlorides when heated strongly in a mixture of chlorine and sulphur chloride,<sup>62</sup> or when heated at 500° in a current of air charged with chlorine.<sup>63</sup> Tungsten trioxide is reduced by hydrogen at 600—900°, and may be then volatilised by treatment with chlorine.<sup>64</sup> G. von Knorre has applied his benzidine method<sup>65</sup> to the estimation of tungsten in steel containing chromium.<sup>66</sup> F. W. Hinrichsen and L. Wolter<sup>67</sup> state that the results are low. They describe other methods of estimating both tungsten and chromium. Methods for the estimation of vanadium in presence or absence of iron are described by T. Warynski and B. Mdivani,<sup>68</sup> and by G. Edgar.<sup>69</sup>

*Electrochemical Analysis.*—The work conducted in this department during the year indicates steady progress, and shows the increasing utility of electrolytic methods. F. Foerster<sup>70</sup> summarises our knowledge of rapid electrolytic methods, especially those in which rotating electrodes are employed. His claim of priority for rotating electrodes has been disputed by A. Classen,<sup>71</sup> and a series of polemical papers by these authors have followed.<sup>72</sup> F. M. Perkin<sup>73</sup> remarks that rotating electrodes were first described by Gooch and Medway, E. Smith, and himself almost simultaneously. F. A. Gooch and F. B. Beyer<sup>74</sup> employ as cathode a Gooch crucible with asbestos filter in the case of precipitates which do not adhere firmly.

The reduction of alkali nitrate to ammonia in presence of copper was studied by Easton in 1904, and subsequently by Ingham in 1905. O. L. Shinn<sup>75</sup> states that in order to realise Ingham's

<sup>59</sup> Adie and Wood, *Trans.*, 1900, **77**, 1076.

<sup>60</sup> *Zeitsch. anorg. Chem.*, 1907, **56**, 223; 1898, **59**, 97; *A.*, ii, 66, 735.

<sup>61</sup> *Centr. Min.*, 1908, 513; *A.*, ii, 897.

<sup>62</sup> F. Bourion, *Compt. rend.*, 1908, **146**, 1102; *A.*, ii, 737.

<sup>63</sup> P. Nicolardot, *ibid.*, **147**, 795; *A.*, ii, 1074.

<sup>64</sup> E. Defacqz, *ibid.*, **146**, 1319; *A.*, ii, 737.

<sup>65</sup> *Ann. Report*, 1905, 192.

<sup>66</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 337; *A.*, ii, 779.

<sup>67</sup> *Zeitsch. anorg. Chem.*, 1908, **59**, 183; *A.*, ii, 900.

<sup>68</sup> *Ann. Chim. anal.*, 1908, **13**, 209, 210; *A.*, ii, 636, 736.

<sup>69</sup> *Amer. J. Sci.*, 1908, [iv], **26**, 79; *A.*, ii, 736.

<sup>70</sup> *Zeitsch. Elektrochem.*, 1908, **14**, 3. <sup>71</sup> *Ibid.*, 90.

<sup>72</sup> *Ibid.*, 141; 208, 239; *A.*, ii, 432, 529. <sup>73</sup> *Ibid.*, 143; *A.*, ii, 432.

<sup>74</sup> *Amer. J. Sci.*, 1908, **25**, 249; *A.*, ii, 529.

<sup>75</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1378; *A.*, ii, 893.

results, the anode must be rotated slowly; the current should be 4—5 amperes at 10 volts, and not more than 20—25 c.c. of  $N/5$ -sulphuric acid should be present. He also finds that it is sometimes necessary to add a second or even a third quantity of copper sulphate in order to complete the reduction.

H. W. Gillett<sup>76</sup> describes the conditions necessary for the deposition of silver in presence of copper from ammoniacal tartrate solutions; an important point is that when the electrolysis is carried out at a temperature below 20° very rapid rotation of the anode is necessary. Miss M. E. Holmes<sup>77</sup> deals with the separation of cadmium from a large number of metals. O. Scheen<sup>78</sup> gives some details for the electrolytic estimation of antimony. In conjunction with his paper should be read that of E. Cohen.<sup>79</sup> H. J. S. Sand has continued his useful studies on the rapid separation of metals,<sup>80</sup> and in a second communication<sup>81</sup> it is shown that by means of the apparatus previously described with rotating anodes, coherent deposits of antimony may be obtained from solutions in sulphuric acid (1:1) in the presence of hydrazine sulphate; the temperature must be kept above 100° with a cathode potential measured against an auxiliary 2*N*-sulphuric acid of 0.65 volt. Tin is not deposited unless the auxiliary potential rises above 0.8 volt. In order to effect its deposition after separating the antimony, oxalic acid is added, the solution neutralised with ammonia, and again acidified with sulphuric acid. Considering the difficulty of this separation on theoretical grounds, the results are extremely good. For the separation of copper from iron, an apparatus is described, including a parchment paper diaphragm. The influence of temperature on the estimation of copper is discussed by J. R. Withrow,<sup>82</sup> whilst E. E. Free<sup>83</sup> deals with the estimation of small quantities of copper. A. Thiel<sup>84</sup> shows that nickel can be estimated accurately by the electrolysis of the nitrate provided no nitrite be present, sufficient excess of ammonia be added, and a straight wire of passive iron used as anode (platinum anodes are attacked); he gives conditions for the separation of nickel and copper quantitatively. F. Foerster and W. Treadwell<sup>85</sup> confirm Thiel and Windel-

<sup>76</sup> *J. Physical Chem.*, 1908, **12**, 26; *A.*, ii, 226.

<sup>77</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1865.

<sup>78</sup> *Zeitsch. Elektrochem.*, 1908, **14**, 257; *A.*, ii, 636.

<sup>79</sup> *Ibid.*, 301; *A.*, ii, 636.

<sup>80</sup> *Ann. Report*, 1907, 207.

<sup>81</sup> *Trans.*, 1908, **93**, 1572.

<sup>82</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 381; *A.*, ii, 432.

<sup>83</sup> *J. Physical Chem.*, 1908, **12**, 28; *A.*, ii, 227.

<sup>84</sup> *Zeitsch. Elektrochem.*, 1908, **14**, 201; *A.*, ii, 538.

<sup>85</sup> *Ibid.*, 89; *A.*, ii, 324.



schmidt's statement,<sup>86</sup> that in separating nickel from zinc by electrolysis an ammoniacal solution containing sodium sulphite as electrolyte, the deposited nickel contains sulphur. As pointed out by A. Fischer, however,<sup>87</sup> without sodium sulphite a much higher current density is required. He gives conditions for the estimation of the two metals. It would appear advisable, taking into account the observations of the various authors, to dissolve the nickel first deposited and again electrolyse. In the electrolytic estimation of nickel, A. Schumann shows<sup>88</sup> that a gauze cathode is preferable to a disk or cone cathode. R. Goldschmidt,<sup>89</sup> in the electrolysis of zinc silicofluoride, uses a stationary slanting anode, over which the solution passes and is returned by a pump. F. J. Metzger and H. T. Beans' method of estimating bismuth by electrolysis in an acetic acid solution seems to be very accurate on the evidence given.<sup>90</sup> J. Peset,<sup>91</sup> after electrolysis of a bismuth salt, adds a known weight of cadmium sulphate, and continues the electrolysis. The deposited cadmium is said to protect the bismuth from oxidation and to render it more adherent.

G. Gallo and G. Cenni<sup>92</sup> state that by electrolysis of a solution of thallium sulphate, faintly acidified with oxalic acid, at the ordinary temperature in a Classen's capsule with a rotating platinum cathode, the whole of the thallium is deposited at the anode apparently as a new oxide,  $Tl_3O_5$ .

J. S. Goldbaum and E. F. Smith<sup>93</sup> have continued their experiments on the separation of the alkali metals<sup>94</sup> to the chlorides of ammonium, caesium, rubidium, and lithium with satisfactory results; attempts to separate potassium and ammonium were unsuccessful.

*General.*—Sir W. Crookes<sup>95</sup> points out the utility of iridium crucibles in analysis, chiefly on account of the high resistance of the metal against the attack of reagents; but he states that rhodium possesses almost the same resistance, and its cost would be less because of its lower density. It is interesting to note that fused silica apparatus, which is adapted for so many purposes in analysis, has recently been considerably cheapened.

<sup>86</sup> *Zeitsch. angew. Chem.*, 1907, **20**, 1137; compare *A.*, 1907, ii, 601.

<sup>87</sup> *Chem. Zeit.*, 1908, **32**, 185; *A.*, ii, 324.

<sup>88</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 2579; *A.*, 1909, ii, 97.

<sup>89</sup> *Bull. Soc. chim. Belg.*, 1908, **22**, 138; *A.*, ii, 536.

<sup>90</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 589; *A.*, ii, 541.

<sup>91</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 401; *A.*, ii, 780.

<sup>92</sup> *Atti R. Acad. Lincei*, 1908, [v], **17**, ii, 276; *A.*, ii, 986.

<sup>93</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1705; *A.*, ii, 1072.

<sup>94</sup> *Ibid.*, 1907, **29**, 447, 1445, 1455; *A.*, 1907, ii, 574, 988.

<sup>95</sup> *Proc. Roy. Soc.*, 1908, **80**, A., 535; *A.*, ii, 702.

A modification of the Ostwald pipette for calibrating burettes and other measuring vessels has been devised by O. von Spindler.<sup>96</sup> Other useful apparatus in connexion with volumetric analysis is described by G. Müller<sup>97</sup> and G. Müller and O. Berchem.<sup>98</sup> A. Gawalowski<sup>99</sup> has devised an apparatus for mixing liquids during a reaction. A simple manometer for use when distilling under diminished pressure is described by N. L. Gebhard,<sup>1</sup> and H. Süchting<sup>2</sup> has devised an automatic stirring arrangement which can be applied to liquids liable to bump when being distilled under diminished pressure. P. A. Kober<sup>3</sup> describes an apparatus whereby Folin's method may be applied to Kjeldahl nitrogen determinations; and, later,<sup>4</sup> he deals with the estimation of carbamide by Folin's method. A new form of pyknometer for very accurate work has been devised by W. R. Bousfield.<sup>5</sup>

*Gas Analysis.*—Useful methods for the detection of ozone, hydrogen peroxide, and nitrogen peroxide in air are described by E. H. Keiser and L. McMaster.<sup>6</sup> P. Ménière<sup>7</sup> gives a method for the estimation of mercury vapour in air, whilst J. Ogier and E. Kohn-Abrest<sup>8</sup> deal with the detection and estimation of small quantities of carbon monoxide in air. C. A. Keane and H. Burrows<sup>9</sup> show that the autolysator for the automatic determination of carbon dioxide in furnace gases gives accurate results. A. Fraenckel<sup>10</sup> deals with the estimation of phosphorus, sulphur, and silica in acetylene. W. A. Bone and R. V. Wheeler<sup>11</sup> describe an apparatus for the analysis of mixtures of hydrocarbon gases, and A. E. Hill<sup>12</sup> describes a new gas burette. A. Stock<sup>13</sup> deals with the uses of the mercury trough in the manipulation of gases and their treatment with reagents. He gives some useful hints on the re-purification of mercury. New gas analysis apparatus has

<sup>96</sup> *Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 145; *A.*, ii, 625.

<sup>97</sup> *Chem. Zeit.*, 1908, **44**, 532; *A.*, ii, 626.

<sup>98</sup> *Ibid.*, 711; *A.*, ii, 775.

<sup>99</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 697; *A.*, ii, 939.

<sup>1</sup> *Proc.*, 1908, **24**, 51.

<sup>2</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 755; *A.*, 1909, ii, 35.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1131; *A.*, ii, 626.

<sup>4</sup> *Ibid.*, 1279; *A.*, ii, 893.

<sup>5</sup> *Trans.*, 1908, **93**, 679.

<sup>6</sup> *Amer. Chem. J.*, 1908, **39**, 96; *A.*, ii, 222.

<sup>7</sup> *Compt. rend.*, 1908, **146**, 754; *A.*, ii, 433.

<sup>8</sup> *Ann. Chim. anal.*, 1908, **13**, 169, 218; *A.*, ii, 631, 632.

<sup>9</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 608; *A.*, ii, 735.

<sup>10</sup> *J. Gasbeleucht.*, 1908, **51**, 431; *A.*, ii, 983.

<sup>11</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 10; *A.*, ii, 221.

<sup>12</sup> *Trans.*, 1908, **93**, 1857.

<sup>13</sup> *Ber.*, 1908, **41**, 3834; *A.*, 1909, ii, 89.

been devised by R. Ross and J. P. Leather.<sup>14</sup> H. Franzen<sup>15</sup> has devised a simple apparatus by means of which a gas may be absorbed from a mixture containing a large proportion of non-absorbable gas. L. M. Dennis and E. S. McCarthy<sup>16</sup> recommend an ammoniacal solution of nickel cyanide as an absorbent for benzene in illuminating gas.

*Water Analysis.*—F. Telle<sup>17</sup> proposes a solution containing 0.344 gram of gypsum per litre as a standard in the Clark process. The method suggested by C. J. Blacher and J. Jacoby,<sup>18</sup> of estimating alkaline earths by titration with potassium stearate and phenolphthalein, is worthy of attention. H. Noll<sup>19</sup> gives a method for the estimation of carbonic acid and carbonates in chalybeate waters. E. Ernyei<sup>20</sup> describes a method of estimating manganese in waters. A useful paper on the systematic investigation of potable waters is that by G. Romyn,<sup>21</sup> who discusses the flora and fauna of potable waters.<sup>22</sup> J. E. Purvis and R. M. Courtauld<sup>23</sup> show that organic nitrogen compounds are attacked to a certain extent by the copper-zinc couple, so that the estimation of nitrates and nitrites by this method in presence of organic nitrogen compounds gives too high results. A simple apparatus for observing the rate of absorption of oxygen by polluted waters has been devised by W. E. Adeney.<sup>24</sup> K. Saito<sup>25</sup> points out that *Bacillus coli communis* is so widely disseminated that great caution must be exercised in condemning a water as polluted because of its presence.

G. O. Adams and A. W. Kimball<sup>26</sup> show that, in the estimation of nitrogen in sewage by the Kjeldahl method, the ammonia formed may be nesslerised. H. W. Clark and G. O. Adams<sup>27</sup> state that the odour and appearance of incubated effluents give a better idea of their putrescibility than does the measurement of the time required to decolorise dyes.

<sup>14</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 491; *A.*, ii, 626.

<sup>15</sup> *Zeitsch. anorg. Chem.*, 1908, **57**, 395; *A.*, ii, 425.

<sup>16</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 233; *A.*, ii, 435.

<sup>17</sup> *J. Pharm. Chim.*, 1908, [vi], **27**, 380; *A.*, ii, 535.

<sup>18</sup> *Chem. Zeit.*, 1908, **32**, 744; *A.*, ii, 897.

<sup>19</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 640, 1455; G. Lunge, *ibid.*, 833; *A.*, ii, 435.

<sup>20</sup> *Chem. Zeit.*, 1908, **32**, 41; *A.*, ii, 133.

<sup>21</sup> *Pharm. Weekblad*, 1908, **45**, 402.

<sup>22</sup> *Chem. Weekblad. Beilage*, 1908, 30/5; *Pharm. Weekblad*, 1908, **45**, 1287.

<sup>23</sup> *Proc. Camb. Phil. Soc.*, 1908, **14**, 441; *A.*, ii, 776.

<sup>24</sup> *Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 280; *A.*, ii, 781.

<sup>25</sup> *Arch. Hygiene*, 1908, **63**, 215.

<sup>26</sup> *J. Amer. Chem. Soc.* 1908, **30**, 1034.

<sup>27</sup> *Ibid.*, 1037.

*Organic Chemistry.*

*Qualitative.*—This portion of the literature is as voluminous as usual, but it will only be necessary to mention a few papers. L. E. Hinkel<sup>28</sup> deals with the detection of methyl alcohol in ethyl alcohol. I. Lifschütz<sup>29</sup> states that the green colour produced by warming an acetic acid solution of cholesterol with benzoyl peroxide, although less sensitive than Liebermann's reaction, has advantages in the position of the absorption bands. Some colour reactions of cholesterol and oxycholesterol are described by L. Golodetz,<sup>30</sup> and, by the same author,<sup>31</sup> a colour reaction with formaldehyde and benzoyl peroxide. In connexion with Hehner's test for formaldehyde in milk,<sup>32</sup> H. D. Dakin<sup>33</sup> characterises a number of aliphatic ketones and aldehydes by the appearances and melting points of their *p*-nitrophenylhydrazones. H. J. H. Fenton and G. Barr<sup>34</sup> tabulate the colour reactions produced by formic, oxalic, dihydroxy-tartaric, pyruvic,  $\alpha\alpha$ -dimethylglutaric, lactic, saccharic, lævulic, and oxalacetic acids when treated with resorcinol, phenol, pyrogallol, or *o*-cresol in presence of concentrated sulphuric acid. According to W. M. Dehn and S. F. Scott,<sup>35</sup> sodium hypobromite gives characteristic colours with phenols and aromatic amines. T. Silbermann and N. Ozorovitz<sup>36</sup> make use of the formation of resinous condensation products (insoluble in ordinary solvents) from formaldehyde and dihydric phenols to detect and identify the latter. F. A. Steensma's observations,<sup>37</sup> that an aromatic or heterocyclic aldehyde in presence of a mineral acid gives a colour with phenols or with heterocyclic compounds containing the group C:CH, are most interesting as showing that certain colour reactions can actually be predicted, a generalisation of which he cites specific instances. The formation of an additive (red) compound with *p*-dimethylaminobenzaldehyde is recommended by B. von Pawlewski<sup>38</sup> as a characteristic reaction of anthranilic acid. Some new differential reactions of the naphthols are described by Voley-Boucher.<sup>39</sup> C. Lefebvre<sup>40</sup> describes some biochemical reactions

<sup>28</sup> *Analyst*, 1908, **33**, 417; *A.*, ii, 1076. <sup>29</sup> *Ber.*, 1908, **41**, 252; *A.*, ii, 233.

<sup>30</sup> *Chem. Zeit.*, 1908, **32**, 160; *A.*, ii, 328. <sup>31</sup> *Ibid.*, 245; *A.*, ii, 330.

<sup>32</sup> See F. von Fillinger, *Zeitsch. Nahr. Genussm.*, 1908, **16**, 226; *A.*, ii, 902.

<sup>33</sup> *J. Biol. Chem.*, 1908, **4**, 235; *A.*, ii, 234.

<sup>34</sup> *Proc. Camb. Phil. Soc.*, 1908, **14**, 386; *A.*, ii, 438.

<sup>35</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1418; *A.*, i, 780.

<sup>36</sup> *Bul. Soc. Sci. Bucuresci*, 1908, **17**, 41; *A.*, 1909, ii, 98.

<sup>37</sup> *Biochem. Zeitsch.*, 1908, **8**, 203; *A.*, ii, 442.

<sup>38</sup> *Ber.*, 1908, **41**, 2353; *A.*, i, 638.

<sup>39</sup> *Ann. Chim. anal.*, 1908, **13**, 335; *A.*, ii, 990.

<sup>40</sup> *Arch. Pharm.*, 1907, **245**, 493; *A.*, ii, 57.

(enzymic) for the detection of sugars and glucosides in the Taxaceæ. B. Tollens and F. Rorive<sup>41</sup> describe colour and spectral reactions of sugars and their derivatives on treatment with naphtharesorcinol. B. Tollens<sup>42</sup> uses the same reagent for the detection of glycuronic acid in urine.<sup>43</sup> E. C. Kendall and H. C. Sherman<sup>44</sup> recommend *p*-bromobenzylhydrazide as a reagent for the detection and identification of various sugars; the hydrazone obtained from galactose is insoluble in boiling alcohol, whilst those of mannose and lævulose are sparingly, and that of dextrose readily, soluble. It is well known that even the hexoses give traces of furfuraldehyde when boiled with acids. C. Fleig<sup>45</sup> shows that furfuraldehyde gives colorations with indole and with carbazole. L. Garnier<sup>46</sup> deals with some colour reactions of digitalis glucosides.

In connexion with alkaloids, C. Reichard<sup>47</sup> describes some reactions of tropacocaine, which serve to differentiate it from cocaine. G. Denigès<sup>48</sup> gives some reactions of hordenine, and L. Krauss<sup>49</sup> some reactions of synthetic supraprenine.

F. Schulz<sup>50</sup> calls attention to the red coloration given when a solution of (crude, not pure) picric acid in benzene is added to a mineral oil, a reaction which serves for the detection of the latter in animal and vegetable oils. Tests for oleic acid are described by A. Manea<sup>51</sup> and I. Lifschütz.<sup>52</sup>

*Quantitative.*—There are a few papers dealing with elementary analysis demanding notice. M. Dennstedt<sup>53</sup> details the precautions to be taken in his simplified method of determining carbon in difficultly combustible substances.<sup>54</sup> He describes<sup>55</sup> a new form of soda-lime absorption apparatus, and A. E. Hill<sup>56</sup> a new form of potash bulbs. W. Lenz<sup>57</sup> points out that the percentage of carbon

<sup>41</sup> *Ber.*, 1908, **41**, 1783; *A.*, ii, 638.

<sup>42</sup> *Ibid.*, 1788; *A.*, ii, 639.

<sup>43</sup> See also K. Tollens, *Zeitsch. physiol. Chem.*, 1908, **56**, 115; *A.*, ii, 740; and compare J. A. Mandel and C. Neuberg, *Biochem. Zeitsch.*, 1908, **13**, 148; *A.*, ii, 993.

<sup>44</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 145; *A.*, ii, 902.

<sup>45</sup> *J. Pharm. Chim.*, 1908, [iv], **28**, 385; *A.*, ii, 1077.

<sup>46</sup> *Ibid.*, **27**, 369; *A.*, ii, 544.

<sup>47</sup> *Pharm. Zentr.-h.*, 1908, **49**, 337; *A.*, ii, 643.

<sup>48</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 786; *A.*, i, 735.

<sup>49</sup> *Apoth. Zeit.*, 1908, **23**, 701.

<sup>50</sup> *Chem. Zeit.*, 1908, **32**, 345.

<sup>51</sup> *Bull. Soc. Sci., Bucuresci*, 1908, **17**, 256.

<sup>52</sup> *Zeitsch. physiol. Chem.*, 1908, **56**, 446; *A.*, i, 754.

<sup>53</sup> *Ber.*, 1908, **41**, 60; *A.*, ii, 321.

<sup>54</sup> Compare J. Zaleski, *Bull. Acad. Sci. Cracow.*, 1907, ii, 646; *A.*, ii, 132.

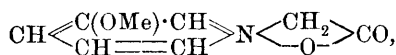
<sup>55</sup> *Chem. Zeit.*, 1908, **32**, 77; *A.*, ii, 225.

<sup>56</sup> *Proc.*, 1908, **24**, 182.

<sup>57</sup> *Zeitsch. anal. Chem.*, 1907, **46**, 557; *A.*, ii, 65.

obtained by the Carrasco-Plancher method<sup>58</sup> is apt to be low on account of the formation of carbon monoxide. O. Carrasco and E. Belloni<sup>59</sup> recommend a modification of the method, in which the organic substance is mixed with powdered platinised biscuit porcelain as catalyst instead of cupric oxide. M. Dennstedt and F. Hassler<sup>60</sup> describe a method and apparatus for the simultaneous estimation of carbon, hydrogen, halogen, and nitrogen, and from the one example given—analysis of pyridine platinochloride—the results would appear to be accurate enough for purposes of check.<sup>61</sup> For the estimation of the halogens and sulphur, W. Parr shows that his method of heating with sodium peroxide and "boromagnesium" mixture (see p. 186) may be used. To estimate sulphur in indiarubber, he burns the sample with sodium peroxide, potassium chlorate, and benzoic acid.<sup>62</sup> According to H. D. Richmond,<sup>63</sup> the higher results obtained when the nitrogen in casein is estimated by Dumas's method, as compared with Kjeldahl's method, is due to the presence of unburnt carbon monoxide in the former case. He also describes a simple method of estimating nitrogen in compounds containing the triazo-group. A series of papers have been published by P. Blackman<sup>64</sup> on a new method of estimating vapour density.

J. Herzog and V. H. Hâncu<sup>65</sup> show that the number of hydroxyl groups present in a phenol may be determined by condensing it with diphenylcarbonyl chloride, hydrolysing the resulting urethane, and weighing the diphenylamine formed. A. Kirpal<sup>66</sup> points out that methoxyl determinations in such a substance as



either by the Zeisel or by the Herzig-Meyer method are invariably low, probably due to the wandering of the methyl group from the oxygen to the nitrogen atom.<sup>67</sup>

G. T. Morgan and T. Cook<sup>68</sup> describe a useful distillation flask adapted for use in many methods for the analysis of organic sub-

<sup>58</sup> *Ann. Report*, 1906, 211.

<sup>59</sup> *J. Pharm. Chim.*, 1908, [vi], 27, 469; *A.*, ii, 631.

<sup>60</sup> *Ber.*, 1908, 41, 2778; *A.*, ii, 984.

<sup>61</sup> Compare J. Zehenter, *Programm d. Oberrealschule, Innsbruck*, 1908; *Chem. Zentr.*, 1908, ii, 635.

<sup>62</sup> See p. 186.

<sup>63</sup> *Analyst*, 1908, 33, 179; *A.*, ii, 530.

<sup>64</sup> *Ber.*, 1908, 41, 768, 881, 1588, 2487, 4141; compare *Proc.*, 1908, 24, 8; *A.*, ii, 157, 564; *A.*, 1909, ii, 21.

<sup>65</sup> *Ber.*, 1908, 41, 638; *A.*, ii, 327.

<sup>66</sup> *Ibid.*, 819; *A.*, ii, 436.

<sup>67</sup> Compare J. Herzig, *Monatsh.*, 1908, 29, 295; *A.*, ii, 638.

<sup>68</sup> *Analyst*, 1908, 33, 118; *A.*, ii, 424.

stances in which distillation is necessary. R. Corradi<sup>69</sup> recommends the gasometric (hypobromite) method of determining the ammonia formed in the Kjeldahl method. V. von Cordier<sup>70</sup> describes a modification of Hüfner's hypobromite method for the estimation of nitrogen, and a special apparatus for carrying it out.

H. Bollenbach<sup>71</sup> has modified de Haën's volumetric process of estimating ferrocyanides, and the evidence he brings forward shows that the results are trustworthy. A valuable paper on the analysis of commercial ferrocyanides is that by H. G. Colman.<sup>72</sup> The paper deals with the direct estimation of the ferrocyanide by titration with copper or zinc sulphate, the estimation of the iron and the calculation of the ferrocyanide from the results, and the estimation of the hydrogen cyanide. G. Heikel<sup>73</sup> has published a useful paper on the limits of accuracy of the Messinger and Denigès' methods of estimating acetone. V. F. Herr<sup>74</sup> describes a new dephlegmator for the fractionation of naphtha. I. Bay<sup>75</sup> shows that carbon disulphide may be estimated in benzene by precipitating with phenylhydrazine, and weighing the resulting phenylhydrazine phenylthiocarbazate,  $\text{CS}_2(\text{Ph}\cdot\text{NH}\cdot\text{NH}_2)_2$ , dried in a vacuum desiccator. This process is, however, not new; it is commonly used, and was first described by Liebermann and Seyewetz.<sup>76</sup> According to F. Utz,<sup>77</sup> when picric acid is heated with sodium hydroxide and hydrogen peroxide, the whole of the nitrogen is obtained as nitrate, and may be estimated by the "nitron" method, whilst M. Busch and G. Blume<sup>78</sup> show that picric acid may be estimated by weighing it as "nitron" picrate; halides and their oxygenated salts, nitrates, nitrites, and chromates must be absent. F. Raschig<sup>79</sup> gives a method for estimating *m*-cresol in presence of the *o*- and *p*-isomerides; it is adversely criticised by J. Herzog.<sup>80</sup>

The methods of estimating starch in cereals, which depend on determining the reducing power after hydrolysis with either diastase or acid, or with both successively, are lengthy and inaccurate, since reducing sugars other than those originating from the starch are invariably present among the products of hydrolysis. Although

<sup>69</sup> *Boll. chim. farm.*, 1907, **46**, 861; *A.*, ii, 130.

<sup>70</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 682; *A.*, ii, 983.

<sup>71</sup> *Ibid.*, 687; *A.*, ii, 996.

<sup>72</sup> *Analyst*, 1908, **33**, 261.

<sup>73</sup> *Chem. Zeit.*, 1908, **32**, 75; *A.*, ii, 235.

<sup>74</sup> *Ibid.*, 148; *A.*, ii, 232.

<sup>75</sup> *Compt. rend.*, 1908, **146**, 132; *A.*, ii, 226.

<sup>76</sup> *Ber.*, 1891, **24**, 788; *A.*, 1891, 684.

<sup>77</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 140; *A.*, ii, 233.

<sup>78</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 354; *A.*, ii, 328.

<sup>79</sup> *Pharm. Zeit.*, 1908, **53**, 99; *A.*, ii, 233.

<sup>80</sup> *Ibid.*, 141; *A.*, ii, 233.



no known method gives anything but approximate accuracy, in the writer's hands the most satisfactory and rapid method is the Dubrunfaut-Effront, which consists in triturating the ground cereal with concentrated hydrochloric acid and polarising the soluble starch. Last year C. J. Lintner<sup>81</sup> proposed a modification of this method, and later O. Wenglein<sup>82</sup> suggested the use of sulphuric acid (D 1·7) instead of hydrochloric, under which conditions the rotatory power of barley starch is found to be  $[\alpha]_D 191\cdot7^\circ$ . Lintner has confirmed Wenglein's results,<sup>83</sup> and adopts his suggestions. E. Ewers<sup>84</sup> points out that substances other than starch are dissolved, and that the results are thereby vitiated. He proposes modifications, his latest suggestion<sup>85</sup> being treatment with one per cent. hydrochloric acid at  $100^\circ$ , and clarification with ammonium molybdate, before polarising. In connexion with sugars, Barfoed's copper acetate solution was put forward as one which was not reduced by maltose and lactose, and F. C. Hinkel and H. C. Sherman<sup>86</sup> have determined the conditions under which in a mixture of dextrose and the reducing bioses mentioned, only the former exhibits reducing power. F. Watts and H. A. Tempany<sup>87</sup> recommend the use of dry basic lead acetate for clarifying commercial sugar solutions. H. C. Prinsen Geerligs<sup>88</sup> points out that the error due to the precipitation of lævulose only occurs in the case of commercial samples containing impurities precipitable by the lead reagent, whilst O. Schrefeld<sup>89</sup> states that this source of error is to be avoided by the employment of neutral lead acetate. F. Watts and H. A. Tempany<sup>90</sup> recommend the Fehling-Violette solution as the least liable to auto-reduction. In the estimation of invert-sugar in presence of sucrose, they find that one gram of the latter exerts a reducing power equal to 0·0033 gram of invert-sugar. The writer and T. Rendle<sup>91</sup> find that sucrose has no influence on the estimation of invert-sugar until its amount exceeds 30 per cent. of the total sugars; with a mixture of equal parts of the sugar, the invert-sugar would be over-estimated by 0·8 per cent., whilst when the invert-sugar only represents one per cent. of the mixture, the

<sup>81</sup> *Zeitsch. ges. Brauwesen*, 1907, **30**, 109; compare *A.*, 1907, ii, 823.

<sup>82</sup> *Ibid.*, 1908, **31**, 53.

<sup>83</sup> *Zeitsch. Nahr. Genussm.*, 1908, **16**, 509; *A.*, ii, 1077.

<sup>84</sup> *Zeitsch. öffentl. Chem.*, 1908, **14**, 150; *A.*, ii, 543.

<sup>85</sup> *Chem. Zeit.*, 1908, **32**, 996.

<sup>86</sup> *J. Amer. Chem. Soc.*, 1907, **29**, 1744; *A.*, ii, 235.

<sup>87</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 53; *A.*, ii, 236.

<sup>88</sup> *Intern. Sugar J.*, 1908, **10**, 500; *A.*, ii, 990.

<sup>89</sup> *Zeitsch. Ver. deut. Zuckerind.*, 1908, 947; *A.*, ii, 1076.

<sup>90</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 191; *A.*, ii, 437.

<sup>91</sup> *Analyst*, 1908, **33**, 167; *A.*, ii, 542.

amount returned may be 14 per cent. too much. These results confirm those of Watts and Tempary,<sup>92</sup> who, however, dealt only with high proportions of sucrose to invert-sugar. The writer and G. C. Jones<sup>93</sup> have shown that the volumetric method of estimating reducing sugars, using ferrous thiocyanate as indicator, gives results quite as accurate as the gravimetric method, and is far more rapid. The writer would point out, however, that with commercial products, such as molasses containing iron, the ferrous thiocyanate indicator cannot be used. It is well known that the rotatory power of lævulose decreases as the temperature is raised, and that at 87° it is equal but opposite in sign to that of dextrose, so that equal amounts of dextrose and lævulose are optically inactive at 87°. For the analysis of commercial invert-sugar, the measurement of the change or rotatory power with rise of temperature is useful, and the apparatus described by A. P. Sy<sup>94</sup> for making polarimetric determinations at high temperatures is much to be appreciated.

T. W. Harrison and F. M. Perkin<sup>95</sup> find that the Valenta method is untrustworthy for the estimation of tar oils in admixture with mineral oils, the latter being not absolutely insoluble in methyl sulphate.<sup>96</sup> W. H. Emerson<sup>97</sup> has redetermined the solubility of stearic acid in alcohol at 0° for the purpose of the Hehner-Mitchell method. R. K. Dons<sup>98</sup> describes a modification of his method of determining the caprylic acid value in butter fat. J. Lewkowitsch<sup>99</sup> gives constants of, and other information on, carapa oil; and<sup>1</sup> he publishes constants of ochoco fat from the seeds of one of the Myristicaceæ. M. Tsujimoto<sup>2</sup> gives some constants of Japanese tea oil. Such processes of determining unsaturated fats as those of Hübl and Wys (iodine absorption) are often used as mere empirical tests; the scientific principle underlying them is brought out, however, by S. Fokin's experiments,<sup>3</sup> showing that the same results may be obtained by determining the hydrogen value (c.c. of hydrogen at 0° and 760 mm. absorbed by one gram of the substance).<sup>4</sup> H. Matthes and O. Rohdich,<sup>5</sup> working on 13 kilos. of

<sup>92</sup> *Loc. cit.*<sup>93</sup> *Analyst*, 1908, **33**, 160; *A.*, ii, 541.<sup>94</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1790; *A.*, ii, 1076.<sup>95</sup> *Analyst*, 1908, **33**, 2; *A.*, ii, 135.<sup>96</sup> Compare Graeffe, *Ann. Report*, 1907, 211.<sup>97</sup> *J. Amer. Chem. Soc.*, 1907, **29**, 1750; *A.*, ii, 236.<sup>98</sup> *Zeitsch. Nahr. Genussm.*, 1908, **15**, 75; *A.*, ii, 238.<sup>99</sup> *Analyst*, 1908, **33**, 184.<sup>1</sup> *Ibid.*, 313; *A.*, ii, 885.<sup>2</sup> *Chem. Rev. Fett Harz. Ind.*, 1908, **15**, 224.<sup>3</sup> *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 700; *A.*, ii, 637.<sup>4</sup> In connexion with the chemistry of Wys' solution, see H. Ingle, *J. Soc. Chem. Ind.*, 1908, **27**, 314.<sup>5</sup> *Ber.*, 1908, **41**, 19; *A.*, i, 199.

cocoa butter, failed to isolate any constituent to which the characteristic odour could be attributed. From the unsaponifiable matter they isolated amyrylene,  $C_{30}H_{48}$ . H. Matthes and E. Ackermann<sup>6</sup> point out that cocoa fat contains two phytosterols, the acetyl-tetrabromides of which melt at  $180^{\circ}$  and  $132^{\circ}$  respectively. The cholesterol of butter does not form an acetyl-tetrabromide. The ethyl ester value of fats is a new constant devised by J. Hanūs and L. Štekl<sup>7</sup> for the detection of cocoanut oil. C. Fleig<sup>8</sup> has carried out a series of experiments which, on the whole, support Mylius's contention that the Camoin-Baudouin colour reaction of sesamé oil and Pettenkofer's similar reaction of bile acids are due to the furfuraldehyde produced by the mineral acid on the sugar, but the evidence is not conclusive, since lævulose and sucrose give better results than certain pentoses. He also shows that the furfuraldehyde in Villavecchia and Fabris's reagent may be replaced by other aromatic aldehydes.

C. H. Herty<sup>9</sup> draws attention to the wide variations in the optical activity of samples of turpentine from trees grown on the same farm in Florida. F. W. Richardson and J. L. Bowen<sup>10</sup> have investigated various methods of detecting and estimating adulterants in turpentine, one of the conclusions being that refractometric determinations of the distilled fractions give some of the most useful data.<sup>11</sup> C. T. Bennett<sup>12</sup> shows that for the estimation of cineol in eucalyptus oil, Schimmel and Co.'s resorcinol method is untrustworthy, and he points out that the fraction of the oil boiling between  $175^{\circ}$  and  $185^{\circ}$  consists mainly of cineol. A. Bloch<sup>13</sup> estimates citral in lemon-grass oil by removing it as the bisulphite compound. E. M. Chace<sup>14</sup> shows that 2 per cent. of turpentine may be detected in lemon oil by conversion into pinene nitrosochloride and examination of the crystals mounted in olive oil under the microscope. P. Jeancard and C. Satie<sup>15</sup> give the optical activity, specific gravity, and ester value of samples of Alpine lavender oil distilled in different years, whilst M. Daufresne<sup>16</sup> has determined some constants of French and German oil of tarragon.

<sup>6</sup> *Ber.*, 1908, **41**, 2000; *A.*, i, 637.

<sup>7</sup> *Zeitsch. Nahr. Genussm.*, 1908, **15**, 577; *A.*, ii, 641.

<sup>8</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 984, 992; *A.*, ii, 994.

<sup>9</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 863; *A.*, i, 434.

<sup>10</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 613.

<sup>11</sup> See also A. K. Turner, *Oil and Colour Trades J.*, 1908, 503.

<sup>12</sup> *Chemist and Druggist*, 1908, **72**, 55.

<sup>13</sup> *Bull. Sci. Pharmacol.*, 1908, **15**, 72; *A.*, ii, 782.

<sup>14</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1475; *A.*, ii, 908.

<sup>15</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 155; *A.*, ii, 232.

<sup>16</sup> *Ibid.*, 300; compare *A.*, i, 436.

S. S. Pickles<sup>17</sup> gives some constants of origanum oil, from which he has isolated a new terpene, origanene.

Among papers dealing with the chemistry of the proteins, the following may be mentioned: G. T. Matthaïopoulos<sup>18</sup> makes use of the fact that casein forms a definite compound with sodium hydroxide, in order to estimate it (volumetrically) in milk. His results confirm Laqueur and Sackur's observation that the molecular weight of casein is 1135. C. F. Cross, E. J. Bevan, and J. F. Briggs<sup>19</sup> have extended the work of F. Raschig,<sup>20</sup> and have shown that, like ammonia, the proteins and their derivatives form chloroamines by the action of hypochlorites. These chloroamines liberate iodine from potassium iodide, and the presence of proteins in an organic tissue may be located by first steeping it in an acid solution of bleaching powder, and, after washing, removing the excess of chlorine by immersion in 2 per cent. sodium phosphate solution at 45°, and finally treating it with a solution of potassium iodide and starch: a blue stain will be produced in those parts in which proteins occur. R. H. Aders Plimmer and F. H. Scott<sup>21</sup> find that when phosphoproteins are digested with a one per cent. solution of sodium hydroxide for twenty-four hours at 37°, the whole of the phosphorus is eliminated as phosphoric acid. This serves, therefore, as a means of distinguishing these compounds from the nucleoproteins. S. P. L. Sørensen<sup>22</sup> proposes to measure the amino-acid formed by the hydrolysis of proteins by a method based on H. Schiff's observation that the basic function of these compounds is annulled by the formation of the group  $N:CH_2$  after treatment with formaldehyde, the carboxyl group being then titrated with alkali hydroxide, using phenolphthalein or thymolphthalein as indicator. The reaction of the amino-acids, formaldehyde, and alkali is reversible, but when thymolphthalein is employed as indicator an end point (bright blue colour, obtained by four drops of  $N/5$  barium hydroxide in excess of that required to produce the first colour indication) may be chosen such that the concentration of the hydrogen ions is as low as  $10^{-9.7}$ .<sup>23</sup> To measure the rate of proteolysis, Grützner has proposed to estimate the carmin liberated from fibrin stained with that dye, but H. E. Roaf<sup>24</sup> states that Congo-red may with advantage be substituted for carmin.

<sup>17</sup> *Proc.*, 1908, **24**, 95.

<sup>18</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 492; *A.*, ii, 783.

<sup>19</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 260; *A.*, i, 374.

<sup>20</sup> *Ber.*, 1907, **40**, 4586; *Chem. Zeit.*, 1907, **31**, 126; *Zeitsch. angew. Chem.*, 1907, **20**, 2065; *A.*, ii, 30.

<sup>21</sup> *Trans.*, 1908, **93**, 1699.

<sup>22</sup> *Bi-chem. Zeitsch.*, 1907, **7**, 45; *A.*, i, 115.

<sup>23</sup> See, further, S. P. L. Sørensen and H. Jessen-Hansen, *ibid.*, 1908, **7**, 407; *A.*, ii, 234.

<sup>24</sup> *Biochem. J.*, 1908, **3**, 188; *A.*, ii, 743.

In the analysis of organic substances, increasing use is being made of physical methods, and numerous papers have appeared recently on the estimation of total solids in molasses, wort, beer, wine, spirits, etc., by means of the refractometer, which can also be used for the estimation of alcohol. The method is principally to be recommended on the score of its rapidity, although in the hands of a skilful worker in a properly equipped laboratory the determination of specific gravity can be carried out very rapidly. On account of the heterogeneous composition of many commercial products, notably the varying amounts of mineral matters present, special tables must be constructed for each kind of product. For practical purposes the assumption that all sugars in solution of like concentration have the same refractive index is quite justified. Tables have been prepared for sugar products by H. Main<sup>25</sup> and by H. C. Prinsen Geerligs.<sup>26</sup> H. Bryan,<sup>27</sup> using Geerligs's tables for honey, syrups, and molasses, finds that the results are in closer accord with the actual determinations of solid matter than are the values obtained by the specific gravity method from Brix's tables. It should be pointed out, however, that this is not due to any defect in the specific gravity method. C. Mai and S. Rothenfusser<sup>28</sup> give a valuable résumé of the application of the refractometric method of detecting the addition of water to milk. From the examination of 5000 samples, they find that the normal refractometer value for milk is 39 divs.; any sample giving a lower reading than 36.5 divs. contains added water. The process fails with sour milks. The application of the method to the estimation of extract in wort is dealt with by O. Mohr,<sup>29</sup> and to that of alcohol and extract in beer and spirits by J. Race.<sup>30</sup> A. Frank<sup>31</sup> observes that the indirect estimation of alcohol by refraction before and after expelling the alcohol is untrustworthy. M. Duboux and P. Dutoit<sup>32</sup> describe a new method of estimating alcohol in wine; it depends on the determination of the temperature at which a clear solution is formed when a fixed amount of the wine distillate is added to a fixed amount of a mixture of aniline or nitrobenzene and alcohol. Some useful data in the pycnometric estimation of alcohol in fermented liquids, with a description of new apparatus, is given by W. Antoni.<sup>33</sup>

<sup>25</sup> *International Sugar J.*, 1907, **9**, 481.      <sup>26</sup> *Ibid.*, 1908, **10**, 68.

<sup>27</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1443.

<sup>28</sup> *Zeitsch. Nahr. Genussm.*, 1908, **16**, 7.

<sup>29</sup> *Wochensch. Brau.*, 1908, **25**, 454.

<sup>30</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 544, 547; *A.*, ii, 738.

<sup>31</sup> *Chem. Zeit.*, 1908, **32**, 569; *A.*, ii, 637.

<sup>32</sup> *Ann. Chim. anal.*, 1908, **13**, 4; *A.*, ii, 136.

<sup>33</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1276; *A.*, ii, 902.

M. E. Pozzi-Escot<sup>34</sup> describes a volumetric method of estimating tartaric acid in wine, whilst the Goldenberg method has been investigated by the Chemische Fabrik vorm. Goldenberg, Geromont and Co.,<sup>35</sup> and conditions laid down whereby accurate results may be obtained. L. Gowing-Scopes<sup>36</sup> has submitted J. von Ferentzy's method of estimating tartaric acid in presence of other acids<sup>37</sup> to a critical examination, and finds it trustworthy. A. Hubert<sup>38</sup> has made the interesting observation that citric acid occurs naturally in wines. This has been confirmed by H. Astruc<sup>39</sup> and by G. Denigès,<sup>40</sup> who suggests that the reason the acid cannot be detected in old wines is to be ascribed to bacterial influences. E. Dupont<sup>41</sup> states that Denigès's mercury method of detecting citric acid may be made approximately quantitative. G. Favrel<sup>42</sup> proposes a test which depends on the formation of acetonedicarboxylic acid (when citric acid is heated with sulphuric acid). This ketonic acid gives a violet coloration with ferric chloride.

P. Dutoit and M. Duboux<sup>43</sup> show that by adding successive quantities of barium hydroxide to a wine, and determining its electrical conductivity after each addition, it is possible to estimate consecutively the sulphates, total acidity, and tannin substances present. Under the name of "abrastol," calcium  $\beta$ -naphthol- $\alpha$ -sulphonate is added to wine as an antiseptic and precipitant of tartrates. The acid may be extracted by amyl alcohol, and identified by the reddish-violet coloration formed on evaporating with mercurous nitrate.

In connexion with brewing materials, A. C. Chapman<sup>44</sup> has devised a valuable method of estimating tannin in hops by weighing the cinchonine compound, and G. C. Jones<sup>45</sup> has communicated two papers on malt analysis.

The paper by J. S. Ford and J. M. Guthrie,<sup>46</sup> on the biochemistry of barley, adds considerably to our knowledge of the nature of the amylolytic enzyme of barley, and the methods they adopt are most interesting and suggestive. J. Wohlgemuth's suggestion,<sup>47</sup> to measure diastatic activity by estimating the quantity of a diastatic

<sup>34</sup> *Bull. Soc. chim. Belg.*, 1908, **22**, 218; *A.*, ii, 740.

<sup>35</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 57; *A.*, ii, 237.

<sup>36</sup> *Analyst*, 1908, **33**, 315; *A.*, ii, 905.

<sup>37</sup> See *Ann. Report*, 1907, 217.

<sup>38</sup> *Ann. Chim. anal.*, 1908, **13**, 139; *A.*, ii, 544.

<sup>39</sup> *Ibid.*, 224; *A.*, ii, 640. <sup>40</sup> *Ibid.*, 226; *A.*, ii, 640.

<sup>41</sup> *Ibid.*, 338; *A.*, ii, 904. <sup>42</sup> *Ibid.*, 177; *A.*, ii, 640.

<sup>43</sup> *Compt. rend.*, 1908, **147**, 134; *A.*, ii, 781.

<sup>44</sup> *J. Inst. Brewing*, 1907, **13**, 646.

<sup>45</sup> *Ibid.*, 1908, **14**, 9, 13.

<sup>46</sup> *Ibid.*, 61; *A.*, ii, 218.

<sup>47</sup> *Biochem. Zeitsch.*, 1908, **9**, 1; *A.*, ii, 444.

solution necessary to hydrolyse soluble starch to the stage at which the products no longer give a coloration with iodine, assumes that this is a linear function of the time, which has not been proved, and the same argument applies to W. A. Johnson's method,<sup>48</sup> although this author does compare the iodine results with those obtained by the cupric reduction method. C. J. Lintner<sup>49</sup> shows that the law of proportionality for malt diastase holds good up to a reducing power of 35 (calculated as maltose). He adopts the writer's method of estimating diastatic activity. J. L. Baker and H. F. E. Hulton<sup>50</sup> and J. S. Ford and J. M. Guthrie<sup>51</sup> have published two most important papers on the question of the so-called "strength" of flour in its relation to enzymes. L. Brieger and J. Trebing<sup>52</sup> call attention to the antitriptic power of human blood-serum, and von Bergmann and K. Meyer<sup>53</sup> give a method for the measurement of its activity.

W. Thörner<sup>54</sup> describes a method of estimating water in foods, consisting in distillation with petroleum and collection of the distillate in a graduated receiver, in which the water separates and its volume may be read off. The method is similar to that of Hoffmann,<sup>55</sup> and of Aschman and Arend.<sup>56</sup>

H. D. Richmond,<sup>57</sup> in his annual report on milk, based this year on the analysis of 35,331 samples, adds to our knowledge of the subject. He has examined eight samples of human milk, and points out that the fat varied from 1.7 to 5.7 per cent. He draws attention to a preservative which he has found in certain samples of milk, namely, formic acid, mixed with dextrose. W. R. G. Atkins<sup>58</sup> states that determinations of the freezing point and specific gravity of milk are sufficient to show if water has been added or fat removed. The freezing point of milk is practically a constant, namely, 0.55°.

A. Kreutz<sup>59</sup> shows that after heating cocoa in a flask on the water-bath with chloral alcoholate until a homogeneous paste is obtained, the fat may be extracted by warming with successive quantities of ether. The chloral is all driven off by heating the

<sup>48</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 798; *A.*, ii, 743.

<sup>49</sup> *Zeitsch. ges. Brauwesen*, 1908, **31**, 421.

<sup>50</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 368.

<sup>51</sup> *Ibid.*, 389.

<sup>52</sup> *Berlin Klin. Wochensh.*, 1908, **45**, 1041.

<sup>53</sup> *Ibid.*, 1673.

<sup>54</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 148; *A.*, ii, 222.

<sup>55</sup> *Wochensh. Brau.*, 1902, **19**, 372.

<sup>56</sup> *Chem. Zeit.*, 1906, **30**, 953; *A.*, 1906, ii, 814.

<sup>57</sup> *Analyst*, 1908, **33**, 113.

<sup>58</sup> *Chem. News*, 1908, **97**, 241; *A.*, ii, 641.

<sup>59</sup> *Zeitsch. Nahr. Genussm.*, 1908, **15**, 680; *A.*, ii, 641.



fat at 110°. The results agree well with those obtained by the ordinary method. Later,<sup>60</sup> he shows that the theobromine is extracted along with the fat by this method; when treated with carbon tetrachloride the fat alone is dissolved, leaving the theobromine, which may be weighed.

P. Biginelli<sup>61</sup> draws attention to the fact that when tannic acid is used as a precipitant for alkaloids in toxicological investigations, it also forms insoluble compounds with certain solvents and mineral acids. L. Dreyer<sup>62</sup> describes the differentiation of tubercular from ordinary pus by its behaviour towards Millon's reagent. It is well known that the formation of indole from proteins is a characteristic of certain microbes, and C. Porcher<sup>63</sup> proposes to detect indole in pus by its colour reaction with *p*-dimethylaminobenzaldehyde.

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<sup>60</sup> *Zeitsch. Nahr. Genussm.*, 1908, **16**, 579.

<sup>61</sup> *Gazzetta*, 1907, **37**, ii, 506; *A.*, i, 40.

<sup>62</sup> *Münch. Med. Wochensh.*, 1908, **55**, 728.

<sup>63</sup> *Compt. rend.*, 1908, **147**, 214; *A.*, ii, 769.