Phthalhydrazidylazoacetylacetone as a Chemiluminescent Complexometric Indicator

K KRISHNAKUTTY & N THANKARAJAN*

Department of Chemistry, University of Calicut, Kerala 673635

Phthalhydrazidylazoacetylacetone has been shown to be a suitable chemiluminescent indicator in EDTA titration of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Ca(II) and Mg(II). Applicability of the indicator in highly coloured solutions has also been demonstrated.

Phthalhydrazidylazoacetylacetone (PHA) has been reported as an efficient chemiluminescent (CL) indicator in acid-base titrations[1]. This note reports the use of PHA as a CL indicator in complexometric titrations with EDTA. The added advantage of PHA is its applicability even in highly coloured solutions.

In alkaline medium, oxidation of PHA by hydrogen peroxide is attended[2] by a weak CL emission at 475 nm. However, in the presence of heavy metal ions which catalyse decomposition of hydrogen peroxide, the CL emission is quite intense. Complexones like EDTA can, however, effectively deprive the heavy metal ions of their catalytic effect, by sequestering them. Thus, when a solution of a catalytic metal ion, admixed with the indicator solution, is titrated in alkaline medium against standard EDTA containing hydrogen peroxide, the end point is marked by the abrupt attenuation of the bright CL emission. If titration is carried out in the reverse direction, the CL emission intensifies suddenly at the end point. Although many azo compounds have been used as indicators in chelatometric titrations, this is the first report of use of an azo compound as a CL indicator in such titrations[3].

The indicator solution was prepared by dissolving PHA (10 mg) in ethanol (50 ml), and diluting to 100 ml with water.

In a typical titration, the metal salt solution (10 ml) containing ammonia buffer (5 ml, pH 10) and the indicator (five drops) was titrated against standard 0.01 M EDTA solution, which was 0.001% with respect to hydrogen peroxide. Mixing was effected by a magnetic stirrer. At the end

point, an excess drop of the titrant produced a sudden change from intense Cl to a dull glow. Although a semi-darkened room is preferable for detection of end point, titrations can be carried out even in daylight by placing the titration flask in a cardboard box with an observation hole on one side. This method was used for the direct determination of copper(II), nickel(II), zinc(II), cadmium(II) and manganese(II).

Results obtained presently and those of complexometric titrations using metallochromic indicators are given in Table 1. In all cases blank titrations were carried out. Variation of results observed was less than ±0.02 mg in replicate determinations of the various metal ions. Concentrations of these divalent metal ions as low as 10^{-4} M could thus be determined.

Calcium and magnesium ions are ineffective in catalysing decomposition of hydrogen peroxide, and hence do not cause intense CL with the indicator. These ions were, therefore, determined indirectly as follows: To a buffered solution (pH 10) of calcium or magnesium ion, a known excess of EDTA, indicator (five drops) and hydrogen peroxide (five drops, 0.01%) were added, and the unreacted EDTA back titrated against standard copper(II) salt solution. At the end point the feeble glow of the solution suddenly became brilliant. Results of these determinations are also included in Table 1. Determination of the total content of calcium and magnesium in hard water yielded accurate results by this method.

Table 1 – Results of Estimations

Analyte metal	Metal content (mg) in 10 ml of metal salt solution			
	Theoretical	Standard method	CL method	
			Without g.v.	With g.v.
Manganese	5.50	5.49	5.51	5.51
Nickel	5.79	5.82	5.78	5.80
Copper	6.51	6.48	6.55	6.54
Zinc	6.59	6.55	6.58	6.61
Cadmium	11.28	11.26	11.31	11.30
Magnesium	2.44	2.43	2.42	2.42
Calcium	4.05	4.02	3.98	4.01

g.v. = gentian violet.

To test the efficiency of the CL indicator in highly coloured solutions, titrations using the indicator were carried out in the presence of gentian violet (0.003%). These results are also included in Table 1. Heavy metal ions which catalyse the decomposition of hydrogen peroxide evidently interfere in these determinations. However, with suitable masking agents the selectivity of the method can be increased so that it becomes viable in the analyses of metal ions in a variety of matrices.

References

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3 Bishop E, *Indicators* (Pergamon Press, New York) 1972.