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**RECOMMENDATIONS FOR PUBLICATION  
OF PAPERS ON METHODS OF  
MOLECULAR ABSORPTION  
SPECTROPHOTOMETRY IN SOLUTION  
BETWEEN 200 AND 800 nm**

Prepared for publication by

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INTRODUCTION

When new reagents for molecular absorption spectrophotometry in solution, or modified methods employing better known reagents, are presented in the literature at an increasing rate, it is inevitable that some confusion and contradiction should result with regard to the best reagent and optimum operating conditions for use in a particular spectrophotometric determination. Because of the non-critical nature of many publications concerning spectrophotometric methods, the advantages and disadvantages of the methods studied are often not made clear, and their comparison in terms of sensitivity and selectivity with well-established methods is not fully described. Such texts as those of Sandell<sup>1</sup>, Boltz<sup>2</sup>, Snell and Snell<sup>3</sup> and the IUPAC Commission on Optical Data<sup>4</sup> assist the critical assessment of various spectrophotometric reagents. The IUPAC publication provides the optical and chemical data necessary to evaluate the methods applicable to a particular problem. These texts are, however, largely concerned with well-established and proven reagents and methods; a newcomer to the field must be bewildered by the wealth of other information available in the literature for a variety of less well-known reagents. The capabilities of these reagents are less easily assessed, and the situation is aggravated by the different approaches employed for the examination of reagents and operating conditions for a particular determination. Different methods are used in the investigation of variables and interferences affecting the reaction which is to be made the basis of a spectrophotometric procedure. Different opinions and individual preferences prevail with regard to the form in which these data are published and concerning the expression of sensitivity, precision and accuracy.

The recommendations of the principal journals of analytical chemistry give a guide to the preferred method of presentation of precision and accuracy data, and most journals recommend that publications conform to a particular format. West<sup>5</sup> and Mellon<sup>6</sup> have made recommendations concerning the general approach to the development of a spectrophotometric procedure, and Yoe<sup>7</sup> presents a suggested outline for a comprehensive study of a new colour reaction and its development into a spectrophotometric method. Although it is obviously desirable, no agreement exists with regard to the presentation of data so that they are of maximum usefulness to other workers.

This report, which is based on the paper by Kirkbright<sup>8</sup> invited by the Editorial Board of *Talanta* as part of its series on publication of analytical methods, has been prepared for the Commission by Dr. G.F. Kirkbright.

NOTE ON NOMENCLATURE

In molecular absorption spectrophotometry the terms 'extinction', 'optical density' and 'absorbance' have been used to express the logarithm of the ratio of the reciprocal internal transmittance  $\left[ \log_{10} (T/T_0) \right]$ .

The term 'absorbance' is preferred because it incorporates the root word which characterises the physical process involved.

RECOMMENDATIONS

The following recommendations are made concerning the minimum amount of data which should be incorporated into a paper which describes a method of analysis using molecular absorption spectrophotometry in solution.

Information pertaining to the following must be given:

1. Reagents

- (a) Purity and stability of solid reagents used to form absorbing component
- (b) Any procedure required for purification of solid reagents
- (c) Data on preparation and properties of new reagents to allow their production and characterization by other workers
- (d) Purity and stability of other reagents used (solvents, buffers, standard solutions, etc.)
- (e) Suitable solvent(s) for any reagents used to form absorbing component and for the reaction to be studied. Reasons for choice of solvent (e.g., to give greatest sensitivity, highest stability, low cost, etc.)
- (f) Stability of reagent solution under laboratory conditions (i.e., effect of daylight, oxygen, CO<sub>2</sub>)

2. Spectral Characteristics

- (a) Absorption spectra for reagent(s) alone and in presence of component to be determined. Statement of concentrations employed and composition of blank solution used to record spectra
- (b) Wavelength chosen for determination. Reasons for choice (e.g., to give maximum sensitivity or precision)
- (c) Effective spectral half-intensity band-width at chosen wavelength of the spectrometer employed
- (d) Report of check on accuracy of wavelength (or frequency) scale

3. Effect of Concentration of Hydrogen Ion

- (a) Details of composition of buffer system and ionic strength of solutions used for absorption measurements
- (b) Method of calibration for 'pH' especially when partly non-aqueous solutions are used
- (c) Effect of pH variation on absorbance at chosen wave-length (and on wavelength of maximum absorbance, if any) over range of pH and ionic strength expected in the examination of real samples

4. Effect of Reagent Concentration

- (a) Effect on yield (i.e. final absorbance) of absorbing component of independent variation of concentration of each reagent used (at concentration of component to be determined and ionic strength similar to that expected in real sample solutions)

5. Order of Addition of Reagents and Rate of Reaction

- (a) Effect of order in which reagents are mixed on rate of reaction and yield (i.e. final absorbance) of absorbing component (at optimum pH, ionic strength and reagent concentration)
- (b) Time required to produce stable absorbance reading against reagent blank

6. Stability of Absorbing Component

- (a) Stability of absorbance readings at wavelength chosen for analysis. Details of any precautions necessary to achieve stable absorbance reading (e.g., storage in dark, absence of dissolved oxygen, etc.)

7. Effect of Temperature

- (a) Effect on rate of formation, yield (i.e., final absorbance) and stability of variation in temperature over range which might be encountered in laboratories (i.e., ca. 15 to 30 °C)
- (b) Recommended temperature for operation of method

8. Calibration Graph and Optimum Concentration Range

- (a) Description of analytical procedure used to establish calibration graph of absorbance vs. concentration of component to be determined
- (b) Shape of graph (or equation for graph). Statement of range of concentration of test component over which linearity is obtained. Ringbom plot<sup>9</sup>. The publication of straight-line calibration graphs is not now the editorial policy of most journals
- (c) Check on photometric accuracy of absorbance scale of spectrometer (with calibrated glass filters or liquid reference standards) (see e.g. ref. 10)

## 9. Sensitivity

(a) Statement of molar (linear) absorption coefficient,  $\epsilon$ , of the absorbing component at wavelength of measurement and spectral half-intensity band-width, temperature and solvent employed.  $\epsilon$  is defined by  $\epsilon = A/(l \cdot c_B)$  where  $A$  = absorbance,  $l$  pathlength through the test system, and  $c_B$  = concentration of absorbing component. The unit employed for  $\epsilon$  must be specified.  $\text{m}^2 \text{mol}^{-1}$  is preferred.

This definition of sensitivity is in accordance with that recommended for use in spectrochemical analysis<sup>11</sup>, i.e.  $\epsilon$  is the differential quotient ( $dA/dc$ ) of the calibration function (analytical graph of absorbance vs concentration) for unit path-length through the test solution.

The absorptivity may be expressed with regard to one mole of the component to be determined per litre of solution instead of to one mole of the absorbing species. This may be termed the analytical molar (decadic) absorption coefficient and does not require knowledge of the molecular formula of the absorbing component or even the presence of the component determined in the solution whose absorbance is measured. This term may be applied readily to statement of sensitivity in combined solvent extraction-photometric and indirect methods of analysis.

(b) The characteristic concentration (sometimes known as the sensitivity index) i.e. number of micrograms of test component, converted to the absorbing component, which in a column of solution of cross-section  $1 \text{ cm}^2$  shows an absorbance of 0.001, should not be used.

## 10. Interference

(a) Definition employed to establish presence or absence of interference from other components present with test component. Definition should be related to precision of method development (i.e., interference when error is greater than 2 or 3 times the standard deviation of method obtained in absence of foreign component)

(b) Effect of large excesses (e.g. 100 or 1000 times the substance concentration of test component) of other components on absorbance produced for test component at several concentration levels (e.g., near to top and bottom of recommended calibration range). Other components investigated must include those which show similar chemical properties to the component to be determined or which are commonly found with it in samples to be analysed. Results to be tabulated without concealment of data (e.g., as 'does not interfere' statement)

(c) Limiting permissible concentrations of those components interfering at concentrations in (b) above

(d) Result of check that when two or more components which do not interfere individually, are present together with the component to be determined, that there is no slight interference from each which is additive

(e) Chemical or physical reasons for interferences observed (e.g., absorption at wavelength of measurement, precipitation, oxidation of reagent or test component).

## 11. Elimination of Interferences

(a) Recommendations for removal of effect of interfering components (e.g., subtraction of absorbance of extraneous component from that caused by component determined, use of masking agent) or preliminary separation of either the component to be determined or interfering component

## 12. Precision

(a) Examination of precision of complete analytical procedure in presence of any necessary masking agents or after preliminary separation procedures

Expression of relative standard deviation (as decimal fraction) for complete analytical procedure at low absorbance value and statement of number of measured values from which this is derived. The best straight line fit for the calibration data may be calculated by the method of least squares and the confidence limits for the slope of the calibration function established.

## 13. Accuracy

(a) Accuracy of method applied to standard or reference samples, or

(b) Comparison of analytical results with those obtained for identical samples by different established procedures.

#### 14. Nature of Absorbing Component

- (a) Report of investigation of nature of component
- (b) Empirical formula of component in solution
- (c) Conditional stability constant of complex (where applicable) under stated conditions of ionic strength, temperature, pH, etc., used in reaction

Many hundreds of methods have been proposed for the spectrophotometric determination of the elements copper and iron and anions such as phosphate and fluoride. Further methods should only be proposed for these and other ions if they are found to be markedly superior in several respects (sensitivity, selectivity, spectrophotometric stability, etc.) to the best of the existing methods. When a new method is proposed for any species its sensitivity and selectivity must be compared with other recommended methods for the spectrophotometric determination of the same species, and any particular advantages or disadvantages of the method proposed must be mentioned. It is again stressed that the above requirements represent the minimum acceptable amount of information which must be included in any report of a new spectrophotometric method of analysis.

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