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COLORIMETRIC DETERMINATION OF LOW PH WITH MALACHITE GREEN

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SUMMARY

A spectrophotometric method was developed for determination of concentration-based pH values from 0 to 2 with malachite green indicator. A quadratic model equation was based on the ratio of the absorbances of the peak at 618 nm and the isosbestic point at 518 nm. Normalization to the isosbestic point was used to stabilize the response because the color faded; the useful time interval was within 5 minutes after indicator addition. Model and verification sets agreed within ± 0.02 pH units between pH 0.3 and 1.8. This excellent precision makes the colorimetric method useful for acid determinations with a relative precision of $>\pm 5\%$. The presence of salts at a salt/acid equivalent ratio >0.1 caused a low pH bias.

INTRODUCTION

Use of color indicators provides a convenient alternative to potentiometric pH measurements for determination of acidity. Modern instrumentation such as diode array spectrophotometry and computerized data reduction has converted this classical technique¹ into one that is practical for field and online applications. Color indicators offer the option of either simple visual estimation or quantitative determi-

nation by spectrophotometry, with fiber optics or flow injection interfaces. Mathematical fitting or modeling of the spectral data can provide instant output values. In this work, preparation of models with standard solutions of known hydrogen ion concentrations makes the measured pH one that is based on hydrogen ion concentrations (i.e., $-\log[H^+]$), rather than on hydrogen ion activities.

Although many pH indicators are available,² only a few have suitable spectra for analytical applications, particularly at the extremes of the pH range. Earlier work described azoviolet indicator for colorimetric pH determinations of solutions such as the concentrated waste solutions with pH >11 at the Savannah River Site.³ The present work describes a similar application of malachite green to solutions with pH <2 for other process streams. Normalization of the data to the isobestic point and development of a quadratic model provides a sensitive method that overcomes the limitations of the indicator due to color fading.

EXPERIMENTAL

The calibration/model was developed by making absorbance measurements with standard solutions of 0.01M to 1M HNO₃. These solutions were prepared from a 1M stock solution standardized against the primary standard tris(hydroxymethyl)aminomethane.⁴ The dilutions were confirmed by nitrate determinations with ion chromatography. Spectra for the acid and base forms of the indicator were established with 2M HNO₃ and 0.1M KNO₃, respectively. Samples were prepared and analyzed by the same

procedure as the standards. A reference spectrum of the test solution without indicator was used for each measurement.

The malachite green solution was 0.1 w/v% of Malachite Green Hydrochloride $[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_5):\text{C}_6\text{H}_4:\text{N}(\text{CH}_3)_2\text{Cl}]$; CAS No. 569-64-2. Baker P451.03 or equivalent] dissolved in water. The solution was filtered. The pH of the indicator solution was about 3. The usual pH adjustment to midrange (about pH 1) was not made because the indicator is unstable at the lower pH, and the acid contribution of the indicator to the test system is negligible.

Procedure

- (1) Pipet 4 mL of solution into a vial.
- (2) Add 50 μL of malachite green solution.
- (3) Transfer solution to a 1-cm cuvette.
- (4) Between 0.25 and 5 minutes after addition of the malachite green, measure absorbance of solution from 400 to 700 nm (618 nm and 518 nm are the specific wavelengths of interest) with a Hewlett Packard Diode Array Spectrophotometer, or equivalent.
- (5) Use the collected data to create a model or to determine pH from the established model, as described below.

RESULTS AND DISCUSSION

Malachite Green Indicator

Figure 1 shows malachite green spectra from pH 0.01 to 2.1. The base form has a strong sharp peak at 618 nm (blue-green), which was used for

the analysis. The acid form has a broader, less suitable, peak in the 425 to 450 nm (yellow) range. The isosbestic point occurs at 518 nm.

Figure 1

Kolthoff reported that triphenylmethane dyes, such as malachite green, were considered to be of no practical value as pH indicators because of instability and salt errors.² Normalization with the isosbestic point absorbance overcame the instability problem; salt error limitations are discussed below. Anionic halide complexes with certain metals (Cd, Co, Ta, Ga, In, Rh, Sn, Zn) are reported to bond with malachite green into extractable ion pairs,⁵ but this possible interference was not investigated because these metals were not significant in our process streams.

Collection and Interpretation of Data

Spectra were collected at intervals of approximately 0.25, 2.5, and 5 minutes after the indicator was added. Spectra at the extremes of the indicator pH range were similarly obtained with 2M HNO₃ and 0.1M KNO₃. Ratios of absorbances at the peak (618 nm) and at the isosbestic point (518 nm) were used for modelling and for pH determinations from the model.

The color of the malachite green faded with time, particularly in more acidic solutions. Normalization to the isosbestic absorbance provided a parameter that was independent of measurement time for the five minute interval after the indicator was added. Figure 2 shows average

values and % relative standard deviations (RSD) for the normalized absorbances taken 0.25, 2.5, and 5 minutes after addition of indicator. %RSD values were <1% except at the lowest pH (0.009), where the %RSD rose to 3.5%. The variables DX_n , DA_n , and DB_n are the ratios of the peak to isosbestic absorbances for the unknown, the acid form and the base form, respectively.

Figure 2

Normalization to the isosbestic point also made the determination nearly independent of indicator concentration. Table 1.A shows DA_n and DB_n , over a three-fold range of indicator concentrations. The peak absorbance at 618 nm for DB_n with 50 μ L of indicator was >3, too high for accurate response.

Table 1

Development of Model

The relationships for fitting single peak data were similar to those used earlier.^{1,3} $DADB_n$ is defined in Equation (1a) in terms of α , the fraction of the indicator in the base form, and in equation (1b) in terms of (DB_n) , (DA_n) , and (DX_n) .

$$DADB_n = \alpha / (1 - \alpha) \quad (1a)$$

$$= (DX_n - DA_n) / (DB_n - DX_n) \quad (1b)$$

The model was developed with a set of 18 nitric acid standards and was verified with measurements of a newly prepared set of these 18 standards. Three sets of data, collected approximately 0.25, 2.5, and 5 minutes after the indicator was added, were averaged for the model. DA_n and DB_n values for the model-building (calibration) set and for the verification set were the average of six experimental values (two samples measured at three different times) for that set. Average DA_n and DB_n and their pooled standard deviations are included in Table 1.B.

The model equation, which had an R squared value of 0.999465, was:

$$pH = 1.298192 + 0.815108 (\log DADB_n) + 0.069844 (\log DADB_n)^2 \quad (2)$$

The good agreement of the model with the test set is shown in Figure 3. Between pH 0 and 1.8, differences between calculated and known values were <0.02 pH unit. The reason for the trend in the data, with a positive bias at pH <1 and a negative bias at pH >1, is not known.

Figure 3

Salt Error

The salt error was investigated with solutions that contained hydrolyzable ions or simple salts. In one set of experiments the solutions were standard 0.1M nitric acid containing 0.1M nitrates of aluminum, uranium, iron, thorium, or chromium, cations of interest in our process

streams. Limits of the salt effect were investigated with the aluminum-nitric acid system with progressively less aluminum, down to 0.0125M aluminum nitrate. The free acid content of these solutions was determined by standard addition in the presence of KSCN^6 or by titration in the presence of KF. Solutions of 0.1N nitric acid or hydrochloric acid solutions spiked with their respective sodium salts were also analyzed.

The spectra of the solutions with hydrolyzable ions, Figure 3, showed that, with the exception of iron, the presence of the metals did not affect the shape of the spectra. The results of these studies, Figure 4, demonstrated that the salt error was related to the number of equivalents of salt present. Equivalent amounts of salt and acid caused a low bias of about 0.06 pH units. To achieve a precision of ± 0.02 pH units the salt/acid equivalent ratio must be < 0.1 .

Figure 4 and Figure 5

Application to Determination of Acid Concentrations

The model was developed for pH defined in terms of hydrogen ion concentration, not for hydrogen ion activity. The excellent precision of ± 0.02 pH units suggested that this colorimetric method might be useful for determination of acid concentrations in systems where a relative precision of $> \pm 5\%$ is adequate.

Table 2 shows application of the model to determination of the acidity of process solutions that contained up to 0.1M $\text{UO}_2(\text{NO}_3)_2$. Confirming analyses were performed by titration with NaOH in KF medium and/or by standard additions in KSCN medium.⁶ Both these methods determine hydrogen ion concentration. Within the range of the model, the colorimetric method gave comparable results. These determinations also demonstrated that in this low-salt system the method could be extended to more concentrated acid solutions by making dilutions as large as ten-fold.

Table 2

Comments on Implementation

Concentration-based pH determinations are useful for many applications. Sometimes the difference between hydrogen ion activity and acid concentration can be compensated. At the higher pH range of the method, samples may be sufficiently dilute that activity coefficients approach unity. For samples with similar ionic strengths, indicator and electrode pH values will be proportional to one another throughout the range.

The model equation in this paper is intended to serve as a guide for application and performance of the method. For actual implementation, a model for the system of interest should be developed. A model that includes the full spectrum can be developed by partial least squares or other techniques, as was done in the previous work with high pH systems

and azoviolet indicator.³ While the full-spectrum model may or may not improve the precision, it most certainly would be useful in flagging inappropriate samples through goodness-of-fit calculations.

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Table 1. Summary of DA_n and DB_n values

μ L Malachite Green per 2 mL sample	DA_n		DB_n	
	Average	Standard deviation	Average	Standard deviation
<i>A. Indicator Volume Study</i>				
10	0.094939	0.007943	14.66812	0.048614
20	0.095574	0.004473	14.64927	0.070567
25	0.09601	0.001847	14.61751	0.042939
30	0.095344	0.000521	14.4231	0.040720
<i>B. Model Development</i>				
MODEL: 25	0.094433	0.001398*	14.83714	0.058613*
VERIFY: 25	0.09166	0.008190*	14.89621	0.079001*

*Pooled Standard Deviations of two sets of timed measurements

Table 2. Determination of Acid Concentrations

Solution#	-----Acid Concentration in Moles per Liter (M)-----		
	Titration in KF	Standard Addition in KSCN	Colorimetric Method (Dilution)
1	0.004	0.066	0.097 (none)
1			0.083 (1:10)
2	nd*	0.55	0.58 (none)
3	nd	3.08	2.51 (1:10)
4	3.45	3.58	3.59 (1:10)
5	5.45	5.42	5.59 (1:10)
6	nd	0.41	0.41 (none)
6			0.43 (1:10)
7	nd	2.19	1.94 (1:10)
8	nd	3.96	3.91 (1:10)
9	nd	5.11	4.88 (1:10)
10	nd	5.51	5.38 (1:10)
11	nd	2.71	2.76 (1:10)
12	nd	0.006	0.008 (none)
13	nd	0.62	0.62 (1:10)
14	nd	2.21	1.91 (1:10)
15	nd	5.11	4.92 (1:10)

*nd=not determined

List of Figures

Fig. 1. Effect of pH on the absorption spectrum of malachite green.

Spectra were taken 0.25 minute after addition of indicator. The concentration of malachite green is $3.4 \times 10^{-5}M$.

Fig. 2. Average values of DX_n , the ratio of absorbances at 618 nm and 518 nm, for different times. The ratios were averaged for measurements 0.25, 2.5, and 5 minutes after indicator addition. $\square$ = average DX_n ; $\circ$ = % relative standard deviation.

Fig. 3. Agreement of the model and the test set with different development times. Minutes after indicator addition: $\square$ = 0.25; Δ = 2.5; $\circ$ = 5.

Fig. 4. Effect of hydrolyzable salts on absorption spectrum of malachite green. Solutions were 0.1M HNO_3 + 0.1M metal nitrate. Spectra were taken 2.5 minutes after addition of indicator. Malachite green concentration is $3.4 \times 10^{-5}M$.

Fig. 5. Salt error in malachite green pH determination. $\diamond$ = 0.1M HNO_3 with pH 1.00; $\square$ = 0.1M HNO_3 + 0.1M nitrate salt of UO_2^{2+} , Ni^{2+} , Cr^{3+} , or Th^{4+} ; $\circ$ = 0.1M HNO_3 + 0.1M $Fe(NO_3)_3$; Δ = 0.1M HNO_3 + 0.1, 0.05, 0.025, and 0.0125M $Al(NO_3)_3$; $\times$ = 0.1M HNO_3 + 0.34M $NaNO_3$ or 0.1M HCl + 0.39M $NaCl$.

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