

## UNIVERSITY OF CALIFORNIA

Department of Chemistry  
Los Angeles, California

September 28, 1942

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Dr. S. S. Prentiss  
1945 Graybar Bldg.  
420 Lexington Ave.  
New York, N.Y.

BEST COPY AVAILABLE

Dear Dr. Prentiss: †

The method employed in the analysis of samples of deteriorated Salcomine is outlined in the following description of the experiment called "Run 2" on page 9 of our monthly report July 15 - August 15:

A sample of 2.00 gms. of deteriorated Salcomine (from Calvin) was suspended in 70 ml. of 2N hydrochloric acid and steam-distilled until the distillate no longer gave a turbidity with the 2,4-dinitrophenylhydrazine reagent (a saturated solution of 2,4-dinitrophenylhydrazine in 2N HCl at room temperature).

The aqueous distillate (500 ml.) was carefully extracted with 5 portions of ether (last ether extract and remaining aqueous layer gave no color with ferric chloride) (Note 1).

The ether solution was shaken with four 20 ml. portions of sodium bicarbonate solution, and the combined extracts washed with fresh ether, which was added to the main ether solution.

Ether solution.-To the ether solution, so obtained, was added 250 ml. of the 2,4-dinitrophenylhydrazine reagent and the ether removed by gentle warming, shaking occasionally. The residual aqueous layer was warmed on the water-bath for 30 minutes, cooled in ice and the orange precipitate collected in a weighed Gooch crucible. After drying in a vacuum desiccator over sulfuric acid, the precipitate weighed 0.825 g. (22.4% of the amount calculated for complete recovery on the basis of undeteriorated Salcomine) (Note 2.)

Sodium bicarbonate extract.-This was acidified and extracted with three 20 ml. portions of ether (aqueous layer then gave no color with ferric chloride). Evaporation of the ether left a crystalline residue (45 mg.) which was recrystallized from water. The product separated as long needles, m.p. 157-9° (corr.), no depression in m.p. when mixed with salicylic acid.

CLASSIFICATION CANCELLED OR

CHANGED TO

*Unclassified*  
BY AUTH. *CF DAR-1 431*  
BY *David J. Am...* DATE *4/11/46*

*By P.E. ... AD 3/15/46*

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Boiler residue.--The aqueous solution remaining in the boiler after steam-distillation was a red-brown in color and contained suspended solid (this was tarry at the boiling-point of water). The solid was collected and dried; it weighed 0.385 g. (see below). The filtrate\* was extracted with ether and the ether extract evaporated, leaving an oily residue (0.37 g.). This was sublimed onto a cold-finger (leaving a tarry residue weighing 0.16 g.). The sublimate (white crystals) was recrystallized three times from water and once from carbon tetrachloride, and then melted at 152-156°. The mixed m.p. with salicylic acid was 154-157°.

\* The Filtrate after ether extraction was evaporated to 30 ml., cooled, filtered and to it was added 3 ml. of benzoyl chloride and enough potassium hydroxide solution to make it strongly alkaline. After the odor of benzoyl chloride had disappeared the mixture was filtered yielding 1.61 g. of a muddy solid containing particles of pink crystalline material. This was dissolved in 20 ml. of glacial acetic acid and the solution diluted with 30 ml. of water. The precipitate (crystalline) was collected and dried. It weighed 0.29 g. A control run on salicylaldehyde ethylenediamine yielded 91.5% of the calculated amount of ethylenediamine dibenzoate by a similar procedure.

The residue from the boiler (0.385 g. referred to above) was a brown, amorphous powder. Analysis of this gave the following figures:

Co	3.74%	(from residue from C-H determination)	
C,	58.40%		
H,	4.00		
N,	6.97	(Kjeldahl)	all on Co-free basis.
O,	20.63	(by difference)	

These figures correspond to the formula  $C_{16}H_{13}O_{4.2}N_{1.6}$ , as compared with salicylaldehyde ethylenediamine,  $C_{16}H_{16}O_2N_2$ , indicating a considerable increase in oxidation-level.

It may be noted that the procedure used in the run described has been modified in other experiments. When all that is desired is to determine the amount of salicylaldehyde recoverable the steam-distillate may be treated (whole or aliquot) with 2,4-dinitrophenylhydrazine directly; the salicylic acid it contains does not interfere. For routine runs on small samples the apparatus pictured on the accompanying drawing was used; any suitable modification of this, such as a Kjeldahl distillation unit, would probably do as well.

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Dr. S. S. Prentiss

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So far, no detailed chemical examination of the solid residue has been carried out. It is planned to examine this further.

Sincerely yours,

/s/ T. A. Geissman

T. A. Geissman

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Note 1. Salicylaldehyde and salicylic acid are both volatile with steam. Both give intense purple colors with aqueous ferric chloride, a test which may be used to follow these substances through extractions and other manipulations.

Note 2. Since control runs on (a) salicylaldehyde standard solutions and (b) undeteriorated Salcomine resulted in 96-97% recovery of the calculated amount of salicylaldehyde, this figure (22.4%) can be corrected to 23.4%.

cc: Dr. J. S. Beekley

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APPARATUS USED FOR QUANTITATIVE DETERMINATION OF SALICYLALDEHYDE RECOVERY  
FROM SALCOMINE

