nitrate, the following analyses were made on a sample of benzyl chloride. The figures given are percentage of chlorine. Theory, 28.07.

Water hydrolysis. Titration with		Alkali hydrolysis. Titrated with 0.1 *N* $AgNO_3$ by Volhard method.	Alcoholic $AgNO_3$ gravimetric.	Drogin-Rosanoff method.
1.0 *N* alkali.	0.1 *N* $AgNO_3$.			
28.1	27.9	27.8	27.9	28.2
28.1	27.9	27.8	28.0	28.2

Summary.

This paper contains a description of a method for the determination of the composition of mixtures of the side-chain chlorination products of toluene. The accuracy attainable is such as to recommend the method for plant control work, although by observing certain precautions outlined in the preceding paper, the accuracy may be increased to such a degree that the method is suitable for a very exact quantitative analysis of these compounds. The analyses given in this paper were made with the object of obtaining rapid results rather than with the idea of securing the highest accuracy.

WASHINGTON, D. C.

[SEVENTH CONTRIBUTION FROM THE COLOR INVESTIGATION LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

THE USE OF BENZALDEHYDE SULFITE COMPOUND AS A STANDARD IN THE QUANTITATIVE SEPARATION AND ESTIMATION OF BENZALDEHYDE AND BENZOIC ACID.

BY G. A. GEIGER.

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Prior to the work of Lubs and Clark, described in the two preceding papers, I attempted to develop methods for the analysis of side-chain chlorinated toluene, based upon the determination of benzaldehyde and benzoic acid. The procedure described in this paper is quite accurate and useful for check analyses, but for ease of manipulation and speed cannot be compared with the methods described by Lubs and Clark. The method is also useful for the determination of benzaldehyde and benzoic acid mixtures derived from other sources than chlorinated toluene. Many difficulties were experienced in obtaining and preserving pure benzaldehyde necessary for developing the analytical method, until the use of the benzaldehyde sulfite compound was suggested to me. This compound is very useful for obtaining benzaldehyde solutions of known concentration, since it is easily prepared pure, keeps well and decomposes quantitatively, giving known amounts of benzaldehyde.

The determination of benzaldehyde has been found by Denis and Dunbar[1] to be best effected by means of the phenylhydrazone compound which

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[1] *J. Ind. Eng. Chem.*, 1, 256 (1909). A review of the literature is given in this article.

is precipitated and weighed. I have had occasion to employ this method in the separation and estimation of benzaldehyde in presence of benzyl alcohol and benzoic acid and, with some modifications in the method, the benzaldehyde and benzoic acid have been satisfactorily determined. In order to test the accuracy of manipulation in the estimation of benzaldehyde and benzoic acid in the presence of each other, test mixtures made from benzaldehyde were found to be unsatisfactory. Even when the benzaldehyde was carefully purified by numerous distillations in an atmosphere of hydrogen, the subsequent handling of the product, in such a way as to prevent oxidation, so many difficulties were encountered and the analyses of the product gave such low results that the use of benzaldehyde was discarded. The sulfite addition product[1] containing half a molecule of water of crystallization was found to be admirable for the purpose, since it is of known composition, comparatively stable, easily dried, can be handled and weighed in the air without fear of change and breaks up into a definite quantity of benzaldehyde on treatment with sodium hyhydroxide in aqueous solution.

This compound was first described by Bertagnini,[2] who ascribed to it the formula $C_6H_5CHO.NaH.SO_3.0.5H_2O$.

The sodium sulfite addition product was made by adding a saturated solution of sodium hydrogen sulfite to an excess of benzaldehyde. The product formed was filtered, washed with 95% alcohol and crystallized twice from 50% alcohol and dried over sulfuric acid or soda lime in a desiccator. Owing to the fact that this compound decomposes *in vacuo* at ordinary temperature, the amount of water present could not be determined by the usual methods. To establish its constitution it was found necessary to determine the proportion of the elements. Sulfur was determined by the Carius method and the carbon and hydrogen by combustion. The results agree with the composition found by Bertagnini.

Samples of the compound are divided in two portions, one dried for 3 days in a desiccator over sulfuric acid and the other over soda lime.

Subst. 0.2236, 0.1793; H_2O, 0.0778, 0.0613; CO_2, 0.3111, 0.2566.

		Found.	
	Calc. for $C_6H_5CHO.NaHSO_3$.-$0.5H_2O$.	I. Dried over sulfuric acid.	II. Dried over soda lime.
C	38.33	38.12	37.94
H	3.68	3.82	3.89
S	14.63	14.60	14.58

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[1] There are statements in the literature which indicate that other sulfite addition products are possible. Otto, *Ann.*, **112**, 308 (1859) describes a substance, made by treating the ammonium sulfite benzaldehyde compound with sodium nitrate, which, when recalculated, indicates the sodium hydrogen sulfite benzaldehyde. See also Allen, *Analyst*, **29**, 87 (1904).

[2] *Ann.*, **85** 188 (1853).

Method.—Solutions containing varying quantities of benzaldehyde and benzoic acid from 0.5 g. of each compound as a maximum to much smaller amounts are treated as follows:

Make distinctly alkaline with caustic soda, avoiding a large excess, and extract with 3 portions, of 25 cc. each, of ether.

To the combined ether extract add 1.5 cc. of freshly distilled phenylhydrazine[1] and 10 cc. of 10% ethereal solution of acetic acid and evaporate to dryness, preferably by a gentle air current from an electric fan. There remains in the beaker a crystalline residue of benzal phenylhydrazone,[2] together with a small amount of phenylhydrazine acetate and acetic acid. Add to this residue about 50 cc. of distilled water, thereby dissolving the phenylhydrazine acetate, let stand for 5 to 10 minutes, and filter the insoluble benzphenylhydrazone into a tared Gooch crucible, dry for two hours at 70° *in vacuo* and weigh.

Make the solution from which the benzaldehyde has been extracted slightly acid with hydrochloric acid (1 to 3), extract once with 25 cc. of chloroform, then saturate the solution with sodium chloride and extract with 3 separate portions of chloroform of 25 cc. each. Evaporate the combined chloroform extracts to dryness in a current of air at room temperature, dissolve the residue of benzoic acid in 50% neutral alcohol and titrate with standard sodium hydroxide[3] solution, using phenolphthalein or thymolsulfophthalein as the indicator.

Known mixtures of pure benzoic acid and the sodium sulfite benzaldehyde compound were made and analyzed by the method above described with the following results:

TABLE I.—ANALYSES OF MIXTURES.

	Composition, gram.			Found by analysis, gram.	
	Benzaldehyde sulfite compound.	Equivalent to benzaldehyde.	Benzoic acid.	Benzaldehyde.	Benzoic acid.
I....................	1.0000	0.4839	0.2500	0.4829	0.2487
				0.4835	0.2483
				0.4842	0.2484
				0.4840	0.2480
				0.4835	0.2487
II....................	0.5000	0.2419	0.2550	0.2416	0.2487
				0.2417	0.2483
III..................	0.5000	0.2419	0.5000	0.2411	0.4915
				0.2413	0.4958

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[1] The phenylhydrazine is best prepared by distilling in an atmosphere of hydrogen and preserving in an atmosphere of this gas.

[2] If small amounts of benzyl alcohol (not more than 0.5 g.) are present in the mixture the accuracy of the estimation of benzaldehyde is not affected, since benzyl alcohol is extracted with the benzaldehyde and remains with the benzphenylhydrazone from which it can be washed with water containing 10% alcohol.

[3] Morey, *Bull. Bur. Standards,* 8, 643 (1913).

By washing the ether solution of benzaldehyde with 25 cc. of 0.2 *N* sodium hydroxide solution the quantity of benzoic acid separated is larger and the accuracy of the method increased.

Benzaldehyde.		Benzoic acid.	
Present, gram.	Found, gram.	Present, gram.	Found, gram.
0.4839	0.4835	0.5000	0.4990
0.2419	0.2423	0.2500	0.2496
0.4839	0.4835	0.2500	0.2494

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE OCCURRENCE OF MELEZITOSE IN A MANNA FROM THE DOUGLAS FIR.

BY C. S. HUDSON AND S. F. SHERWOOD.

Received July 6, 1918.

At the suggestion of Miss Helene M. Boas, of the New York Botanical Garden, Bronx Park, we have recently examined a sample of manna which had been collected by Mr. James A. Teit near Spence's Bridge, British Columbia, from Douglas fir trees (*Pseudotsuga Taxifolia* [(Lamarck) Britton]). This tree is also known as the Douglas spruce and the Oregon pine. It was reported that the manna formed in large quantities on the twigs and needles of the firs during summer droughts, but it was not definitely known whether it was an exudation or was produced by aphids or other insects. The sample of manna that was received from Miss Boas consisted of several small stems and needles of the Douglas fir encrusted with a hard, white, crystalline coating. The stems and needles weighed 4 g., while the manna that surrounded them weighed 42.5 grams. The manna possessed an agreeable, mildly sweet flavor, contained very little moisture, and was not hygroscopic. On drying to constant weight at 100° it lost 2.2% water and became slightly yellow in color. The manna was soluble in cold water and only traces of insoluble matter were left behind.

In order to purify the crystalline substance of which the manna largely consisted, 32 g. of the powdered dry manna was digested with 300 cc. absolute alcohol at 25° during 48 hours. The insoluble residue was dissolved in 25 cc. water, the solution was decolorized with carbon and to it was added an equal volume of absolute alcohol. Crystallization proceeded rapidly and after 12 hours' standing in the ice box the solution yielded 15 g. of pure white crystals of the rare trisaccharide *melezitose*. From the mother liquor 1.5 g. melezitose were also obtained after concentrating to a sirup and adding an equal volume of glacial acetic acid.

The identification of the sugar as melezitose was fully established. Its