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IDENTIFICATION AND CONTROL OF PURITY OF ACID-BASE INDICATORS

Prepared for publication by

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Identification and control of purity of acid-base indicators

Abstract - A series of tests to be applied to acid-base indicators to establish their purity is recommended. These include the determination of moisture content, residue after combustion, elemental analysis, spectral characteristics and chromatographic examination. The tests may also be used for spectrophotometric reagents and compleximetric indicators where their purity is in doubt.

Commercially available acid-base indicators often are a mixture of different compounds, the nature of which depends on their origin. The objective of the present report is not to give methods for the characterization of these compounds, but to provide the analyst with some simple guidelines for the evaluation of the purity of an acid-base indicator. The methods of testing recommended here are also useful for other organic reagents, especially those used in photometric analysis or as compleximetric indicators.

Impurities, especially if they are highly coloured, can interfere seriously with the practical use of these reagents. For the determination of the acid-base equilibria of such compounds only very pure substances can be used.

If the purity of the indicator is not declared by the manufacturer, it must be established by the user. This may be done by comparing the results of the following tests with those obtained with compounds of known purity, or with data published in the chemical literature.

Contaminated substances can in general be purified using the conventional techniques of organic chemistry, especially recrystallization or column chromatography.

The following tests are proposed:
Determination of moisture content.
Determination of combustion residue or sulphated ash.
Determination of elemental composition by combustion analysis.
Recording and evaluation of the UV/VIS spectrum.
Determination of the isosbestic point.
Recording the IR and/or NMR spectrum.
Examination by thin-layer chromatography.
Further methods.

Determination of moisture content

Dry a suitable amount (e.g. 500 mg) of the air-dried indicator in a drying oven, at 110°C, to a constant mass. In doing so, it must be assumed that no decomposition of the sample takes place.

Different methods of preparation and purification can give rise to considerable variation in the moisture content of the substances.

Determination of combustion residue or sulphated ash

Heat a suitable amount (e.g. 100-500 mg) of the indicator in a porcelain crucible to dull red heat (650-700°C) either over a gas burner or in an electric furnace.

The mass of the residue is related as a percentage to the mass of the air-dried sample. It may be necessary to fume the residue with sulphuric acid, in which case the mass of the residue (sulphated ash) is also related to the mass of the air-dried sample.

Determination of the elemental composition by combustion analysis

Sometimes it can be useful to obtain elemental analysis (i.e. content of carbon, hydrogen, nitrogen, sulphur, phosphorus, halogen) for the identification or verification of the purity of an indicator. This type of analysis is generally used to show if the substance is pure or not. It must however be realised that the precision of the combustion method is not sufficiently high to discriminate between compounds of similar molecular mass. No information on the nature of any impurity is obtained.

Recording and evaluation of the UV/VIS spectrum

Prepare solutions of the indicator in suitable buffer solutions of 2 pH units below and 2 pH units above the beginning and the end of the transition interval. For indicators used in non-aqueous titrimetry use appropriate buffer systems. The concentrations of the solutions to be tested should be such that the resulting absorption at λ_{max} does not exceed an absorbance of 1.2. Use the buffer solution as a reference.

The UV/VIS spectrum, or more commonly, the spectrum in the visible region only, is a useful means for the identification and for the verification of purity of an organic reagent. Read from the spectrum the wavelength(s) of maximum absorption (λ_{max}) and calculate, if the relative molecular mass is known, the conditional molar absorptivity (ε_λ) at λ_{max}. To describe samples of the same type but unknown composition, it is convenient to calculate the special absorptivity (ε_λ*) of a 1% (m/v) solution.

Compare these results with those obtained using pure samples or with values published in the literature. The wavelength(s) of maximum absorption, λ_{max}, and the value(s) of the conditional absorptivity, ε_λ (or the value(s) of the special absorptivity, ε_λ*) are suitable criteria on which to base the purity of the sample; in many cases, it allows identification to be made.

It should not be overlooked, however, that impurities (generally by-products from the synthesis) of chemical constitution similar to the indicator often have very similar spectral characteristics. Inorganic impurities (arising from salting-out or neutralisation of reaction mixtures with acid or alkali) cannot be detected spectrophotometrically because they usually make little or no contribution to the absorbance of the solution. Their presence will, however, result in a lowering of the ε values. It is also useful to examine the behaviour of the indicator solution at values of pH far from the pH range over which the colour change occurs. Therefore spectra should also be obtained from solutions containing 0.1$\underline{M}$ hydrochloric acid or 0.1$\underline{M}$ sodium hydroxide. This procedure may also provide useful information concerning the stability of the indicator solutions.

If the indicator is to be used for titrations in non-aqueous systems, it may be useful to know how the compound behaves in an appropriate solvent or solvent mixture. In this case the above measurements should be repeated with a solution in the particular non-aqueous solvent.

Determination of the isosbestic point

Prepare a solution of the indicator with the same concentration as used for the spectral measurements described above, and a pH corresponding to one end of the colour transition. Record the spectrum of this solution and of further solutions of the same concentration for steps of 0.2 pH units until the colour change is complete (usually over a range of 2 pH units).

If a system in equilibrium changes directly from the initial to the final state, all absorbance curves intersect at one point, the isosbestic or isoabsorptive point.

The isosbestic point only occurs if, in the pH range tested, only one equilibrium is present. It does not if other equilibria are involved, such as those from other protolytic equilibria of the indicator with dissociation constants similar to those of the first equilibrium. Lack of an isosbestic point is also observed if reactions take place between different coloured substances present as impurities in the solution under test.

Recording the IR and/or NMR spectrum

Generally the VIS spectrum gives sufficient information to identify an indicator and it is unnecessary to record an IR or NMR spectrum. If it is desired to have more knowledge of the nature of other substances present, an IR and/or NMR spectrum can be recorded under suitable experimental conditions.

Examination by thin-layer chromatography

A useful and fast method for the identification and checking of the purity of indicators is thin-layer chromatography. (Paper chromatography can also be used.)

The success of the separation depends greatly on the selection of a suitable substrate for the chromato-plate and especially of the solvent mixture to be used.

Because of the very different chemical structures of the dyestuffs used as indicators and their behaviour in the separation process, it is not practicable to recommend here one or more separation systems. Therefore, for any particular case it is necessary to consult the literature. To confirm the results obtained, it is recommended that a second separation involving a different solvent system be used.

Normally only coloured or fluorescent by-products can be detected. Inorganic components can be made visible after spraying with suitable reagents.

Solutions of some indicators show a tendency to decompose during storage. This decomposition is also evident if the substance is kept on the thin-layer plate (or on the paper sheet) some hours before the separation is begun. It should also be recognised that any coloured by-products present in the sample are only visible in the chromato-plate (or on the paper strip) if they are present in not too low a concentration.

The tailing effect common in such separations can be prevented by using an optimum concentration of the sample. General experience with TLC has shown that good results are obtained when 10 µL volumes of a 0.1-0.2% (w/v) solution are used.

Further methods

The methods of analysis listed above are useful for rapid, initial examination of an indicator. For more detailed knowledge, several other methods are available. For the determination of the nature and concentration (quantity) of the by-products, HPLC is invaluable. The higher sensitivity of HPLC compared with TLC and PC also enables very small concentrations of impurities to be detected or determined.

Instead of simple combustion in a crucible, methods of thermal analysis can be used to examine the process of decomposition.

It must be mentioned that the methods listed above are suitable for the examination of known indicators. When new compounds are being recommended, information regarding their acid-base equilibria, their chemical structure, etc., should always be given.

Conclusions

Normally, acid-base indicators used in analytical chemistry are available in sufficiently good quality. However, storage for even relatively short periods can lead to some decomposition. Therefore, it is desirable also to test such substances before they are used.

Small concentrations of by-products normally do not disturb the detection of the end-point in volumetric analysis, but in work involving high precision, the results are dependent on the purity of the indicator used, simply because the titration errors are influenced by the purity of the indicator.