in synthetic telluride solution could not be accomplished because of the precipitation of rhodium telluride.

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References

Titrimetric Methods in the Determination of Acidity of Solids
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Different indicators having the same $pK_a$ give different end points when used for the determination of the acidity of an $SiO_2 \cdot Al_2O_3$ surface by n-butylamine titration, despite of control of parameters like time of equilibration, concentration of indicator, nature of solvent and mode of mixing.

A number of methods have been reported\textsuperscript{1-10} for the determination of acidity and acid strength distribution of solid catalysts to obtain correlations between catalytic activity and acidity. Titration in nonaqueous media for the determination of acidity of surfaces was proposed initially by Tamele\textsuperscript{7}, Walling\textsuperscript{8} and Johnson\textsuperscript{10} and later extended to the study of the distribution of acid strengths by Benesi\textsuperscript{10} using a complete set of available Hammett indicators. Though this method is based on some assumptions and has a number of limitations in its actual application, it is the most commonly used method due to its simplicity. The present study is an attempt to ascertain whether the acidity of a solid determined titrimetrically using various indicators having almost the same $pK_a$ is constant within the limits to be expected for the very small differences in $pK_a$.

$SiO_2 \cdot Al_2O_3$ (0.5 g) was taken in each of a few tubes. The solvent was added to each of them so that the solid was completely wetted. Definite amounts of the solution of indicator in the appropriate solvents were then added and the tubes shaken to achieve complete mixing. To each of these tubes a solution (0.1M) of purified n-butylamine solution in the appropriate solvent was added in increasing amounts so that the titrant added to each tube differed by 0.25 ml. The tubes were stoppered, shaken for 30 min and then left for equilibration. After 48 hr the visual end point was noted. The error in the detection was found to be within ±0.1 ml of the titrant (0.01 mmole). The various indicators used are listed in Table 1. Indicator solutions were prepared by adding 0.1 g of the solid indicator to 100 ml of the respective solvents, shaken thoroughly and then filtered. The volume of indicator solution added was so chosen as to suit the convenience in visual observation of the end point.

It has been reported\textsuperscript{11} that for the determination of acidity, the solid-liquid system should be left for equilibration for about 50 hr. It is found that other conditions being the same this time differs

<table>
<thead>
<tr>
<th>No.</th>
<th>Indicator*</th>
<th>$pK_a$</th>
<th>10 Butylamine titre (mmole/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$p$-Ethoxychrysoidin (pEC)</td>
<td>5·0</td>
<td>0·290</td>
</tr>
<tr>
<td>2</td>
<td>Methyl red (MR)</td>
<td>4·8</td>
<td>0·465</td>
</tr>
<tr>
<td>3</td>
<td>Brom cresol green (BCG)</td>
<td>4·7</td>
<td>0·265</td>
</tr>
<tr>
<td>4</td>
<td>Bromothymol blue (BTB)</td>
<td>7·1</td>
<td>0·590</td>
</tr>
<tr>
<td>5</td>
<td>$p$-Nitrophenol (pNP)</td>
<td>7·1</td>
<td>0·415</td>
</tr>
<tr>
<td>6</td>
<td>Neutral red (NR)</td>
<td>6·8</td>
<td>0·465</td>
</tr>
<tr>
<td>7</td>
<td>Benzenazoazodiphenylamine (BADA)</td>
<td>1·5</td>
<td>Already shown basic colour</td>
</tr>
<tr>
<td>8</td>
<td>$p$-Nitroaniline (pNA)</td>
<td>1·1</td>
<td>Indication not shown</td>
</tr>
<tr>
<td>9</td>
<td>4-Phenyloxazaphthylamine (PANA)</td>
<td>4·0</td>
<td>Indicator does not get adsorbed</td>
</tr>
<tr>
<td>10</td>
<td>Bromphenol blue (BFB)</td>
<td>4·1</td>
<td>0·050</td>
</tr>
</tbody>
</table>

 Vol. of indicators used: pEC, 1·5 ml; BCG, 0·5 ml and others 0·25 ml.

TABLE 1 — n-Butylamine Titre for the Different Indicators Used

*Mode of mixing: solid + $C_6H_4$ + indicator + amine; time of equilibration: 48 hr
from indicator to indicator and could be as low as a few hours. Mode of mixing e.g., (i) solid + indicator + amine + benzene, (ii) solid + benzene + amine + indicator and (iii) solid + benzene + indicator + amine shows that unlike the MR system BCG and pEC systems are not affected much. Even though small, the differences observed in the case of the MR system are beyond the experimental uncertainty. However, it is a little surprising to note that the mode of mixing should affect the end point since an indicator should undergo a colour change when the last of the acid sites disappears. As enough time (48 hr) is given for equilibration such a difference in the titre value should not occur.

The effect of concentration of indicator on the acidity is quite interesting. The pEC and BCG systems show very little dependence of titre value on the concentration of the indicator. But in the case of the MR system the volume of titrant required to reach the end point steadily increases with increasing amounts of the indicator. Even 0.25 ml of MR indicator is enough to show the end point clearly. The chemisorption of MR over the solid may be responsible for the variation in the titre value at higher concentration of MR. It is possible that this chemisorption creates additional acid sites on the solid thereby increasing the volume of titrant required for neutralization. The more the amount of indicator, the greater the number of additional sites created and hence the greater the titre value. pEC apparently does not seem to create acid sites while BCG affects the system only to a very small extent.

If one looks at the structure, pEC and MR should behave alike as they both contain the azo linkage. Since they do not affect the system in a similar manner the structure may not be responsible for such a behaviour. Both MR and BCG contain acidic groups. Assuming that these acidic groups influence the titre value through interaction with the solid, it is reasonable to expect MR, having a -COOH group to affect the end point much more than the BCG which has only SO2H group. pEC which has no acid group, should affect the end point least. The results show that these indicators do behave in the aforesaid manner supporting the above reasoning. However the dual functionality of the MR indicator should also be taken into consideration. So the correct amount of indicator to be used varies from indicator to indicator and for quantitative measurements one has to predetermine this amount for each of the indicators. It is not advisable to use indicators like MR which show a steady variation of titre value with concentration.

The solvent medium is also found to affect the end point. Benzene, cyclohexane and decalin were used as solvents. The trend for the titre value in these solvents in the case of indicators MR and BCG having an acid group could be given as C6H5 > decalin > cyclohexane. pEC, containing a basic group shows a different trend — decalin > benzene > cyclohexane. Hence for comparative studies of acidities the same solvent should be employed and a similarity in solvents implied in the statement ‘benzene, isooctane, decalin or cyclohexane may be employed as solvents’ is not correct.

A comparative study of the volume of titrant required to neutralize the same solid using indicators of same pKa was made. Table 1 shows that the titre values are different for indicators with almost identical pKa.

The results indicate that the choice of an indicator depends on various factors like the time of equilibration, the concentration and nature of the indicator and the solvent used. If an acidity measurement is to be made, the minimum concentration of the indicator to be employed, the time of equilibration required and the mode of mixing has to be determined in a few solvents to choose the proper conditions. A number of indicators with the same pKa have to be tried if one has to study the acidity distribution in order to be assured that the extent of acidity does not depend on the nature of the indicators used. All these conditions cannot be standardized and have to be determined for each of the solids because the nature of solid-indicator interaction may vary from one to another. It can be concluded that titration in non-aqueous media is incapable of providing a reliable value for the acidity even at room temperature.

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References
Extractive Spectrophotometric Determination of Microgram Amounts of Codeine, Narcotine, Papaverine & Thebaine by Solochrome Green V 150

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A direct spectrophotometric method for the quantitative determination of microgram amounts of codeine, narcotine, papaverine and thebaine is described. The method is based on the formation of ion-pair complexes between these alkaloids and Solochrome Green V 150 and measurement of the absorbance of chloroform extract at 520 nm. The spectral characteristics, the pH values for maximum formation of the complexes, composition of the complexes and the effect of various foreign substances have been described.

Trace determination of various opium alkaloids is one of the topical problems in organic analysis because of their toxicological and pharmacological importance. Most commonly employed methods are indirect and time-consuming. A few direct spectrophotometric methods based on the use of acid dyes are available for the determination of codeine and papaverine but these are apparently not applicable to narcotine and thebaine.

A search for acid dyes for the determination of various opium alkaloids revealed that the dye, Solochrome Green V 150, forms extractable ion-pair complexes with codeine, narcotine, papaverine and thebaine, and the colour of the extract can be used for their spectrophotometric determination. Quantitative determination of morphine by this reagent is not possible because of very poor extraction of the complex into organic solvents. Since the extracted ion-pairs obtained with four of the five opium alkaloids absorb at the same wavelength, the alkaloids need to be separated prior to their determination in a mixture.

Absorbance measurements were carried out using a Bausch and Lomb Spectronic-20 spectrophotometer.

Solochrome Green V 150 dye was obtained from the Imperial Chemical Industries Limited, Calcutta.

Samples of pure opium alkaloids were procured from Central Forensic Science Laboratory, Hyderabad. Walpole and Clarke and Lub buffers were used. All the other chemicals used were of analytical grade.

Procedure — An aliquot of the alkaloid solution containing 0-025-0-1 mg of alkaloid was transferred to a separating funnel and 5 ml of 10⁻⁴ M aqueous dye solution and 10 ml of suitable buffer solution added. The mixture was extracted by shaking with 15 ml of chloroform for 1 min. The chloroform layer was separated and the absorbance measured at 520 nm.

The unique feature of the reagent Solochrome Green V 150 is its universality and convenience for the determination of four of the five major opium alkaloids in spite of the fact that it requires their separation when present together. Most of the commonly associated impurities do not interfere and the sensitivity is better than that obtained in the commonly used methods. Since the dye is not extracted into chloroform the absorbance of the reagent blank is negligible.

Aqueous solutions of Solochrome Green V 150 have a maximum absorbance at 490 nm. Change in pH of the solution does not affect the λmax of the dye. The dye is not extracted into chloroform at any pH in the range 1-11. The ion-pair complexes of the four alkaloids extracted in chloroform show a maximum at 520 nm and change in pH does not affect this maximum. Of the three halogenated solvents, chloroform, 1,2-dichloroethane and dichloromethane, chloroform has been found to be the best extractant. The pH values for maximum extraction of ion-pair of alkaloids into chloroform are given in Table 1. About one min of shaking is sufficient for complete extraction. Excess of shaking sometimes results in emulsion formation. The colour of the extract is stable for about 24 hr, after which sedimentation starts. The compositions of ion-pair complexes of four alkaloids as found by continuous variation and mole ratio methods, the concentration range in which the Beer's law is obeyed and Sandell's sensitivity are listed in Table 1. Five-fold excess of the dye is required for maximum colour development. Concentrated solutions of the dye result in emulsion formation. The precision of the method for the determination of various opium alkaloids was found to be ±2%. The effect of foreign substances has been checked. Citric acid, acetylsalicylic acid, sodium salicylate, sodium benzoate, sodium diethyl barbiturate and saccharine sodium do not interfere even in ten-fold excess. A statistical evaluation

| Table 1 — Spectral Characteristics, pH of Extraction, and Sensitivity for the Determination of Codeine, Narcotine, Papaverine and Thebaine by Solochrome Green V 150 |
|---------------------|---------------------|---------------------|---------------------|
| Alkaloid            | pH of maximum absorption | Range of Beer's law | Compositional sensitivity |
|                     | (pH) | (in μg) | (Alk: Dye) | (in μg/cm²) |
| Codeine             | 6-0  | 50-1000 | 1:1       | 2.5/cm²/0.002  |
| Narcotine           | 2-0  | 5-300   | 1:2       | 0.5/cm²/0.005  |
| Papaverine          | 2-0  | 5-30    | 1:2       | 0.03/cm²/0.004  |
| Thebaine            | 3-6  | 5-200   | 1:2       | 0.2/cm²/0.003  |