

## Physical Methods, Apparatus, etc.

**Crystallographic Data.** Armour Research Foundation of Illinois Institute of Technology (*Anal. Chem.*, 1948, 20, 683-684)—Data for two modifications of thiamine hydrochloride (vitamin B<sub>1</sub>) are given (*cf. Ibid.*, 1948, 20, 275; *Analyst*, 1948, 73, 579). M. E. DALZIEL

**Crystallographic Data.** Armour Research Foundation of Illinois Institute of Technology (*Anal. Chem.*, 1948, 20, 779-780)—Crystal properties of  $\alpha$ -pyridinesulphonic acid in three polymorphic forms, only one being well-defined, are described under the headings given in the original publication (*Ibid.*, 1948, 20, 275; *Analyst*, 1948, 73, 579). M. E. DALZIEL

**Storage and Titration with Oxygen-Sensitive Solutions.** H. W. Stone (*Anal. Chem.*, 1948, 20, 747-749)—The system described uses nitrogen under a slight pressure and avoids the necessity of maintaining inert gas pressure by means of a Kipp's apparatus or a cylinder, and also of scrubbing the inert gas over a long period.

**Apparatus**—In Fig. 1 the gas pressure compensating systems for storage and the burette are separate.

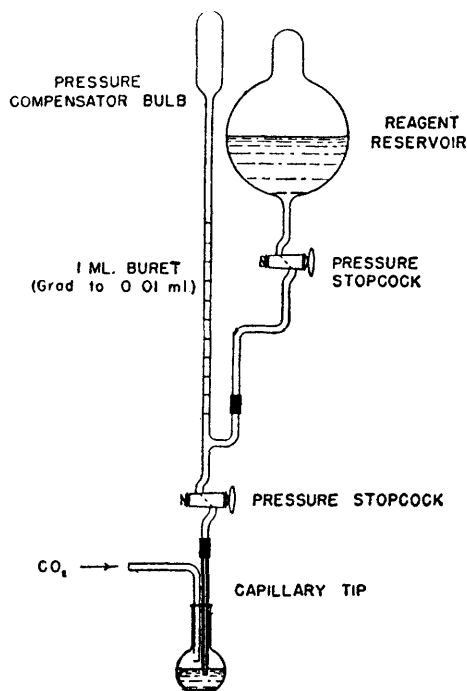


Fig. 1

The nitrogen pressure in the reservoir, made from a round-bottomed flask, must be just sufficiently greater than that in the burette to allow the burette to fill, and that in the burette must be high enough to expel the solution during titration. The apparatus shown in Fig. 2 requires a reservoir above the burette graduations, as gravity controls the flow of solution; thus, only one pressure adjust-

ment is necessary in preparing the apparatus, but if the burette is allowed to empty, the nitrogen becomes contaminated and the whole system must be recharged.

**Introduction of reagent**—The necessary apparatus is shown in Fig. 3, the top stop-cock representing the burette tap in Fig. 2. At the start, screw-clamps B, C, and E are open and D is closed. Pass air at 2 atmospheres pressure and vent through B, which is gradually closed until the chromic chloride solution in hydrochloric acid is forced up

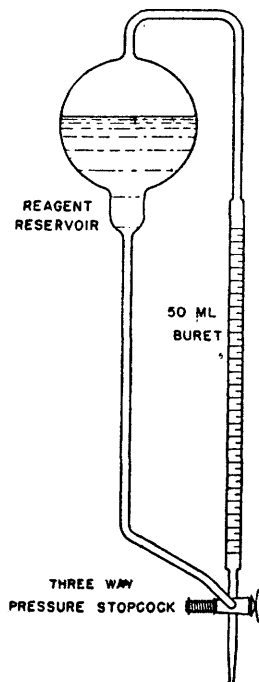


Fig. 2

through the reductor, through E to C, thus clearing air from the line. Open the burette stop-cock, close C, and regulate the flow into the reservoir (Fig. 2) by adjusting B. When enough solution is in the burette and reservoir to absorb all the oxygen, close the stop-cock and E and shake the apparatus, allowing nitrogen through D and the stop-cock to compensate for the decrease in pressure. The pressure of nitrogen should be reduced to about 1 atmosphere by means of a valve on the cylinder. Close the stop-cock and shake the apparatus again lest the nitrogen contains any oxygen. Clear the storage flask of the partly-spent solution and the excess of nitrogen by closing D and opening the burette stop-cock and C and adjusting the pressure to 1 atmosphere by venting through C. Then charge with the reagent by closing C, opening E and forcing the solution up with B closed until the reservoir is half full, the pressure then being 2 atmospheres.

To dispense oxygen-free water, pump out the system with an oil pump and fill with oxygen-free nitrogen alternately until the partial pressure of oxygen is adequately reduced, then admit distilled

water, previously boiled and cooled in a stream of nitrogen.

Nitrogen can be replaced by hydrogen, but carbon dioxide is not suitable as its solubility is too variable. Diffusion of oxygen through the

rotations of the screw. Since the plunger moves at a constant speed, the volume delivered can also be related to the time of delivery.

An indicator electrode and a saturated calomel reference electrode are coupled to a recording potentiometer fitted with a mercury switch, which can be set to stop the titration at the equivalence point, if this is desired. The nature of the indicator electrode depends on the electrode reaction taking place, and is usually a strip of an appropriate metal.

Since additions can be made more accurately from a syringe than from a burette of the same volume, this apparatus is capable of giving results that are more accurate than those obtained by the usual methods. By using a syringe of smaller volume, the method can be applied on the semi-micro scale.

For routine purposes in which the shape of the titration curve is known, the recording potentiometer is replaced by any potentiometer control of rapid response, set to stop the titration at the equivalence point.

J. G. WALLER

#### "Micro"-Kjeldahl Distillation Apparatus.

R. Johanson (*J. Proc. Austral. Chem. Inst.*, 1948, 15, 183-184)—In the apparatus shown the outer jacket serves as a steam jacket for the inner distillation tube and as a vacuum jacket for collecting the spent sample, the inner tube being suspended in it by means of a rubber stopper. The sample is admitted through the thistle funnel, and the

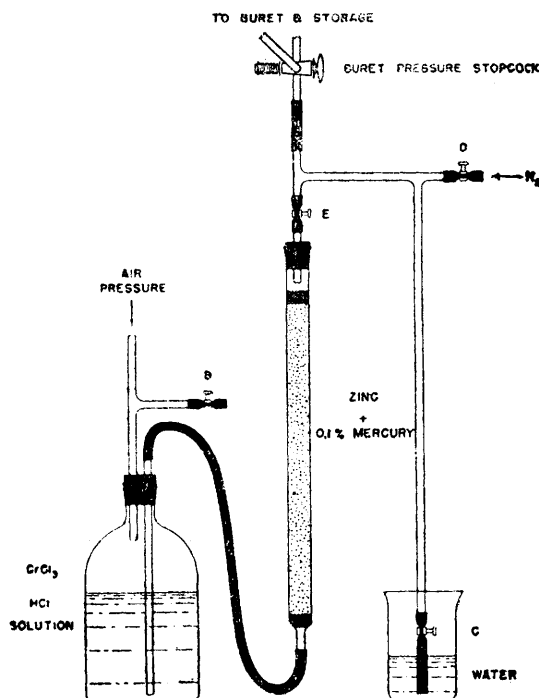


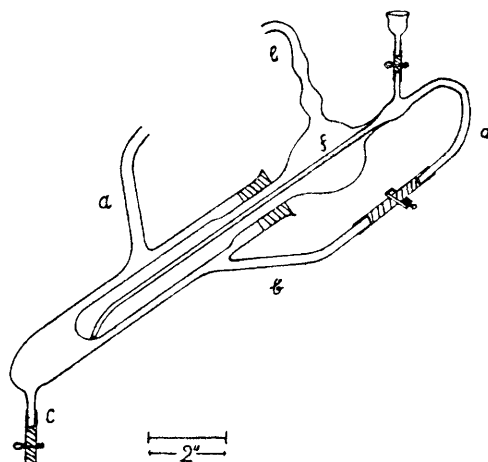
Fig. 3

rubber is compensated for by replacing the reagent in the lines with fresh solution before a fresh group of titrations. During titrations a capillary tip is fitted to the burette and allowed to dip below the surface, so restricting diffusion and oxidation, while commercial carbon dioxide is blown over the liquid surface at a rate of 200 to 300 ml. per min. The gas stream is started about 5 min. before titration to sweep out the vessel, but longer time is necessary to clear the line from the cylinder.

Solutions of 0.03 N chromous chloride in hydrochloric acid showed no variation in titre in 10 months. The apparatus requires no attention when not in use, and is ready at a moment's notice.

M. E. DALZIEL

**Automatic Potentiometric Titrations.** J. J. Lingane (*Anal. Chem.*, 1948, 20, 285-292)—Potentiometric titrations applicable to any type of electrode reaction can be carried out with the apparatus described, which will either record the complete titration curve or stop the titration at the equivalence point. The titrant is delivered from a 50-ml. hypodermic syringe, the plunger being driven by a screw thread turned by a synchronous motor. The number of rotations of the screw are recorded by a revolution counter and the syringe is calibrated by weighing the water forced out by a definite number of complete



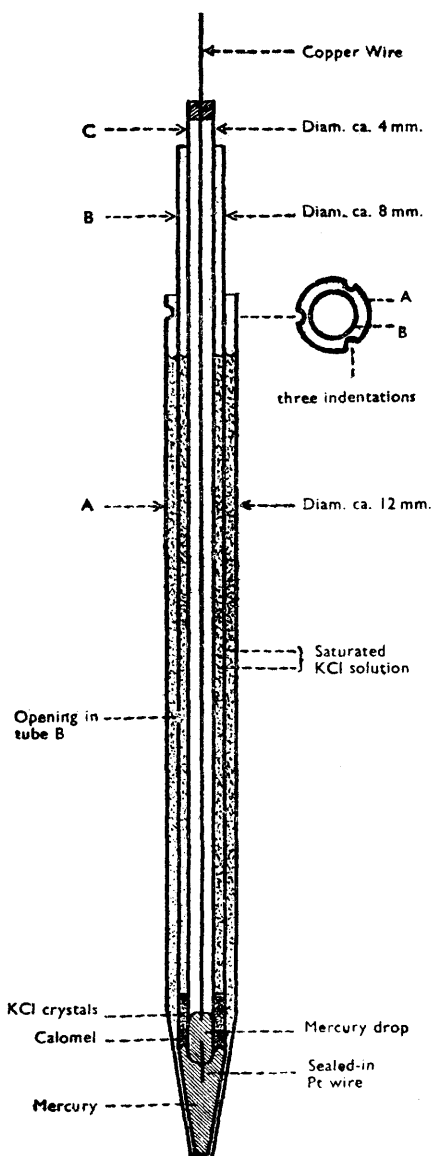
clip on the connection closed; steam is then allowed to enter through the tube *a*, is led through *b* into *d* and tube *f*, and bubbles through the sample liquor into *e* and the condenser, which is not shown. Distillation is rapid and smooth, and emptying out of the spent liquor into the outer jacket is automatic at the close of a determination.

M. E. DALZIEL

**Calomel Electrode.** B. van der Burg (*Chem. Weekblad*, 1948, 44, 417-418)—The simple and easily made calomel electrode described is composed of a glass tube, A, of 140 mm. length, drawn out at the lower end and provided with three indentations at the upper end. A second tube, B, inserted

into the first one, has the lower end drawn out and sealed off, the drawn-out portion being ground into the corresponding part of the tube A. In B

liquid of which the pH is to be determined. After use it is washed with distilled water and dried with filter paper, and a drop of potassium chloride solution is allowed to flow out. The level of the liquid in the electrode must always be above the hole connecting the two tubes. G. MIDDLETON



is placed a small amount of re-distilled mercury, then some calomel and a layer of potassium chloride crystals, after which the innermost tube, C, which is closed at the bottom and has a platinum wire sealed through the lower end, is inserted into the tube B. Contact is made with the platinum wire by means of a bead of mercury in the tube C and an amalgamated copper wire. At the upper end this tube is closed by wax. Finally, the tubes A and B are filled with saturated potassium chloride solution. The prepared electrode is placed in the

**Chemical Analysis Based on X-ray Absorption Measurements with a Multiplier Photo-tube. I. Solids and Liquids.** H. A. Liebhafsky, H. M. Smith, H. E. Tanis, and E. H. Winslow. II. Gases. E. H. Winslow, H. M. Smith, H. E. Tanis, and H. A. Liebhafsky (*Anal. Chem.*, 1947, 19, 861-865, 866-867).—The use of X-ray absorption as a method of chemical analysis has long been appreciated, but simple and precise measurement of X-ray intensity has only recently become possible. These papers describe how the method may be used when X-ray intensity is measured by means of a phosphor and multiplier photo-tube coupled to an amplifier.

**METHOD**—Polychromatic X-rays are passed through sheets of the material being analysed or, for gases, liquids, or divided solids, through a cell in which a known weight of sample is placed. The absorption is then measured and the mass absorption coefficient deduced. Absorption, being an atomic property, independent in general of the physical state, depends upon the elements and their relative proportions present in the sample. The method of analysis is based upon this principle.

A constant-voltage source is necessary for accurate work.

**RESULTS—Solids and Liquids**—Preliminary experiments show that materials such as polystyrene, saflex, butvar, ethyl cellulose, cellulose acetate, cellophane, koroseal, and saran, can be distinguished from one another.

The uniformity and, very roughly, the quality of coal can be assessed in a few minutes, and the chlorine contents of chlorinated hydrocarbon polymers determined in about one-tenth the time required for the conventional analysis.

A limitation of the method is exemplified by methyl alcohol and sucrose which give identical absorption coefficients.

This ambiguity arises from the use of polychromatic X-rays, changes in "effective wavelength" of the X-rays occurring from one measurement to the other. The "effective wavelength" of a polychromatic beam is defined as that of a monochromatic beam absorbed to the same extent under the experimental conditions.

**Gases.**—Measurements made on hydrogen, methane, air, oxygen, methyl chloride, and chlorine, show that, as would be expected, the softest radiation is best for analytical work, but it is found that when longer wavelengths are used, particular attention must be paid to changes in the "effective wavelength."

The temperature and pressure of the gas should be known in order to calculate the density of the sample.

Curves for the absorption of methyl chloride at reduced pressures are given. E. G. STEWARD