Uses of Total Organic Carbon and Inorganic Carbon Analysis in the Sugar Beet Factory

CARLSON, JEFFREY L, UPASIRI SAMARAWEERA, KEN A. KUBAT,
Minn-Dak Farmers Cooperative, 7525 Red River Road, Wahpeton, ND 58075-9698.

Introduction

Personnel at Minn-Dak Farmers Cooperative use a total organic carbon (TOC) and total inorganic carbon (IC) analysis in a number of ways. First, they use TOC to monitor and control the wastewater treatment system. Second, they employ TOC to keep track of sewer and flume losses. Third, they use IC to monitor carbonate in the second carbonation and evaporator juices. Finally, Minn-Dak has experimented with determining the amount of organic species removed in carbonation using TOC. These measurements are easy to do, highly accurate and reproducible and can be more useful than alternative methods.

The total carbon content (TC) of a sample is composed of the total inorganic carbon and total organic carbon. The inorganic carbon is defined as the carbon in carbonate, bicarbonate and dissolved CO_2. Total organic carbon is defined as all carbon atoms covalently bonded in organic molecules. A variety of methods are available to analyze for TOC and IC. Most TOC instruments are easy to use and dependable. The instrument from Rosemont Analytical that Minn-Dak uses, requires two sample injections. The analyst first injects a sample into phosphoric acid, which expels all inorganic carbon as CO_2 into a carrier gas. She injects a second aliquot from the same sample into a heated platinum catalyst. The combination of high temperature (680°C), platinum catalyst and gas (O_2) convert organic and inorganic carbon into CO_2. Once the instrument converts either sample to CO_2 it purges the CO_2 through a dehumidifier and a halogen scrubber, then measures it with an infrared detector. The instrument calculates the TOC by the difference between the TC and IC values.

The analyst calibrates the instrument once each eight-hour shift, usually using sugar and sodium carbonate. He usually uses a fifty :-liter sample. Both the accuracy and precision of this instrument are less than one percent and its response is linear over large range. TOC instruments range in cost from $15 to $30 thousand. However, their day-to-day operation cost is low. Minn-Dak uses about one high-grade oxygen cylinder each year for about $200. Other consumables include injection syringes, filter papers and normal laboratory glassware.

Wastewater Treatment

Wastewater treatment operators commonly use for TOC measurements for evaluating the performance of wastewater-treatment systems. As presented at the 30th ASSBT, Minn-Dak has found TOC correlates well to both the five-day biological oxygen demand (BOD_5) and the chemical oxygen demand (COD) measurements. In a sugar factory the vast majority of either BOD_5 or COD is organic, so a TOC analysis works well for wastewater treatment of sugarbeet wastewaters. Wastewater treatment personnel at Minn-Dak have found that they needed to establish correlations between TOC and these parameters for each step of the wastewater treatment system (Table I). Once established the correlations hold well over time.

Table I: Relation between TOC and BOD_5 for Wastewater Treatment at Minn-Dak

	TOC (PPM)	BOD_5 (PPM)	Ratio
	Wastewater Ponds		
11/3/00	3,410	8,960	0.38
2/16/01	9,336	22,120	0.42
	Anaerobic System Effluent		
11/3/00	350	316	1.11
2/16/01	613	312	1.96
	Aerobic System Effluent		
11/3/00	205	18	11.4
2/16/01	205	19	11.0

Sugar Losses

Measurement of the sugar losses in the factory sewer is always problematic. Many solutions that workers discharge to the sewer are acid or caustic and highly colored. This can interfere with sugar determination by the alpha-naphthol test or polarimetry. If sugar is chemically inverted, TOC will report an accurate sugar amount where polarimetry will not. Minn-Dak lab personnel monitor the factory sewer using both pol and TOC. Each hour a lab technician samples the factory sewer, measures the pol and records the flow. The analyst then saves five grams of the sample in a composite, which is analyzed for TOC at the end of the day. The results are shown in Figure 1. The TOC analysis closely matches the pol readings. To calculate sucrose from TOC in the sewer, the TOC values was divided by 0.421 (fraction of carbon in sugar) and multiplied by the fractional raw juice purity.

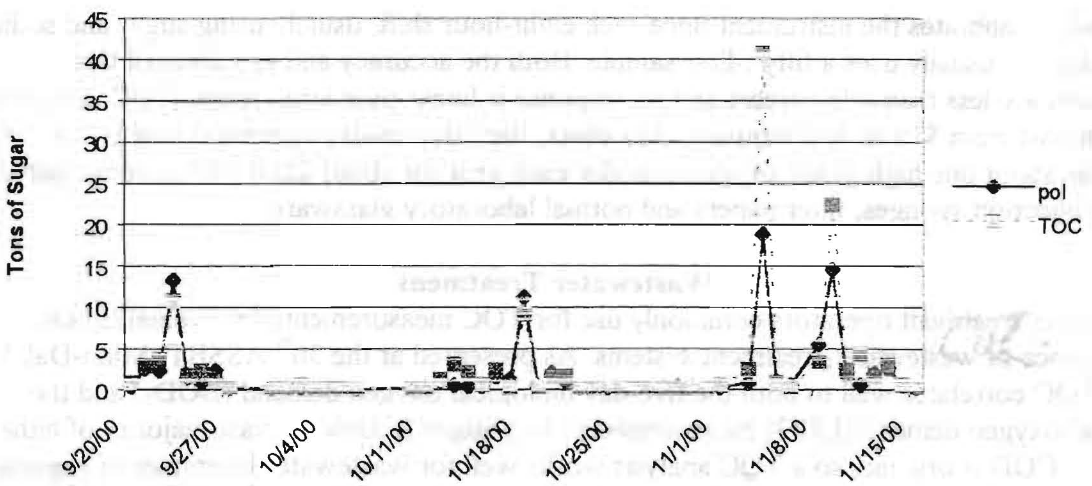

Figure 1. Measurement of sugar lost in the factory sewer using polarimetry and total organic carbon analyses

Minn-Dak personnel measure sugar loss to the flume water using TOC. At Minn-Dak the flume system volume is about one million gallons. Washhouse personnel control flume-water infection by adding milk of lime to keep the pH above 10. At this pH, Minn-Dak still experiences some infection primarily in the mud at the bottom of the clarifier. Because the bacterial action inverts sugar and converts it to various acids, sugar measurement alone will not report the total sugar leached into the flume. Once each day, an analyst measures the TOC of a 24-hour composite sample. To calculate the sugar loss the chief chemist multiplies the sugar concentration by the mass of flume water pumped to the wastewater ponds. Figure 2 shows the flume sugar losses for the current campaign.

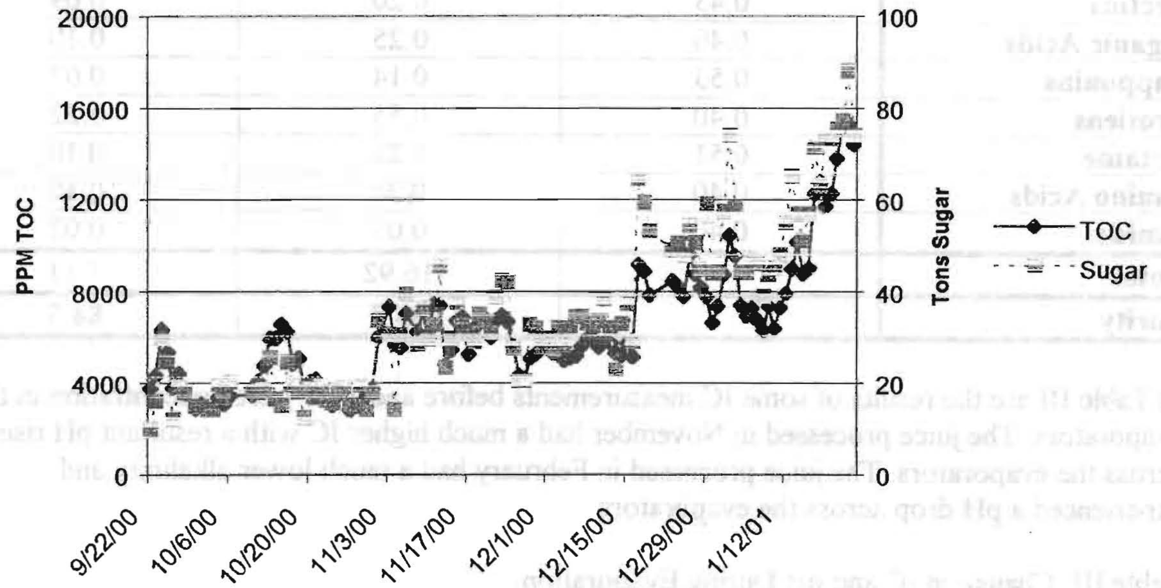

Figure 2. Sugar lost to the flume water calculated using total organic carbon measurements

TOC Purity

During beet juice purification, some organic nonsugars are removed and some are not. Research at Minn-Dak has shown that measuring both purity and TOC purity of juice before and after purification personnel can achieve a better understanding than by measuring purity changes alone. By measuring a juice's sugar content and TOC, an analyst can determine its TOC purity (defined as the total sucrose carbon divided by the total organic carbon). Table II lists the organic species and TOC for each species in a typical raw juice. At the bottom of the two columns is the organic purity (88.7) and the TOC purity (88.5). These values are about the same because the weighted average of the organic nonsugar carbon content (0.43) is only slightly higher than that of sugar.

Inorganic Carbon

In concentrating juice and crystallizing out sugar, factory personnel subject the juice to high temperature for a prolonged period. Under these conditions, nonsugars and sugar react to produce acid. One economical way for factory personnel to prevent pH drop during subsequent processing is to ensure that purified raw juice has adequate carbonate/bicarbonate alkalinity to neutralize generated acid. Traditionally, personnel measure alkalinity by titration. Using a TOC analyzer to measure the residual IC is experimentally much easier than doing a titration.

Table II: Organic and TOC Content of a Typical Raw Juice

	Fraction Carbon	Typical Raw Juice Content (%)	TOC in Typical Raw Juice (%)
Sucrose	0.42	15.00	6.32
Glucose	0.40	0.10	0.04
Fructose	0.40	0.05	0.02
Raffinose	0.43	0.08	0.03
Pectins	0.43	0.20	0.09
Oganic Acids	0.40	0.25	0.10
Sapponins	0.53	0.14	0.07
Protiens	0.40	0.55	0.22
Betaine	0.51	0.25	0.13
Amino Acids	0.40	0.25	0.10
Amides	0.40	0.05	0.02
Total		16.92	7.13
Purity		88.7	88.5

In Table III are the results of some IC measurements before and after juice concentration in the evaporators. The juice processed in November had a much higher IC with a resultant pH rise across the evaporators. The juice processed in February had a much lower alkalinity and experienced a pH drop across the evaporators.

Table III: Change in IC and pH During Evaporation.

	Thin Juice	Thick Juice	Change
		11/16/2000	
IC/PPM	82 (236)*	12.8	-223
RDS	18.8	54	X 2.9**
PH	9.0	9.2	+0.2
		2/7/2001	
IC/PPM	21 (78)*	4.1	-74
RDS	17	63	X 3.7**
PH	8.7	8.3	-0.4

* The value in parentheses is the measured valued multiplied by the RDS concentration factor
** The RDS concentration factor

Summary

Both TOC and IC measurements are valuable with a variety of uses in a sugar factory. The modern instruments are relatively inexpensive, economical and easy to operate and reliable. The uses presented in this paper are meant only as examples with many others possible.