

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. V. INTERNAL INDICATORS SUITABLE FOR USE IN DIRECT TITRATIONS

BY G. FREDERICK SMITH AND H. H. BLISS¹

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Introduction

The present paper is the continuation of a series of studies dealing with the extended application of the use of bromates in volumetric analysis.² Undesirable features previously associated with the use of bromate in volumetric analysis have been the following: first, that the reduction of bromic acid may take either of two courses, reduction to bromide as in the oxidation of trivalent arsenic or antimony or to free bromine as in the oxidation of ferrous iron or chromic salts, oxalic and nitrous acids; second, that many of the possible applications of bromate in volumetric analysis involve the use of an excess of bromate followed by back titration requiring the undesirable use of an additional standard solution; third, suitable indicators have not been found for bromate oxidation reactions except in the case of the determination of arsenic and antimony, in which case methyl orange and indigo-sulfonic acid are employed which require undesirably high concentrations of hydrochloric acid at temperatures near the boiling point.

The first of these undesirable features has been eliminated by the use of the mercuric ion,² which brings about the reduction of bromate to bromide rather than to free bromine as in the cases already cited. The present paper has for its object the elimination of the second and third difficulties by the selection of a number of organic dyes suitable for use as indicators in bromate reactions. Back titrations following the use of an excess of bromate can be shown in various cases to be unnecessary through the use of these new indicators. Cold titrations at lower acid concentrations are possible. By selection of the indicator having the most desirable color transformation the interference of foreign colored ions is eliminated. It is to be observed that the application of the electrometric determination of the end-point would in many cases solve the problems. Visual end-point phenomena are more difficult to devise but are more practical in application.

In subsequent papers of this series, specific applications of the new indicators to individual determinations will be disclosed.

¹ A portion of the thesis presented by H. H. Bliss in partial fulfilment of the requirements for the Ph.D. degree in the Graduate School of the University of Illinois.

² Smith and co-workers, *THIS JOURNAL*, **45**, 1115, 1417, 1666 (1923); **46**, 1577 (1924).

Method Used in Selection of Dyes

In the familiar bromate titration of trivalent arsenic or antimony in hot concentrated hydrochloric acid solution using methyl orange as indicator, the end-point reaction consists in the liberation of bromine from the action of the first drop excess of bromate on the hot hydrochloric acid of the solution. Under these conditions the helianthin indicator is destroyed by halogenation and the end-point of the reaction is defined. It is, therefore, logical in the study of possible new dyes for similar bromate reactions to select from that group least "fast" in color when chlorinated. Such use was made of the "Colour Index."³

This method of attack was found to be satisfactory after it was learned that a "chlorine fastness" number of 5 indicated too great ease of halogenation and that the red and yellow colors seemed better adapted than colors of the remainder of the spectrum. Quite as certain selections were subsequently made from those dyes unclassified in chlorine fastness by the British Colour Index (wool and silk dyes), using other and more intuitive methods of selection. The list of dyes about to be described is only a small portion of those examined and is not supposed to be an exhaustive one. The selections made, however, are thought to cover a wide range of possible working conditions and to include desirable color changes. With a single exception the color change is from colored to colorless. This naturally follows from the nature of the reaction bringing about the end-point change. The dyes examined and found satisfactory are classified and identified in Table I.

In the data of Table I the first column is given for convenience in referring to the various dyes in the British Colour Index and in the second column the compact formula is given for convenience in referring to the compounds in Beilstein. In column three a common name is given which seems to be quite generally accepted. In most cases it seems best to refer to the indicators by their British Colour Index number. Column four indicates that the chemical classifications most abundantly represented are the mono-azo dyes and those of the triphenylmethane series. Column four indicates the variety of colors to be selected from the various classes of dyes and it is observed that the greatest variety in color is shown by the triphenylmethane class. Chief qualifying characteristics for the various indicators are given in column six. As indicated in column five all the indicators are sufficiently soluble in water and the color produced is not materially affected by the addition of hydrochloric acid. In some cases the depth of color is favorably affected by the addition of hydrochloric acid and in the other cases the color is unfavorably affected. In general those indicators are most desirable which produce the deepest color, since this is less masked by colored ions.

³ "Colour Index," The Society of Dyers and Colourists, 1924.

TABLE I
NEW INTERNAL OXIDATION INDICATORS FOR USE IN VOLUMETRIC BROMATE REACTIONS

British Colour Index number	Compact formula	Common name	Chemical Classification	Color in water and HCl solution	Remarks
21	$C_{13}H_{15}N_4Cl$	Chrysoidine R	Mono-azo	Yellow-red	Color bleached with reducing agents. Restored at end-point, then destroyed
27	$C_{16}H_{10}N_2O_7S_2Na_2$	Rainbow Orange G	Mono-azo	Orange-yellow	Suitable at moderate P_H and temp.
56	$C_{18}H_{13}N_3O_9S_2Na_2$	Chromotrope 6 B	Mono-azo	Violet red	Bright red to colorless, moderate P_H , low temperature
88	$C_{20}H_{12}N_2O_7S_2Na_2$	Bordeaux	Mono-azo	Red	Suitable at moderate P_H and low temperature
128	$C_{24}H_{14}N_3O_7ClS_3Na_2$	Diamine pink	Mono-azo	Red	Unsuited to low P_H and temp.
184	$C_{20}H_{11}N_2O_{10}S_3Na_3$	Amaranth	Mono-azo	Red	Suitable at moderate P_H and low temperature
185	$C_{20}H_{11}N_2O_{10}S_3Na_3$	Brilliant Ponceau 5R	Mono-azo	Scarlet red	Advantageously resists fading
246	$C_{22}H_{14}N_6O_9S_2Na_2$	Naphthol Blue-black	Di-azo	Blue	Quite satisfactory under ordinary conditions
375	$C_{32}H_{21}N_6O_7S_2Na_2$	Congo Corinth	Di-azo	Red-blue	Satisfactory for moderate P_H and boiling temperature
471	$C_{34}H_{26}N_5O_8S_2Na_2$	Bensoasurin 3 R	Di-azo	Violet	Faint color but satisfactory end-pt.
657	$C_{23}H_{25}N_2Cl$	Malachite green	Triphenylmethane	Green-reddish yellow	Satisfactory at moderate P_H and boiling temperature
667	$C_{37}H_{34}N_2O_6S_2ClNa$	Fast Acid Green B	Triphenylmethane	Blue-green	Satisfactory only at lower P_H
678	$C_{22}H_{24}N_3Cl$	Fuchsine	Triphenylmethane	Red-yellow	Very satisfactory. For lower temperature only
683	$C_3H_3N_3Cl$	Methyl violet	Triphenylmethane	Violet-brown	Very satisfactory at low P_H and boiling temperature
698	$C_{41}H_{44}N_3O_6S_2Na$	Acid violet	Triphenylmethane	Violet-green	Satisfactory at low P_H and higher temperature
793	$C_{19}H_{16}N_4O_3$	Phosphine	Acridine	Orange (fluorescent)	Satisfactory at low temp. and high P_H

A selection of indicators shown in Table I consists in a preference for the three numbers 185, 246 and 678. Indicator number 678 serves admirably for the oxidation of trivalent to pentavalent arsenic and antimony. For this determination it is much more satisfactory than the commonly employed methyl orange since titrations may be made at room temperature and at lower acidities as was done electrometrically by Zintl and Wattenberg.⁴

Further data of a comparative nature relating the speed of the reaction of the oxidation of the indicators under varying conditions of hydrogen-ion concentrations are given in Table II.

TABLE II
CONDITIONS PRODUCING END-POINT INDICATOR OXIDATIONS AT VARIOUS ACID CONCENTRATIONS

0.2 cc. of 0.2% solution in water per 100 cc. of solution of chosen PH = indicator concentration. Oxidizing agent, 0.05 cc. of *N*/10 solution of KBrO_3 or HgOHBrO_3 . Temperatures in degrees centigrade $\approx 5^\circ$. One star, slow reaction; two stars, moderately fast reaction; three stars, fast reaction

Indicator number	Equivalent normality of acid					
	0.1-0.15	0.25-0.3	0.5-0.6	0.9-1.0	1.5	3.0
21	..	80 ^{o*}	...	60 ^{o**}	45 ^{o***}	45 ^{o***}
27	..	90 ^{o**}	...	55 ^{o**}	65 ^{o***}	...
56	..	90 ^{o*}	...	65 ^{o**}	25 ^{o*}	...
88	..	80 ^{o**}	...	55 ^{o***}	25 ^{o**}	...
128	..	85 ^{o**}	85 ^{o**}	85 ^{o**}
184	..	75 ^{o*}	...	50 ^{o***}	25 ^{o**}	5 ^{o**}
185	..	80 ^{o**}	...	60 ^{o***}	25 ^{o**}	...
246	..	75 ^{o**}	...	45 ^{o**}	25 ^{o**}	...
375	..	100 ^{o**}	40 ^{o**}
471	100 ^{o**}	80 ^{o**}	55 ^{o**}
657	..	90 ^{o***}	85 ^{o**}	55 ^{o**}	...	25 ^{o**}
667	..	75 ^{o**}	...	60 ^{o**}	45 ^{o**}	...
678	25 ^{o**}	...	25 ^{o**}
683	..	75 ^{o***}	...	25 ^{o**}
698	..	80 ^{o**}	...	60 ^{o**}	60 ^{o**}	...
793	95 ^{o*}	80 ^{o**}	55 ^{o**}	50 ^{o**}

Interesting comparisons result upon examination of the data of Table II. All the indicators are rapidly destroyed in one normal acid by a concentration of 5×10^{-5} of bromate ion at a temperature ranging from 25-85°. Helianthin requires the same concentration of bromate ion at an acid concentration of three normal and a temperature not less than 60°.

It is not necessary to build up the required concentration of hydrogen ion using only hydrochloric acid. For example, it may be provided using sulfuric acid and enough hydrochloric acid added to increase the acid normality 0.1-0.2 unit just before the titration is begun or at a point slightly before the titration is complete, other conditions being equal. The same principle is applied in the following section of this paper and the results are similar to those reported in Table III.

⁴ Zintl and Wattenberg, *Ber.*, 56, 472 (1922).

Indicator Oxidation Conditions Using Sulfuric and Hydrobromic Acid Solutions.—It would be a distinct advantage in many cases to be able to adjust conditions for the indicator oxidation in the absence of hydrochloric acid. The use of hydrobromic acid would be undesirable if it were substituted for hydrochloric acid without limiting the necessary concentration to a small amount for two reasons. One, because of the increased cost, and the other as a result of the low solubility of mercuric bromide. The reduction of bromate to bromide as influenced by the presence of mercuric mercury is more satisfactory in the absence of hydrochloric acid, as proved in previous papers of this series,² since mercuric bromide is less dissociated in solution than mercuric chloride.

A study was therefore made of the oxidation of the various indicators as influenced by moderate concentrations of sulfuric acid and small additions of hydrobromic acid. The results are recorded in Table III.

TABLE III

CONDITIONS PRODUCING END-POINT INDICATOR OXIDATIONS AT VARIOUS CONCENTRATIONS OF SULFURIC AND HYDROBROMIC ACIDS

0.2 cc. of 0.2% solution of indicator per 100 cc. of solution at normality of acid given. Oxidizing agent, 0.05 cc. of *N*/10 solution of HgOHBrO_3 . Temperature in degrees centigrade $\pm 5^\circ$. One star, slow reaction; two stars, moderately fast reaction; three stars, fast reaction

Indicator number	H_2SO_4 normality	Hydrobromic acid concentration normal				Color change
		0.01	0.02	0.4	0.6	
683	1.0	68 ^{****}	43 ^{***}	25 [°]	45 ^{****}	Yellow to lavender
	1.5	66 ^{****}	63 ^{****}	50 ^{****}	30 ^{***}	
	2.0	58 ^{****}	48 ^{****}	40 ^{****}	25 ^{***}	
246	1.0	85 ^{****}	65 ^{****}	Greenish-blue to colorless
	1.5	78 ^{****}	
	2.0	67 ^{****}	59 ^{**}	
185	1.0	75 ^{****}	70 ^{****}	45 ^{**}	Red to colorless
	1.5	50 ^{****}	30 ^{**}	
	2.0	40 ^{****}	25 ^{**}	

All the indicators described were employed under the various conditions given using the oxidation of trivalent arsenic (and in some cases trivalent antimony) and quantitative results obtained within a maximum error of 0.2 mg. in the titration of 100 milligrams of the element determined. More complete quantitative data using the indicators studied will appear in subsequent papers of this series.

Summary

1. Description has been given of the selection of a group of sixteen organic dyes suitable for use as internal indicators for volumetric bromate reactions.

2. The dyes described have been tabulated by chemical classes and the mono-azo dyes and those of the triphenylmethane series shown to be most abundantly represented.

3. A study has been made of the limitations of temperature and acidity for which the various indicators are suitable.

4. Colors ranging from red through yellow, green, blue and violet are included. Interfering colored ions may therefore be counteracted by the selection of the proper indicator color from the group described.

5. All the indicators described are suitable for use in the quantitative estimation of trivalent arsenic with an accuracy ordinarily required from the usual volumetric determinations.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. XII. DIPOLE MOMENT DATA FOR (A) NAPHTHALENE AND CERTAIN OF ITS DERIVATIVES. (B) ALPHA AND BETA BENZENE HEXACHLORIDES

BY JOHN WARREN WILLIAMS AND JOHN M. FOGELBERG

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In the last years it has been amply demonstrated that the symmetrical hydrocarbons have zero dipole moments. Such a molecule will become electrically dissymmetrical and possess a finite dipole moment if one of its hydrogen atoms is replaced by another atom or group of atoms; furthermore the moment will vary with the nature of the substituent. When two of its hydrogen atoms are replaced by these substituents, it will not generally be possible to compute the electric moment of the resulting molecules from the assumption that it is the vector sum of individual moments characteristic of the substituent groups because (a) it is necessary to take into account the stereochemistry of the atoms forming the substituent group and (b) it is necessary to take into account mutual attractions or repulsions between the groups unless they be sufficiently removed from one another in the molecule. These factors, first suggested by one of us¹ as possibilities in order to explain the fact that hydroquinone diethyl ether possesses a finite dipole moment, have now been quite completely described.^{2,3} These studies, and now many others, have assisted materially in assigning configurations to benzene, methane and ethane, cyclohexane and certain of their derivatives.

In a few individual cases difficulties with the measurement and interpretation of the electric moment data have been encountered. Thus, iodine, symmetrical trinitrobenzene, and naphthalene have appeared to

¹ Williams, *Physik. Z.*, 29, 271 (1928).

² Höjendahl, "Dissertation," Copenhagen, 1928; *Physik. Z.*, 30, 391 (1929).

³ Williams, *THIS JOURNAL*, 50, 2350 (1928); *Z. physik. Chem.*, [A] 138, 75 (1928); Williams and Fogelberg, *THIS JOURNAL*, 52, 1356 (1930).