# ION CHROMATOGRAPHIC DETERMINATION OF CATIONS
# IN SUGAR BEET PROCESS SAMPLES

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## INTRODUCTION

Ion chromatographic (IC) analysis techniques have been extensively applied to sugar factory process streams over the last fifteen years and examples of these applications have been reported by a number of authors.[1-10] For the most part, these applications have involved the use of ion chromatography to determine either carbohydrate or anion levels although several of the listed authors have used the technique for cation determination.[1,8,10] The principal reason for the application of ion chromatography in the determination of carbohydrates and anions is the absence of faster or more convenient analysis techniques. In the case of carbohydrate determination, ion chromatography is comparable in sample analysis time to high performance liquid chromatography (HPLC) and offers some improvements in specificity and precision. In the case of determination of anions, IC is one of the few fast, convenient method for determination of multiple anions in a mixture.

For the determination of multiple metal cations in complex mixtures such as factory process streams, ion chromatography can certainly give good results for levels of common cations (such as sodium, potassium, calcium, and magnesium) but it suffers in sample analysis time when compared to the use of atomic absorption (AA) spectrometry for the analysis of large sets of samples. Although ion chromatography can give levels for several cations in a single 8 to 10 minute chromatographic run, if one has a set of 10 or 20 samples for cation analysis the required analysis time becomes from 1 1/2 to 3 hours while for AA spectrometry samples can be analyzed for a single element essentially as fast as they can be aspirated into the AA flame (as fast as several samples per minute). In addition, ion chromatography usually requires a significantly longer period of time for instrument warm-up and equilibration of analysis conditions than AA spectrometry. Thus ion chromatography for cation determination in multiple samples cannot compete in ease of analysis and time requirements, provided that one is willing to put up with the weaknesses of AA itself: matrix effects, possible interferences, and a generally lower precision. Atomic spectrometry rarely attains precision levels of 1 to 2% relative standard deviation[11] under the best of conditions while chromatography, given good separation and detection conditions, can frequently attain relative standard deviations under 1%. In addition, the fact that ion chromatography involves of separation of components would be expected to result in a lower possibility for interferences and matrix effects of varying samples.

For routine questions related to the beet quality or the quality of process samples, the precision and accuracy of cation determination by AA spectrometry are usually adequate but there are situations in which the most precise cation measurements possible would be very useful. A particular case is the use of accurate levels of a cation, such as potassium, as a reference material in the determination of sucrose destruction during specific factory process steps. Sucrose levels in streams before and after a factory step, evaporation for example, can be measured precisely by polarimetry or chromatographic methods but the amount of sucrose lost

during the step cannot be determined solely from the sucrose level without accurate mass flow information, that is the flow rate or, better yet, the mass of material entering and leaving the process. Since the flow rate or mass of material proceeding through a continuous factory process cannot normally be measured precisely enough to detect small sugar losses the best alternative is to examine the ratio of the level of sucrose to some material that is not chemically changed through the step. If the quantity of reference material does not change, then any decrease in the ratio of sucrose to the reference material reflects a destruction of sucrose. To some extent, the common purity determination is such a measurement. In that case the ratio of sucrose to total dissolved solids is monitored to look for significant changes in sucrose level. However, the level of total dissolved solids is not an ideal reference point because it may also be affected by many process steps. Among many examples of changes in the quantity of measured dissolved solids during a process step are: (1) the destruction of sucrose to produce non-carbohydrate components with refractive indices different than carbohydrates; (2) the loss of ammonia from solution by the hydrolysis of amides during evaporation; and (3) the precipitation of non-sugars during liming and carbonation. Although other fairly stable compounds, such as betaine, have been considered as reference materials for sucrose loss measurement, any organic compound may always be suspected of undergoing thermal destruction or microbiological degradation during various process steps and thus not be an ideal candidate for producing well-behaved ratios of sucrose to reference material.

Some of best possibilities for a stable reference material in the determination of sucrose losses are offered by metal cations, which , unlike organic materials, are not subject to any kind of thermal, chemical, or microbiological destruction. Metal cations can typically only be removed from a stream by mechanisms such as precipitation, ion exchange, or ion exclusion. In particular, the common alkali metal cations, sodium and potassium, are good reference materials because virtually all of their salts are water soluble and no precipitation occurs under any normal factory conditions (unless concentrations are quite high). Of these two, potassium has the advantage of being present in higher concentrations in sugar beet process streams. In addition, potassium is not normally present in process additives while many sources of added sodium (soda ash addition, salt added to the lime kiln, etc.) would complicate the use of sodium as a reference material in the determination of sucrose losses. Therefore, the measurement of sucrose to potassium ratio across any process step should be a reliable indicator of sucrose loss provided that potassium is not removed by some mechanism such as ion exchange and that the level of potassium can be measured precisely enough.

The calculation, using sucrose to potassium ratios, of the quantity of sucrose destroyed is a fairly straightforward procedure for any process step in which there is no significant mechanism for the removal of potassium. Examples could include: juice heating; liming and carbonation; and evaporation. In any of these cases, given proper sampling techniques to avoid the effects of routine process stream composition variation, the overall ratio of sucrose to potassium before the step should equal the ratio of sucrose to potassium after the step unless sucrose is being chemically destroyed during the process step. Consideration of the sucrose material balance in relation to the sucrose to potassium ratio for such processes leads to the following expression for the ratio of sucrose destroyed to sucrose entering:

1)
$$\frac{Sucrose\ destroyed}{Sucrose\ entering} = 1 - \frac{Sucrose\ out\ /\ Potassium\ out}{Sucrose\ in\ /\ Potassium\ in}$$

where the two ratios of sucrose to potassium may be measured in any convenient units. The form of this equation now demonstrates the necessity for precise potassium measurements. Since sucrose loss is directly related to the ratio of sucrose to potassium, the potassium value is just as important as the sugar level in determining sugar loss. In Equation (1), if the sucrose/potassium ratio before the process step is identical to the ratio after the step then the fraction on the right side is equal to one and the loss is zero. However, a 1% relative variation in one of the sucrose/potassium ratios produces an apparent 1% sugar loss and 1% variations in both ratios (in the opposite direction) produce an approximately 2% apparent sugar loss. Thus the potassium level measurement has to be just as precise as the sugar measurement. (Interestingly, since the loss ratio is calculated by dividing two ratios, although both the sugar and potassium levels have to be measured precisely, or reproducibly, neither has to be an accurate value. That is, they do not have to reflect the true level of sucrose or potassium they just have to be proportional to the actual level by the same factor in all samples.)

The factory process step that is perhaps the most interesting to monitor for sucrose destruction is the diffusion step. Unfortunately, loss calculations for the diffusion step are complicated by the presence of a second outgoing process stream, pressed pulp, that, due to its behavior as an ion exchanger, may carry potassium with it. In this case, the ratio of sugar to potassium in pulp may be also measured, in addition to the ratios in beets and diffusion juice, but an additional measurement must be made to determine how potassium is proportioned between the diffusion juice and pulp. One approach to this problem is the measurement of potassium to marc ratios in beets and pulp but this has not been investigated further.

RESULTS AND DISCUSSION

The goal of this project is a detailed examination of the determination of cations, particularly potassium, in various sugar beet process streams by ion chromatography in comparison with atomic absorption spectrometry. Initial work was carried out with potassium standards to give some idea of the precision of both methods. Figure 1 shows a typical plot of peak area versus concentration for a set of potassium standards.
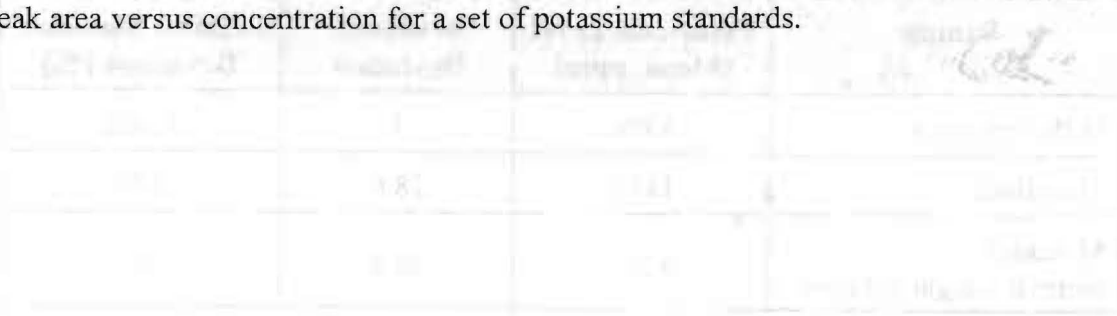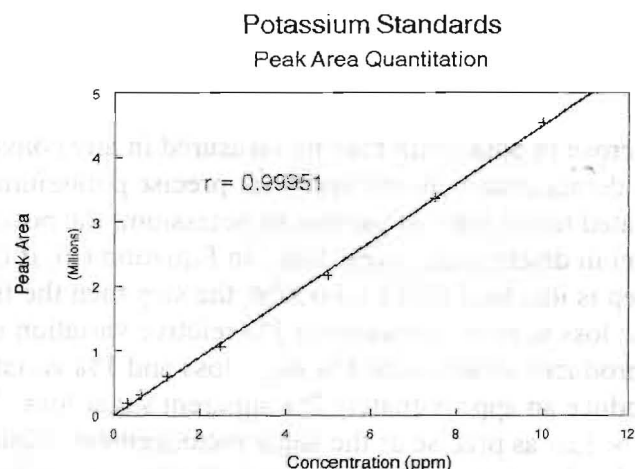
Figure 1

Potassium Standards

Peak Area Quantitation



In a typical test of precision, ten replicate IC injections of an approximately 5 ppm potassium standard gave a mean potassium concentration of 4.77 ppm and a relative standard deviation (RSD) of 1.44% by electronic peak height quantitation. Another five replicate injections of the same standard with electronic peak area quantitation gave a mean concentration of 4.78 ppm with a RSD of 0.47%. In this case, peak area quantitation gave better precision but in general peak height measurement is less susceptible to inconsistencies introduced by the changing baselines or overlapping peaks obtained with juice samples. A similar potassium standard, approximately 4 ppm in concentration, subjected to ten replicate AA determinations gave a mean concentration of 3.68 ppm with a relative standard deviation of 5.50%.

Preliminary tests of potassium level reproducibility in factory samples by triplicate analysis of samples gave the mean and standard deviation values given in Table 1. Note that the standard deviation for diffusion juice samples was unusually low.

**Table 1**
**Factory Sample Analysis**

| Sample | Potassium Level (Mean, ppm) | Standard Deviation | Relative Standard Deviation (%) |
|---|---|---|---|
| Diffusion Juice | 1896 | 1 | 0.053 |
| Thin Juice | 1811 | 28.0 | 1.55 |
| Molasses Normal weight solution | 8764 | 56.8 | 0.65 |

To obtain an indication of how IC potassium values relate to actual potassium levels in factory samples, standard addition tests were carried out with diffusion juice and thin juice.

50

Results for diffusion juice are shown in Figure 2 and those for thin juice in Figure 3.

**Figure 2**

## Thin Juice
### Standard Addition



r = 0.9994
y-intercept = 1.02

Measured K (no std added)
IC 0.79
AA 0.92

Measured Potassium (ppm, dilute sample) vs Added Potassium (ppm, dilute sample)

**Figure 3**

## Diffusion Juice
### Standard Addition



r = 0.9991
y-intercept = 0.96

Measured K (no std added):
IC 0.75
AA 0.88

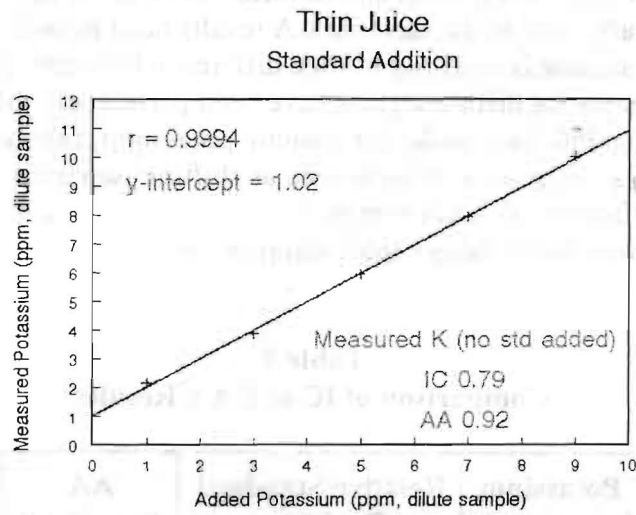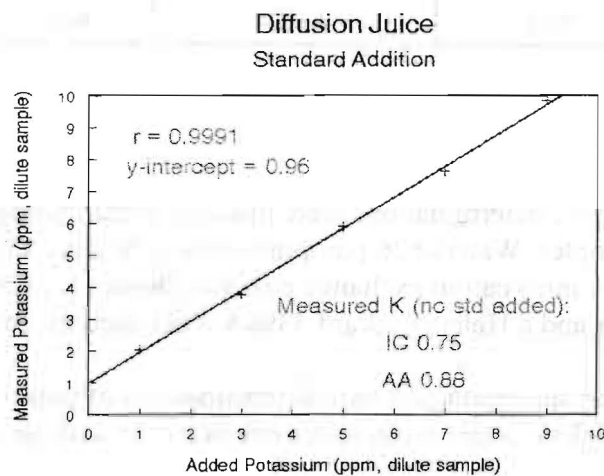Measured Potassium (ppm, dilute sample) vs Added Potassium (ppm, dilute sample)

Both tests showed good linear agreement between the level of added potassium and IC results although the differences between the standard addition potassium levels (y-intercept) and measured potassium levels without standard addition are higher than desired. These tests were run at quite a high dilution (potassium level without standard addition is under 1.0 ppm) which probably affects the agreement between y-intercept, standard addition predicted value, and AA value. In any event, the tests do show a good linear relationship between potassium level and IC measurements, which is the important factor with respect to loss determination using sucrose to potassium ratios.

Extensive tests of the precision of ion chromatographic potassium determination in comparison with AA results have, unfortunately, given somewhat mixed results. Unlike early tests with potassium standards, where IC give a lower relative standard deviation than AA analysis, analysis of thin juice, thick juice, and diffusion juice gives similar precision results by both methods. This is partly due to the fact that AA results have actually been more precise with juice samples than with standards resulting in little difference between AA and IC in tests of precision. Precise IC results for diffusion juice have been particularly difficult to obtain because diffusion juice chromatograms have peaks for sodium, potassium, calcium, magnesium, and ammonium cations with some peak overlap as well as shifting baselines. Examples of results for replicate analysis of factory juice samples by IC and AA are given in Table 2. Work aimed at obtaining consistent IC results for factory juice samples, with the best possible precision is continuing.

**Table 2**
**Comparison of IC and AA Results**

| Sample | IC Potassium (Mean, ppm) | Relative Standard Deviation | AA Potassium | Relative Standard Deviation |
|---|---|---|---|---|
| Thin Juice | 1460 | 1.83 | 1497 | 0.48 |
| Thick Juice | 7145 | 1.33 | 6504 | 1.87 |
| Diffusion Juice | 955 | 6.22 | 808 | 1.99 |

EXPERIMENTAL

Ion chromatographic determinations were made on a chromatographic system consisting of a Waters 717 Autosampler, Waters 626 pumping system, Waters 432 conductivity detector, Dionex IonPac CS12A (4 mm) cation exchange column, Dionex CSRS-Ultra (4mm) Self-Regenerating Suppressor and a Helett-Packard 3396A electronic integrator.

Atomic absorption spectrophotometric determinations of potassium were made using a Thermo-Jarrell Ash Model 11 single beam spectrophotometer with air/acetylene flame.

ACKNOWLEDGEMENTS

The authors would like to thank Alla Bagramyan, of our laboratory, for performing atomic absorption potassium determinations.

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