5-METHYL-1,3,4-THIADIAZOLYL-(2-AZO-6)-3,4-DIMETHYLPHENOL AS NEW ANALYTICAL REAGENT*

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A synthesis of the new reagent 5-methyl-1,3,4-thiadiazolyl-(2-azo-6)-3,4-dimethylphenol (MTDADF) is described. The dissociation constant of the OH group is determined by spectrophotometry ($pK_a = 7{\cdot}88 \pm 0{\cdot}05$). The reaction of MTDADF with Ni(II) is quantitatively studied. Beer's law is obeyed in the interval of 0–2·4 ppm of Ni(II), the optimum range being 0·4 to 2·0 ppm, as deducted from a Ringbom graph. The stoichiometry of the complex corresponds to the ML_2 type. Many other ions interfere seriously in the determination of Ni(II).

Heterocyclic azo-compounds are widely used for the photometric and the extraction-photometric determination of ions of almost all metals except of alkali and alkaline-earth ones[1]. Their use is promoted by the high sensitivity of their reaction with a series of ions. Amines of nitrogenous heterocycles as pyridine[2], benzothiazole, quinoline, pyrimidine[3], antipyrine[4], triazole[5–7], thiazole[8] and thiadiazole were used as bases. It is important to remark that the presence of a further N heteroatom in the heterocyclic ring substantially modifies properties of the reagent such as absorption maxima and colour intensity of the complexes with metallic ions.

However, ther are few studies pertaining to the analytical properties of thiadiazole azo compounds in the literature[9,10]. In a previous paper[11], we proved that a compound with a 1,3,4-thiadiazol ring is a more sensitive reagent for Cd and Zn (ref.[12]) determination than a similar thiazol derivative. Moreover, the thiadiazol derivative has proved to be more selective than the thiazol. Ther are few theoretical papers studying the influence of methyl groups in the coupling component of the azo derivatives on the sensitivity and selectivity of those reagents.

In a review about the analytical properties of azo derivatives of heterocyclic compounds in which the thiadiazol ring was not included, Ivanov[13] suggests that the presence of methyl groups in different positions in the coupling component produces a decrease in the sensitivity of the reagents.

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In order to verify the influence of these methyl groups in the thiadiazol derivatives we have synthetized the 5-methyl-1,3,4-thiadiazolyl-(2-azo-6)-3,4-dimethylphenol and studied its reactivity with metallic ions and the spectrophotometric determination of Ni. The results obtained are compared with those corresponding to thiazolyl-azo-4-methylphenol (TAC).

EXPERIMENTAL

Apparatus and Reagents

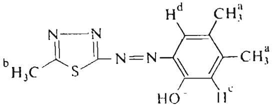
A Pye Unicam SP8-100 spectrophotometer with 1 cm silica cells was used for measuring absorbance and a Radiometer 51 pHmeter for pH measurements. MTDADF solution, 0·01% (m/V) in ethanol, was stable for several weeks. Buffers solutions according to Clark and Lubbs were used. A standard nickel solution (1 gl^{-1}) was prepared by dissolving pure metal (Merck).

Synthesis of MTDADF

2-Amino-5-methyl-1,3,4-thiadiazol (1·18 g) was dissolved in 15 ml of H_2SO_4, 50% (m/V), and cooled below +5°C. A saturated, cooled (< 5°C) solution of sodium nitrite (0·69 g) was added, while stirring, into the solution of 2-amino-5-methyl-1,3,4-thiadiazol. The diazonium salt solution obtained was then poured slowly, while stirring, into a concentrated solution of 3,4-dimethylphenol (1·22 g) in ethanol. This reaction mixture was diluted to 50 ml with cold water and set to pH 3—4 with sodium hydroxide. The red orange precipitate was filtered off and washed with cold water. The product was recrystallized from ethanol. Its purity was checked by TLC on silica gel with $CHCl_3$-methanol mixture as the eluent. The yield approx. 100%, m.p. 177 ± 1°C. For $C_{11}H_{12}N_4OS$ (248·3) calculated: 53·22% C; 4·83% H; 22·58% N; found: 53·79% C; 4·95% H; 22·53% N.

Properties of the Reagent

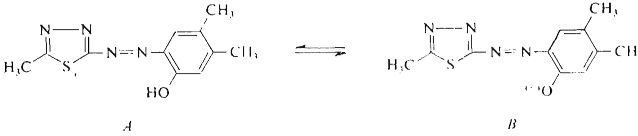
MTDADF (red orange needles) is sparingly soluble in water, moderately soluble in methanol and ethanol and very soluble in $CHCl_3$. The infrared spectrum (potassium bromide pellet) ν_{max} (cm^{-1}) was as follow:s —OH stretching (3 500); —C=N-heterocyclic (1 660, 1 640); C—O def. (1 300); —CH_3 vibr. (1 400—1 180); C—H aromatic (760, 740). The NMR spectrum (^1H, $CDCl_3$, δ, ppm) was as follows: 2·25 (6 H, s, —CH_3^a); 2·8 (5 H, s, —CH_3^b); 6·85 (H, s, —H^c); 7·75 (H, s, —H^d).



SCHEME 1

RESULTS AND DISCUSSION

MTDADF dissolves in concentrated sulfuric acid to violet solution which turns yellow when diluted with water. From pH 2 to pH 12 the MTDADF solution changes its colour from yellow (pH < 7) to red violet (pH > 8). This can be explained by the existence of two forms: (Scheme 2)



SCHEME 2

and confirmed by one isosbestic point ($\lambda = 477$ nm) in the absorption spectra of reagent between pH 2 and pH 12 (Fig. 1). At pH < 4·2 the reagent form *A*, at pH >

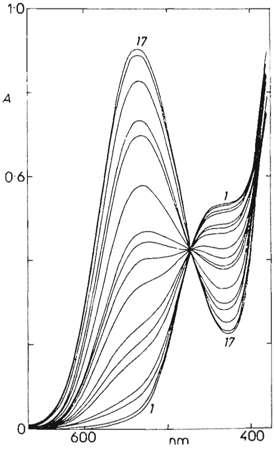


FIG. 1

Absorption spectra of the reagent at different pH values. $C_R = 8{\cdot}06 \,.\, 10^{-2}$ mol l^{-1}. pH: *1* 4·20; *2* 5·33; *3* 6·40; *4* 6·60; *5* 6·98; *6* 7·00; *7* 7·11; *8* 7·49; *9* 7·65; *10* 7·73; *11* 7·81; *12* 8·14; *13* 8·63; *14* 8·80; *15* 9·25; *16* 10·48; *17* 11·32. 25°C. $I = 0{\cdot}1$

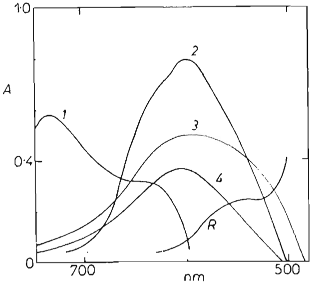


FIG. 2

Absorption spectra of several complexes with MTDADF at pH 7·2 $C_R = 8{\cdot}06 \,.\, 10^{-3}$ mol . . l^{-1}. *1* Fe(III), $C_M = 3{\cdot}58 \,.\, 10^{-5}$ mol l^{-1}; 2 Ni(II), $C_M = 3{\cdot}4 \,.\, 10^{-5}$ mol l^{-1}; 3 Co(II), $C_M = 3{\cdot}4 \,.\, 10^{-5}$ mol l^{-1}; *4* Cu(II), $C_M = 3{\cdot}14 \,.\, 10^{-5}$ mol l^{-1}, *R*-reagent

$> 11{\cdot}4$ the reagent form B are predominating. At pH < 0 the spectrum changed, and in this pH range the decomposition of the reagent was observed. The dissociation constant determined by Stentrom and Goldsmith method[14] and from A–pH curves was $pK_a = 7{\cdot}88 \pm 0{\cdot}05$ (at 25°C and $I = 0{\cdot}05$).

The MTDADF forms green, blue or violet complexes with several ions. The absorption spectra of some complexes are shown in Fig. 2. The optimum pH for the complex formation and λ_{max} as well as ε_{max} are given in Table I, together with similar values for TAC.

Thus, the optimum wavelength for nickel determination is 625 nm. The absorbance of the reagent at this wavelength is negligible which is advantageous because a large excess of reagent can be employed. As Ni–MTDADF complex is moderately soluble in water, ethanol should be added to get its volume ratio 0·6.

The colour of the complex develops instantly. It remains stable for at least 30 min at 25°C, but 3·8% decrease of absorbance at 625 nm was observed after 60 min. The absorption spectrum of the nickel complex measured against a reagent blank shows two maxima in the range 380–700 nm. One absorption maximum lies in the range from 580 nm to 650 nm and with increasing pH a bathochromic shift occurs.

TABLE I

Optimum pH values, λ_{max} and molar absorptivities of several complexes with MTFADF and TAC

Ion	MTDADF			TAC			Ref.
	pH	λ_{max}	ε/l mol^{-1} vm^{-1}	pH	λ_{max}	ε/l mol^{-1} cm^{-1}	
Cu(II)	7·9	610	$1{\cdot}07 \cdot 10^4$	8·2–8·3	610	—	—
Fe(III)	9·9	412	$7{\cdot}00 \cdot 10^3$	—	—	—	—
Pb(II)	6·9	580	$5{\cdot}90 \cdot 10^3$	—	—	—	—
Hg(II)	7·1	590	230	4·5–8·8	602	$1{\cdot}03 \cdot 10^4$	15
Hg(I)	6·9	605	$3{\cdot}40 \cdot 10^3$	—	—	—	—
Zn(II)	7·0	550	$5{\cdot}2 \cdot 10^3$	—	565	—	15
Pd(II)	5·1	495	$1{\cdot}52 \cdot 10^4$	—	—	—	—
Co(II)	7·3	570	$6{\cdot}95 \cdot 10^3$	—	—	—	—
Cd(II)	7·5	553	$4{\cdot}30 \cdot 10^3$	—	565	—	15
U(VI)	6·5	550	$8{\cdot}70 \cdot 10^3$	—	—	—	—
Ce(III)	6·8	520	957	—	564	7 950	15
Sb(III)	7·1	515	975	—	—	—	—
La(III)	6·8	505	928	—	565	800–1 300	15
Ni(II)	7·9	625	$1{\cdot}98 \cdot 10^4$	6–10	617	$3{\cdot}0 \cdot 10^4$	15

The second absorption maximum lies in the wavelength range from 340 nm to 430 nm and its hypsochromic shift is observed with increasing pH values. At pH $\geqq 8$ the Ni–MTDADF complex has an absorption maxima at 625 and 413 nm. They do not change with the pH change, the ε_{max} values, however, do change. The optimum pH value used is 8. The molar absorptivity (625 nm, pH 8) is $1{\cdot}98 \,.\, 10^4$ l mol^{-1} cm^{-1} and the Sandell sensitivity is 0·0029 μg cm^{-2}. Beer's law is obeyed from 0·2 ppm to 2·8 ppm at the optimum conditions before described, and the relative error of the method is 0·18%.

The stoichiometry of the complex determined by the continuous variation method and the molar ratio method showed that the metal to ligand ratio is 1 : 2. The complex formation constant estimate from Job's method of continuous variations is $\beta_2 =$ $= 1{\cdot}0 \,.\, 10^{10}$.

TABLE II

Determination of Ni(II) in the presence of various ions. Given 100 μg Ni

Ion	Added, μg	Ni found, μg	Relative error, U
Co(II)	80	134·7	+ 34·74
V(IV)	59	106·9	+ 6·90
Zn(II)	150	101·7	+ 1·69
Pb(II)	100	102·7	+ 2·78
Cd(II)	500	101·1	+ 1·09
	1 000	113·8	+ 13·86
Mg(II)	10 000	100·7	+ 0·73
La(III)	400	100·2	+ 0·24
	1 000	100·2	+ 2·31
Pd(II)	75	101·2	+ 1·22
Cu(II)	20	106·6	+ 6·63
Hg(II)	100	92·4	− 7·60
Hg(I)	90	98·1	− 1·99
Mo(VI)	1 000	99·0	− 1·20
	2 000	98·0	− 2·40
Mn(II)	2 000	101·2	+ 1·21
Th(IV)	100	89·7	− 10·27
Zr(IV)	1 000	93·8	− 6·21
Fe(III)	20	83·0	− 17·08
Ce(III)	1 000	92·2	− 7·80
Ag(I)	1 000	104·7	+ 4·75
Au(III)	1 000	95·7	− 4·26
Sb(III)	1 000	83·6	− 16·46
Bi(III)	1 000	110·3	+ 10·36

Recommended Procedure for Nickel Determination

To a solution of Ni $<$ 2·4 ppm in a 50 ml volumetric flask add 10 ml of MTDADF solution (0·01%) in ethanol and 10 ml of buffer solution (borax–NaOH, pH = 8) and 20 ml of ethanol. Dilute to the mark with distilled water. Measure the absorbance of the solution at 625 nm against a reagent blank.

Effect of Other Ions

Synthetic solutions containing a known amount of Ni (100 μg) and various amounts of other ions were prepared and the proposed procedure for the determination of Ni was followed. The results are given in Table II.

It is observed (Table I) that the wavelength of the absorption maximum for the Ni complex is scarcely affected by the second methyl group, but the molar absorptivity is greatly diminished. This results are in agreement with those of Ivanov for pyridyl-azo-compounds. The marked decrease in sensitivity can be attributed to steric hindrance. However, the color change from free reagent to nickel complex is very sharp. This reagent is, therefore, suggested for the use as metallochromic indicator in the complexometric titration of Ni. This aspect is studied in another communication[16].

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