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Determination of Saccharin in Watts Nickel Plating Solutions by First Derivative Ultraviolet Spectrometry

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An accurate method for determining small concentrations of saccharin in the presence of plating salts is discussed. First-derivative ultraviolet spectrometry is employed to enhance, separate, and quantify saccharin's spectral features from those of the plating solution. A detection limit of 0.1 ppm has been obtained by simple electronic differentiation of the absorbance spectrum. The effects of a sample's absorbance background, temperature, and pH have been studied and are also discussed. The data suggest that the saccharate anion is the actual chemical species which is determined and that this method could easily be applied to determine sodium saccharin as well.

Saccharin is one of many organic compounds which are often added to Watts nickel plating solutions to improve the ductility, brightness, and uniformity of the plating. The analytical procedures for determining saccharin cited in the literature, however, were developed for food and beverage samples (*1–4*). Most of these methods cannot be successfully applied to determining saccharin in electroplating solutions, where plating salt concentrations typically exceed 1.0 M and saccharin concentrations can be as low as 1.0×10^{-6} M. In addition, many of the above mentioned methods are indirect and, as a minimum, require that the saccharin be extracted from the sample. The analytical procedure for saccharin discussed in this paper is a direct method. Although it was developed for determining saccharin in plating solutions, upon examination it is also applicable to food and beverage determinations.

The technique of derivative spectrometry, recently reviewed in this journal by O'Haver (*5*), has, among its advantages, enhancement of minor spectral features found on a broad background and quantitive separation of overlapping absorption peaks. The enhancement and separation of saccharin's spectral features by first-derivative ultraviolet spectrometry permit the direct determination of saccharin in plating solutions, foods, and beverages. The derivative spectra presented within this text were obtained by electronic differentiation of the analog absorbance signal of the spectrophotometer with respect to time. Although this is not necessarily the true mathematic derivative, they are proportional, as can be seen by the following equation.

$$\frac{dA}{d\lambda} \propto \frac{dA/dt}{d\lambda/dt} \qquad (1)$$

Since the magnitude of this derivative signal is a function of the scan speed of the spectrophotometer, the scan speed is kept constant throughout the quantitative analyses. Electronic differentiation has proved to be sufficiently sensitive to detect 0.1 ppm of saccharin in aqueous solution with a precision of ±0.05 ppm.

EXPERIMENTAL

Apparatus. Ultraviolet (UV) and visible light (VIS) spectra were taken with a Beckman ACTA MVII spectrophotometer. Derivative spectra were obtained by use of the above with a Beckman first-derivative absorbance module. Temperature adjustments were carried out in the Beckman variable temperature sample compartment for use with the above instrument. Quartz UV cells of 1.0-cm pathlength were supplied by Beckman. pH measurements were made on a pH/mV electrometer, model 265, supplied by Instrumentation Lab., Inc.

Chemicals. Saccharin (*o*-benzoic sulfimide) was supplied by Eastman Kodak Company; nickel sulfate and nickel chloride were products of J. T. Baker Chemical Company; boric acid was obtained from Rexall Drug Company, and the buffers utilized were supplied by Fisher Scientific Company.

Reagents. Sodium hydroxide was purchased from J. T. Baker Chemical Company, and hydrochloric acid was purchased from a Mallinckrodt Chemical Works distributor. All water used was deionized tap water of greater than 1.0-mΩ/cm resistivity.

Preparation of Calibration Curve. A master solution of 1.0 mg/L aqueous saccharin is prepared, with successive dilutions into volumetric flasks forming concentrations of 0.1, 0.2, 0.4, 0.6, and 0.8 mg/L solutions. A spectrum is then taken of each sample with the derivative module incorporated into the spectrophotometer. The spectral region scanned is from 270 to 210 nanometers (nm). A plot of the magnitude of the derivative peak at 236 nm vs. concentration is then established.

Plating Solutions. A plot of the derivative peak height vs. concentration, similar to that established for aqueous saccharin, was obtained in a corresponding manner for saccharin in Watts nickel plating baths. The Watts nickel plating bath consists of 1.2 mol/L nickel sulfate, 0.1 mol/L nickel chloride, and 0.3 mol/L orthoboric acid. Exact concentrations of these constituents are not crucial.

Temperature Dependence. An aqueous solution containing 1.8 mg/L of saccharin was placed in the temperature-controlled sample compartment of the spectrophotometer. Derivative spectra were taken at various temperatures within the range of 10 → 80 °C.

Background Effects. An aqueous solution of 2.0 mg/L saccharin was prepared. Another stock solution of 4% by volume of acetone in water was prepared. Aqueous solutions of 0.4% acetone and saccharin concentrations of 0.2, 0.4, 0.6, and 0.8 mg/L were prepared from the stock solutions. The magnitude of the derivative signal at 236 nm was measured for each sample.

pH Dependence. A stock aqueous saccharin solution containing 18.4 mg/L was prepared. Twelve tenfold dilutions were made, each with a different arbitrary amount of HCl or NaOH to obtain a full range over the pH. Additional dilutions were made using buffers of pH values 1, 2, 6, 7, 8, and 9 to alter the pH. The particular buffers were chosen for their lack of interfering absorbance in the UV spectrum. The samples were then tested for pH and inserted into the spectrophotometer. The magnitude of the derivative signal at 236 nm was measured for each sample to assess the effects of pH.

RESULTS AND DISCUSSION

Saccharin in aqueous solution exhibits two discrete absorption shoulders at about 228 and 236 nm and a broad absorption peak near 270 nm. Although the molar absorptivities of these wavelengths are sufficiently large and have been employed for quantitative analysis (*1*), the detectability and differentiation of these maxima by conventional absorbance spectrometry in the presence of a highly absorbing background is very poor. This is illustrated in Figure 1. The

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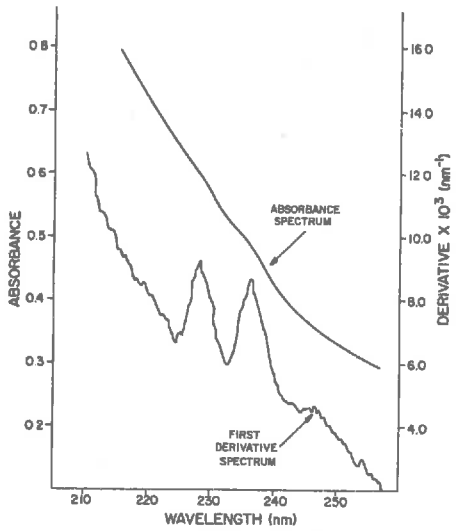

Figure 1. Absorbance and first-derivative spectra of a tenfold dilution of a Watts nickel plating solution containing 12.0 mg/L saccharin

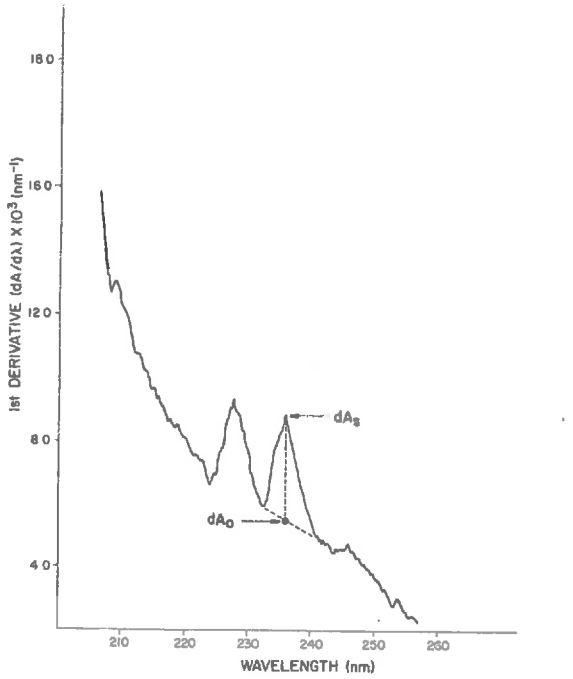

Figure 2. Graphic method of measuring the first-derivative intensity, $dA_s - dA_0$, attributable to saccharin.

absorbance background of this sample is demonstrated by the fact that if it were run undiluted at a 1.0-cm pathlength, the two inflections at 236 and 228 nm attributable to saccharin would lie between 4 and 6 absorbance units. The characteristic of derivative spectrometry enhancing fine spectral features is also shown in Figure 1 in the first-derivative spectrum of the same sample. Although the presence of saccharin is discernible from the inflections in the absorbance spectrum, quantitative determination is not possible. The first-derivative spectrum, however, quantitatively demonstrates the presence of saccharin in a way similar to standard colorimetric methods. Since the first derivative of an inflection or shoulder results in a derivative peak proportional to the intensity of the inflection, saccharin can be quantified by the magnitude of the change in the first-derivative spectrum. As seen in Figure 2, the magnitude of the change in the derivative spectrum is measured graphically in a manner identical to that which one would apply to measure an absorbance peak. The derivative base line in the absence of saccharin is approximated graphically by drawing a straight line between the adjacent minima.

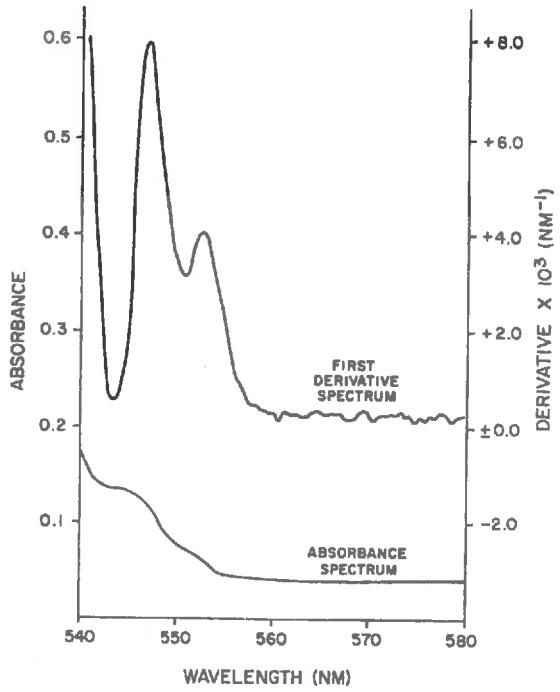

Figure 3. Absorbance and first-derivative spectra of a holmium oxide filter

The value of the base line, dA_0, at the wavelength of the derivative maximum, dA_s, is substracted from the derivative maximum. The resultant quantity, $dA_s - dA_0$, has the units of reciprocal nanometers and is proportional to the saccharin concentration. Either the 236-nm or the 228-nm maxima may be used for the quantitative determination of saccharin. The magnitude of the 236-nm maximum, however, is approximately 20% larger and is the one utilized for the saccharin determinations presented within this paper. Additionally, the ratio of the intensities of the two maxima could possibly be used for the qualitative determination of saccharin.

The derivative spectra obtained on the Beckman ACTA MVII are a result of electronic differentiation of the absorbance signal. Consequently, the magnitude of the derivative signal and, naturally, its associated noise are a function of the monochromator scan speed and response period of the recorder. For the Beckman ACTA MVII a scan speed of 1.0 nm/s and a recorder period of 4.0 produce derivative spectra for saccharin equivalent to those measured graphically. Consequently, the slope of our derivative calibration curve, 2.43×10^{-3} L/mg cm nm, should not be considered a precise value. As with any calibration curve, it should be regenerated for a different instrument or operating parameters.

A calibration check of the electronics which generate the derivative signal was routinely performed throughout this investigation. Using the same instrument parameters as those employed for the saccharin analyses, the first derivative spectrum of a holmium oxide filter was scanned from 570 to 540 nm. Figure 3 shows both the absorbance and first-derivative spectra for the holmium oxide filter over this wavelength range. The shoulder at 547 nm in the absorbance spectrum of holmium oxide is similar to the spectral features exhibited by saccharin. Operating parameters identical to those employed for determining saccharin yield an average derivative signal for the 547 nm shoulder of 7.87×10^{-3} nm^{-1} and an RSD of ±1.7% for a sample field of twelve. By comparison, the repetitive determination of a 4.0 mg/L aqueous solution of saccharin gave a RSD of ±1.2% for 12 samplings. These data are listed in Table I and represent a precision of ±0.05 mg/L for determining saccharin by this first-derivative method. The fact that the holmium oxide filter is a solid and

Table I. Reproducibility of the Derivative Method

sample no.	holmium oxide calibration standard, $nm^{-1} \times 10^{-3}$ @ 547 nm	4.0 mg/L saccharin: derivative intensity, $nm^{-1} \times 10^{-3}$ @ 236 nm	4.0 mg/L saccharin: saccharin measured, mg/L
1	7.88	9.60	3.95
2	7.82	9.92	4.08
3	7.56	9.82	4.04
4	8.06	9.60	3.95
5	7.88	9.84	4.05
6	7.80	9.56	3.93
7	7.82	9.64	3.97
8	7.90	9.76	4.02
9	8.06	9.70	3.99
10	7.88	9.62	3.96
11	7.82	9.58	3.94
12	8.00	9.62	3.96
mean	7.87	9.69	3.99
± RSD, %	1.7	1.2	1.2

Table II. Actual and Measured Aqueous Saccharin Concentrations in the Presence of 0.4 vol % Acetone

saccharin concentration: actual	saccharin concentration: measured	% error
0.2	0.06	−70
0.4	0.22	−44
0.6	0.31	−48
0.8	0.54	−33
2.0	1.73	−24
5.4	5.0	−7.4
10.7	10.3	−3.7

relatively inert affords a rapid and reproducible means for checking instrument calibration.

Background Effects. In the instance of Watts nickel plating solutions, the UV spectrum is highly absorptive but does not contain any discrete absorption maxima. As this may not always be the case for whhich one might desire to apply the method, the effect of a neighboring absorption maxima on the accuracy of the saccharin determination was evaluated. Acetone was selected as an interfering substance because it exhibits a broad absorption maximum at about 264 nm in aqueous solution. The presence of acetone was determined to have an effect on the accuracy of the method. A 2.0 mg/L sample of saccharin in the presence of 0.1 vol % acetone analyzed as 1.95 mg/L. In the presence of 0.4 vol % acetone, it analyzed as 1.73 mg/L.

In addition to testing the effect a varying background has on the computed value of saccharin, the error a fixed background induces on varying saccharin concentrations was also evaluated. Table II lists actual saccharin concentrations, the measured values using the standard calibration curve, and the corresponding percent error for determining saccharin in the presence of 0.4 vol % acetone. The table illustrates that as the concentration of saccharin decreases over a fixed background, the error increases. Obviously, if one wishes to determine minute saccharin concentrations in the presence of an interfering background, an amended calibration curve must be generated.

Temperature Dependence. An aqueous solution of 1.8 mg/L saccharin was contained in a glass stoppered cuvette and placed in a temperature controlled sample compartment. The magnitude of the 236-nm maximum of the derivative spectrum was recorded at various temperatures. The slope of the straight line obtained by linear regression analysis of the data corresponds to a decrease in the derivative maximum of approximately 2.0×10^{-5} nm^{-1} per degree centigrade. Regarding the error which a particular sample's temperature may introduce into a determination, the effect corresponds to approximately 0.5% error per degree centigrade.

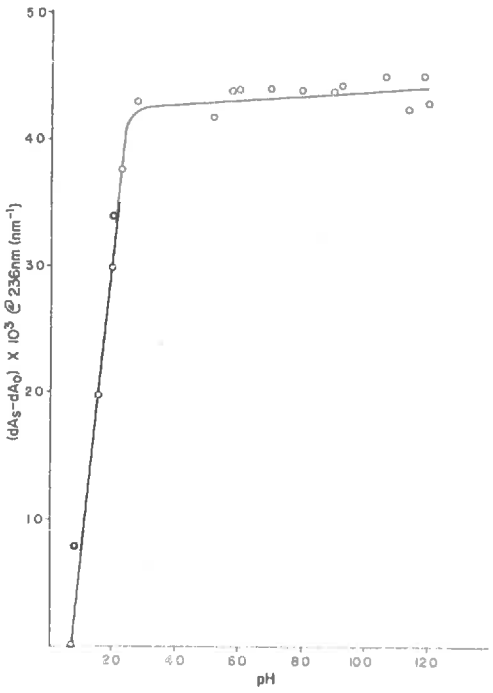

Figure 4. Magnitude of the first derivative at 236 nm of aqueous saccharin, 1.8 mg/L, as a function of pH

pH Effects. Since the working pH of plating solutions can vary considerably, the effect pH has on the determination of saccharin by derivative spectrometry was also investigated. Figure 4 shows the magnitude of the derivative maximum at 236 nm as a function of the pH of a solution containing 1.8 mg/L of saccharin. Clearly, the derivative technique for determining saccharin should not be applied to samples whose pH is less than 3. In general, it is advantageous to dilute the sample with a buffer solution which does not absorb in the UV spectrum. This was not possible for our particular plating solution because other proprietary additives were found to precipitate when the buffer was added to the sample. The Watts nickel plating solution, which was of particular interest to us in this investigation, typically exhibits a pH of ~3.0. Since there is a possibility of significant error of measurement at this pH, we have limited the application of the method to tenfold dilutions of the plating solution. Understandably, this raises the pH of the sample to ~4.0 where minor variations in pH will not significantly affect the derivative signal. Fortunately, the concentration of saccharin in the plating solution is sufficiently large to afford the tenfold dilution and remain well above the detection limit of 0.1 mg/L.

In light of the facts that a solid sample of saccharin dispersed in potassium bromide does not exhibit either the 227 nm or the 236 nm absorption shoulders and that the effect of pH on the intensity of the shoulders is reversible, we believe that the absorptions at 227 nm and 236 nm are attributable to resonance stabilization of the deprotonated saccharin anion. This is further supported by the fact that the point on Figure 4 where the effect of hydronium ion concentration halves the magnitude of the derivative signal corresponds to a pH of approximately 1.6. This is in close agreement to the reported pK_a value for saccharin of 1.60 (6).

Food and Beverage Samples. Cursory studies show that food and beverage samples which contain sodium saccharin exhibit similar spectral features and that this method can easily be applied. These data are shown in Table III. For those products which listed sodium saccharin as the sweetener,

Table III. Saccharin in Food and Beverage Samples

sample	reported value	sachharin concentration: calculated	sachharin concentration: measured
Tab	9.2 mg/fl. oz.	310 mg/L	350 mg/L[a]
Pepsi Light	8.87 mg/fl. oz.	303 mg/L	305 mg/L[a]
Fresca	6.7 mg/fl. oz.	230 mg/L	275 mg/L[a]
D-Zerta Lemon Gelatin	1.5%[b]	1.3%	1.2%[c]
Sweet N' Low	4.0%[d]	3.6%	2.8%[c]

[a] Analyzed directly as a 1/100 dilution of the beverage. [b] Dry sample. Reported as 1.5% sodium saccharin. [c] Analyzed directly as a 100 mg/L solution of the sample. [d] Dry sample. Reported as soluble saccharin. Calculated value assumes it to be sodium saccharin.

the proportional concentration of saccharin was calculated. Since it is not the intent of this work to report on the determination of saccharin in foods and beverages, the data have been presented solely to demonstrate a potential area of application for the method. Although there appears to be a significant error in the determination for some samples, it is questionable whether the error is in the method or in the reported values. Samples of artificially sweetened puddings and cocoa were attempted but interfering absorptions and turbidity prohibited the direct determination of saccharin by this method.

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Continuum Spectrum Source Excited Coherent Forward Scattering Spectrometry for Detection of Elements

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An element detection method utilizing coherent forward scattering of resonance radiation from atoms irradiated by continuum spectrum sources is described. Analytical curves for nine elements, As, Cd, Cr, Cu, Fe, Mn, Tl, V, and Zn, are measured with a xenon lamp. Detection limits and dynamic ranges are compared with those using the atomic absorption method. Although the detection limits are larger than with the atomic absorption method, except for Tl, and depend on the spectral radiance of the xenon lamp, the quantitatively analyzable least amounts are of the same order. The dynamic ranges are limited on the upper side by the saturation effect; they are 10^2 for Tl and V and between 10 and 100 for the other elements.

A detection method for element analysis based on the coherent forward scattering (CFS) of resonance radiation by atomic vapor (*1*) has recently been proposed by T. Hadeishi (*2*, *3*).

In CFS, changes in the polarization state caused by the magnetooptical effects, the Faraday effect, or the Voigt effect are detected. The intensity of the signal is proportional to the square of the number of scattering atoms due to the coherence of the light scattered forward by different atoms (*4*). This quadratic dependence is the main point of difference from the usual methods. High sensitivity is expected from this feature.

We previously reported experiments on CFS (*5*, *6*), in which the Voigt effect was used to detect signals. High sensitivity was confirmed when a resonance line spectrum source was used.

In atomic absorption spectrometry (AAS), narrow spectral width resonance line sources, such as hollow cathode lamps, have been used as exciting light sources. In AAS, the relative decrease in light intensity due to light absorption by the sample atomic vapor is taken as the signal.

As shown in Figure 1a, the spectral resolving power of the dispersive system used in the conventional AAS apparatus is quite wide compared with the absorption line width of the atomic vapor. Light irrelevant to atomic absorption but within the instrumental width in the hatched area in Figure 1a can also transmit to the detector, so line spectrum sources narrower than the absorption width of the atomic vapor, such as hollow cathode lamps, are needed to maintain high sensitivity in AAS.

In CFS, scattering occurs predominantly in the resonance condition. As a result, signals are composed only of the resonance lines of sample atoms and appear against a dark background as illustrated in Figure 1b. Owing to the application of a magnetic field, the pressure broadened scattering profile of the atomic vapor is further broadened by the Zeeman effect. Therefore, in contrast with AAS, a continuum spectrum source can be used and may be better suited for CFS.

The availability of a continuum spectrum source has very important practical meanings. Measurements of various kinds of elements can be done with a single lamp. Qualitative analysis is also possible if wavelength scanning of the dispersive system is done. In this case, as mentioned above, only resonance lines appear in the signals, and identification of the lines is easy. In addition, simultaneous multielement analysis can be done in conjunction with a polychromator. In CFS, the population of the ground state atoms is measured, but in atomic emission spectrometry (AES), the population of the

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