

bismuth, zinc, cobalt, uranium(VI), EDTA and ascorbate. Several sequestering agents were used to eliminate the interference of some of the ions, e.g. antimony(III), rhodium, ruthenium, zirconium and cerium(IV) were masked with tartaric acid whereas manganese was masked with oxalic acid. The interference due to palladium and iron(III) was eliminated by selective extraction¹² with dimethylglyoxime and acetylacetone respectively.

The method is rapid as extraction and determination required only 30 min. As little as 0-126 µg per ml of gallium can be determined. The results are reproducible. The average recovery of gallium is $99.8 \pm 0.2\%$. The relative standard deviation is $\pm 1.12\%$.

References

1. KRISHNAN, A. & FREISER, H., *Analyt. Chem.*, **31** (1959), 923.
2. STEINBACH, J. F. & FREISER, H., *Analyt. Chem.*, **26** (1954), 375.
3. JASKÓLSKA, H. & MINCZEWSKI, J., *Chem. Anal. (Warsaw)*, **12** (1967), 697.
4. SWEET, T. R., *Anal. Chim. Acta*, **37** (1965), 1552.
5. STARY, J. & HLADKY, E., *Anal. Chim. Acta*, **28** (1963), 227.
6. RAHAMAN, M. S. & FINSTEN, H. L., *Analyt. Chem.*, **40** (1968), 1709.
7. DHOND, P. V. & KHOPKAR, S. M., *Talanta*, **23** (1976), 51.
8. BERG, E. W. & REED, K. P., *Anal. Chim. Acta*, **36** (1966), 372.
9. KOLTHOFF, I. M. & ELVING, P. J., *Treatise on analytical chemistry* (Interscience, New York), 1964, 252.
10. CHARLOT, G., *Colorimetric determination of elements* (Elsevier, Amsterdam), 1964, 252.
11. SANDELL, E. B., *Colorimetric determination of traces of metals* (Interscience, New York), 1959, 210.
12. DE, A. K., KHOPKAR, S. M. & CHALMERS, R. A., *Solvent extraction of metals* (Van Nostrand-Reinhold Co., London), 1970, 98, 48.

Use of Some Phenolic & Pyrazolone Derivatives as Acid-Base Indicators

S. C. MISHRA, (Mrs) SAROJBASINI DAS & A. S. MITTRA*
Mayurbhanj Chemical Laboratory, Ravenshaw College
Cuttack 753003

Received 23 October 1976; accepted 24 February 1977

Nitro, nitroso, amino, hydroxylamino, hydroxy and carboxy derivatives of some phenols and 2-pyrazolin-5-ones have been prepared and their use as acid-base indicators studied. The pK_{in} values, pH range, and colour in acidic and alkaline media are reported for the indicators. It is found that the pK_{in} value for 1-phenyl-3-methyl-4-amino-2-pyrazolin-5-one tallies with that of methyl orange (3.7), and it has also comparable stability. Hence its use as a substitute for methyl orange is suggested.

WHILE preparing various phenolic and 2-pyrazolin-5-one derivatives in the course of our investigation on fungicides against blast disease of rice plant, we observed that some of these

compounds behave as neutralization indicators. It is known¹ that phenolic derivatives like *p*-nitrophenol, cresol red, etc., act as indicators in acid-base titrations. According to chromophore theory, the presence of $-NO_2$, $-NH_2$, $-NHOH$ and $-OH$ groups enhances the sharp colour change from acidic to alkaline medium or vice versa. The present seventeen compounds, having both chromophore and auxochrome groups, satisfy all the requisites of ideal indicators².

2-Nitroso-, 2-carboxy- and 2-nitro-resorcinols, 2-nitro-1-naphthol, 2-nitro-1-naphthol-3-carboxylic acid, 3-nitro-1-naphthol-2-carboxylic acid, 1-nitro-2-naphthol, 1-nitro-2-naphthol-3-carboxylic acid and 3-nitro-2-naphthol-1-carboxylic acid (Sr No. 1-9, Table 1) were prepared by standard methods³⁻⁵. 1-(2,4-Dinitrophenyl)-3-methyl-2-pyrazolin-5-one (Sl No. 16, Table 1) was also prepared by a reported procedure⁶.

For the preparation of 6-nitro-*o*-cresol, 3-nitro-*p*-cresol and 6-nitro-*m*-cresol (Sl No. 10-12, Table 1), each of the compounds, *o*-cresol, *p*-cresol and *m*-cresol (2 g) was dissolved separately in pyridene (20 ml) and conc. HNO_3 (10 ml) added dropwise until effervescence stopped. The contents were cooled for 1 hr and ice-water (20 ml) was added. The separated compounds were filtered, recrystallized from ethanol; m.p. 69.5° (Sl No. 10), 77° (Sl No. 11), 56° (Sl No. 12); yield 65-75%.

For the preparation of 1-phenyl-3-methyl-, 1-acetamido-3-methyl- and 3-methyl-4-hydroxy-amino-2-pyrazolin-5-ones (Sr No. 13-15, Table 1), the three different 4-nitroso-2-pyrazolin-5-ones⁷ (1 g each) were dissolved separately in the minimum amount of absolute ethanol and zinc (1 g) and calcium chloride solution (10 ml) were added. The mixtures were then refluxed over a water-bath for 1 hr, or until there was a marked colour change in the solution. The reaction mixture was filtered hot and excess of ethanol evaporated off. It was then allowed to cool (kept overnight) when crystals separated. The compounds were filtered, recrystallized, analysed for C, H and N. The analytical data are given in Table 2.

For the preparation of 1-phenyl-3-methyl-4-amino-2-pyrazolin-5-one (Sl No. 17, Table 1), 1-phenyl-3-methyl-2-pyrazolin-5-one³ (1 g) was dissolved in the minimum amount of sodium hydroxide solution (10%). The solution was heated over a low flame while stirring it continuously. Solid sodium dithionite was added in small portions until the yellow colour of the solution changed to orange-red. The reaction mixture was kept overnight, when dark red crystals separated. The compound was filtered, recrystallized from ethanol, m.p. 186° , yield 70%. The same compound was also obtained, by carrying out the reduction in zinc and acetic acid medium (Found: C, 63.39; H, 5.81; N, 22.12. $C_{10}H_{11}N_3O$ requires C, 63.49; H, 5.82; N, 22.22%).

Preparation of the indicator solutions — 0.05 g of the indicator sample was dissolved in the minimum volume of ethanol at room temperature and volume made up to 100 ml by the addition of distilled water. In some cases, a slight precipitate was formed at this stage, which was filtered off.

*To whom all correspondence should be addressed.

TABLE 1 — INDICATOR PROPERTIES OF THE VARIOUS COMPOUNDS

Sl No.	Chemical name	pH range*	Colour change during acid-base titration	pK _{In} †
1	2-Nitrosoresorcinol	3.3-4.9	Yellow to orange	4.15
2	2-Carboxyresorcinol	3.1-4.6	do	4.0
3	2-Nitroresorcinol	5.0-6.7	do	5.9
4	2-Nitro-1-naphthol	5.5-6.9	do	6.4
5	2-Nitro-1-naphthol-3-carboxylic acid	5.1-6.6	do	6.0
6	3-Nitro-1-naphthol-2-carboxylic acid	5.1-6.7	do	6.1
7	1-Nitro-2-naphthol	5.3-6.8	do	6.2
8	1-Nitro-2-naphthol-3-carboxylic acid	5.2-6.6	do	6.15
9	3-Nitro-2-naphthol-1-carboxylic acid	5.2-6.7	do	6.2
10	6-Nitro- <i>o</i> -cresol	2.6-4.0	do	3.3
11	3-Nitro- <i>p</i> -cresol	2.7-4.2	do	3.16
12	6-Nitro- <i>m</i> -cresol	2.6-4.1	do	3.5
13	1-Phenyl-3-methyl-4-hydroxylamino-2-pyrazolin-5-one	4.9-6.4	Red to pink	5.8
14	1-Acctamido-3-methyl-4-hydroxylamino-2-pyrazolin-5-one	2.8-4.3	Yellow to red	3.55
15	3-Methyl-4-hydroxylamino-2-pyrazolin-5-one	3.2-4.6	Yellow to pink	4.1
16	1-(2,4-Dinitrophenyl)-3-methyl-2-pyrazolin-5-one	4.9-6.5	Colourless to orange	5.8
17	1-Phenyl-3-methyl-4-amino-2-pyrazolin-5-one	2.8-4.6	Orange-yellow to red	3.7

*pH range was determined by buffer solution method⁸.†pK_{In} value was measured by pH meter⁹.

TABLE 2 — ANALYTICAL DATA AND MELTING POINTS OF THE NEW COMPOUNDS PREPARED

Sl No. of compounds in Table 1	m.p. (°C)	Yield (%)	Calc. (%)			Found (%)		
			C	H	N	C	H	N
13	170	70	58.54	5.37	20.49	58.24	5.17	20.48
14	209	60	34.88	4.65	32.56	34.68	4.35	32.54
15	>300	80	37.21	5.43	32.56	37.01	5.40	32.36

Prior to this work, some investigations have been reported on the use of pyrazolone compounds as colour formers in colour photography¹⁰. A large number of reports on the use of pyrazolone compounds, e.g. picrolonic acid, 4-nitroso-2-pyrazolin-5-ones, in the gravimetric and colorimetric estimation of a number of metal ions have also appeared¹¹. However, no instance could be found of the use of pyrazolone compounds as acid-alkali indicators. It is interesting to note that 1-phenyl-3-methyl-2-pyrazolin-5-one does not behave as an indicator, whereas 1-(2,4-dinitrophenyl)-3-methyl-2-pyrazolin-5-one (Sl No. 16), 4-hydroxylamino derivatives of 3-substituted 2-pyrazolin-5-ones (Sl Nos. 13-15, Table 1), 1-phenyl-3-methyl-4-amino-2-pyrazolin-5-one (Sl No. 17), having the same nucleus, behave as good indicators. The acetyl derivatives of the above compounds do not show indicator properties. It can be seen from Table 1 that the acetyl derivatives of compounds (Sl Nos. 13-15 and 17, Table 1) have the same potential for keto-enol tautomerism as the original compounds. So loss of indicator property must be due to change of the chromophore groups from -NHOH, -NH₂ to -NHOAc, -NHAc respectively. Moreover, it has been observed that the compounds having chromophore groups, but having no scope for keto-enol tautomerism, for example, 4-nitrosoantipyrine, 4-aminoantipyrine, etc., do not behave as acid-alkali indicators. Therefore, a conclusion may be drawn that tautomerism favours indicator property in 2-pyrazolin-5-one nucleus, which must also carry chromophore at the 4-position.

The indicator solutions of all the compounds were found to be quite stable even after keeping for six months. The pK_{In} value (3.7) of 4-amino-3-methyl-2-pyrazolin-5-one tallies exactly with that of methyl orange (3.7). Hence the use of the former as an alternative indicator is suggested in the place of methyl orange in acid-alkali titrations. The titre values of all these compounds remained same, when the titration was carried out in ethanolic medium¹².

One of the authors (S.D.) is thankful to the CSIR, New Delhi, for the award of a junior research fellowship to her.

References

1. VOGEL, A. I., *A textbook of qualitative inorganic analysis* (ELBS & Longmans, London), 1961, 55.
2. KING, J., *Analyst*, **77** (1952), 752.
3. GILLMAN, H., *Organic synthesis*, Coll. Vol. I (John Wiley, New York), 1958, 33.
4. GORE, T. S., INAMDAR, P. K. & NAGARKAR, M. P., *Indian J. Chem.*, **12** (1974), 946.
5. HODGSON, H. H. & KILNER, E., *J. chem. Soc.*, (1924), 807.
6. KHROMOV-BORISOV, N. V., *Zhur. obsch. Khim.*, **25** (1955), 36.
7. NANDA, B., PADMANABHAN, S., TRIPATHY, B. & MITTRA, A. S., *J. Indian chem. Soc.*, **52** (1975), 533.
8. SMITH, T. B., WHITE, C. A., WOODWARD, P. & WYATT, P. A. H., *J. chem. Soc.*, (1952), 3848.
9. BATES, R. G., *Encycl. Ind. Chem. Anal.*, **3** (1966), 146.
10. WILEY, R. H. & WILEY, P., *The chemistry of heterocyclic compounds*, Vol. 20 (Interscience Publishers, New York), 1964, 148.
11. WILEY, R. H. & WILEY, P., *The chemistry of heterocyclic compounds*, Vol. 20 (Interscience Publishers, New York), 1964, 155.
12. PALIT, S. R. & BAG, J. K., *J. Indian chem. Soc.*, **53** (1976), 526.