IMPROVING ACCURACY AND PRECISION OF CALCULATED PROCESS VARIABLES BY USING DIRECTLY MEASURED NONSUGARS

Jeffrey L. Carlson
Gregory W. Golovanoff
Kenneth A. Kubat
Minn-Dak Farmers Cooperative
7525 Red River Road
Wahpeton, ND 58075

Introduction

Precision is a term that is used to denote the reproducibility of data, while accuracy denotes how close measured values are to the true values. The four targets in figure 1 give examples of accuracy and precision with the "bull's eye" representing the true value. In 1a the marks all over the target represent inaccurate and imprecise data. In 1b the loosely grouped points around the center show the data to be accurate but imprecise. In 1c tight grouping outside of the "bull's eye" indicates precise but inaccurate data, and the tight grouping at the center of target 1d symbolizes data that is both accurate and precise.

In the beet-sugar industry, data coming from the process laboratory are used for purposes with different accuracy and precision requirements. Some uses require precise but not accurate data, some uses require accurate but not precise data, and some uses require both precise and accurate data. The process laboratory analyzes raw material, process and product streams, and produces some data of each kind (and even some that is both inaccurate and imprecise). Unfortunately, the data does not always meet the end use accuracy and precision requirements.

Ideal analytical tests are inexpensive, timely, and give results that are both precise and accurate. Even though this is not yet a reality for all analyses, many ion determinations meet these criteria. This paper illustrates how ion analyses can be used to improve information coming from the sugar-factory, process laboratory.

Propagation of Errors

For many calculations done in the sugar factory, juice and syrup streams are considered to have three components-sugar (S), nonsugars (NS), and water. The two analytical techniques that are used most often to measure these are polarimetry for sucrose w/w ([S]), and refractometry for dry substance w/w (dissolved solids or 100-%water, [DS]). The major advantage of these methods is speed and good precision, but neither method is analyte specific and thus they are slightly inaccurate. When values determined by these methods are used in calculations, their errors propagate through to the results.

Propagation of measured errors through calculations has been extensively studied and the mathematics is well known. In general, for any value, Q, that is calculated from n measured quantities x_i

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such that $Q = Q(x_1, x_2, x_3, \ldots, x_n)$ and each measurement differs from its true value, μ_i, by and amount θ_i, ($\theta_i = x_i - \mu_i$), the error in the calculated value θ_Q can be estimated by equation 1. Most often, θ_i is not known, but by using estimates of the uncertainties, ϵ_i, and a derivation of equation 1, a good estimate of θ_Q, ϵ_Q can be calculated (equation 2)[1]

$$\theta_Q = \left(\frac{\partial Q}{\partial x_1}\right)\theta_1 + \left(\frac{\partial Q}{\partial x_1}\right)\theta_2 + \ldots + \left(\frac{\partial Q}{\partial x_n}\right)\theta_n \qquad (1)$$

$$\epsilon_Q^2 = \left(\frac{\delta Q}{\delta x_1}\right)^2\epsilon_1^2 + \left(\frac{\delta Q}{\delta x_2}\right)^2\epsilon_2^2 + \ldots + \left(\frac{\delta Q}{\delta x_n}\right)^2\epsilon_n^2 \qquad (2)$$

The equations for calculating both [NS] and $\epsilon_{[NS]}$ are shown (equations 3 and 4). If it is assumed that the two uncertainties are independent and equally likely to be positive or negative the cross term ($2\epsilon_{[NS]}\epsilon_{[S]}$) will be zero. These equations show that the absolute uncertainty for [NS] will always be of the same order of magnitude as the largest of the uncertainties from [DS] and [S] (Table I).

$$[NS] = [DS] - [S] \qquad (3)$$

$$\epsilon_{[NS]} = \sqrt{\epsilon_{[DS]}^2 + \epsilon_{[S]}^2 - 2\epsilon_{[NS]}\epsilon_{[S]}} \qquad (4)$$

Probably the most frequently used quantity for sugar-process evaluation is purity (P). Purity is the percentage of [DS] that is sugar (equation 5) and its relative error is calculated with equation 6. The relative uncertainty of the calculated purity value will always be of the same order of magnitude as the largest of the relative uncertainties from which it is calculated (Table I)

$$Purity = \frac{[S]}{[DS]} \qquad (5)$$

$$\frac{\epsilon_{[P]}}{P} = \sqrt{\left(\frac{\epsilon_{[DS]}}{[DS]}\right)^2 + \left(\frac{\epsilon_{[S]}}{[S]}\right)^2} \qquad (6)$$

Use of Specific Nonsugars in
Calculating Crystallizations

An example of how substitution of an ion concentration for [NS] improves data can be given with the sugar elimination equation. When this calculation is used to evaluate pan and

Table I: Propagation of Errors from Measured [RDS] and [S] to Calculated [NS] and Purity.

	Measured		Calculated	
		Values		
	RDS	S	NS	Purity
Thin Juice	17.2	15.7	1.5	91.3
A-Pan Mass	91.0	84.6	6.37	93.0
A-Green	80.0	68.8	11.2	86.0
Molasses	80.0	44.8	35.2	56.0

Absolute Error

	RDS	S	NS	Purity
Thin Juice	± 0.2	± 0.2	± 0.3	± 1.6
A-Pan Mass	± 1.0	± 1.0	± 1.4	± 1.5
A-Green	± 1.0	± 1.0	± 1.4	± 1.6
Molasses	± 1.0	± 1.0	± 1.4	± 1.4

Relative Error

	RDS	S	NS	Purity
Thin Juice	± 1.2	± 1.3	± 19	± 1.7
A-Pan Mass	± 1.1	± 1.2	± 22	± 1.6
A-Green	± 1.4	± 1.5	± 13	± 1.9
Molasses	± 1.4	± 2.2	± 4.0	± 2.6

crystallizer performance it is known as percent gross crystallization (%GC). The %GC is the amount of sugar crystals produced (w/w) as a percent of the total sugar in a syrup. It is generally calculated using equation 7 where P_m and P_g are the massecuite (or feed) and green syrup purities, respectively[2]. Substitution of [S] + [NS] for [DS] in this equation followed by simple algebraic manipulation results in the mathematically equivalent equation 8.

An assumption implicit in %GC calculations is that the absolute amount of nonsugars does not change during crystallization. This assumption should be very good as there is little destruction of sucrose or nonsugars during this process.

$$\% \, GC = \frac{10,000 \, (P_m - P_g)}{P_m (100 - P_g)} \tag{7}$$

$$\% \, GC = 100 \times \left[1 - \frac{[S]_g [NS]_m}{[S]_m [NS]_g} \right] \tag{8}$$

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$$\epsilon_{\%GC} = \sqrt{\left(\frac{P_g(100-P_g)}{P_m^2 - \dfrac{2P_m^2 P_g}{100} + \dfrac{P_m^2 P_g^2}{10000}}\right)^2 \epsilon_{P_m}^2 + \left(\frac{P_m(-100+P_m)}{P_m^2 - \dfrac{2P_M^2 P_g}{100} + \dfrac{P_m^2 P_g^2}{10000}}\right)^2 \epsilon_{P_g}^2} \qquad (9)$$

Just as the errors in the [DS] and [S] values propagate to the purity value, so will the error in purity propagate to the %GC calculation (equation 9). An example can be made using the purity and error values from Table I in equations 7 and 9. The resultant %GC is 53.8 with an absolute error of 12.3% or a relative error of 22.9 %.

The high absolute error results primarily from the two subtractions where the absolute error for each is large with respect to the differences. The larger the purity drop between the massecuite and syrup, the larger the difference in the numerator. Thus, the magnitude of error in the %GC calculation will diminish with greater purity differences. Also, because of the difference in the denominator, the lower the purity of the green syrup, regardless of the mass purity, the smaller the error for a given error in purity.

Equation 8 gives an alternative method for calculating %GC. However, the [NS] values as calculated from equation 3, are determined from the same [DS] and [S] values as the purity. Thus, use of these [NS] values in equation 8 gives the same result and error as use of purities in equation 7.

Since the % GC calculated from equation 8 uses the [S] and [NS] ratios in the massecuite and the green syrup, their actual values are not needed, just numbers that are proportional to the actual values. This means that any specific nonsugar can be substituted for [NS].

Modern analytical instrumentation allows the easy and accurate measurement of many specific nonsugars. The concentrations of ions like potassium $[K^+]$, sodium $[Na^+]$, chloride $[Cl^-]$ and nitrate $[NO_3^-]$ can be determined with low relative errors. This makes them attractive replacements for [NS] in many sugar-factory calculations including %GC.

For the work presented here, potassium ($[K^+]$) was the nonsugar chosen for three reasons. First, beet-sugar syrups contain enough of these ions for easy quantification by atomic absorption; second, contamination from environmental potassium is not a problem; and finally, these ions are very soluble in sugar solutions so they do not precipitate or scale out of solution, but pass completely through the process to molasses.

In equation 8 there is no error in the first term of the parentheses as it is an absolute number which represents complete crystallization. Application of equation 2 to the second term gives equation 10. This is the propagation-of-error expression for $[K^+]$ and [S] errors to the fraction of sugar that is retained in

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the syrup after crystallization (R). The absolute error for this term will be the same absolute error for the crystallized fraction (equation 8: the term in the parentheses) $100\epsilon_R = \epsilon_{\%CG}$. When %GC is calculated with equation 8, the greater its value, the smaller the propagated error.

$$\frac{\epsilon_R}{R} = \sqrt{\left(\frac{\epsilon_{[K^+]_m}}{[K^+]_m}\right)^2 + \left(\frac{\epsilon_{[S]_m}}{[S]_m}\right)^2 + \left(\frac{\epsilon_{[K^+]_g}}{[K^+]_g}\right)^2 + \left(\frac{\epsilon_{[S]_g}}{[S]_g}\right)^2} \qquad (10)$$

Table II compares values of %GC for hypothetical A-, B- and C-pan crystallizations as calculated with both purities and $[K^+]$. The %GC and error estimates in this table were determined by applying equations 8 and 10 to [DS], [S] and [K+] values given. The absolute error in [DS] and [S] values are assumed to be 1.0%. Two different relative errors for $[K^+]$ 1.0% and 5.0% are assumed. For all three pans, the 1.0% errors in [DS] and [S] had more impact in the %GC calculated with purities than the 5.0% error in $[K^+]$ had using the other equation.

Another advantage that individually measured nonsugars have is the minimization of the effect that systematic errors have in %GC calculations. This can be illustrated by considering a hypothetical strike with the A-mass and A-green parameters given in Table II. The % GC for this strike would be 53.8. Typical systematic errors manifest themselves as either absolute offsets (intercept errors) or a relative offsets (slope errors). In either case, all measurements have these errors. Figure 2 illustrates the relative offset in the %GC calculation. The %GC determined using $[K^+]$ will be unaffected, but the same calculation using purities will have significant error.

The above difference that exists in these calculations can be understood if equation 8 is examined. Since [NS] and [S] values appear in both the numerator and denominator of the second term, a systematic relative error will divide out. Systematic absolute errors essentially divide out as well.

Results

%GC of A-Pan Strikes

Figure 3 shows the %GC for 30 A-pans calculated with equations 7 and 8. Apparent purities were used for equation 7, and AA determined [K+] with polarimetry determined [S] values for equation 8. Equation 8 values have a higher average %GC (54.6) than those calculated with apparent purities (50.6). In addition, the variation from pan-to-pan was much less with estimated standard deviations for the thirty of 1.2 and 4.0 respectively.

Sugar-End Extraction

Figures 4 and 5 compare sugar-end extraction over a 17-week period as calculated using equations 7 and 8. Sugar-end extraction is the percent of the sugar entering in the thick juice that is

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Table II: Errors in %-Gross-Crystallization as Calculated with Purities and Potassium Ions.

<u>CRYSTALLIZATION</u>

Substance	$[DS]^1$ ± 1.0	$[S]^1$ ± 1.0	P	[NS] ppt	[K+]	$\%GC_P$ ± 1.0	$\%GC_{K+}^2$ ± 5.0
A-PAN							
Massecuite	91	84.6	93	6.4	5.1		
Green	80	68.8	86	11.2	9.0		
						53.8	53.9	53.9
Absolute Error						± 12	± 1.1	± 3.3
B-PAN & CRYSTALLIZERS							
Massecuite	93	74.4	80	18.6	10.0		
Green	81	55.9	69	25.1	13.5		
						44.4	44.3	44.3
Absolute Error						± 6.7	± 1.5	± 4.1
C-PAN & CRYSTALLIZERS							
Massecuite	94	64.9	69	29.1	20.0		
Molasses	82	46.7	57	35.2	24.3		
						40.6	40.8	40.8
Absolute Error						± 5.7	± 1.9	± 4.5

[1]The absolute error in the [DS] and [S] is 1.0.
[2]The error in %GC is calculated for relative errorss of 1.0 and 5.0% in the potassium determination.

extracted as granulated sugar. It is assumed that all nonsugars entering exit with molasses and that no extra nonsugars are added.

The sugar-end extraction calculation will be one of the most accurate elimination calculations for either equation 7 or 8. Because of large differences in thick juice and molasses purities, and the fact that molasses has a low purity, propagation of errors through both equations is minimized. If a 1.0% absolute error is assumed for the purity values, then $\epsilon_{\%GC} = 1.6$. (equation 9). If 1.0 % relative errors are assumed for [K+]'s and 1.0% absolute errors for [S]'s, Then $\epsilon_{\%GC} = 0.3$ (equation 10).

Figure 4 compares weekly calculations using apparent purities with the ones using [K+] and polarimetry determined [S]. Over this period, both calculations show gradual drop in the sugar-end extraction but value calculated from equation 8 shows a 2.0% higher extraction than the one calculated with apparent purities.

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Figure 5 compares calculations using true purities with those using [K+] and IC determined [S]. The calculated average extraction during this period is about the same for each method, however, the trending over time is more definite with the potassium calculation.

Figure 6. compares the extractions calculated from equation 8 using the two methods for [S] determination. Both types sucrose determinations give virtually identical results.

Conclusions

The improvements in both the precision and accuracy of calculated values through the use of a specifically measured nonsugar have been demonstrated. Use of this method will be helpful in a number of ways. First, there are many laboratory and on-line instruments available for measuring specific nonsugars. This expands the chemist's or process engineer's choice of instruments for determining traditional sugar-factory parameters. Second, greater accuracy and precision of these calculations improves the numbers engineers and managers have when they are evaluating processes and planing for changes. Finally, increased accuracy and precision of real-time calculated values can be used for control purposes instead of just being after-the-fact evaluations.

Use of specifically measured nonsugars and parameters calculated from them can be invaluable tools for increasing productivity in the sugar industry.

Experimental

%GC of A-Pan Strikes

Sampling: Samples of the A-massecuite were collected by the sugar boilers just before each pan was dropped. The pan-floor helper separated mother liquor from the massecuite by using a Buchner funnel equipped with a filter that had been cut from a used, white-centrifugal screen. The mother liquor was drawn through the screen with vacuum, and all samples were brought to the laboratory where 70 g of each was weighed into a bottle and 230 g of reverse-osmosis water added. The samples were thermostated to 20°C.

Sucrose analysis: The thermostated samples were analyzed for sucrose with a CTI-501 Dark Solution Polarimeter

Dry substance analysis: A CTI-601 Precision Refractometer, both manufactured by Crystal Tek International was used.

Ion analysis: The diluted samples were further diluted so the ion concentration would be between 0 and 5 ppm and analyzed for potassium with a Perkin-Elmer 3100 Atomic Absorption Spectrophotometer equipped with an acetylene/air burner.

Sugar-End Extraction

Sampling: Production thick juice and molasses samples were

collected every two hours and composited over a 24-hour period. Each 24-hour composite was analyzed for as above.
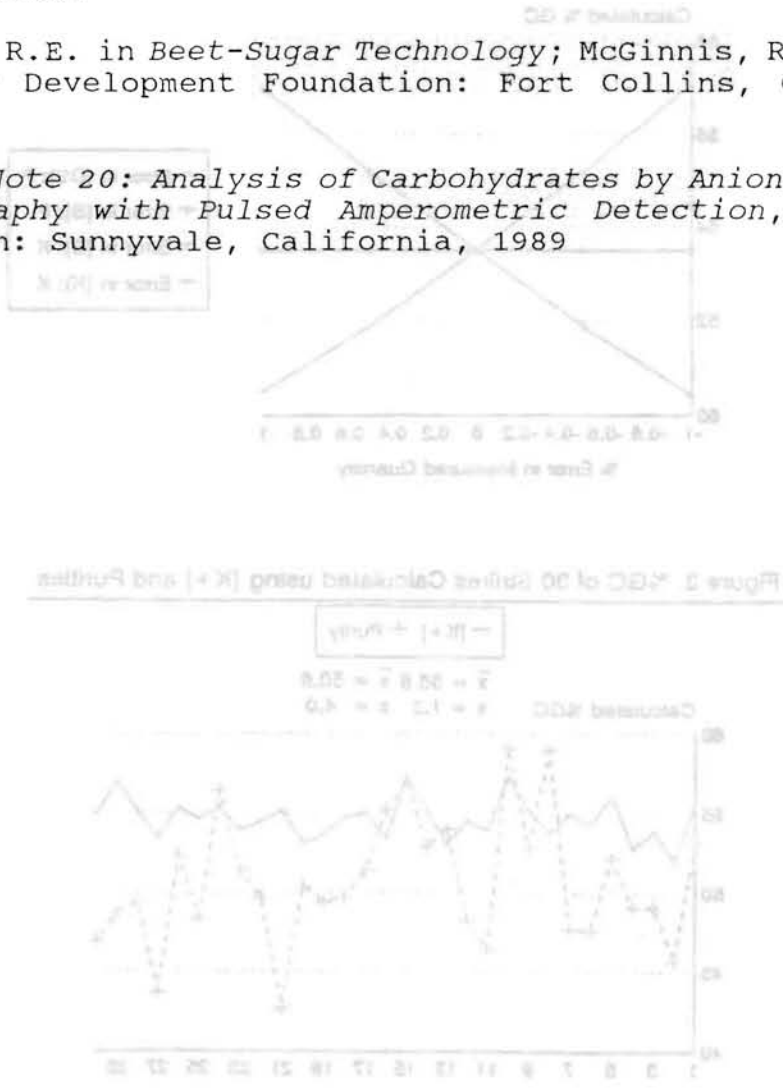
Dry substance: Duplicate determinations of each 24-hour composite were made by weighing between 1 and 2 grams of the composites into aluminum weighing boats on an analytical balance, then drying in a convection oven at 100 C for about 24 hours. The samples were reweighed and the difference taken to be the amount of water in the original samples.

Sucrose: Sucrose concentration of each composite was determined on a Dionex ion chromatograph using 1.4 g of lactose as an internal standard.[3]

Calculations: Weekly averages were calculated for results from the daily-composite analyses. The average weekly concentrations were used in equations 7 and 8.

References

1. Halpern,A.M.; Reeves,J.H. *Experimental Physical Chemistry: A Laboratory Textbook*; Scott, Foresman and Company: Glenview, Illinois, 1988.

2. Hallabeck, R.E. in *Beet-Sugar Technology*; McGinnis, R.A., Ed.; Beet Sugar Development Foundation: Fort Collins, Colorado, 1982, 756.

3. *Technical Note 20: Analysis of Carbohydrates by Anion Exchange Chromatography with Pulsed Amperometric Detection*, Dionex Corporation: Sunnyvale, California, 1989
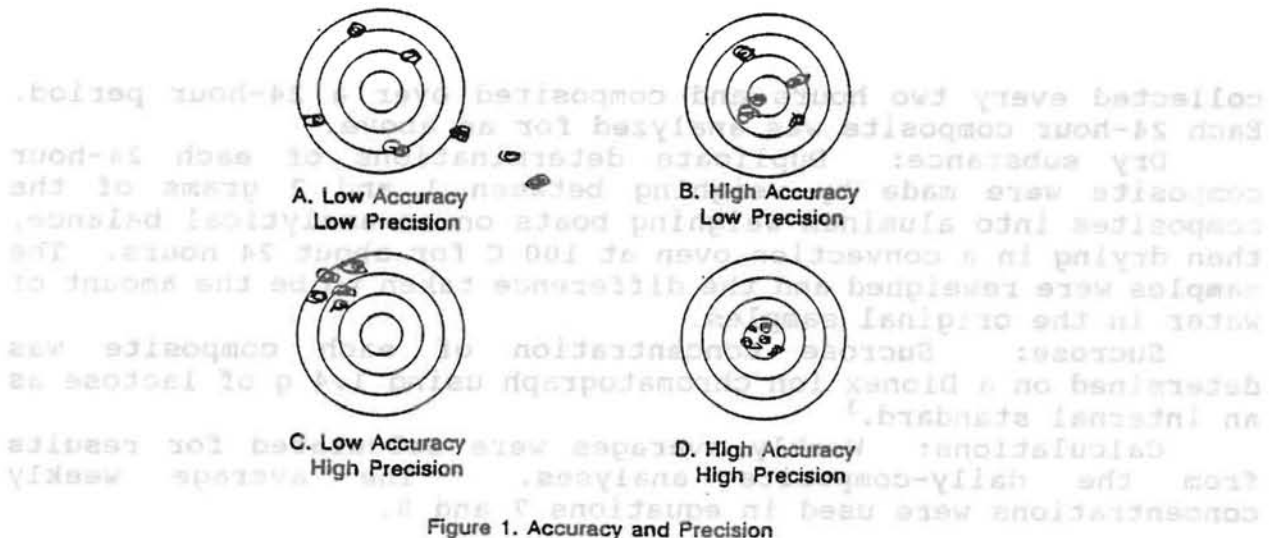
A. Low Accuracy
Low Precision

B. High Accuracy
Low Precision

C. Low Accuracy
High Precision

D. High Accuracy
High Precision

Figure 1. Accuracy and Precision

Figure 2. Effect of Systematic Error on %GC Using Purity and [K+] Calculations

Calculated % GC

— Error in [DS]: P
+ Error in [S]: P
＊ Error in [S]: K
→ Error in [K]: K

% Error in Measured Quantity
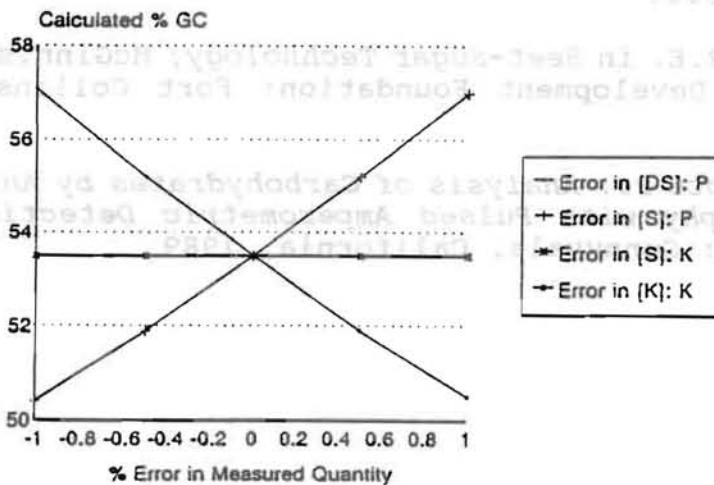
Figure 3. %GC of 30 Strikes Calculated using [K+] and Purities

— [K+] + Purity

$\overline{x} = 56.6$ $\overline{x} = 50.6$
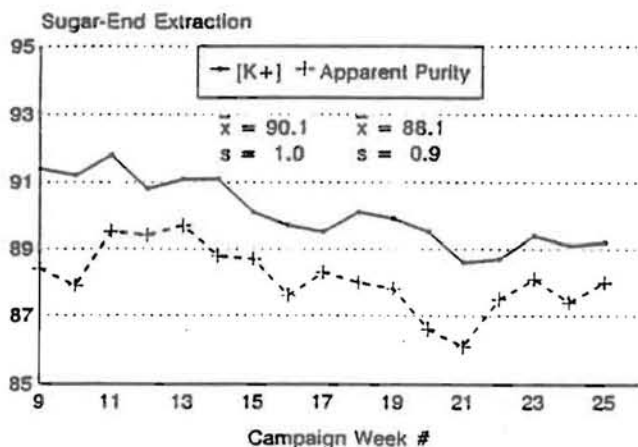$s = 1.2$ $s = 4.0$

Calculated %GC

Strike

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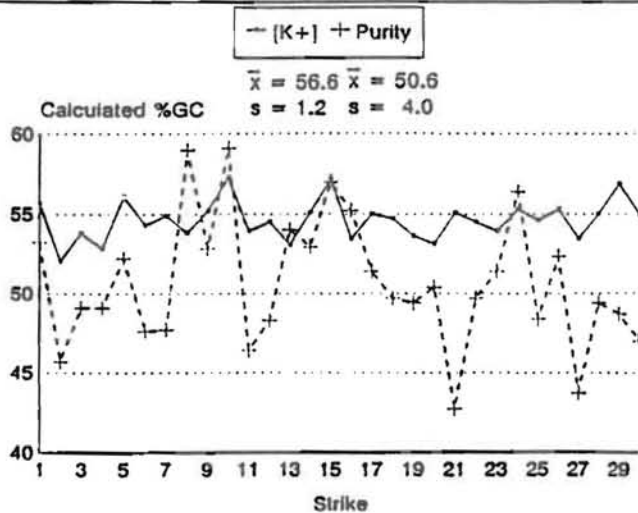
Figure 4. Sugar-End Extraction Calculated with Apparent Purities and [K+]
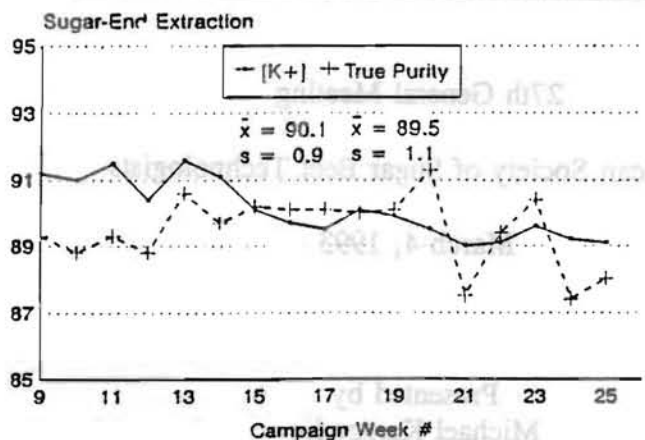Analytical Methods: Refractive Index, Polarimetry, and Atomic Absorption

Values taken from Minn-Dak's 1992-1993 Campaign.

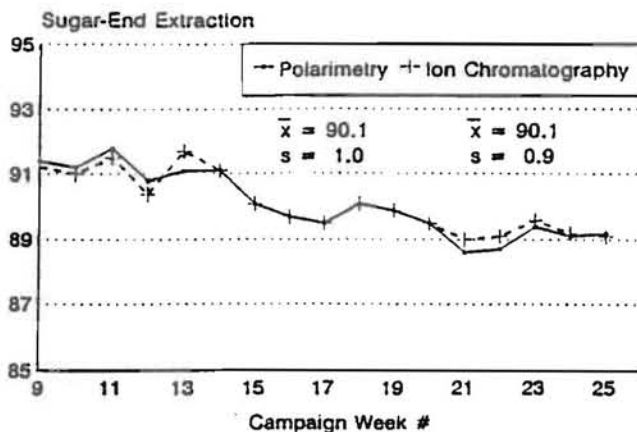**Figure 5.** Sugar-End Extraction Calculated with True Purity and [K+].
Analytical Methods: Gravimetric, IC, and Atomic Absorption.

Values taken from Minn-Dak's 1992-1993 Campaign.

Figure 6. Sugar-End Extraction Calculated Using [K+]
Analytical Methods: Ion Chromatography, Polarimetry, and Atomic Absorption

Values taken from Minn-Dak's 1992-1993 Campaign.

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