

volume of water and make a new test, using 1 cc. of the diluted urine, and multiplying the percentage found in the table by two.

In compiling this table, sixteen aqueous solutions of serum albumin varying in strength from 0.1% to 2.0% were prepared. These solutions were standardized in the following manner. The albumin was precipitated with potassium mercuric iodide, heated in a water bath, separated by filtration and determined by the Kjeldahl method using the factor 6.3. About forty determinations were made upon each of these solutions by the acetone precipitation method. A curve was plotted from the average results obtained, and from this the table was constructed. The use of normal urine instead of water in making up the albumin solutions caused no difference in the results; and in a number of pathological specimens gave results which agreed closely with those obtained gravimetrically. While it can not be expected that a method of this kind will give accurate results, yet if carried out with proper attention to details it will be found to give more accurate results than those obtained by other methods based upon the volume of the precipitate.

The results are not influenced by ordinary variations in temperature; nor by the changes in acidity or amount of phosphates caused by the varying composition of different urines.

Considerable variations in the diameter of the measuring tube or in the manner of mixing the liquids were found to affect the results.

The precipitate settles so rapidly that after fifteen minutes the volume changes very slowly. For this reason, it did not seem necessary to consider centrifugal separation as a means of shortening the method, although it is probable that good results might be obtained in that way.

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## THE ASSAY OF SOME U. S. P. CHEMICALS.

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Assay processes for chemicals should be made as simple as possible and with the aid of as little apparatus as is consistent with good work. Comparison of past Pharmacopoeias shows remarkable advance in the number of assays directed, and the ninth revision now in progress will undoubtedly show the greatest advance; this is shown by the consideration given to chemicals for which no assay processes have ever been officially prescribed, as in the case of nitrates, chlorates, etc., owing to manipulative difficulties and the need of special apparatus.

### ASSAY OF CHLORATES.

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A number of processes for the assay of this class of salts have been published which will be briefly outlined:

1. Decomposition of the chlorate by heat into the corresponding chloride

and determining this either volumetrically or gravimetrically; results apt to be low, due to the volatility of the chloride.

2. Reduction by means of sulphuric or acetic acids and metallic zinc; satisfactory results are obtained by gravimetric, but unsatisfactory by volumetric methods (residual titration), owing to difficulty with the end reaction.

3. Reduction with  $\text{Na}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ ; results as above.

4. Reduction with  $\text{SnCl}_2$  and  $\text{HCl}$  and titrating excess of  $\text{SnCl}_2$  with Iodine V. S.; results vary, probably due to atmospheric oxidation of  $\text{SnCl}_2$ , which can, however, be prevented by working in an atmosphere of  $\text{CO}_2$ .

5. Reduction with  $\text{KI}$  and  $\text{HCl}$  and measuring the liberated iodine with  $\text{Na}_2\text{S}_2\text{O}_3$  V. S.; results vary, due to the liberation of iodine from the reagents in presence of air, but can be made satisfactory by boiling the reagents in a current of  $\text{CO}_2$  and allowing the decomposition of the chlorate to proceed after expelling the air by means of  $\text{CO}_2$ .

6. Reduction with an excess of a ferrous salt in presence of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ , determining the excess with  $\text{K}_2\text{Cr}_2\text{O}_7$  V. S. or  $\text{K}_2\text{Mn}_2\text{O}_8$  V. S.; the presence of  $\text{HCl}$  interferes in the titration with  $\text{K}_2\text{Mn}_2\text{O}_8$ , while with  $\text{K}_2\text{Cr}_2\text{O}_7$  the end reaction is obtained by spotting. The atmospheric oxidization of the ferrous salt is also a source of error.

The following method gave satisfactory results and is free from the objections indicated in the preceding methods, but attention should be called to the ratio between the chemical and the number of cc. of a decinormal V. S., thus:

0.1 gm.  $\text{KClO}_3$  (99.5%) requires 48.7 cc. N/10  $\text{Na}_2\text{S}_2\text{O}_3$  V. S.

0.1 gm.  $\text{NaClO}_3$  (99.5%) requires 56.1 cc. N/10  $\text{Na}_2\text{S}_2\text{O}_3$  V. S.

Place 0.1 gm. of the salt in a glass stoppered bottle (150-200 cc), dissolve in 10 cc. water, add 15 cc.  $\text{KBr}$  sol. (10%) and 20 cc.  $\text{HCl}$  (sp. gr. 1.20) and allow to stand forty minutes; after cooling the bottle and its contents by immersion in cold water, carefully rinse stopper, using 20 cc.  $\text{KI}$  solution (10%) and titrate with decinormal  $\text{Na}_2\text{S}_2\text{O}_3$  V. S. (Results 99.5%; 99.73%; 99.85%  $\text{KClO}_3$ ). 1 cc. N/10 V. S. = 0.00204266 gm.  $\text{KClO}_3$  or 0.0017743 gm.  $\text{NaClO}_3$ .

A blank test should be made to prove that the combined reagents do not liberate iodine.

#### ASSAY OF BENZOATES AND SALICYLATES.

JOSEPH W. EHMAN.

Methods which have been used in the assay of these classes of organic salts are as follows:

1. Ignition to change into the corresponding carbonates or oxides, which if soluble, are extracted with water and titrated with Acid V. S., methyl orange indicator. Complete ignition to remove separated carbon is likely to entail loss due to the volatility of alkali carbonates; incomplete ignition is followed by a tenacious retention of the alkali carbonate by the charcoal.

2. Ignition to thoroughly char, treating residue with an Acid V. S. in excess, filtering, thoroughly washing with water and titrating the excess of Acid V. S. with an Alkali V. S., methyl orange indicator. Suitable for organic salts of those non volatile metals whose oxides or carbonates can be titrated.

3. Ignition with  $\text{H}_2\text{SO}_4$ , changing organic salt to sulphates; suitable for

organic salts of those metals whose sulphates are stable; in the case of salts of K and Na, persulphates are likely to be formed, giving an excessive weight, but this can be prevented by treatment with ammonia or ammonium carbonate solution, evaporation to dryness and re-ignition.

4. Ignition with  $(\text{NH}_4)_2\text{SO}_4$  as above; this does not form persulphates.

5. In the case of organic salts, the acid of which when liberated may be removed by immiscible solvents, as ether, chloroform, etc., a measured excess of an Acid V. S. may be added, the organic acid extracted with the solvent and the excess of Acid V. S. titrated with an Alkali V. S., (in the aqueous portion), methyl orange indicator.

6. Extraction of the acid as in (5), but allowing the volatile solvent to evaporate at ordinary temperature and weighing the residue of free organic acid.

The following modification of (5) and (6) gave satisfactory results:

0.200 to 0.500 gm. of the salt, placed in a separator and dissolved in 20 to 30 cc. water, add 2 to 4 cc. N/1  $\text{H}_2\text{SO}_4$  (or HCl) (note); a mixture of ether 1 vol. and chloroform 2 vols. is used for extraction, of which three portions of 15-20 cc. each are usually sufficient for complete extraction; to the mixed ether-chloroform extractions in a flask, add a little water (10cc.) and titrate with N/10 NaOH V. S., phenolphthalein indicator; or, the first portion separated may be titrated, then the second added, titration continued and so on until no more Alkali V. S. is required to give a permanent pink color to the aqueous layer after thorough agitation.

The following results were obtained:

Sodium Salicylate	Ammonium Salicylate	Strontium Salicylate	Sodium Benzoate	Lithium Benzoate
98.088%	98.28%	98.38%	99.063%	99.059%
99.32%	98.147%	98.38%	97.41%	
99.72%				
100.039%				
100.12%				
98.82%				

Note.—The amount of acid required here is slightly more than the calculated amount to decompose all the salt (e. g. each 0.100 gm. sodium salicylate requires a little over 0.6 cc. N/1 V. S. for an excess).

Chloroform is the most convenient solvent, but more of it is required than of ether; the latter is less convenient to separate, but a heavy mixture of the two has been found quite satisfactory.

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## THE QUALITY OF DRUGS.\*

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*Asafetida*.—*Asafetida* is a drug that cannot be powdered without considerable loss of the active volatile constituents present. Of five lots of the pow-

\* Notes made from the files in the Analytical Department of Smith, Kline and French Co. upon the drugs examined from June 1, 1911, to June 1, 1912.