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CO-DETERMINATION OF SODIUM METABISULFITE AND STARCH IN CORN SYRUP BY FLOW INJECTION COULOMETRY

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Summary—During the processing of corn syrup for commercial use, starch, in the form of α-amylose, must be completely broken down to its D-glucopyranose units. Sodium metabisulfite is added to the corn syrup as a preservative. Flow Injection Coulometry was used to perform an automated assay of these analytes, both individually and jointly. The sodium metabisulfite concentration, over a range of 3.5×10^{-4}–$2.9 \times 10^{-2}M$, is determined by coulometric flow injection titration with generated iodine, using spectrophotometric endpoint detection at 530 nm. Analysis over this range produced a relative standard deviation of $< 1.5\%$ and was found to correlate very well with manual titrations. The determination was performed in the presence of varying amounts of starch, and was found to be independent of the starch concentration. Starch was determined, when no sodium metabisulfite was present, from the absorbance level after the reaction of the sample with a specific amount of iodine. In the presence of sodium metabisulfite, the rate of the accumulation of the starch/iodine interaction product after the metabisulfite titration endpoint, at a constant reagent generation rate, was used. A relative standard deviation of $< 1.4\%$ was obtained for all starch analyses, with a very good correlation (correlation coefficients ≥ 0.997) with the known relative concentration. The use of the FIC technique to perform analyses by specific amount and excess reagent generation is demonstrated, along with dual analyte determination.

Methods and techniques for performing titrations using the Coulometric Flow Injection Titration (CFIT) method have been previously described.[1,2] The generation of reagents by electrolysis, however, does not have to be limited to use in conventional titrations. The generation of a specific amount of reagent, or an excess of reagent, are areas in which the Flow Injection Coulometry (FIC) can be applied. Also, for specific chemical systems in which the generated reagent reacts preferentially with one specie of interest and then, when that specie is completely reacted, reacts with a second specie, the possibility of performing a dual component analysis is presented.

One such chemical system is the assay of commercially produced corn syrup. In order to produce an acceptable product, the raw starch of the corn syrup must be broken down to the point where it is effectively removed. In order to preserve the corn syrup, which is susceptible to biological degradation, SO_2, in the form of sodium metabisulfite, must be added. There is a need, therefore, to determine both the starch and the sodium metabisulfite concentration of the corn syrup. These species, in their reaction with iodine, allow a dual-component analysis using FIC.

The method of performing CFIT has recently been developed in this laboratory.[1] It combines the advantages of flow injection analysis and coulometric titrations. In this method, a sample is injected into a flow system containing a gradient chamber which contains a generating electrode and serves as the detector flow cell. At any specified time after the sample zone enters the chamber, a selected portion of the dispersed sample can be isolated within the chamber by stopping the flow. This portion of the injected sample reacts with the reagent as it is produced at the generating electrode. The chamber serves as the flow cell for a spectrophotometer, which constantly monitors the chamber to detect the titration endpoint. As stated, the use of a reagent generated through electrolysis does not have to be limited to use in a titration.

Faraday's law, which states that the quantity of electricity passed through a cell is directly proportional to the quantity of chemical change

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that occurs at the cell electrode, can be used to calculate the amount of reagent which has been generated at any time after the application of current.[3] For this study, the reagent, iodine, is produced by electrolysis at the platinum anode of a pair of electrodes from an electrolyte containing iodide.

The degree of dilution obtained for a sample injected into a gradient chamber at a specific delay time, at a constant flow rate, can be predetermined by application of the single mixing tank mode of the tanks-in-series model.[4–6] It has been shown that, using this model, for any time after all of a sample has entered into a flow system gradient chamber the dilution factor at that time can be predicted by an equation of the form

$$X^{-1} = k_1 e^{k_2 t_d}$$

where X^{-1} is the dilution factor expressed as the inverse mole ratio, k_1 is a constant dependent upon the factors governing the dispersion of the sample zone prior to entering the chamber, k_2 is a constant ($\sec^{-1}$) dependent upon the system flow rate and the chamber volume, and t_d is the time (sec) after injection.[1]

The presence of starch in corn syrup is determined by the interaction of the starch and iodine. Though there has been much debate on the issue of this interaction, it is currently believed that the iodine is held in an adsorption complex within the helical chain of the amylose component of the starch, and that the exact nature of the adsorption complex is dependent upon the initial starch concentration and the length of the starch chain.[7,8] The spectra resulting from the addition of an equivalent amount of iodine to solutions of varying starch concentration are shown in Fig. 1. The broadness of the adsorption peak and the effect of concentration on the complex formation would account for the production of different colors when a constant amount of iodine is reacted with corn syrup samples with differing starch concentrations. The starch present in corn syrup exists mainly in the α-amylose form, which produces a coloration considered to be nonreversible.[9]

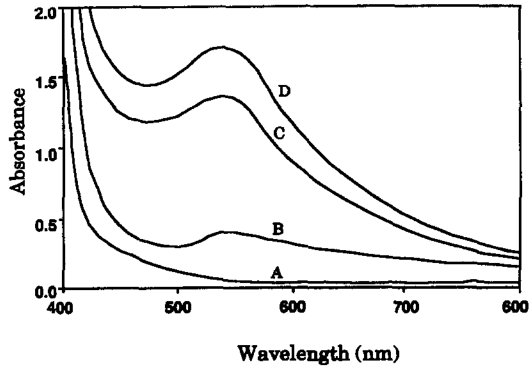

Fig. 1. Spectra of the product resulting from the addition of 0.5 ml of $2 \times 10^{-2} M$ iodine to 50 ml of diluted (1:1 (w:v) in de-ionized water) corn syrup samples of varying starch concentration. A = 3%, B = 20%, C = 65%, D = 80%.

Currently the raw starch content of corn syrup is determined by dissolving an aliquot of corn syrup in water, adding a specific amount of iodine, then observing visually and reporting the resulting color which develops, and is used in a strictly qualitative manner.[10] The color which is produced is dependent upon the concentration of the raw starch in the corn syrup. This is a simple and easy test to perform, yet it has some disadvantages. Iodine solution must be frequently standardized to ensure normality. The detector, the human eye, cannot be calibrated, and the color of a solution is based on the subjective opinion of the observer. While this test can be performed quickly with all solutions pre-prepared, it does involve manual solution handling, which potentially introduces errors dependent upon the skill of the operator performing the test.

In order to overcome the drawbacks of the present technique, the possibility of performing this test using the CFIT technique was investigated. A specific number of moles of I_2 reagent are generated and the resulting reaction with starch is spectrophotometrically monitored by light transmitted through the gradient chamber. The absorbance due to the accumulation of the iodine/starch interaction product can be correlated with the raw starch concentration of the samples. The application of the CFIT technique could be used to perform a much more reproducible analysis on the corn syrup during the course of processing, allowing for a much more cost-effective control of the process, and provide a more in-depth knowledge of the progress of the process sequence.

The concentration of sodium metabisulfite is conventionally determined by titration with iodine to a starch indicator endpoint.[11] The reaction which occurs is

$$Na_2S_2O_5 + 2I_2 + 3H_2O \rightarrow 2H_2SO_4 + 4I^- + 2Na^+ + 2H^+$$

When all sodium metabisulfite has been reacted, the excess iodine will be present to interact with

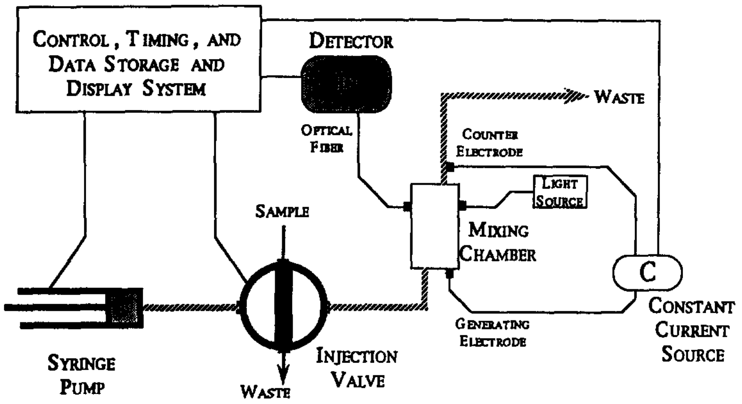

Fig. 2. Schematic of the system for performing flow injection coulometry.

the starch indicator. It is not necessary for the starch to be present, however, since iodine in solution absorbs in the visible range, allowing the titration to be self indicating.

The titration of sodium metabisulfite can be performed by the previously described CFIT technique, whereby the sample is injected and transported to a stirred mixing chamber containing a generating electrode, the flow is stopped at a pre-determined delay time, and then current is applied across the electrodes to produce the reagent. The endpoint is detected spectrophotometrically by the accumulation of excess iodine, or, if starch is present, by the accumulation of the I_2/starch interaction product.

The time at which the endpoint is detected is used to calculate the concentration of sodium metabisulfite in the injected sample. The absorbance increase occurring after the endpoint can be used to determine the starch concentration. Thus it is seen that the concentration of the two components can be determined by a single analysis.

EXPERIMENTAL

Reagents and samples

The carrier for experiments on samples containing starch only (no metabisulfite) was an electrolyte solution consisting of 0.2*M* potassium iodide (Mallinckrodt) in a pH 8 buffer of sodium phosphate dibasic (Mallinckrodt) and potassium phosphate monobasic (J. T. Baker). A non-buffered solution of the same KI concentration was used for all other analyses, because the presence of the buffer was found to interfere with the analysis of sodium metabisulfite. A 0.2% starch solution, for use as an indicator for manual titrations, was made from soluble potato starch powder (J. T. Baker) in deionized water. Arsenic trioxide (Mallinckrodt) was used as a primary standard for the determination of iodine concentration, and a 0.02*N* iodine (J. T. Baker) solution was used in the manual starch experiments and titrations of sodium metabisulfite (Allied Chemical). Samples of corn syrup with varying starch concentrations were provided by Cargill, Inc.

Apparatus

A single line FIA manifold using the single zone injection method, identical to that previously described, was used in all experiments (Fig. 2).[2] The system used a Harvard Syringe Infusion Pump 22 (South Natick, MA), and an electronically actuated 10-port, 2-way injection valve (Valco Instrument Co. Inc., Houston, TX). The valve was furnished with a 50 μl sample loop. The gradient chamber was as previously described.[2] The tubing downstream of the gradient chamber was a 28 cm long piece of 0.25 inch i.d. stainless steel tubing which served as the counter electrode. All other tubing was 0.8 mm i.d. polytetrafluoroethylene (PTFE), or Microline® (Cole Palmer, Chicago, IL) using Tefzel® and Delrin® fittings (Upchurch, Oak Harbor, WA). The net chamber volume could be varied by adjustment of the end cap positions. A volume of 0.90 ml was used for all experiments.

The electrodes were connected to a lab built constant current source. Current measurement and spectrophotometric detection were as previously described.[2] A wavelength of 530 nm was used for all experiments. The pump controllers, injection valve actuator, and constant current source were controlled and data were collected using an IBM Data Acquisition and Control Adapter (DACA) (Mendelson Electronics, Dayton, OH) in conjunction with an IBM PC/XT computer. For the manual determination of starch a Hewlett Packard 8452A diode array spectrophotometer was used.

General procedure

This study is divided into two sections, the investigation of starch determination and the co-determination of starch and sodium metabisulfite. The general procedure for the starch determination was performed in the following steps: (1) a sample or blank (H_2O) was injected into the carrier containing electrolyte; (2) at a specified delay time the flow was stopped, causing a selected portion of the sample to be arrested in the chamber; (3) at that point current was applied for a given time, electrochemically producing a specific quantity of I_2 reagent; (4) the current was stopped and the absorbance of the reacted sample was monitored and measured; (5) the flow was resumed to flush out the chamber. This automated sequencing was controlled by an IBM PC/XT computer using the general FIA control software previously described.[12] A typical FIA absorption profile is shown in Fig. 3.

For the titration of sodium metabisulfite and the co-determination of starch and sodium metabisulfite, the procedure was only slightly altered. The time during which iodine was generated was extended, and the time delay prior to the resumption of flow to flush the chamber and after the end of reagent generation, was excluded. A typical FIA absorption profile for this section of the study is shown in Fig. 4.

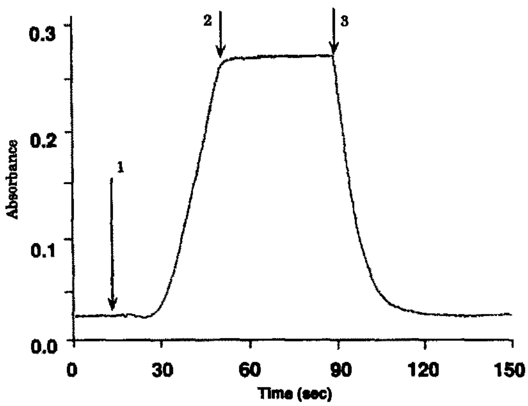

Fig. 3. FIA profile of the analysis of starch in corn syrup at a current of 0.96 mA for 30 sec, with a sample volume of 50 μl, and a flow rate of 5.0 ml/min. The flow is stopped at a selected delay time after injection, and current is applied to begin reagent generation (1). After the desired amount of reagent has been generated the current is stopped (2) and the resulting absorbance is monitored and related to the starch concentration. Flow is then resumed to flush the chamber (3).

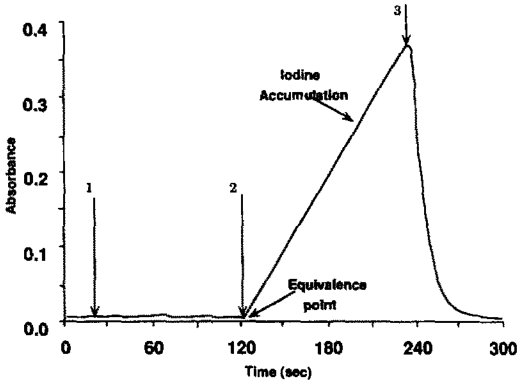

Fig. 4. FIA profile of a sodium metabisulfite titration at a current of 4.20 mA, with a sample volume of 50 μl, and a flow rate of 5.0 ml/min. The flow is stopped at a selected delay time after injection at which the desired dilution has been obtained, and current is applied to begin titration (1). After the metabisulfite endpoint (2) is reached and excess iodine has accumulated, the current is stopped and flow is resumed to flush the chamber (3). The slope of the excess iodine curve is related to the starch concentration.

RESULTS AND DISCUSSION

In order to test the current efficiency of the reagent generation, solutions made with known amounts of As_2O_3 were injected and titrated at a delay time of 5.6 sec, at which point 93.7% of the sample is within the gradient chamber. The concentrations of As_2O_3 determined by titration agreed with the calculated values of these standards within 0.5%. The results of these experiments indicate that the current efficiency was >99.8%.

Starch determination

The nature of the corn syrup samples, which are both viscous and adhesive ("sticky") did not allow them to be pumped into the sample loop. Thus all corn syrup samples were pre-diluted into a volume of de-ionized water, in milliliters, equal to the mass, in grams, of a syrup aliquot prior to injection into the system.

All of the provided corn syrup samples were then analyzed with a current of 0.96 mA for 30 sec, which produced 1.49×10^{-7} moles of iodine, at a rate of 4.67×10^{-9} moles/sec, which reacted with the 23.4 μg of the corn syrup isolated within the chamber. A composite FIA profile for four of the samples is shown in Fig. 5. A set of manual measurements were performed, using a Hewlett-Packard 8452A diode array spectrophotometer, in which the final sample-

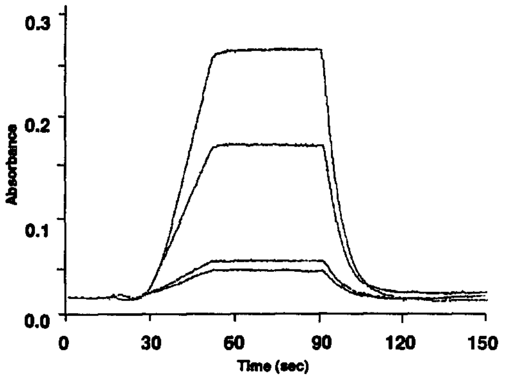

Fig. 5. Overlay of the FIA profiles of four different samples of corn syrup containing 10%, 20%, 60%, and 100% relative starch concentration. All were performed at a current of 0.96 mA for 30 sec, producing an equivalent amount of iodine for each experiment, with a sample volume of 50 μl of the 1:1 diluted sample, and a flow rate of 5.0 ml/min. The detected intensity of the absorbance of the product of the reaction (during the period from 51 to 88 sec) correlates with the concentration of starch in the sample.

to-reagent concentration ratio was equivalent to that which existed in the FIC method. When the absorbance level values obtained manually were compared with those obtained using the CFIT system the correlation of the resulting linear plot was very good ($R^2 = 0.996$). The intercept was slightly greater than zero (0.012) due to the presence of the electrolyte in the CFIT system carrier, which produced a refractive index effect upon mixing with the injected sample which was not encountered in the manually performed analyses. A t-test value of 1.389 was obtained, which, when compared to a tabulated t value at a 95% confidence level ($n = 10$) of 2.262, indicates there is no significant statistical difference between the two methods.

When the starch determination was performed, it was observed that, for a given amount of iodine added, a specific absorbance plateau level was obtained dependent upon the starch concentration of the injected sample, independent of the rate of iodine generation. It was further observed that, if the rate of iodine production is constant for different samples, the rate of I_2/starch interaction product accumulation, as well as the absorbance plateau level, is dependent upon the starch concentration. This can be observed in Fig. 5, from 29 sec after the initiation of injection, in which the sample is transported to the chamber and mixed, to 51 sec during which 1.49×10^{-7} moles of iodine are produced and reacted with samples of differing starch concentration. Thus, since the iodine is generated at a constant rate, the rate of the product production is expected to be constant and the slope of the absorbance increase should correlate to the starch concentration in a manner identical to the absorbance profile plateau.

Determination of starch in the presence of metabisulfite

The use of the slope of the absorbance profile as an assay parameter was investigated. The concentration of the starch in the provided corn syrup samples was not known, and no standards were available. In order to define a concentration value, the corn syrup sample with the greatest starch concentration, as determined in the previous experiments, was assigned a relative concentration of 100% starch, and dilutions of this corn syrup sample were used for all further measured starch samples.

A series of starch samples were analyzed in the presence of a fixed concentration of metabisulfite and the slope of absorbance increase beyond the metabisulfite titration endpoint was determined from several selected points on the absorbance–time curve using a CricketGraph^{tm} computer plotting program. It was observed that there was a slight curvature of the absorbance increase in the region between 0.1 and 0.4 AU, which was more pronounced at the lower starch concentrations (Fig. 6). This was not observed in the previous set of experiments since the maximum absorbance obtained for samples containing a low starch concentration did not exceed 0.1 AU. The curvature is believed to be due to the complex nature of the I_2/starch interaction which may vary due to a relative

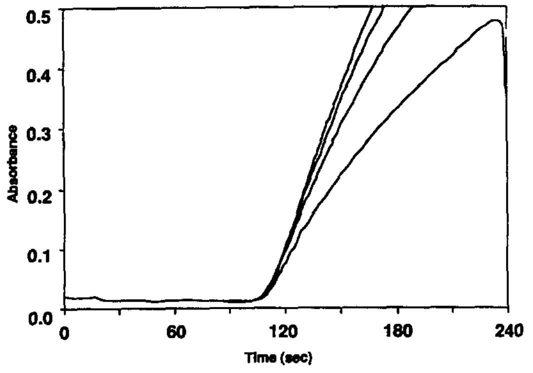

Fig. 6. Overlay of the absorbance profiles of the analysis of four samples having a sodium metabisulfite concentration of 0.0047M with relative starch concentrations of 30%, 45%, 52%, and 55%. Note that the titration endpoint is constant while the slope of the absorbance increase is different for each sample. (The entire profile is not shown, with the portion in which the chamber is flushed having been omitted.)

decrease of the starch concentration, as was discussed in the Introduction. The slope of several portions of the absorbance increase, and the estimated slope of the whole curve, were compared to the starch concentration. The intercept of 0.0328 AU/sec corresponded to the value of the slope obtained due to the absorbance of the accumulated iodine which occurred when no starch was present (starch concentration = 0%). When the curved portion of the increase was omitted, a linear plot was obtained with a correlation coefficient of 0.998, an intercept of 0.0328 AU/sec, and a slope of 170 AU/sec%. When the entire absorbance increase was used, with the slope obtained by fitting the selected points to a straight line in the CricketGraph^{tm} program, a straight line with a slope of 121 AU/sec%, an intercept of 0.0350 AU/sec and a good correlation ($R^2 = 0.997$) was obtained. The very first portion of the absorbance increase, however, is that which would most likely be used in a routinely performed analysis. When the slope of the absorbance increase between 0 and 0.3 AU was plotted against the sample concentration a curve, which could be fit to a second order polynomial with extremely good correlation ($R^2 = 0.999$), was obtained (Fig. 7). Therefore it was determined that the use of the slope of the absorbance profile, for a given rate of reagent production, is a valid parameter for use in determining starch concentration.

Metabisulfite titration

Attention was next turned to the determination of sodium metabisulfite concentration. Prepared samples of known concentration were titrated volumetrically with I_2 to a potato starch endpoint and by the CFIT method. When the two sets of results were compared the correlation was very good ($R^2 = 0.999$) with a straight line plot having a slope of 1.008 and an intercept of -1.26×10^{-4}. A Student t-test was performed and a value of 0.507 was obtained. The comparison of this value with the tabulated t value at a 95% confidence level ($n = 16$) of 1.746 indicates there is no significant statistical difference between the two methods.

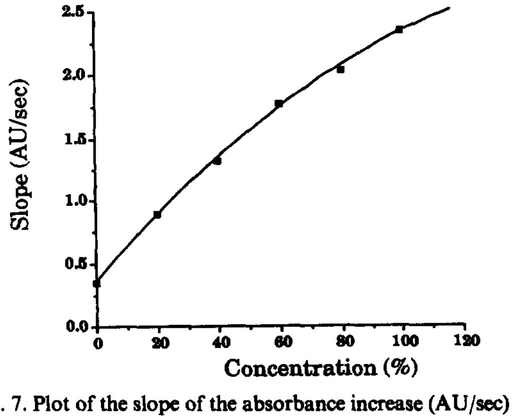

Fig. 7. Plot of the slope of the absorbance increase (AU/sec) in Fig. 6, between 0 and 0.3 AU, with respect to the starch concentration in percent (%).

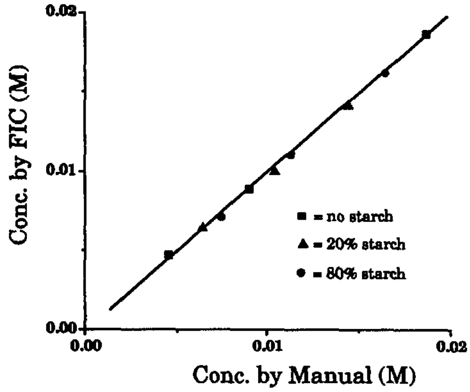

Fig. 8. Comparison of the concentration of sodium metabisulfite determined by manual titration (manual) and by the use of the FIC technique (FIC) for samples containing various amounts of starch from corn syrup. ■ = no starch, ▲ = 20% starch, ● = 80% starch.

Simultaneous metabisulfite and starch determination

Samples containing both starch and sodium metabisulfite were analyzed. The time at which the initial formation of the iodine/starch product was observed was used as the endpoint of the sodium metabisulfite titration, and the slope of the absorbance profile after the endpoint was used to determine the starch concentration. Since the time at which the titration endpoint occurred varied with each sample, it was extremely difficult, with the control program used, to generate a specific amount of iodine after the endpoint. Therefore, it was much more convenient to use the slope, instead of the absorbance level after reaction with a specific amount of iodine, to perform the starch determination. Figure 8 shows the metabisulfite results by manual titration and the CFIT for a selected number of the samples, indicating the starch levels present. As seen, the response is not affected by the starch concentration.

Figure 6 shows the absorbance profiles of samples having the same sodium metabisulfite concentration with differing starch concentrations. Note that the titration endpoint occurred at the same time while the slopes of the absorbance increase were different for each. Plots of the absorbance increase slope, between 0 and 0.30 AU, with respect to the starch concentration at different levels of sodium metabisulfite are seen in Fig. 9. The system response does not follow a specific trend with metabisulfite concentration, and the starch response is considered to be unaffected by the metabisulfite concentration. Differences are due to physical variations in the system between runs.

The absorbance profile of samples with a constant starch concentration with varying levels of sodium metabisulfite are shown in Fig. 10. In this case, note that the slope of each absorbance increase is the same, while the titration endpoint is different. These analyses indicated that the response of each of the species was not affected by the concentration of the other, allowing for two independent analyses to be performed in a single assay.

Multiple analyses (≥3) were performed for all samples analyzed. For the analysis of starch, in the absence of metabisulfite, by the addition of a specific amount of iodine, a relative standard deviation of <1.5% was obtained for corn syrup samples containing >20% starch concentration and <3.5% for samples containing <20% starch. For the analysis of the starch using the slope of the absorbance increase, a relative standard deviation of <1.2% was obtained for all corn syrup samples regardless of the starch or metabisulfite concentration. The analysis of the data from the determination of sodium metabisulfite produced a relative standard deviation of <1.4% for all samples, irrespective of the starch concentration.

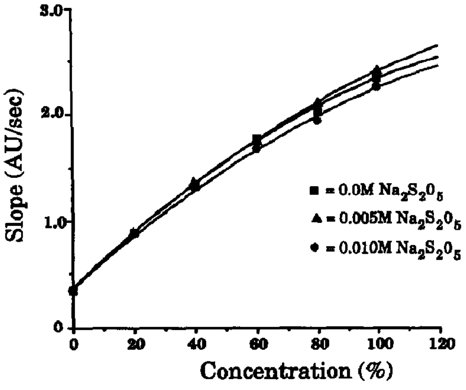

Fig. 9. Analysis of the starch in corn syrup samples with various amounts of sodium metabisulfite. The slope of the absorbance increase between 0 and 0.3 AU is used. ■ = no $Na_2S_2O_5$, ▲ = 0.005*M* $Na_2S_2O_5$, ● = 0.010*M* $Na_2S_2O_5$.

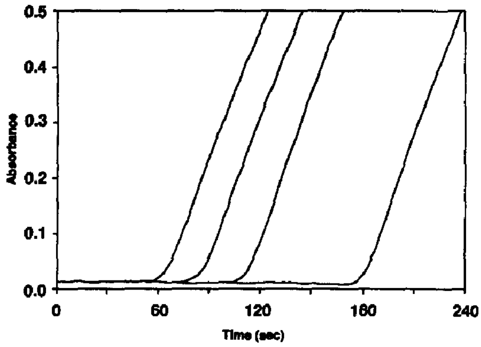

Fig. 10. Overlay of the absorbance profiles of the analysis of four samples having a relative starch concentration of 55% and sodium metabisulfite concentrations of 0.0020*M*, 0.0033*M*, 0.0047*M*, and 0.0083*M*. Note that the slope of the absorbance increase is constant while the titration endpoint is different for each sample. (The entire profile is not shown, with the portion in which the chamber is flushed having been omitted.)

CONCLUSIONS

This investigation revealed advantages and disadvantages of flow injection coulometry for starch assays. The iodine used in the assay was generated electrochemically, which was an advantage when compared with the conventional preparation of an iodine solution. The 0.20*M* KI and the 0.20*M* KI in pH 8 phosphate buffer solutions did not have to be at exactly pH 8 or 0.20*M* KI. The amount of iodine reacted with the sample was dependent only upon the intensity of the generating current and the time which this current was applied.

Due to their high viscosity and their tendency, even at elevated temperatures, to adhere to surfaces it was not possible to inject undiluted samples directly into the system. Thus the use of the FIC system did not fully avoid manual sample handling. Through the electrochemical generation of reagent and automated solution handling within the FIC system, the amounts of reagent and sample reacted in each analysis were more reproducible than when performing the test manually, and the amounts of sample and reagent used per determination were substantially reduced.

The time required for a single analysis was 150 sec, and although this time could be reduced with the use of a peristaltic pump in place of the syringe pump, which required re-filling during the analysis, it would still be longer than that required for the current manual method when all solutions are pre-prepared. The automated nature of the present method, however, caused the sequence of events during the test to occur at the same time for each analysis, removing variance in the result due to any kinetic effects. When the same sample-to-reagent ratio as that in the FIC analysis was used to perform the test manually, the correlation was very good, indicating that the FIC method is an adequate substitute for the manual method of the starch determination and was found to be statistically equivalent.

The advantages listed for starch analysis also apply for sodium metabisulfite determination. The only drawback of this assay was the necessity to increase the analysis time to 300 sec, which was required by the nature of the control software to insure adequate titration time for the entire concentration range of the metabisulfite samples. The CFIT method was also found to be statistically equivalent to the manual sodium metabisulfite titration.

Analysis by generation of a specific amount of reagent was demonstrated. The ability to generate a reagent at a desired rate and observe a reaction in progress allows for departure from conventional assays where a reaction between sample and reagent must go to completion in order to perform the analysis. The analysis of starch can be viewed as an example of the ability to perform an analysis in which an analyte reacts with an electrochemically generated reagent to form a readily detectable specie.

Simultaneous determination of starch and sodium metabisulfite by the CFIT method was performed, illustrating the advantages of combining titration with another measurement.

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