Lime-Salts Determination by Direct Colorimetric Titration

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The standard soap method (1)[2] for determination of total hardness of water is being largely superseded by a convenient titration method employing a color indicator. This new method is based on the titration of a water sample with an organic sequestering agent which has the ability to form soluble non-ionic chelates with calcium and magnesium. The titration is performed on a solution buffered to pH 10, utilizing an indicator which is red in the presence of calcium and magnesium ions and blue in their absence.

Chelates formed in the alkaline pH range between Versene[3] (Disodium dihydrogen ethylene diamine tetraacetate dihydrate) and calcium and magnesium are particularly stable, and in the determination of total hardness in water the Biedermann and Schwarzenbach method (1) or a modification thereof is almost universally used. Because of the simplicity and accuracy of this method, an investigation was conducted during the 1951-52 campaign with the aim of adapting this method to the determination of lime salts in factory process syrups. It was known that the Schwarzenbach method is not applicable if the solution to be tested contains more than 0.07 ppm of copper or 1 ppm. of manganese; and that in this case an inhibited indicator must be used (2). Such an indicator may be obtained from the Hach Chemical Company of Ames, Iowa.

The indicator has a deep blue color in solution at pH 10. In the presence of magnesium, however, a wine-red complex is formed. When, in the presence of a small amount of this dye, sufficient Versene has been added to chelate all of the magnesium present, a sharp color change from red to blue occurs. When calcium is also present in solution it is titrated before the end point since Versene will first chelate calcium ions. For this reason magnesium is usually deliberately introduced into the standard Versene solution.

Procedure

The Versene solution used in these tests was prepared as follows; To 7.0 gm. of reagent grade disodium dihydrogen ethylene diamine tetraacetate dihydrate dissolved in 750 ml. distilled water add 0.1785 gm. $MgCl_2.6H_2O$ and "dissolve to a perfectly clear solution. This solution is standardized against a primary calcium standard containing .001 gm. CaO per ml. and adjusted before titration to a pH of not less than 5.0. The Versene solution is adjusted to exact equivalence with the standard by utilizing the following titration procedure:

To 10 ml. of the calcium standard pipetted into an Erlenmeyer flask, add distilled water to make 100 ml. and add approximately 1 gm. (measured in a plastic or stainless-steel dipper) of Uni-Ver Buffer-Indicator powder (Hach Chemical Co.) which has been finely ground in a mortar. Swirl and titrate to the discharge of the red tint; the end point is signified by the appearance of a true blue color.

When applied to determinations of lime salts in factory syrups, 20 ml. of the syrup (diluted if necessary to 13-15 Brix) is pipetted into a 250-ml. Erlenmeyer flask and made up to 100 ml. with distilled water. To this solution is added the Uni-Ver (1 gm., measured by the dipper) and the titration is carried out as outlined above. In most cases the water blank will be zero; almost certainly so small that it may be ignored in interpreting the results by the use of the standard tables for CaO by soap solution *in thin juices.*

It would be well to point out here that the reaction is not a rapid one, and it is very important that the Versene solution be added at a moderate but fairly constant rate so that the reaction does not lag behind the additions of solution and thus cause the end point to be overshot. Once the operator understands that the final additions of titrating solution must be added slowly, little difficulty will be experienced.

Experimental Results

In the investigational work 15 Brix pure sucrose solutions as well as factory syrups were employed, known increments of calcium and/or magnesium being added previous to the titration. Comparisons were made against standard soap solution (1 ml. = .001 gm CaO) prepared by conventional procedures.

Table 1 presents a summary of 156 determinations and shows the improved accuracy which may be realized from the Versene method as compared to the soap solution method. This table represents average and maximum deviations from the known conditions found when comparing the two methods.

Table 1.

Solution	CaO Added Mg	MgO Added Mg	Versene		Soap Solution	
			Average Deviation	Maximum Deviation	Average Deviation	Maximum Deviation
Pure Sucrose	1 to 10		.01	.02	.05	.11
		1 to 6	.01	.03	.07	.13
	.8 to 8	.2 to 2	.01	.03	.07	.16
Thin Juice	1 to 10		.02	.05	.11	.19
		1 to 6	.01	.04	.09	.16
	.8 to 8	. to 2	.02	09	-13	.31
Standard Liquor	1 to 10		.02	.06	.10	.17
		1 to 6	.03	.04	.11	.16
	.8 to 8	.2 to 2	.04	.09	.14	.29

It can be plainly seen from Table 1 that the error in determination is considerably less when using the Versene than when using soap solution; however, an even greater difference would be noted if variations experienced by different operators running duplicate determinations were tabulated. It is quite generally established that the soap solution method introduces a great deal of variation from one operator to another, primarily in the matter of just exactly what distinguishes the end point.

Table 2.—Variation in Quadruplicate Analyses.

Solution	Versene		Soap Solution	
	Average Deviation	Maximum Deviation	Average Deviation	Maximum Deviation
Pure Sucrose	.01 ml	.03 ml	.03 ml	.09 ml
Thin Juice	.02	.05	.06	-12
Standard Liquor	.03	.05	.07	.16

Table 2 illustrates the reproduceability encountered under average operating conditions by the same operator. Two different known amounts of calcium and magnesium were added to each solution for the titrations shown.

Table 3 shows the reproduceability obtained when duplicate analyses were made by several operators in different laboratories.

In the Versene method in these experiments, it was found possible to obtain duplication of results within an accuracy of .05 to .1 ml. over a titration range of 0-10 ml. This represents an accuracy of about .002 to .004 percent lime salts on 100 Brix over a range of 0.350 percent lime salts on 100 Brix for average syrups. A few practice determinations by even an inexperienced operator should enable him to recognize the end point so that a reproduceability of about .1 ml. for routine analyses should be obtainable in the factory laboratory. That this is possible has been well substantiated during the past campaign, as little difficulty was encountered in training operators to run the analyses.

Table 3.—Lime Salts Found in Factory Syrups—CaO on 100 Brix.

Sample		General Laboratory Results		Factory Results
		Ver senate	Soap Solution	Versenate
Thin Juice	No. 1	.068	.081	.066
	2	.074	.090	.074
	3	.070	**.079**	.066
	4	.112	**.130**	**.109**
	5	.088	**.101**	.090
Standard Liquor	No. 1	.048	**.061**	.048
	2	.052	.059	.050
	3	.072	**.091**	**.071**
	4	.080	**.097**	**.080**
	5	.063	**.071**	.062

Interfering ions were investigated as shown in Table 4. Tests were run on 15 Brix pure sucrose solutions containing .2 mg. CaO plus .05 mg. MgO per ml. In all cases where the addition of the ion in question caused a great deviation from neutrality, adjustment was made to near neutrality in order that the buffer mixture might function correctly. In some cases the interfering ion altered the typical red-to-blue color change at the end point. However, accuracy of end point determination at the maximum color change was unaffected. Table 4 lists only that concentration above which the error may exceed an arbitrary maximum of 0.1 ml. in a 5.0 ml. titration.

Observations

Up to a lime salts concentration of about .160 percent CaO on **100** Brix it was found possible to obtain a one-drop end point with the Versene, using a 10 ml. Koch automatic burette with a micro-tip delivering 42 drops per ml. Beyond this concentration, and in certain dark-colored syrups, it was necessary to exercise considerable care in the recognition of the end point, but in all cases it could be determined within a range which would correspond to 1-2 drops from a conventional burette. Such a small variation introduces only an inconsequential error in the actual lime salts value.

As the very nature of the soap solution determination made the use of such equipment impractical, a standard burette delivering 22 drops per ml. was used *in* the soap determinations. As in the case of the Versene, 1 or 2 drop end points could be realized on solutions containing very low lime salts concentrations, but in most cases the end point was quite indistinct, often requiring the addition of 3-5 drops of soap solution beyond the first false end point indication to obtain a final value. This represents a far greater possible error than in the case of the Versene, and in all cases re- quired considerably more time per analysis.

Table 4.—Tolerance Levels for Interfering Ions.

Ion	ppm in Syrup
Cu++	100
Fe+++	100
Fe++	100
SOs−	1000
PO*	1000
NOa-	1000
COs-	1000
Cl-	10000
SO4-	10000
Sucrose	500000

Conclusions

The Versene method of lime salts determination on factory syrups offers several advantages over the conventional soap solution method, fore- most being greater speed, greater accuracy, and greater reproduceability. It enables different operators to produce highly consistent and comparable results, and gives better indication of true lime salts concentration. In no respect did the Versene method prove to be inferior to the soap method; rather, it was in every case **tested equal to or superior to the soap method.**

Xherefore, it is believed that this method is fully worthy of inclusion into the methods of factory syrup analyses.

Literature Cited

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