

AN ABSTRACT OF THE THESIS OF

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Title-----STUDIES OF THE METHOXYL DETERMINATION-----
Modification of Apparatus and Preparation of Hydriodic Acid-----

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In this thesis a modified Pregl apparatus for the determination of methoxyl groups has been introduced. Some of the modifications are the use of an evacuated flask for the absorption of the alkyl iodides, the use of an U-tube for the gas scrubber, and the introduction of the carbon dioxide from the bottom of the reaction flask. This apparatus gave consistent results.

Hydriodic acid obtained from various sources gave high blanks. The major interfering impurity was found to be a volatile organic iodide. This hydriodic acid could be purified by distillation through an all-glass distilling unit.

By distilling a mixture of potassium iodide and phosphoric acid under reduced pressure in an all-glass distilling unit, hydriodic acid free from a large blank was prepared.

STUDIES OF THE METHOXYL DETERMINATION
Modification of Apparatus and Preparation
of Hydriodic Acid

by

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STUDIES OF THE METHOXYL DETERMINATION
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Introduction

The methoxyl group is found widely distributed in nature. It is found in many naturally occurring organic compounds, in alkaloids, in various constituents of volatile oils, and in all lignified plant materials, such as straw, hulls, cobs, stalks, leaves, trunks of trees, and shrubs (18). Hence the importance of its quantitative estimation cannot be overstated.

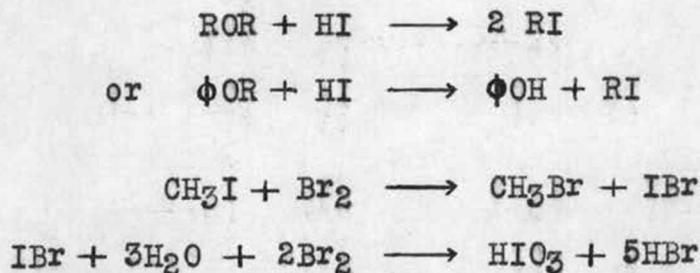
Since the micro-gravimetric method of Zeisel (24) was introduced in 1885, numerous attempts have been made to determine the alkoxylys volumetrically. Among these a modified macro method of Kirpal and Bühn (14) was the most noted. In this method pyridine was substituted for the usual silver nitrate solution and the resulting methyl iodide titrated with standard silver nitrate. This method, however, gave inaccurate results for micro quantities and, further, involved the use of objectionable pyridine.

In 1930 Vieböck and Brecher (20) devised a micro volumetric method free from these objections, especially the interfering influence of sulfur. This is the volumetrical procedure universally adopted at the present time.

In running micro volumetric determinations on known samples of methoxyls by the apparatus of Pregl (19), erratic results were obtained in this laboratory. This, we were able to trace to the reagents. The importance of using highly purified reagents, especially hydriodic acid is generally recognized (6, 10); however a review of the literature indicates that little has been published (5) regarding the nature and probable origin of the interfering impurities. For this reason the following investigation was undertaken.

Theory

The method of F. Vieböck and C. Brecher (20) depends upon the collection of the alkyl iodide, formed by treating the sample with hydriodic acid, in the receiver in which a solution of sodium acetate and glacial acetic acid together with a few drops of bromine is present. The following reactions occur:



The sodium acetate present neutralizes the hydrobromic acid formed and the excess bromine is decomposed by formic acid. Finally, the resulting iodate is treated with

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potassium iodide in an acid medium and the liberated iodine titrated with standard sodium thiosulfate solution.

Experimental

Discussion of the apparatus. The original Pregl (19) apparatus in the opinion of the authors presented many difficulties in running determinations. For example:

- a. The solutions in the scrubber and absorption flask being drawn back into the reaction flask by an uneven or interrupted supply of carbon dioxide.
- b. The risk of losing some alkyl iodide upon the forcing of carbon dioxide at too rapid a rate through the system.

Many modifications (1,2,3,16,17,21) of the original methoxyl apparatus have been reported and much attention has been given to the question of absorption (7,9,12,16,22).

The problem of absorption was overcome by using an evacuated flask (containing the bromine-sodium acetate - glacial acetic acid solution) as a receiver for the alkyl iodide. Besides preventing loss of alkyl iodide, this arrangement provided an excellent control on the rate of gas flow by manipulation of the stopcock on the cap of the glass stoppered Erlenmeyer flask.

A simple U - tube was used for the scrubber which prevented the sucking back of the solution into the reaction flask.

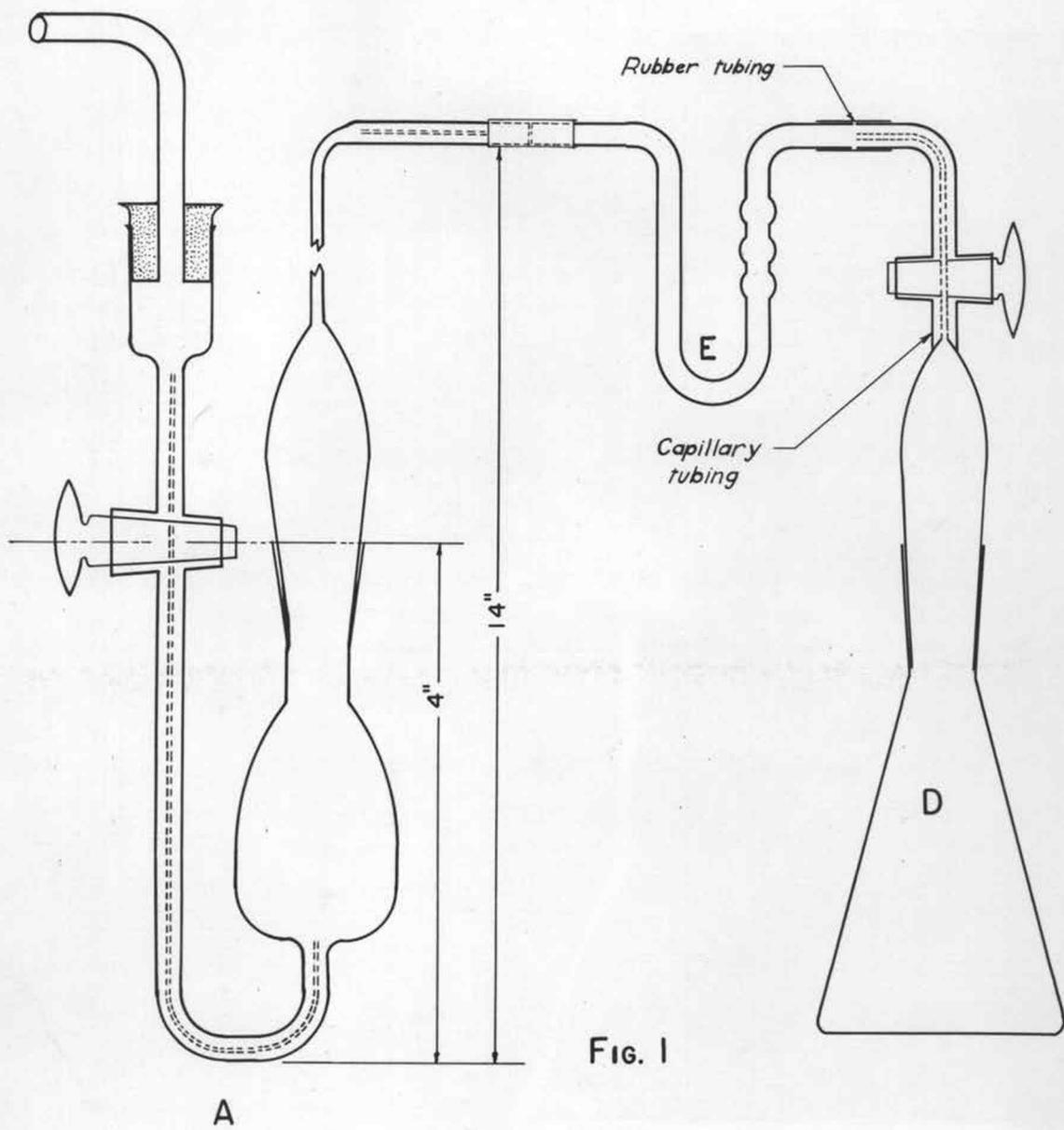
Another improvement was brought about by introducing the carbon dioxide through the bottom of the reaction flask instead of the side as in the original Pregl (19) apparatus. This prevented bumping which is always a major problem in this determination.

Description of apparatus. The modified apparatus is shown diagrammatically in Figure 1. The reaction unit, A, was constructed from a 14/35 standard taper joint and a capillary stopcock, and had a volume of 7 ml. to the ground-glass joint. The condensing unit, made from 5 mm. and capillary Pyrex tubing was 35 cm. over-all in length. It was equipped with a water jacket (not shown) and was connected to U-tube B, which in turn was connected to absorption flask C. The absorption flask for the analysis of the alkyl iodides was constructed from a 250 ml. Erlenmeyer flask, a 24/40 standard taper joint, and a two-way capillary stopcock.

A phosphoric acid bath (4) served as a heating medium for the reaction vessel. The temperature was maintained by a micro-burner within 5°C.

Procedure

Approximately 5 mg. of material weighed in a glass boat were introduced into the reaction chamber along with a few crystals of phenol and 4 to 5 drops of acetic anhydride, and the vessel was connected to the air-condensing unit. The U-tube was removed, charged with 0.5 cc. each of 5 per



cent cadmium sulfate and sodium thiosulfate solutions, and then connected to the apparatus. 5

The absorption flask was charged with 2 ml. of 10 per cent sodium acetate-glacial acetic acid solution and 5 drops of bromine. The joint was lubricated with glycerol and the flask was evacuated by means of a water pump and connected to the open arm of U-tube B.

After making sure that the charge had dissolved, 2ml. of hydriodic acid was introduced through the capillary stopcock, which was then connected to an open Kipp generator for carbon dioxide. The gas flow was regulated to approximately 15 to 30 bubbles per minute (depending on time of heating) and the reaction vessel brought to a temperature of 125° to 135°C. by means of a phosphoric acid bath.

After the heating operation (from 30 to 60 minutes) the flask was disconnected and the male joint sufficiently opened to permit the pipetting of 5 ml. of 20 per cent sodium acetate solution. The joint was again closed, and by inverting and shaking the flask, the entire inner surface was washed with solution. Formic acid was added dropwise until the solution was colorless, 4 to 6 drops in excess then being used. Two ml. of 10 per cent potassium iodide were introduced, and the solution was acidified with 5 ml. of 2 N. sulfuric acid. The liberated iodine was then titrated with standard thiosulfate. From these data, the methoxyl content was readily calculated by using the

following formula:

$$\% = \frac{(\text{cc. thiosulfate})(N)(31.02)(100)}{(\text{Wt. of sample})(1000)(6)}$$

Discussion and Results

Blank runs made with hydriodic acid obtained from various sources, gave values varying from 0.04 to 1.50 cc. of 0.02 N. thiosulfate. Initial experiments indicated that the magnitude of the blank was due mainly to the hydriodic acid used. It was thus evident that the interfering impurities must be both volatile and readily converted to an oxidizing agent by the bromine--probably arsenic compounds (AsH_3) or alkyl iodides.

A Gutzeit determination showed only traces of arsenic which could not account for the large blanks. To prove the presence of alkyl iodide as an interfering impurity in the hydriodic acid, the gases from a blank determination (using carbon dioxide-free air as a carrier gas) were passed over a heated platinum spiral. The iodine was caught in a potassium iodide trap and carbon dioxide in barium hydroxide and both determined quantitatively. They were found in sufficient quantities to account for practically all of the blank. These experiments gave reasonable assurance that a volatile organic iodide must have been present in

the hydriodic acid. Clark (5) appears to have recognized this fact when he suggested refluxing in a stream of carbon dioxide as one step in its preparation.

The nature of the impurities in hydriodic acid depends, of course, upon the reagents used in preparing it. Various methods are reported for its preparation (5, 8, 13, 23), some involving the use of organic materials. In order to avoid either sulfur or organic contaminants, the author prepared a number of samples of hydriodic acid by distilling a mixture of 85% phosphoric acid and potassium iodide (15) under reduced pressure in an all-glass distilling unit. Constant boiling acid obtained from this source gave the values noted in table I (a).

TABLE I. BLANK RUNS

Hydriodic Acid Sample	Blank, 0.02 N Thiosulfate ml.
(a) From H_3PO_4 and KI	
1	0.04
2	0.04
3	0.06
(b) Baker's, sp. gr. 1.5 (not redistilled)	0.05
After first redistillation (ordinary distilling unit with cork-stoppers)	0.56
After second redistillation (same unit as above)	1.24
After third redistillation (All-glass unit)	0.08

This method of preparing hydriodic acid proved to be rapid and simple.

In connection with this work the deleterious effect of cork on purity of hydriodic acid was observed. To measure the relative effect of cork, a sample of hydriodic acid was distilled several times in an ordinary distilling unit provided with two cork stoppers. The blank rose to approximately 25 times the original blank as can be seen from Table I (b). When this was redistilled through an all-glass distillation unit, the blank fell to nearly the original value. The importance of keeping the hydriodic acid out of contact with organic matter such as cork is readily proven by this experiment.

To illustrate the precision of the modified apparatus, a number of successive runs with it are tabulated in Table II.

TABLE II
PRECISION OF APPARATUS

	Sample Weight Mg.	Methoxyl Found %	Methoxyl Calculated %
Anisic acid	3.176	20.6	20.4
	4.380	20.3	
Dibromo-p-dimethoxybenzene	5.665	21.3	21.0
	4.159	21.1	
Vanillin	2.050	20.1	20.4
	3.030	20.2	
	2.775	20.1	
	4.048	20.2	
	3.731	20.3	

Summary

1. A simple and efficient modified Pregl apparatus has been devised and tested.
2. The detection and removal of the probable impurities in hydriodic acid have been accomplished.
3. Hydriodic acid from potassium iodide and phosphoric acid have been prepared.

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