action of the relay operates the second clock or recorder which registers the interval between contact with the object or control manipulated and any succeeding manipulation which may be made. When clocks are used in the apparatus, a third clock is employed for obtaining a measurement of total time. This total time value serves as a check on the component times obtained from the other two clocks. Clocks which may be read with precision to 0.001–0.005 sec are being used in present work with the apparatus.

The technique, as described, may be applied to any work situation or psychomotor task in which it is possible to insulate the subject operator from the controls or objects to be manipulated. Subject operators cannot detect the fact that they are acting as electrical conductors in the use of the equipment.

Rate of tapping of different members of the body, operation of hand and foot controls, manual grasping and manipulation of objects, repetitive movements involving transient contact with equipment, adjustment reactions in operation of scales, and operation of machines may all be analyzed by means of the simple principles involved here. The apparatus can be set up to obtain continuous records of repetitive movements in work situations in order to make studies of learning and fatigue and to obtain continuous performance records in manual and pedal motion. Recording apparatus which makes provision for cumulatively recording the time intervals involved can be attached to the device to secure separate rate records of travel and manipulation motions in continuous work.

The development of the technique described has provided a foundation for standardized dimensional analysis of predefined patterns of movement. One example of this application is shown in Fig. 2. A large panel 5 ft long and 3 ft high is constructed with switch controls and pins arranged at regular intervals on the panel. The pins are attached to small springs located behind the panel so that they will return to their original position after being grasped and released. Electrical connections are made between each of the switches and pins on the panel and a terminal board located in the housing of the apparatus. Appropriate controls for selected combinations of switches and pins to be operated are made through this terminal board. When hooked up with the motion analyzer, precise data can be obtained with respect to such dimensions of motion as the pattern of manipulation, plane of movement, direction of movement, length or extent of the movement, continuity or uniformity of the movement patterns, distance of travel from the body, number of repetitions of the movement, the body member involved, force requirements in manipulation, amplitude of manipulation, uniformity in pattern of manipulation, and any other quantitative dimension affecting the motions involved. Stimulus variations may be introduced for analysis of their effects on the motions under investigation. Through such application of the motion analyzer, standardized investigation of human work and control situations may be evolved to answer practical and theoretical questions of work arrangement, control arrangement, and physical conditions affecting performance. The same application of the analyzer constitutes a standardized test situation of significance for the appraisal of individual psychomotor performance which may be of vocational, medical, or military significance in certain situations.

In preliminary studies of learning aspects of movement patterns, it has been determined that the manipulative and travel components of simple movements are affected by practice quite differently. Detailed examination into the effects of training, and related phenomena of inhibition, transfer, and fatigue, which may be of prime significance in various aspects of human engineering work, are made possible by the techniques described.

Investigation of the Forms of Phosphorus in Neutron-Bombarded Phosphates: Role of Hypophosphate[1, 2]

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In attempts to establish the states of combination of P^{32} in neutron-bombarded orthophosphates, use has been made of phosphite as a carrier (*1–3*). The basis for such a use of phosphite apparently has been the work of Wilson (*4*) relative to the possibility of exchange of P^{32} between orthophosphorous and orthophosphoric acids. Wilson considered it possible that the hydration of hypophosphoric acid was to some extent reversible. This was apparently the only reference in recent literature on the states of combination of P^{32} in neutron-bombarded phosphates, which is indicative of the possibility that the hypophosphate form of phosphorus should be considered in such investigations. Work recently completed by the writer has indicated, however, that the formation of hypophosphate by interaction of orthophosphate and phosphite may be of considerable significance, more especially in the case of systems containing calcium.

According to Mellor (*5*) hypophosphoric acid has been prepared by (*a*) slow oxidation of phosphorus in moist air, (*b*) oxidation of phosphorus by cupric nitrate or silver nitrate in the presence of dilute nitric acid, (*c*) by the action of phosphorus on copper sulphate solutions, (*d*) by the slow oxidation of phosphorous acid in air, or (*e*) by oxidation of phosphorous acid with silver nitrate in neutral or ammoniacal

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solution. More recently (*6*) this acid has been prepared by oxidation of red phosphorus with sodium chlorite.

Hitherto the hypophosphates seem invariably to have been prepared from hypophosphoric acid. Thus Mellor (*5*) has not recorded any instance of the preparation of a hypophosphate by reaction of phosphites with phosphates and has indicated that hypophosphoric acid apparently was not formed either by interaction of phosphorous and phosphoric acids in solution or by heating mixtures of the more concentrated forms of these acids. The writer has obtained evidence that the interaction of phosphites and phosphates in aqueous solution may give rise to hypophosphate. This evidence was obtained by the reaction of labeled magnesium ammonium phosphate with (*a*) ammonium orthophosphite, (*b*) sodium hypophosphite, and (*c*) with calcium hypophosphite.

Radioactive magnesium ammonium phosphate believed to contain all the phosphorus in the orthophosphate form was prepared by the following procedure:

> Weigh out 0.1000 g neutron-bombarded monocalcium phosphate (N.R.C. No. 510–3) into a 150-ml Kjeldahl flask. Add 20 ml persulfate-perchloric mixture containing 10 g ammonium persulfate and 10 ml reagent perchloric acid/100 ml. Heat to fumes of perchloric acid. Cool, add 1 ml of the above acid mixture, and again strongly fume the perchloric acid. Add 50 ml distilled water. Neutralize with ammonium hydroxide and precipitate with the molybdate reagent recommended by Jones (*7*). Filter, discarding the filtrate and dissolve the precipitate with ammonium hydroxide. Add 5 ml of the molybdate reagent. Acidify with 1:1 nitric acid and allow the molybdate to precipitate at 24° C for 15 min. Filter and dissolve the precipitate with 1:1 hydrochloric acid into a clean flask. Add 70 ml of magnesia mixture, neutralize with concentrated ammonium hydroxide, and then add 5 ml excess of the latter reagent. Stir repeatedly and let stand overnight at 4° C. Filter the precipitate and wash with 1:20 ammonium hydroxide. Redissolve with hydrochloric acid into a clean Erlenmeyer flask, add 4 ml of magnesia mixture, and reprecipitate with ammonium hydroxide, using the same procedure as the first precipitation. Filter the precipitate, wash with 1:20 ammonium hydroxide, twice with ethyl alcohol, and once with ether. Confirm the absence of hypophosphate in the magnesium ammonium phosphate by precipitation of a portion of the salt with silver nitrate at pH 1 to 2 (*8*) in the presence of carrier hypophosphate. The absence of activity in this silver hypophosphate precipitate indicates the absence of hypophosphates in the magnesium ammonium phosphate.

The preparation of the inactive ammonium orthophosphite was conducted by the action of phosphorus trichloride on distilled water (*5*). The phosphorus trichloride was allowed to drop slowly from a separatory funnel into a suction flask containing distilled water, stoichiometric amounts being reacted. The flask was partially immersed in ice and water, and under suction from a water aspirator. The reaction mixture boiled rapidly at relatively low temperature, indicating possible removal of hydrochloric acid in the process. The reaction mixture was reduced to small volume on the steam bath. Ammonium hydroxide was added until the acidity was pH 3 by glass electrode measurement. Evaporation was continued to dryness. This salt was washed 3 times with alcohol, the filtration being carried out under suction, for the removal of ammonium chloride and any other alcohol-soluble impurities. The dry salt was found to have a melting point of 124° C and a gram-molecular ratio 1:3 of ammonia to total phosphorus. Orthophosphate was not detected by Jones' method (*7*). There was a slight silver precipitate at pH 1.5 in formic or phosphoric acid that suggested the presence of either some hypophosphate or chloride, or both.

The calcium hypophosphate which was used as carrier in testing for hypophosphate formation was prepared by reacting sodium hypophosphate with excess calcium nitrate. The gelatinous precipitate was washed thrice with distilled water and once with ethanol. The sodium hypophosphate for this reaction was prepared by the action of sodium chlorite on red phosphorus as described by Leininger and Chulski (*6*), and was twice recrystallized from water. Both the sodium and the calcium hypophosphates, prepared in this manner, could be quantitatively precipitated by silver nitrate at pH 1 to 2 in either formic or phosphoric acid, a property which Wolf and Jung (*8*) have found to be characteristic of hypophosphate.

The other reagents used in the experiments were reagent grade chemicals. The silver nitrate was made by dissolving 25 g reagent silver nitrate in 100 ml distilled water. The pH for the silver hypophosphate precipitations was adjusted by either 85% formic acid or 85% phosphoric acid. No hypophosphate could be detected in the phosphoric acid.

The procedure initially used for the phosphate-phosphite reaction was as follows:

> Weigh out 0.100 g of the ammonium orthophosphite into a 250-ml Erlenmeyer flask. Weigh out 0.100 g of the radioactive magnesium ammonium phosphate and add to the flask. Add 5 ml distilled water and swirl the Erlenmeyer to mix the salts. After less than 5 min for the above process add 0.100 g calcium hypophosphate to serve as a carrier for any hypophosphate formed in the reaction. Adjust the pH to 1.5 by a predetermined volume of formic or phosphoric acid and add 2 ml of the silver nitrate reagent. Agitate for 1 min. Filter off the silver hypophosphate and wash 3 times with water acidified to pH 1.5. Dry the precipitate on a steam bath. Count the activity by a bell-window counter.

The activity in the silver precipitate was found to be approximately 50% of the activity originally present in the 0.100-g sample of the radioactive magnesium ammonium phosphate. Wolf and Jung (*8*) have found that neither phosphites nor phosphate precipitates under the above conditions. This point was confirmed by the writer. As has been pointed out above, the magnesium ammonium phosphate did not exchange activity with the hypophosphate during precipitation of the hypophosphate by silver at pH 1.5 in either formic or phosphoric acid. Since the hypophosphate contained active phosphorus under the conditions of the above reaction, hypophosphate formation was suspected.

Evidence of a similar nature also has been obtained indicating that the hypophosphites of sodium and calcium react with radioactive orthophosphate to produce radioactive hypophosphate.

The following additional observations made in the course of this work seem pertinent to the point under consideration, namely, the validity of using phosphite as a carrier:

a) A solution containing 0.156 g of radioactive magnesium ammonium phosphate per ml at a pH of 5.5 in acetic acid was added to a solution containing 0.0045 g of the ammonium orthophosphite per ml at pH 2.3. Reacting different volumes of the phosphate and phosphite solutions gave incomplete recovery of activity in the orthophosphate fraction determined by the method of Jones (*7*). The recovery of activity was measured on the magnesium ammonium phosphate salt derived from the ammonium phosphomolybdate precipitate that was formed at 24° C in 15 min. It was noted that the apparent loss was 5–15% of the original activity. This test was conducted many times, varying the amounts of phosphate and of phosphite and the pH. The filtrate from the orthophosphate test in each case possessed activity recognized as P^{32}.

b) The former tests were repeated using 0.100 g magnesium ammonium phosphate with 0.100 g of the orthophosphite or the hypophosphite in 5 ml water and 0.100 g calcium hypophosphate as carrier. Instead of the silver precipitation, 70 ml of the molybdate reagent was added and orthophosphate precipitated at 24° for 15 min, as recommended by Jones (*7*). The ammonium phosphomolybdate was counted as the magnesium ammonium phosphate, and again a loss in activity of about the same value as that obtained in the silver hypophosphate precipitations was obtained. The writer was able to confirm the quantitative precipitation of a solution of magnesium ammonium phosphate in the absence of the phosphites, and in the presence of the hypophosphate. Phosphites and hypophosphate gave no precipitate with molybdate at 24° C over periods up to 24 hr.

Addition of sodium metaphosphate or of sodium pyrophosphate to the active filtrate and heating at 70° C for 1 hr produced ammonium phosphomolybdate having only a trace of activity. This indicated that the precipitation of the orthophosphate in the previous treatment had been quantitative.

The filtrate remained radioactive. Additional molybdate reagent and 10 ml bromine water were added to this filtrate, which was then allowed to stand on the water bath at 80° C for several hours. A further crop of ammonium phosphomolybdate was obtained which possessed appreciable activity. The filtrate, however, still remained radioactive from P^{32} emanations. Further phosphite or hypophosphite carrier was easily precipitated by the bromine treatment, but the filtrate in each case remained radioactive. Sodium hypophosphate was oxidized rather easily by bromine water under the above conditions and the ammonium phosphomolybdate from the sodium hypophosphate was visually normal.

If the calcium hypophosphate accounts for the final activity in the filtrate, then this salt must indeed be very resistant to oxidation by bromine in the presence of molybdate.

c) When magnesia mixture was added to solutions containing both hypophosphate and radioactive orthophosphate in the presence of phosphite no activity was found in the filtrate. This same combination, however, was shown above to yield activity in the silver hypophosphate precipitate and also to result in low recovery of activity in the orthophosphate precipitate derived from the ammonium phosphomolybdate.

d) Some caution was justified in the use of ammonium phosphomolybdate precipitation as an indication of orthophosphate after heating the molybdate, because Mellor (*5*) has pointed out the existence of molybdate-hypophosphate complexes. The author has found that the hypophosphate gave no turbidity with the molybdate reagent at 24° C nor over short periods of heating; however, the light-yellow precipitate formed on prolonged heating on the water bath or at temperatures above 70° C might have contained this complex.

Using calcium hypophosphate as a carrier, the following neutron-bombarded phosphates have been found to possess activity in the silver hypophosphate precipitate at pH 1.5 in phosphoric acid: monocalcium phosphates, superphosphate, calcium pyrophosphates, and calcium hypophosphite.

More complete details on the quantitative analysis of the forms of phosphorus in neutron-bombarded phosphates and some evidence for the possible significance in studies of the utilization of phosphorus by plants will be published elsewhere.

References

1. Fried, M., and MacKenzie, A. J. *Science*, **111**, 492 (1950).
2. Libby, F. W. *J. Am. Chem. Soc.*, **62**, 1930 (1940).
3. Whitmore, F. E. *Nature*, **164**, 240 (1949).
4. Wilson, N. J. *J. Am. Chem. Soc.*, **60**, 2697 (1938).
5. Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. Vol. VIII, 926–940. London: (1928).
6. Leininger, E., and Chulski, T. *J. Am. Chem. Soc.*, **71**, 2385 (1949).
7. Jones, L. T. *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).
8. Wolf, L., and Jung, W. *Z. anorg. u. allgem. Chem.*, **201**, 333 (1931).

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