A Quantitative Total Aldehydes Test Useful in Evaluating and Blending Citrus Essences and Concentrated Citrus Products

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The recovery and concentration of the volatile flavor and aroma constituents of citrus juices and their subsequent addition to concentrated juice products is being practiced by approximately 50% of the Florida commercial citrus processors. This industrial interest in flavor enhancement necessitated the development of an analytical method to evaluate recovered essence so that it could be added to concentrated juice products at the desired level. A quantitative colorimetric test using *N*-hydroxybenzenesulfonamide in an isopropanol system to determine the total aldehyde content of citrus juices, essences, and processed citrus products is discussed. Data and results are given, illustrating the applicability of the test for blending citrus essence and concentrated citrus products.

The use of fruit essence as a flavor enhancing material is a rather recent addition to the processing methods of the Florida citrus concentrate industry. The recovery and concentration of the volatile flavor and aroma constituents of citrus juices (Wolford *et al.*, 1968) with their subsequent addition to concentrated juice products for flavor enhancement is now being practiced by approximately 50% of the commercial processing companies. Along with this industrial interest in flavor enhancement has come the need for an analytical method to determine the strength or concentration of the recovered essences so that they can be added back to the concentrated juice products at the desired level. While numerous papers have been published providing valuable knowledge of the chemical composition of citrus and other juice essences, very little has been reported covering the quality-control-type of analyses which can be run in the normally unsophisticated laboratories found in the citrus industry.

Jansen (1961) and Charley (1962) reported methods for analyzing for volatile constituents of fruit juices. These were based on distillation followed by dichromate oxidation of the volatile substances in the distillate. Dougherty (1968) developed the chemical oxygen demand (COD) method of analysis which measures all of the oxidizable compounds in citrus essences and has been used with some success in blending essences in concentrated citrus products. Attaway *et al.* (1967) reported chemical methods for determining oxygenated terpenes, saturated, and unsaturated aldehydes and ester concentrations in aqueous citrus essences. Peleg and Mannheim (1969) criticized the saturated aldehyde test of Attaway *et al.* and proposed a method for the determination of carbonyl compounds in aqueous citrus essences using 2,4-dinitrophenylhydrazine. Ismail and Wolford (1970) developed a method for determining aldehydes in aqueous solutions using *N*-hydroxybenzenesulfonamide. The method was based on a spot test developed by Feigl (1966).

The present paper describes a quantitative test, in an isopropanol system, for the determination of total aldehydes in citrus essences, juices, and processed citrus products. Isopropanol was selected as the solvent because it is relatively safe and inexpensive to use, and part of the distillate from the juice distillation can be used for the oil determination as reported by Scott and Veldhuis (1966). The results of the test are useful for blending essences and concentrated citrus products. It may also be used for the determination of total aldehydes in other solutions or solvents, providing that the proper dilution in 90% isopropanol can be made.

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EXPERIMENTAL

Apparatus. Distillation is necessary in preparing the samples for analysis of any distillation apparatus having a water cooled condenser is satisfactory. The absorbance measurements were made with a Fisher Electrophotometer II using the small cuvettes having a 10 mm light path. However, other colorimeters can be adapted to the procedure. The chemical reactions and color development are most conveniently carried out in 50-ml Erlenmeyer flasks.

Preparation of Standard Solution and Samples. The standard stock aldehyde solution for the test contains 1000 mg per l. of aldehydes and is made by diluting 0.25 g of octanal and 0.25 g of *trans*-2-hexenal to 500 ml with reagent grade isopropanol. The 10 to 50 mg per l. of aldehydes working standards are prepared by diluting portions of the stock aldehyde solution with 90% isopropanol (v/v, reagent grade isopropanol plus distilled water). The juice samples are prepared by diluting 50 ml of juice to 100 ml with reagent grade isopropanol and distilling this mixture at atmospheric pressure to obtain 50 ml of distillate. The essence samples are prepared by making a 1 to 100 (v/v) essence to water dilution. Then 50 ml of this dilution are diluted to 100 ml with reagent grade isopropanol and distilled at atmospheric pressure to give 50 ml of distillate, which is the sample. The aldehyde values obtained with the distilled essence samples are used when blending orange essences and concentrates. However, when blending is not to be considered, the essence sample is prepared by making a 1 to 100 (v/v) essence to 90% isopropanol dilution and using this dilution directly for the aldehyde determination.

The test calls for a 1.5% *N*-hydroxybenzenesulfonamide (HBS) solution (w/v) in reagent grade isopropanol. This solution should be kept in the refrigerator and discarded if not used in 5 days. The *N*-hydroxybenzenesulfonamide reagent should be stored in a desiccator. All of the standard aldehyde solutions should be refrigerated when not in use and allowed to warm to room temperature before using. The standard solutions should last for 6 months or longer.

Analytical Procedure. The procedure for conducting the test is as follows: To 10 ml of sample or working standard

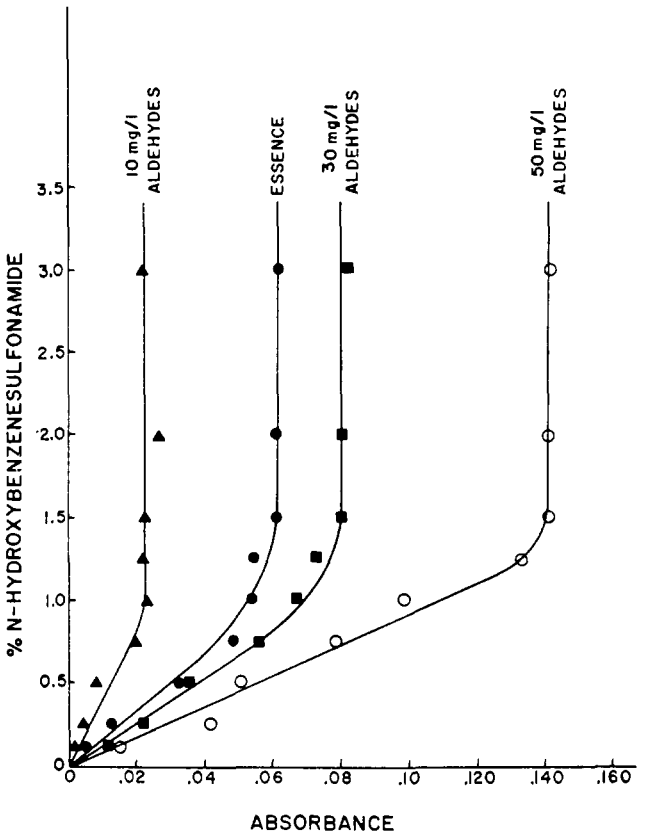

Figure 1. The effect of *N*-hydroxybenzenesulfonamide concentration on absorbance when the test was conducted on standard aldehyde solutions and a typical orange essence

add 1.0 ml of 1.5% HBS solution and 1.0 ml of 1*N* KOH solution. Swirl gently until mixed and let stand for 10 min. Add 1.0 ml of a 1.0% $FeCl_3$ (w/v) in 2*N* HCl solution. Once again swirl gently and allow the mixture to stand for 10 min. The absorbance of the mixture is measured in the electrophotometer using a 525 mμ filter. Maximum absorption was observed at 510 mμ; therefore, if possible, this wavelength should be used.

A blank and working standards of 10, 30, and 50 mg per l. of aldehydes should be run with each series of samples. The blank is 90% isopropanol and is used for zeroing the instrument used to measure the absorbance. The working standards are used to plot a curve from which the results for samples are obtained. The curve is linear in the range of concentrations used.

The values for fresh juices or reconstituted concentrates are the values obtained from the curve. The values for essences must be the values from the curve multiplied by 100, since a 1 to 100 dilution of the essence is made in preparing the essence samples.

Octanal and *trans*-2-hexenal were selected as the aldehyde standards, since both occur in citrus essences and they represent both saturated and unsaturated aldehydes.

RESULTS AND DISCUSSION

It was necessary to determine the minimum concentration of HBS solution required to detect *all* of the aldehydes present in the concentration range in which the test was applied. Figure 1 is a plot of the percent HBS *vs.* absorbance when the test was run on 10, 30, and 50 mg per l. standard aldehyde solutions and on a typical orange essence. It can be seen that

Table I. Triplicate Analyses of Three Orange Essence Samples Demonstrating Reproducibility of the Aldehyde Test

Sample		Absorbance	Difference in Absorbance	Aldehyde Content (mg/l.)	Difference in Aldehydes (mg/l.)
	a	0.028		1100	
1	b	0.029	0.001	1130	30
	c	0.028		1100	
	a	0.052		2000	
2	b	0.052	0.000	2000	00
	c	0.052		2000	
	a	0.033		1280	
3	b	0.033	0.001	1280	30
	c	0.034		1310	

Table II. Addition of Orange Essences to Concentrates on the Basis of Total Aldehyde Content

Essence Sample	Essence Aldehydes (mg/l.)	Concentrate Aldehydes (mg/l.)	Essence Added (ml/l. Recon. Juice)	Recon. Juice Aldehydes (mg/l.)
1	1695	7.4	17.7	39.0
2	2315	7.4	13.0	39.7
3	2170	7.4	13.8	39.3
4	3170	6.7	9.5	38.6
5	2630	6.7	11.4	38.6
6	2370	6.7	12.6	38.4

1.5% HBS is the minimum concentration necessary to quantitatively detect all of the aldehydes in a 50 mg per l. standard. This is evident in that the absorbance does not change when the concentration of HBS is increased beyond this level. Samples to be analyzed, such as the typical essence shown, should be diluted to fall within this range.

Optimum reaction time was determined to be 10 min after the addition of HBS and KOH solutions. Color stability was observed 10 min after the addition of ferric chloride.

Reproducibility of the test is shown in Table I. Three orange essences were analyzed in triplicate for total aldehydes. The results show a change in absorbance of only 0.001 unit and a change in total aldehydes of only 30 mg per l. The reproducibility of the test is very good and is well within experimental and instrumental error.

When using the total aldehyde values for blending essences and concentrated juices, it is necessary to analyze both the essence to be used and the concentrate to which it is to be added for total aldehyde content. These values are substituted in equation 1 to obtain the volume of essence required:

$$\frac{(a - b) \times c}{d} = \text{volume of essence} \qquad (1)$$

where: a = desired mg/l. aldehydes in reconstituted product; b = mg/l. aldehyde, before essence addition, in the reconstituted concentrate; c = total volume of reconstituted product; and d = mg/l. total aldehydes in the essence. The blending can be checked by analyzing the reconstituted product which should contain the concentrate aldehydes plus the essence aldehydes.

To evaluate the applicability of the test for blending essence and concentrated juices, six fresh essence samples were analyzed and addition was made to concentrates on the basis of the aldehyde content of each essence. An amount of each essence was added to the concentrates to give an additional 30 mg per l. aldehydes in the reconstituted juices (Table II). The use

of equation 1 is illustrated below for the calculation of the amount of essence sample 1 to be added to orange concentrate:

$$\frac{(37.4 - 7.4) \times 1000}{1695} = \text{vol of essence} = 17.7 \text{ ml}$$

The results of these additions show that when essence was added to the two concentrates on the basis of this aldehyde test, the aldehyde content of the reconstituted juices agreed closely with the calculated values of 37.4 and 36.7 mg per l. The average total aldehyde values for the reconstituted juices were, respectively, 1.9 and 1.8 mg per l. greater than the calculated values.

It may be concluded that this aldehyde test may be used as a means of determining the total aldehyde content of citrus juices, essences, and processed citrus products. The values obtained can be used to blend essences and concentrates to obtain a desired aldehyde content in the reconstituted juice, as may be reflected in flavor preference determined organoleptically. The test is a measure of essence strength and not of essence quality.

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