THE ASSAY OF SPIRIT OF ETHYL NITRITE.*

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INTRODUCTION.

The Netherlands' Pharmacopœia (1) employs an argentimetric assay for its preparation "Spiritus Nitri dulcis," an alcoholic solution containing between 2 and 2.5 Gm. of ethyl nitrite in 100 cc. This process was recommended by Herting (2) as a substitute for the official gasometric assay. The method was studied extensively by L. van Itallie, *et al.* (3) and certain desirable modifications were established. The principle depends upon the oxidation of ethyl nitrite to nitrate by means of potassium chlorate in acid solution, and the argentimetric estimation of the resulting potassium chloride. In the method as given by the Netherlands' Pharmacopœia, the silver chloride after precipitation is not filtered from the reaction mixture and hence a permanent end-point with the indicator, iron alum, is not obtained.

With the purpose of investigating the possibilities of the simple volumetric assay for a Pharmacopœial method this study was begun.

EXPERIMENTAL.

After various modifications of the argentimetric method the following procedure was adopted as giving the best results.

> Introduce into a 50-cc. volumetric flask, successively 10 cc. of distilled water, 5 cc. of 5 per cent solution of potassium chlorate, 5 cc. of Spirit of Ethyl Nitrite, accurately measured and 5 cc. of diluted nitric acid. Stopper the flask, shake well and allow it to stand fifteen minutes. Add 15 cc. of tenth-normal silver nitrate solution. Make up to volume with distilled water, filter and titrate the excess of silver nitrate in 25 cc. of the filtrate with tenth-normal potassium sulphocyanate using ferric ammonium sulphate T.S. as an indicator. Each cc. of tenth-normal silver nitrate consumed corresponds to 0.0225 Gm. of $C_2H_5.NO_2$.

Several commercial samples and other samples of Spirit of Ethyl Nitrite prepared in this laboratory were assayed by this method and also by the present official gasometric method. The results are given in Table I.

TABLE I.—GM. ETHYL NITRITE PER 100 CC.

Sample.	Volumetric Assay.	Gasometric Assay.
1	4.41	(1) 4.51
	4.41	4.50
2	7.02	(2) 6.82
	7.09	6.82
	6.95	....
	6.95	....
3	2.61	(3) 2.42
	....	2.42
4	3.33	(4) 2.99
	3.33	3.02
5	2.86	(5) 2.72
	2.86	2.72
6	4.40	(6) 4.07

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	4.40		3.94
	4.40		....
	4.40		....
	4.40		....
7	3.65	(7)	3.52
	3.65		3.54
8	3.12		3.09
	3.12	(8)	3.08
	3.12		....
	3.01		....
	3.20		....
9	1.80	(9)	1.80
	1.98		1.76
10	2.65	(10)	2.54
	....		2.54
11	4.00	(11)	3.83
	4.00		3.74

These results indicate that there is a reasonable agreement between the gasometric and volumetric methods, however the results obtained by the volumetric method are somewhat higher.

It is a generally accepted procedure when gas volumes are measured for the purpose of analysis, to make a substractive correction for the vapor tension of the liquid over which the gas is measured. The Pharmacopœia makes no provision for this correction. It was thought advisable, therefore, to determine the vapor tension of the reaction mixture resulting from the decomposition in the assay. A small portion of this liquid was sealed in a gelatin capsule and inserted in an inverted tube containing dry mercury. When the capsule rose to the surface of the mercury it was broken by the expansion of the vapor of the liquid caused by the application of gentle heat. The height of the column of mercury was measured before the introduction of the liquid and at various temperatures after equilibrium was established. These data are given in Table II.

TABLE II.

	Temperature.	Vapor Pressure, mm.
Column in mm. before 755	17.2°	23
	19.2°	26
	20.0°	24
	21.5°	31
	22.0°	33
	24.3°	38
	25.0°	39
	27.8°	42
	29.1°	45
	30.3°	50

This correction of the barometric pressure is quite large at 25° C. corresponding to approximately 5 per cent of the entire gas pressure. If this correction were applied to the foregoing determinations, the results would be brought further below the volumetric determination.

In a subsequent communication the authors propose to report the results of an investigation designed to determine which of these two methods gives the more accurate results and the applicability of the determined vapor tension correction.

SUMMARY.

1. The vapor tension of the reaction mixture in the assay of Spirit of Ethyl Nitrite has been determined.

2. Results on the argentimetric and gasometric methods have been compared.

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A TOXICOLOGICAL INVESTIGATION OF PHENOL AND IODINE.*

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Few of the modern poisons are as easily accessible to the public as phenol and iodine, owing to their widespread use as household disinfectants and germicides. In the last few years they have been very near the top of the list of poisons causing death in the United States and England.

Toxicologists are therefore many times called upon to examine chemically viscera containing one or the other of these drugs. Methods for analysis of both chemicals are well worked out but there are still certain questions pertinent to toxicology which should have further attention. They are the effect of the common tissue preservants on the recoverable amount of the drugs; the probable rate of disappearance of the specific poison in a preserved or decomposing cadaver; the possibility of organic combinations with the tissue rendering the lethal material, in the case of phenol, not amenable to the ordinary analytical technics; and in the case of iodine the possibility of a shorter method for its determination which is sufficiently accurate for chemico-legal work.

To make the necessary quantitative observations which would in a broad way answer these questions furnish thereby certain standard or comparative data for medico-legal cases, a series of specimens of organic material in contact with known quantities of phenol or iodine and one or no preservative were set up. The procedure for this part of the work was that used in similar previous investigations of other poisons.[1]

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[1] The plan was to subject the poisons as nearly as possible to all of the conditions they might encounter in a body after death. Some of the specimens to be made up for analysis were to be preserved with the common tissue preservatives, including embalmer's cavity fluid, and others left unpreserved and allowed to undergo natural putrefaction. Therefore, using stomachs from freshly killed sheep as carriers for the drugs, a series of 4-ounce wide-mouthed bottles were set up, each containing a weighed amount of minced stomach together with a known quantity of one poison and one or no preservative. All bottles were stoppered and sealed with paraffin. In all, enough specimens were arranged so that there were three complete sets of bottles containing the poison in contact with one or no preservative. This permitted during the period of the investigation three quantitative determinations of the poison under every condition considered.