

## 5-METHYL-1,3,4-THIADIAZOLYLAZO-RESORCINOL AS A NEW METALLOCHROMIC INDICATOR FOR COMPLEXOMETRIC TITRATION OF LEAD\*

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The synthesis, characteristics and analytical reactions of 5-methyl-1,3,4-thiadiazolylazo-resorcinol (MTDAR) are described. Their dissociation constants of OH groups in *ortho* and *para* position are respectively  $pK_1 = 8.09 \pm 0.01$  and  $pK_2 = 5.72 \pm 0.02$ . For the Pb-MTDAR complex, the molar absorptivity is  $2.0 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 525 nm and pH = 8.0. The complex of ML type is formed. Beer's law is obeyed between 0 and 9 ppm of Pb. The formation constant is  $7.9 \cdot 10^5$ . The studied reagent can be employed as a metallochromic indicator in chelometric titrations with visual and photometric indication. The interferences and their elimination are studied, too. The tristimul coordinates to chromatic transition are determined. This transition is increased by adding indigo carmine as an inert dyestuff.

The research of azoderivatives of heterocyclic compounds containing more than one nitrogen atom in the ring as analytical reagents has awakened interest during the last years. Among these compounds, the derivatives of 1,3,4-thiadiazol have been shown to have very interesting properties related to the sensitivity and selectivity of their reactions with several metal ions. Domagalina and Zareba<sup>1</sup> have synthesized and studied several unsubstituted derivatives of 1,3,4-thiadiazol and those containing in 5 position the group-SH (ref.<sup>2,3</sup>), —SCH<sub>2</sub>COOH (ref.<sup>4</sup>) and NH<sub>2</sub> (ref.<sup>5</sup>) and we have studied some derivatives of 5-methyl-1,3,4-thiadiazol<sup>6-8</sup> previously.

Quantitative studies of Ni(II), Co(II), Fe(III), Cu(II), Cd(II) (ref.<sup>9</sup>) and Zn(II) (ref.<sup>7</sup>) complexes have been and their application to the photometric and complexometric determinations have been studied. However, no information has been given about the complexes of Pb(II), probably due to the lower sensitivity of the reactions of 1,3,4-thiadiazol derivatives with Pb(II).

In the present paper, a study of MTDAR reagent, of its Pb-complex and of its application to complexometric determination is shown. This paper is part of a syste-

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matic investigation that aims at establishing the influence of introducing a new nitrogen atom in the thiazol ring.

## EXPERIMENTAL

### Apparatus and Reagents

A photometric titration unit, Radiometer TTA 4 (Copenhagen, Denmark) with several filters. A Pye Unicam SP8 100 Spectrophotometer (Great Britain) with 1 cm silica cells was used for measuring absorbance and a Radiometer 51 pH meter (Copenhagen, Denmark) for pH measurements.

All the reagents were p.a. quality (E. Merck, Darmstadt). MTDAR solution, 0.01% (m/V) in ethanol, was stable for at least 4 days. Buffer solutions according to Clark and Lubbs were used.

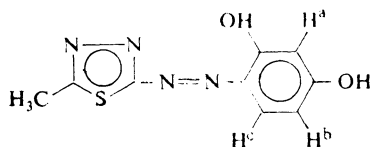
### Synthesis of MTDAR

2-amino-5-methyl-1,3,4-thiadiazol (1.18 g) was dissolved in 20 ml of 50% (m/V)  $H_2SO_4$ , cooled below  $+5^\circ C$  and a saturated, cooled ( $<5^\circ C$ ) solution of sodium nitrite (0.69 g) was added, while stirring. The diazonium salt solution obtained was then poured slowly, while stirring, into a concentrated solution of resorcinol (1.10 g) in ethanol. This reaction mixture was diluted to 50 ml with cold water and set to pH 3–4 with sodium hydroxide. The yellow precipitate was filtered off and washed with cold water. The product was recrystallized from ethanol-water mixture (2 + 1) and yellow needles were obtained. Its purity was checked by TLC on silica gel with  $CHCl_3$ -methanol (10 + 1) mixture as the eluent.  $R_F = 0.56$ , m.p. =  $236 \pm 1^\circ C$ .

For  $C_9H_8N_4O_2S$  (236) calculated: 45.76% C; 4.49% H; 23.73% N; found: 45.97% C; 3.38% H; 23.73% N.

### Properties of the Reagent

MTDAR is sparingly soluble in water and moderately soluble in methanol and ethanol. The infrared spectrum (potassium bromide pellet)  $\nu_{max}$  ( $cm^{-1}$ ): —O stretching (3 480); —C=N-heterocyclic (1 640, 1 590, 1 330, 1 260); —C=C-aromatic (2 000–1 660); —C—H-aromatic (980). The NMR spectrum ( $^1H$ ,  $DMSO-d_6$ ,  $\delta$  ppm): 2.65 (3 H, s, — $CH_3$ ); 6.45 (2 H, m,  $H^a$ ,  $H^b$ ); 7.60 (H, m,  $H^c$ ) (Scheme A).

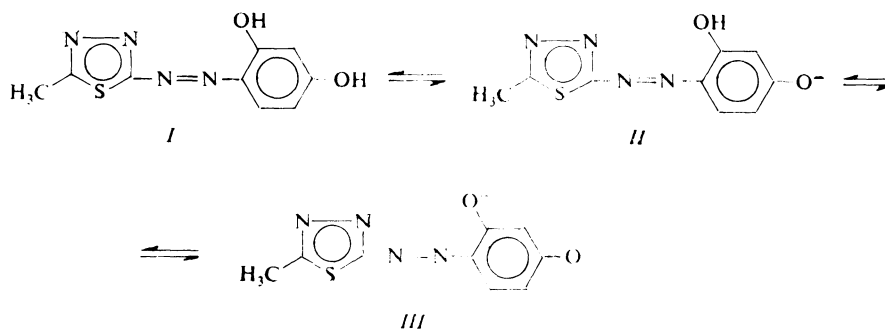


SCHEME A

## RESULTS AND DISCUSSION

MTDAR dissolves in concentrated sulphuric acid to a brownish yellow solution which turns yellow, orange and red when pH increases. This fact can be explained by the existence of three different forms in solution (Scheme B) and confirmed by the

presence of two isobestic points in the absorption spectra of aqueous solutions of reagent in the pH interval from 4 to 9.25 (Fig. 1).



SCHEME B

Between pH 1 and pH 3.7, the spectrophotometric curves are overlapped corresponding to a non dissociated form of reagent. The reagent shows an absorption maximum at 399 nm with a molar absorptivity of  $2.1 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

From pH 3.70 to pH 6.70 an isobestic point appears at 432 nm, which corresponds to dissociation equilibrium of OH group in *para* position with respect to azo group.

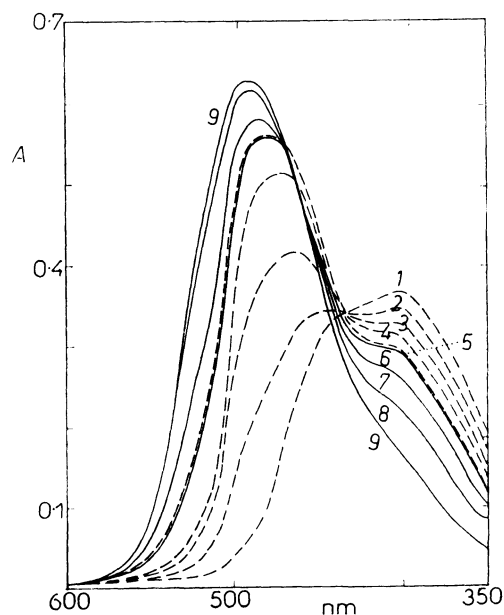


FIG. 1

Absorption spectra of MTDAR versus pH. Curve-pH: 1 4.00; 2 5.42; 3 5.72; 4 6.18; 5 6.71; 6 7.68; 7 8.29; 8 8.67; 9 9.25

At pH 6.70 the predominant form is *II*, which presents an absorption maximum at 480 nm, with a molar absorptivity of  $3.1 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

Between pH 6.75 and pH 9.25 an isosbestic point appears at 466 nm corresponding to dissociation equilibrium of the second OH group. At pH 9.25, only form *III* exists, which shows a maximum at 490 nm with a molar absorptivity of  $3.7 \cdot 10^4 \text{ l} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ . The dissociation constants, determined by the Stentrom and Goldsmith method<sup>10</sup> and from absorbance-pH curves were:  $\text{p}K_1 = 5.72 \pm 0.02$ ,  $\text{p}K_2 = 8.09 \pm 0.01$  (at 25°C and  $I = 0.05$ ) for a confidence limit of 95% and for 4 determinations.

It can be deduced from these figures that MTDAR is not appropriate as acid-base indicator.

MTDAR forms mainly orange, pink and red complexes with several ions. For  $C_M = C_R = 10^{-4} \text{ mol l}^{-1}$  the following reactions occur: pH 1.5: Bi(ochreous), Zr (orange), Pd (green). pH = 6.5: Hg(II) (pink), Pb (pink), Bi (orange-reddish), Co(II) (orange-reddish), Zr (pink), Th (orange-reddish), V(V) (red), Pd (brownish). pH 10: Hg, Pb, Bi and Zr complexes give a precipitate.

Among these complexes, the Pb-complex has a very bright colour. For this reason we made a quantitative study.

Fig. 2 shows the absorption spectra of the Pb-complex *versus* pH. It can be observed that a maximum appears at pH 8 and  $\lambda = 525 \text{ nm}$ . The colour of the complex is reached immediately. Beer's law is obeyed between 0 and 9 ppm of Pb and fol-

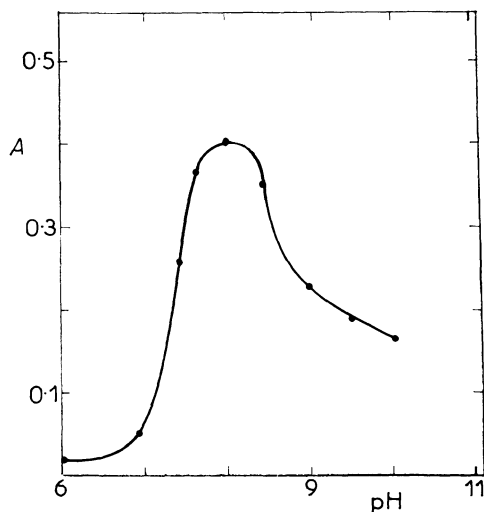


FIG. 2  
Absorbance-pH curves for Pb-complex

lows the equation:

$$y = 0.0785x + 0.023, \quad (1)$$

where  $y$  is absorbance and  $x$  ppm of Pb.

The optimum range is 2–8 ppm of Pb from Ringbom plot<sup>11</sup>. The molar absorptivity of the complex is  $2.0 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ . The stoichiometry of the complex, determined by molar ratio<sup>12</sup> and continuous variations methods<sup>13</sup> is 1 : 1. The complex formation constant estimated from Job's method of continuous variations at pH 8 is  $\beta = 7.9 \cdot 10^5$ .

In the photometric determination of Pb, ions such as Cu(II), Cd(II), Zn(II), Sn(II), Mg(II), Ca(II), Sr(II), Ba(II),  $\text{F}^-$  and  $\text{CN}^-$  in molar ratio 10 : 1 with respect to Pb, do not cause interference, while Fe(III), Zr(IV), W(VI) and V(V) in proportion 1 : 1, Al(III) in proportion 2 : 1 and Mn(II) and Co(II) in proportion 5 : 1 produce serious interferences.

With respect to these results, we have concluded that MTDAR could be appropriate to spectrophotometric determination of Pb, but it is more useful as metallochromic indicator for EDTA titrations.

To find the best conditions for a complexometric titrations the photometric titration unit was used. Using the 921–221 green filter, a maximum quantity of indicator of 4 drops of ethanolic solution 0.2% (m/V) in 50 ml of Pb solution was found. The best pH to the titration is 8, and the concentration range to which the method is applied is 5–50 mg.

The relative standard deviation of 10 photometric titrations of 10 mg Pb is  $1.14 \cdot 10^{-2}$ . The error is  $-0.09\%$ .

Under these conditions, the colour change produced at the equivalent point is from red to yellowish-orange.

The visual determination of the end point is sharp without having to heat the solution. The change in colour can be seen in the same way in any kind of light.

The result of 10 visual titrations of less than 30 mg Pb in 100 ml of solution shows an error of 0.19%, with a variation coefficient of 0.25%.

The chromatic transition of the indicator in this titration was carried out by applying the CIE (ref.<sup>14</sup>) and Reilley<sup>15</sup> methods.

Table I shows the values of complementary chromatic coordinates, dichromatism and optic concentration values to initial and final points of Pb titration with several well-known metallochromic indicators. The graph of these chromatic transitions in the complementary colour diagram (Fig. 3) suggests that MTDAR is of a greater quality than Erio T and methyl thymol blue. Moreover, due to the location in the diagram, this MTDAR-transition can be improved by adding an inert dyestuff.

The chromatic transition will thus pass through the grey point just before reaching the end point of titration.

Among appropriate inert dyestuff methylene blue and indigo carmine are found, as Vytřas and Kotrly<sup>16</sup> proved in their study of the screening applied to acid-base indicators.

TABLE I

Complementary colour coordinates, dichromatism and optic concentration values for some well known indicators for the complexometric titration of Pb with EDTA

Indicator		$Q_x$	$Q_y$	$D$	$J$
Xylenol orange	0	0.380	0.485	0.176	0.5816
	1	0.198	0.195	-0.120	0.2835
Erio T	0	0.344	0.405	0.009	0.2459
	1	0.346	0.394	0.126	0.3890
Methyl thymol blue	0	0.387	0.420	0.091	0.2577
	1	0.281	0.304	-0.172	0.1553
MTDAR	0	0.142	0.347	0.234	1.1907
	1	0.125	0.136	-0.037	1.2177
MTDAR + indigo carmine	0	0.316	0.385	-0.074	1.7636
	1	0.301	0.261	0.061	1.8202

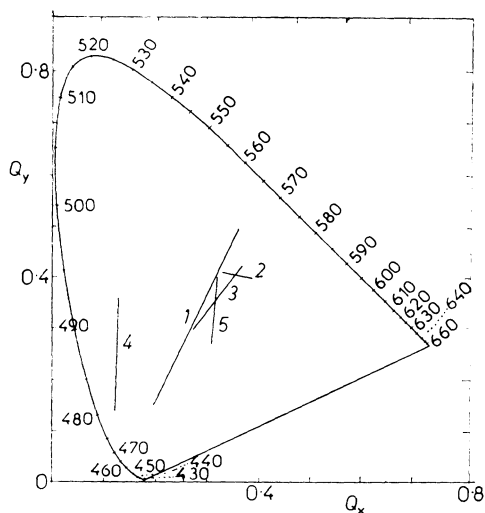


FIG. 3

Chromatic transitions of several indicators to the complexometric titration of Pb. 1 Xylenol orange; 2 Erio T; 3 Methyl thymol Blue; 4 MTDAR; 5 MTDAR + indigo carmine

When the ratio MTDAR-indigo carmine is 2.2 : 3.7 the colour change of the indicator mixture in the titration of Pb is from violet to brilliant green. The titrated solution is almost colorless just before the end point.

The new chromatic transition here obtained is plotted in Fig. 3 and the corresponding data are included in Table I. The  $F^-$  and  $CN^-$  do not cause interference in the titration, even in 10 times higher mass concentrations than Pb. Ca(II), Sr(II), Ba(II) and Mg(II) do not interfere. The interference of Cu(II), Hg(II), Co(II) and Ni(II) can be avoided by adding  $CN^-$  and the interference of Al by adding  $F^-$  in excess. Zn(II) and Cd(II) interfere.

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