

POTENTIOMETRIC TITRATION OF TRIAZOLETHIOLS AND TETRAZOLETHIOLS WITH IODINE IN ALKALINE MEDIUMWitold CIESIELSKI^{1,*} and Anna KRENC²

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The iodimetric determination of triazolethiols and tetrazolethiols in alkaline medium is presented. The volumetric titration with potentiometric end-point detection was applied. The range of determination, in which the error is lower than 1%, is 20–2 000 μmol for 1*H*-1,2,4-triazole-3-thiol (**1**), 25–1 000 μmol for 3-phenyl-1*H*-1,2,4-triazole-5-thiol (**2**), 25–500 μmol for 4-methyl-5-(trifluoromethyl)-4*H*-1,2,4-triazole-3-thiol (**3**), 50–500 μmol for 3-amino-1*H*-1,2,4-triazole-5-thiol (**4**), 10–1 000 μmol for sodium (5-mercapto-1*H*-tetrazol-1-yl)acetate (**5**), 125–500 μmol for 1-phenyl-1*H*-tetrazole-5-thiol (**6**) and 50–1 000 μmol for 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**). The relative standard deviation for all determinations was below 1%. The shape of potentiometric titration curve of **6** and **7** is noteworthy at higher concentrations of sodium hydroxide and depends on the type of the indicator electrode (platinum, gold). An introduction of iodine results in a strong potential drop. Some systems do not follow the Nernst equation.

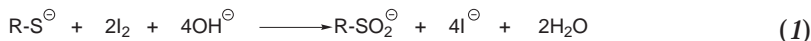
Keywords: Iodimetry; Potentiometry; Volumetry; Triazolethiols; Tetrazolethiols; Thiols; Determination.

Thiols are used in various spheres of industry and technology as corrosion inhibitors, stabilizers for radiolabelled nucleothiol and collectors in flotation. They are also used in production of photographic emulsions, developers and lithographic plate materials. 1*H*-1,2,4-Triazole-3-thiol (**1**) is applicable as an antidote in nitrogen mustard poisoning. Thiols are also used in medicine, e.g. tetrazolethiols are useful for treatment of hyperthyroidism.

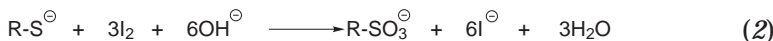
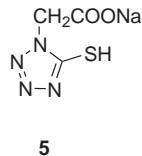
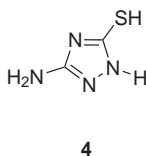
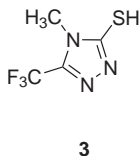
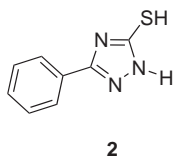
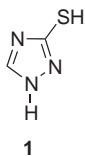
We found only few methods of determination of the studied compounds. 1-Phenyl-1*H*-tetrazole-5-thiol (**6**) was determined by coulometric titration with generated mercury(II)¹, silver(I) or vanadium(V)^{2,3}. The determination of thiols has been also carried out using kinetic^{4,5}, spectrophotometric⁶ and polarographic⁷ methods.

The iodimetric determination of pyrimidine-2-thiols⁸, pyridine-2-thiols⁹ and 2-thiouracils¹⁰ in alkaline medium was worked out.

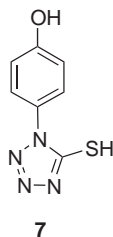
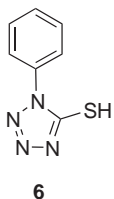
In this paper, the determination of triazolethiols and tetrazolethiols by direct titration with iodine in an alkaline medium is presented. The reaction between iodine and the thiols is based on the Eqs (1) and (2).



for thiols 1-5:



for thiols 6 and 7:



EXPERIMENTAL

Reagents and Apparatus

The double-distilled water in glass apparatus and the following reagents of analytical grade purity: sodium hydroxide, potassium iodide, iodine (Factory of Chemical Reagents, Gliwice, Poland), 1*H*-1,2,4-triazole-3-thiol (1) (Fluka), 3-phenyl-1*H*-1,2,4-triazole-5-thiol (2) (Lancaster), 4-methyl-5-(trifluoromethyl)-4*H*-1,2,4-triazole-3-thiol (3) (Lancaster), 3-amino-1*H*-1,2,4-triazole-5-thiol (4) (Avocado), sodium (5-mercapto-1*H*-tetrazol-1-yl)acetate (5) (Lancaster), 1-phenyl-1*H*-tetrazole-5-thiol (6) (Aldrich) and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (7) (Aldrich) were used. 4-Methyl-5-(trifluoromethyl)-4*H*-1,2,4-triazole-3-thiol (3) and 1-phenyl-1*H*-tetrazole-5-thiol (6) were purified by dissolving in 3 M sodium hydroxide solution and reprecipitating with glacial acetic acid. For purification of 3-phenyl-1*H*-1,2,4-triazole-5-thiol (2) and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (7), crystallization from water was used. Standard solutions were obtained by dissolving a weighed amount of the particular reagent in a suitable solution of sodium hydroxide. A type CP-315 pH meter made by Elmetron (Gliwice, Poland), with a saturated calomel electrode and platinum electrode, was used.

Procedure

Samples of thiols were dissolved in 50 ml of a suitable solution of sodium hydroxide (concentrations are given in Tables I and II) and titrated with iodine, using the potentiometric detection of the end-point with a platinum electrode as the indicator electrode and a saturated calomel electrode. The equivalence point of the reaction was the inflection point on the titration curve.

RESULTS AND DISCUSSION

The results of the determination of compounds have been presented in Tables I and II. In titrations of the larger or smaller amount of thiols than given in Tables, the error increased above 1%.

TABLE I

Results of potentiometric determination of triazolethiols in alkaline medium; $n = 6$

Compound	NaOH concentration mol l ⁻¹	Taken μmol	Found
			$\bar{x} \pm t_{0.95} \frac{s}{\sqrt{n}}$ μmol
1 <i>H</i> -1,2,4-Triazole-3-thiol (1)	2	20.00	20.18 ± 0.04
		50.00	50.06 ± 0.10
		100.0	100.2 ± 0.13
		250.0	249.2 ± 0.4
		500.0	495.9 ± 1.1
		1 000	1 006 ± 2
		2 000	2 007 ± 3
3-Phenyl-1 <i>H</i> -1,2,4-triazole-5-thiol (2)	0.5	25.00	25.14 ± 0.05
		50.00	50.10 ± 0.08
		125.0	124.8 ± 0.5
		250.0	249.8 ± 0.8
		500.0	497.6 ± 1.1
		1 000	1 007 ± 1
4-Methyl-5-(trifluoromethyl)-4 <i>H</i> -1,2,4-triazole-3-thiol (3)	1	25.00	25.14 ± 0.06
		50.00	50.08 ± 0.16
		125.0	124.9 ± 0.7
		250.0	250.1 ± 0.7
		500.0	496.8 ± 0.7
3-Amino-1 <i>H</i> -1,2,4-triazole-5-thiol (4)	5	50.00	49.69 ± 0.14
		100.0	99.72 ± 0.15
		200.0	198.9 ± 0.7
		500.0	497.6 ± 2.2

In acid and neutral media, the reaction rate of iodine with thiol was very low and iodimetric determination of these compounds was impossible. A change of the stoichiometry of the reaction between thiol and iodine in alkaline medium compared with the course of reaction in neutral or acid media was observed.

Iodine disproportionates quickly in alkaline medium to give iodide and hypiodite ions, so hypiodite is the actual oxidizing agent. The titration in alkaline medium is possible if the reaction rate of hypiodite ions with thiol is higher than the rate of disproportionation of hypiodite ions. It was found that the number of electrons transferred in the reaction of 1 mol of 1*H*-1,2,4-triazole-3-thiol (**1**), 3-phenyl-1*H*-1,2,4-triazole-5-thiol (**2**), 4-methyl-5-(trifluoromethyl)-4*H*-1,2,4-triazole-3-thiol (**3**), sodium (5-mercapto-1*H*-tetrazol-1-yl)acetate (**5**) and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**) with iodine depends on the concentrations of sodium hydroxide solutions only to a certain degree. However, the number of electrons transferred in the reaction of 1 mol of 1-phenyl-1*H*-tetrazole-5-thiol (**6**) with iodine de-

TABLE II
Results of potentiometric determination of tetrazolethiols in alkaline medium; $n = 6$

Compound	NaOH concentration mol l ⁻¹	Taken μmol	Found $\bar{x} \pm t_{0.95} \frac{s}{\sqrt{n}}$ μmol
Sodium (5-mercapto-1 <i>H</i> -tetrazol-1-yl)- acetate (5)	2	10.00	9.943 ± 0.027
		20.00	20.08 ± 0.05
		50.0	49.95 ± 0.20
		100.0	99.97 ± 0.22
		250.0	250.0 ± 0.9
		500.0	502.7 ± 1.4
		1 000	1 005 ± 1
1-Phenyl-1 <i>H</i> -tetrazole-5-thiol (6)	0.1	125.0	125.3 ± 0.4
		250.0	251.1 ± 0.9
		400.0	399.7 ± 0.7
	0.5	500.0	497.4 ± 0.8
1-(4-Hydroxyphenyl)-1 <i>H</i> -tetrazole- 5-thiol (7)	1	50.00	50.37 ± 0.05
		100.0	100.8 ± 0.2
		200.0	200.3 ± 0.5
		500.0	502.8 ± 1.4
		1 000.0	1 006 ± 2

depends on the concentration of sodium hydroxide, increasing with increasing NaOH concentration. At lower NaOH concentrations, the reaction between 1-phenyl-1*H*-tetrazole-5-thiol (**6**) and iodine did not proceed stoichiometrically and the number of electrons transferred in the reaction of 1 mol was less than 6. An increase in NaOH concentration over 1 mol l⁻¹ caused an increase in the number of electrons transferred in the reaction of 1 mol because the product of reaction (1) reacted with iodine. In the case of 3-amino-1*H*-1,2,4-triazole-5-thiol (**4**), an increase in concentration of sodium hydroxide solution brought about a decrease in the number of electrons transferred in the reaction of 1 mol of this compound.

Every concentration range of titrated compounds needs a suitable concentration of sodium hydroxide to run the reaction according to Eqs (1) or (2). In the titration of 25–500 μmol of 3-phenyl-1*H*-1,2,4-triazole-5-thiol (**2**), the results were valid when the initial concentration of sodium hydroxide was 0.5 mol l⁻¹, but the titration of 1 000 μmol of this compound requires a higher initial concentration of sodium hydroxide (1 mol l⁻¹). The determination of 500 μmol of 1-phenyl-1*H*-tetrazole-5-thiol (**6**) also requires a higher concentration of sodium hydroxide (0.5 mol l⁻¹) than the titration of 125–400 μmol of **6**.

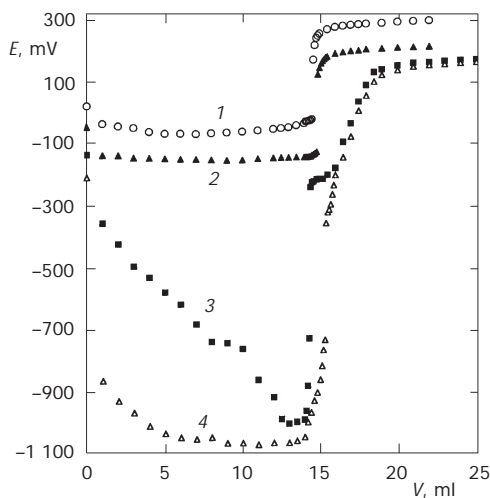


FIG. 1

Potentiometric titration curves for 250 μmol of 1-phenyl-1*H*-tetrazole-5-thiol (**6**) with 0.1 M iodine in: 0.1 M sodium hydroxide (1), 1 M sodium hydroxide (2), 5 M sodium hydroxide (3), 10 M sodium hydroxide (4)

The shape of potentiometric titration curves of 1-phenyl-1*H*-tetrazole-5-thiol (**6**) and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**) is noteworthy at higher concentrations of sodium hydroxide (Fig. 1, curves 3 and 4). A small amount of iodine added brings about a strong potential drop in the initial part of the curve. Similar curves were obtained in the titration of pyrimidine-2-thiol⁸, thiopental¹¹ and 2-thiocytosine¹². We did not observe such a phenomenon in potentiometric titration of these compounds using a gold electrode as indicator electrode (Fig. 2, curve 1). The shape of the titration curves obtained at high sodium hydroxide concentrations depends on the material of the indicator electrode and is associated with adsorption processes and charging of the double electric layer at the phase boundary.

It was found that 1,2,4-triazole-3-thiol substituted with phenyl, trifluoromethyl and methyl groups requires lower concentrations of sodium hydroxide in the titration with iodine than the titration of 1*H*-1,2,4-triazole-3-thiol (**1**). The determination of 3-amino-1*H*-1,2,4-triazole-5-thiol (**4**) requires higher concentrations of NaOH in the reaction solution. The acceptor groups cause lower electron density at the sulfur atom in SH group and this is the reason why 3-phenyl-1*H*-1,2,4-triazole-5-thiol (**2**) and 4-methyl-5-(trifluoromethyl)-4*H*-1,2,4-triazole-3-thiol (**3**) are oxidized easier than 1*H*-1,2,4-triazole-3-thiol (**1**).

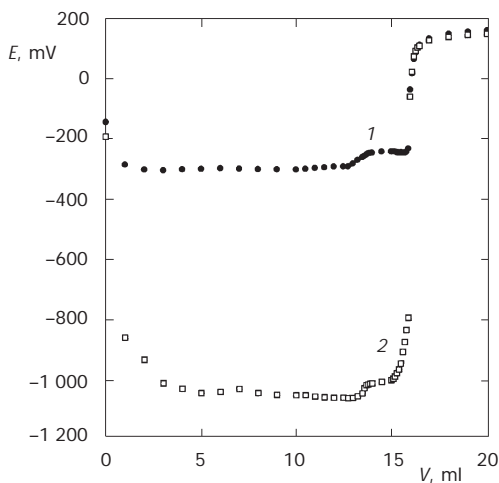


FIG. 2

Potentiometric titration curves for 250 μmol of 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**) with 0.1 M iodine in 10 M sodium hydroxide using a gold indicator electrode (1), a platinum indicator electrode (2)

Comparing the conditions of determination of sodium (5-mercapto-1*H*-tetrazol-1-yl)acetate (**5**), 1-phenyl-1*H*-tetrazole-5-thiol (**6**) and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**), we observed changing stoichiometry of the reaction. The number of electrons transferred per mol of 1-phenyl-1*H*-tetrazole-5-thiol (**6**) and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**) is 6. Moreover, the determination of **6** requires a lower concentration of sodium hydroxide. A hydroxy group in aromatic ring makes the oxidation difficult and the determination of 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (**7**) requires higher concentrations of sodium hydroxide than the determination of 1-phenyl-1*H*-tetrazole-5-thiol (**6**).

The new method of iodimetric determination of triazolethiols and tetrazolethiols is characterised by a short analysis time, high precision and accuracy, determination over a broader range of concentrations of thiols, simplicity and the use of commonly available reagents.

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