[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI.]

A COMPARISON OF THE EFFICIENCY OF SOME COMMON DESICCANTS.

BY MARY V. DOVER AND J. W. MARDEN.

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In a recent paper,[1] alumina has been shown to be a good drying agent for use in desiccator jars and it seemed worth while to compare its efficiency, using rather more refined methods of work, with that of a few other commonly employed desiccants. Baxter and Warren[2] and, also, Baxter and Starkweather[3] have already determined the comparative efficiencies of calcium chloride, sodium hydroxide and potassium hydroxide. In the present work the methods of the above authors were applied to aluminum oxide, magnesium oxide, and copper sulfate. The fact that the Association of Official Agricultural Chemists is investigating the use of calcium oxide and some other substances in place of sulfuric acid in ordinary desiccators, lends some special interest to the investigations of the drying efficiency of this substance.

Alumina ($Al_2O_3XH_2O$) was prepared by the precipitation of the hydroxide from purified alum solution with ammonium hydroxide solution. This first precipitate, after repeated washing with water containing ammonium hydroxide, was redissolved in hydrochloric acid, reprecipitated with ammonium hydroxide, and repeatedly washed with dilute ammonium hydroxide. This precipitate was first dried at 100°, then in the full heat of the non-luminous flame of a small combustion furnace (about 500°). During this last heating, air dried by sulfuric acid was passed over the oxide.

Calcium oxide was prepared as follows: The hydroxide was precipitated from a solution of the nitrate by sodium hydroxide solution; this first precipitate was redissolved in hydrochloric acid, reprecipitated as before and washed until free from chlorides. The hydroxide was then dried and the oxide prepared by heating above 500° in a current of air, previously passed through a sodium hydroxide solution and dried by sulfuric acid as before. The amounts of calcium carbonate in samples thus prepared were found to be small.

Magnesium oxide was prepared by precipitation of the hydroxide by means of ammonium hydroxide. The precipitate was redissolved in hydrochloric acid, reprecipitated, washed and dried as above, *i. e.*, first at 100° and then in a combustion furnace at 500° in a current of dried air.

Cupric sulfate was prepared from a good grade of blue vitriol three times recrystallized from water, the most and least soluble portions being dis-

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[1] *J. Ind. Eng. Chem.*, **7**, 320 (1915).

[2] THIS JOURNAL, **33**, 340 (1911).

[3] *Ibid.*, **38**, 2038 (1916).

carded from each recrystallization. This recrystallized blue vitriol was first dried at 100° and then heated for some time at about 400° to render it as nearly anhydrous as possible.

In each case the freshly prepared desiccant was transferred to the U-tube, in which the experiments were made, while still warm, with almost no exposure to the air.

The apparatus, similar to that used by Baxter and his coworkers consisted of the following parts, arranged in the order mentioned: (I) Aspirator. (II) A wash bottle containing 20% sodium hydroxide solution; this serves to regulate, in some degree, both the amount of moisture carried by the air and the rate at which the air is driven over the substance under observation. (III) A glass-stoppered U-tube containing a column of the material under observation about 30 cm. long and 15 mm. wide. This U-tube was hung in a thermostat. (IV) A glass-stoppered U-tube containing resublimed phosphorus pentoxide for absorption of the residual moisture. This was carefully weighed before and after each experiment. (V) A second glass-stoppered U-tube containing commercial phosphorus pentoxide. The purpose of this U-tube was to prevent moisture from the air penetrating the apparatus.

The U-tube, hung so as to catch the residual moisture, was weighed by means of counterpoise and calibrated platinum fractional weights. Though the attempt was made to weigh to 0.01 mg., no claim is made to an accuracy greater than 0.1 mg.

It was found essential, in order to obtain concordant results, that the air be passed over the drying agents at, as nearly as possible, a uniform rate (not more than one and one-half to two liters per hour).

In each determination the first phosphorus pentoxide tube was carefully weighed, the U-tubes hung in place and a measured volume of air ladened with moisture was passed over the substance under observation. The residual moisture was absorbed by the first phosphorus pentoxide tube which was again carefully weighed after the experiment. From the increase of weight of the phosphorus pentoxide tube and the volume of air passed through the apparatus, Baxter and Warren calculate the pressure of the aqueous vapor in the air which was in equilibrium with the desiccant under observation, *i. e.*, the vapor pressure of the desiccant itself.

Johnson[1] has shown that aluminum trioxide is an excellent drying agent, superior to sulfuric acid, and frequently suitable where phosphorus pentoxide cannot be used. This trioxide (of Johnson) was prepared by heating the hydroxide at the temperature of the "smoky flame" in a current of air dried by sulfuric acid. Marden and Elliott[2] prepared alumina by

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[1] THIS JOURNAL, 34, 911 (1912).

[2] *J. Ind. Eng. Chem.*, 7, 320 (1915).

heating the hydroxide at the temperature of the smoky flame of the combustion furnace and compared its efficiency for use in desiccators with that of 95% sulfuric acid and of calcium chloride. For small amounts of moisture this aluminum trioxide seemed rather better than either of the other substances, but for the absorption of large quantities of moisture it appeared to be of about the same efficiency as the sulfuric acid.

In the present investigation, the question very soon arose as to the drying efficiency of alumina after being heated at various temperatures. The above authors considered that the hydroxide should be dehydrated, using no higher temperature than the "smoky flame." Blum,[1] however, states that 0.1 g. of ignited aluminum trioxide, allowed to stand open for five minutes, gains as much as 1 mg. in weight. This author considers that alumina, after blasting at 1100°, takes up moisture rapidly and that not even by blasting at 1400° is the anhydrous compound obtained. Martin,[2] in his exhaustive investigation of the hydrates of aluminum, gives the following table for the decomposition of the hydroxide by heat.

TABLE I.

Decomposition of Aluminum Hydroxide Heated to Various Temperatures (Martin).

Temperature.	Percentage moisture.
150°	0.0
170	0.54
200	4.82
225	11.72
250	26.50
380	29.02
657 (M. P. Al)	33.66
820 (M. P. Na_2CO_3)	34.38
955 (M. P. Ag)	34.40
White heat	35.57 (total)

This table would indicate that the compound prepared by Johnson can probably be expressed by the formula AlO(OH), that it must, therefore, contain quite a considerable amount of moisture. In view of these statements, it seemed necessary to make a few rough determinations of the effect of heating on the desiccating power of this compound. In each case a quantity of the compound was heated in a combustion furnace to a definite temperature, for two hours, in a current of air dried by sulfuric acid. After heating, the substance was transferred to a weighing bottle. Each weighing bottle was allowed to stand, uncovered, in a closed vessel over a 30% sodium hydroxide solution. The results obtained are recorded in Table II. Although the experiments were continued for several days, the results are given here for the first 24 hours only, this being expressive of the order of increase in weight of the alumina throughout the entire period.

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[1] Bureau of Standards, *Scientific Papers*, No. 286 (1916).

[2] Martin, "Le Moniteur Scientifique Quesneville," October, 1915.

TABLE II.

Increase in Weight of Alumina, Heated to Various Temperatures, over 30% Sodium Hydroxide Solution.

No. expt.	Temp.	Wt. Al_2O_3 used.	Increase per g. in 24 hours.
1	220°	3.220	0.0357
2	250	3.578	0.0306
3	300	2.538	0.0372
4	360	3.080	0.0351
5	500	2.804	0.0382

These results, though not very concordant, due no doubt to the difference of surface exposed, seem to indicate that the temperature to which the compound is heated does not affect, to any marked degree, its ability to absorb moisture. The sample which was heated to 500° does show, however, the greatest efficiency in this respect.

Alumina ($Al_2O_3xH_2O$) at 25° proved to be a very efficient drying agent. On passing many liters of moist air over this substance, no weighable amount of residual moisture was absorbed by the phosphorus pentoxide tube at this temperature.

TABLE III.

Aqueous Pressure of $Al_2O_3.xH_2O$, Calculated after Baxter and Warren.

No. expt.	Temp.	Liters air per hour.	Liters air S. T. P.	Mg. H_2O.	Cc. water vapor S. T. P.	Internal press.	V. P. mm. Hg.
1	50°	1.5	24	0.20	0.25	748	0.007
2	50	1.5	19	0.20	0.25	742	0.009
						Average,	0.008

Since it has been found that the vapor pressure of such materials increased about three times in a raising of the temperature an interval of 25°, the value for alumina at 25° is estimated to be 0.003 mm.

Calcium oxide soon became exhausted. The vapor pressure at 50.7° was about 0.75 mm. At 25° the vapor pressure of calcium oxide is estimated to be 0.2–0.3 mm.

TABLE IV.

The Vapor Pressure of Calcium Oxide, Calculated after Baxter and Warren.

No. expt.	Temp.	Liters air per hour.	Liters air S. T. P.	Mg. H_2O.	Cc. water vapor S. T. P.	Internal press.	V. P. mm. Hg.
1	50.7°	2.0	5.2	4.7	5.83	746	0.83
2	50.7	1.3	2.6	1.9	2.36	748	0.68
						Average,	0.75

Magnesium oxide proved to have a very small capacity for moisture. Six liters of moist air were passed over the substance before a weighable increase of the phosphorus pentoxide could be detected. The vapor pressure, therefore, could not have exceeded 0.02 mm. at 50°.

TABLE V.

The Vapor Pressure of Cupric Sulfate, Calculated after Baxter and Warren.

No. expt.	Temp.	Liters air per hour.	Liters air S. T. P.	Mg. H_2O.	Cc. water vapor S. T. P.	Internal press.	V. P. mm.
1......	0°	1.0	4.80	2.40	2.98	748	0.46
2......	...	1.4	4.31	1.40	1.74	748	0.30
3......	...	1.3	6.28	2.90	3.60	745	0.42
						Average,	0.4
4......	25°	0.8	3.51	4.73	5.88	754	1.26
5......	...	1.2	2.68	4.70	5.88	748	1.62
6......	...	1.2	6.08	8.85	11.00	754	1.36
7......	...	1.0	10.00	13.50	16.00	752	1.26
						Average,	1.3

Cupric Sulfate.—The color of material indicated that the first few centimeters absorbed practically all of the moisture.

The drying efficiency of sulfuric acid was observed by a method somewhat similar to that used for the other substances. The 30 cm. U-tube was filled with glass beads which had previously been soaked in 95.1% acid. Due to the fact that sulfuric acid is a liquid, the results are not comparable with those obtained with the other substances. At 25°, however, one liter of air passed through a 30 cm. tube containing beads soaked in this acid still contained about 0.3 mg. of water.

For the sake of comparison, the values obtained in this work and those of Baxter are included in Table VI. The values marked "B" are due to Baxter.

TABLE VI.

Weights of Residual Moisture in One Liter of Air at 25°, after Having Passed a U-tube Containing 30 cm. of Desiccant.

Substance.	Mg. water.	Substance.	Mg. water.
$CuSO_4$	1.4	$CaBr_2$	0.2 (B)
$ZnBr_2$	1.1 (B)	CaO	0.2[2]
$ZnCl_2$	0.8 (B)	NaOH	0.16 (B)
$CaCl_2$	0.36 (B)[1]	MgO[3]	0.008[2]
H_2SO_4 (95.1%)	0.3	$Al_2O_3.xH_2O$	0.003[2]
		KOH	0.002[3]
		P_2O_5 (resublimed)	Practically none[4]

The values in Table VI are given as milligrams of water passing through a 30 cm. tube of desiccant, 15 mm. wide, at 25°, while the air is being driven at a rate of one to three liters per hour. This table shows three substances, aluminum trioxide ($Al_2O_3.xH_2O$), potassium hydroxide and resublimed phosphorus pentoxide, to be much more efficient drying agents

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[1] Two 30 cm. tubes used.

[2] Estimated from determinations at higher temperatures.

[3] The total weight of water absorbed is small.

[4] Morley, *J. chim. phys.*, 3, 241 (1905).

than any others. The potassium hydroxide has the advantage of the alumina because it is easily prepared (by fusing the commercial material) but the alumina is much more easily handled.

Columbia, Mo.

NOTES.

The Separation of Isotopes: *A comment on the paper by T. W. Richards and N. F. Hall.*—In their recent paper,[1] T. W. Richards and N. F. Hall do not state the existing position very fairly with regard to the evidence upon which the chemical non-separability of isotopes is based. In their opening remarks they say that the methods used have been fractional crystallization and precipitation but these processes have seldom been carried out more than ten times in a particular case, and frequently six or seven crystallizations have been through a sufficiently thorough test of inseparability. I have no intention of giving a complete bibliography of the subject here, for I do it periodically in my Report on Radioactivity.[2] But I may mention that in the original work in which the conception of isotopes was first put forward, my wife carried out for me a very long fractionation of the barium-radium-mesothorium-I chloride derived from thorianite. I looked up the record and find in the preliminary work 80 fractionations were done. After that it did not seem worth while counting as the progress of the removal of the barium was quite regular. The original concentration of the barium to the radium was increased 340 times, but the ratio of mesothorium to radium was, within the 1 or 2% possible error of radioactive measurements, the same as before. In the technical separation of mesothorium and radium from monazite such fractionations are carried on from year to year continuously and the barium is eliminated completely, without separating in the least the mesothorium from the radium.

My work was published in 1910,[3] and the abstract in the Proceedings concludes, "The cases of complete identity between groups of radioactive elements differing presumably in atomic weight, which now appear to include all the radioactive elements of period of average life longer than a year, are in direct conflict with the principle of the periodic law." The general question was also discussed in the Annual Report on Radioactivity for that year. The authors cited attribute the generalization to Fajans, Russell, Fleck and Soddy, but in 1910 Fajans had not commenced his contributions to radioactivity and did not contribute anything on this subject to 1913. The generalization, that when an α-ray is expelled in radioactive change the product occupies a place in the Periodic Table

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[1] This Journal, **39**, 531 (1917).

[2] "Annual Reports of the Progress of Chemistry," published by the Chemical Society.

[3] *Proc. Chem. Soc.*, **26**, 336 (1910); *Trans. Chem. Soc.*, **99**, 72 (1911).