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The use of tetrazolium salts in inorganic analysis

K B Gavazov, A N Dimitrov, V D Lekova

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Abstract. The use of tetrazolium salts for extraction, spectrophotometric and potentiometric determination of various elements and ions is described. The optimum conditions for extraction of tetrazolium ion-associated complexes are analysed. Chromogenic and other systems derived from tetrazolium salts and their applications in the analysis of industrial and natural samples are discussed. The bibliography includes 118 references.

I. Introduction

Tetrazolium salts (TS) are heterocyclic compounds the five-membered rings in which contain four nitrogen atoms; one of these atoms bears a positive charge. The methods for synthesis, properties and applications of TS have been described.[1] Substituted TS usually contain up to three substituents, *viz*., at the carbon atom in position 5 and at two nitrogen atoms. The following combinations of positions of substitution in the tetrazolium ring are possible: 1, 2, 5; 1, 3, 5; 1, 4, 5 and 2, 3, 5. The most extensively studied 2,3,5-trisubstituted TS (Table 1) are the topic of the present review.

The first tetrazolium salt, *viz*., 2,3,5-triphenyltetrazolium chloride, was synthesised in the late 19th century independently by H von Pechman and E Bamberger. Tetrazolium salts attracted the attention of investigators by virtue of their ability to be converted into coloured formazans under the action of chemical and biological reducing agents. Commercial production of TS began half a century later. Tetrazolium salts came into wide use as redox indicators for determination of enzymes and other systems.[1, 2] At present, tetrazolium salts are among the most efficient reagents in cell biology designed for determination of metabolic activities of various cells (from mammalian to bacterial).[2] In addition, TS have found application as catalysts and photosensitive materials.[1]

In the 1960 – 1970s, a new trend in the chemistry of TS emerged, namely, the chemistry of ion-associated complexes (IAC) of tetrazolium cations with simple and complex anions.[3, 4] Unlike the original salts, these complexes are poorly soluble in water and can selectively be extracted with appropriate organic solvents. Due to the ability to form IAC, tetrazolium salts served as the basis for the development of analytical (*e.g*., extraction – photometric, *etc*.) techniques for the determination of metal ions and non-metal derivatives incorporated in such complexes.

The first surveys[3, 4] of the extraction and analytical applications of tetrazolium ion-associated complexes (TIAC) published before 1983 appeared in 1984. Since then, numerous data have been reported on ion-associated complexes with different tetrazolium cations and their applications for the extraction of various ions and elements. Competitive extraction – photometric and potentiometric methods making use of TIAC and photometric and catalytic photometric methods based on TS reduction were also developed.

The aim of the present review is to generalise and to systematise the data on the applications of TS in inorganic analysis published between 1984 and 2006.

II. Preparation and properties of tetrazolium ion-associated complexes

Tetrazolium ion-associated complexes are crystalline compounds that are stable under ordinary conditions, poorly soluble in water and easily soluble in diverse organic solvents. They are decomposed upon heating to 180 – 220 °C (Refs 5 and 6) or under direct sunlight.[3, 4, 7, 8] In weakly basic solutions, *e.g*., at pH ~10, the N(2) – N(3) bond of the tetrazolium ring is cleaved to yield coloured formazans.[1, 3, 4, 7]

The chromophore properties of TIAC usually represent a combination of chromophore properties of the constituent ions, *viz*., tetrazolium cations and complex anions. This suggests the predominantly ionic nature of the chemical bond in TIAC. The tetrazolium salts absorb light in the visible and UV spectral regions, their absorption maxima usually lie at 200 – 260 nm with exception of MTT, which has an absorption maximum in the visible region (~380 nm).

TIAC are widely employed in analytical chemistry as components of extraction systems. They are used for both isolation of ions from complex mixtures and quantitative determination of metal cations and other inorganic ions in various natural and industrial samples by extraction – spectrophotometric methods. The properties of TIAC allow their extraction from aqueous solutions and govern the extraction characteristics of systems employed in the analysis (Tables 2 and 3). In addition to the general characteristics of the method (*e.g*., solvents, extraction time, pH, *etc*.), these tables list the extraction constants (which

K B Gavazov, A N Dimitrov, V D Lekova Department of Chemistry, Plovdiv University 'Paisii Hilendarski', Tsar Assen st. 24, 4000 Plovdiv, Bulgaria. Fax (359-32) 62 83 90, tel. (359-32) 26 14 20, e-mail: kgavazov@abv.bg (K B Gavazov), vanlek@pu.acad.bg (V D Lekova), tel. (359-32) 26 13 24, e-mail: andim@pu.acad.bg (A N Dimitrov)

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Table 1. Tetrazolium salts used for the preparation of ion-associated complexes.

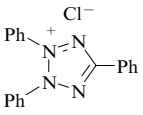
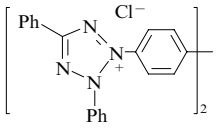
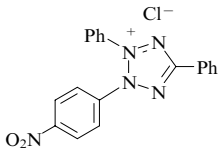
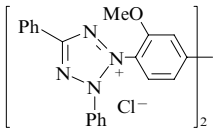
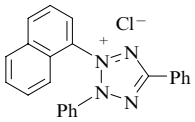
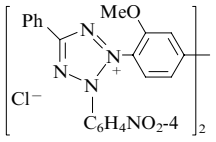
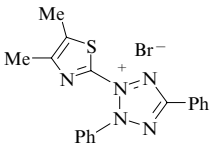
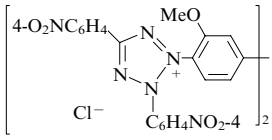
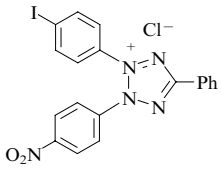
Formula	Name	Abbreviation	Mol. mass	Formula	Name	Abbreviation	Mol. mass
	2,3,5-triphenyl-2*H*-tetrazolium chloride	TT	334.41		3,3′-(4,4′-biphenylene)-bis(2,5-diphenyl-2*H*-tetrazolium) chloride (Neotetrazolium chloride)	NT	667.60
	2-(4-nitrophenyl)-3,5-diphenyl-2*H*-tetrazolium chloride	p-NT	379.82		3,3′-(3,3′-dimethoxy-4,4′-biphenylene)bis(2,5-diphenyl-2*H*-tetrazolium) chloride (Tetrazolium Blue chloride)	BT	727.66
	3-(1-naphthyl)-2,5-diphenyl-2*H*-tetrazolium chloride (Tetrazolium Violet)	TV	384.86		3,3′-(3,3′-dimethoxy-4,4′-biphenylene)bis[2-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium] chloride (Nitro Blue Tetrazolium chloride)	NBT	817.65
	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide (Thiazolyl Blue Tetrazolium Bromide)	MTT	414.31		3,3′-(3,3′-dimethoxy-4,4′-biphenylene)bis-[2,5-di(4-nitrophenyl)-2*H*-tetrazolium] chloride (Tetranitro-tetrazolium Blue chloride)	TNBT	907.6
	3-(4-iodophenyl)-2-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride	INT	505.70				

Table 2. Extraction characteristics of tetrazolium ion-associated complexes with inorganic anions.

Extraction system		pH	Time of extraction /min	log K_{ex}	log K_D	log β	R (%)	Ref.
TIAC	solvent							
$(INT^+)BrO_3^-$	$CHCl_3$	broad range	3	1.9	1.19	0.7	93.9	9
$(MTT^+)BrO_3^-$	$CHCl_3$	the same	3	1.9	1.29	0.6	95.1	9
$(TT^+)BrO_3^-$	$CHCl_3$	"	3	0.8	0.35	0.4	69.1	9
$(TNBT^{2+})[Cd(SCN)_4]^{2-}$	$C_2H_4Cl_2$ + + $(CH_3)_2O$	2–6	2	2.8	0.85	2.0	87.6	10
$(TT^+)_2[Cd(SCN)_4]^{2-}$	$C_2H_4Cl_2$	broad range	3	5.6	1.52	4.1	97.1	11, 12
$(INT^+)_2[Cd(SCN)_4]^{2-}$	$C_2H_4Cl_2$	the same	3	5.9	1.35	4.5	95.7	11, 12
$(MTT^+)_2[Cd(SCN)_4]^{2-}$	$C_2H_4Cl_2$	"	3	5.9	1.13	4.7	93.1	13
$(NBT^{2+})[Cd(SCN)_4]^{2-}$	$C_2H_4Cl_2$	"	4	2.9	0.60	2.3	80.2	11, 14
$(NT^{2+})[Cd(SCN)_4]^{2-}$	$C_2H_4Cl_2$	"	4	2.8	0.64	2.2	81.3	11, 14
$(INT^+)ClO_3^-$	$CHCl_3$	"	3	3.2	0.88	2.4	88.6	15
$(MTT^+)ClO_3^-$	$CHCl_3$	"	3	3.3	1.04	2.3	91.7	15
$(TT^+)ClO_3^-$	$CHCl_3$	"	3	2.3	0.14	2.2	58.4	15
$(INT^+)ClO_4^-$	$CHCl_3$	"	3	4.0	1.42	2.6	96.3	9
$(MTT^+)ClO_4^-$	$CHCl_3$	"	3	4.0	1.57	2.4	97.4	9
$(TT^+)ClO_4^-$	$CHCl_3$	"	3	3.6	1.27	2.3	94.9	9
$(TT^+)_2[Co(SCN)_4]^{2-}$	$C_2H_4Cl_2$	"	3	6.5	2.07	4.5	99.2	16
$(NBT^{2+})[Co(SCN)_4]^{2-}$	$C_2H_4Cl_2$	1–8 (0.01–0.66 M H_2SO_4)	3	4.1	2.07	2.0	99.2	16, 17
$(TV^+)_2[Co(SCN)_4]^{2-}$	$C_2H_4Cl_2$	2.7–7.6	3	6.4	1.86	4.6	98.6	8
$(MTT^+)_2[Co(SCN)_4]^{2-}$	$C_2H_4Cl_2$	2.7–7.6	3	6.6	1.81	4.8	98.5	13
$(TNBT^{2+})[Co(SCN)_4]^{2-}$	$C_2H_4Cl_2$ + + $(CH_3)_2O$	2–6	2	4.3	2.08	2.3	99.2	10
$(MTT^+)_3[Cr(SCN)_6]^{3-}$	$C_2H_4Cl_2$	1.8–7.2 M HCl	0.5	–	–	–	–	18

Table 2 (continued).

Extraction system		pH	Time of extraction /min	log K_{ex}	log K_D	log β	R (%)	Ref.
TIAC	solvent							
$(MTT^+)_3[Cr(ClO_4)_6]^{3-}$	$CHCl_3$	2.4 – 5.5 M HCl	–	–	–	–	–	18
$(NT^{2+})[CrO_3Cl]_2^-$	$C_2H_4Cl_2$	0.36 – 1.08 M HCl	0.17	–	–	–	–	19
$(NBT^{2+})[CrO_3Cl]_2^-$	$C_2H_4Cl_2$	0.25 – 0.6 M HCl	0.25	–	–	–	–	20
$(TT^+)[CrO_3Cl]^-$	$C_2H_4Cl_2$	0.3 – 1.5 M HCl	1	2.9	0.76	2.1	85.2	21
$(INT^+)[CrO_3Cl]^-$	$C_2H_4Cl_2$	0.1 – 1.1 M HCl	0.5	4.2	1.36	2.8	95.6	8, 22
$(TV^+)[CrO_3Cl]^-$	$C_2H_4Cl_2$	0.07 – 0.36 M HCl	0.5	4.5	1.42	3.1	96.4	8, 22
$(MTT^+)[CrO_3Cl]^-$	$C_2H_4Cl_2$	0.15 – 0.42 M HCl	1	4.0	1.38	2.6	96.0	23
$(MTT^+)[GaCl_4]^-$	$CHCl_3$	6.1 – 6.6 M HCl	15	4.7	0.67	4.0	82.4	24
$(TV^+)[HgBr_3]^-$	$C_2H_4Cl_2$	broad range	1	4.5	1.60	2.9	97.6	25
$(TV^+)[HgI_3]^-$	$CHCl_3$	1 – 9	1	4.1	1.03	3.1	91.5	25
$(INT^+)[HgI_3]^-$	$C_2H_4Cl_2$	0.2 – 5.5 M H_2SO_4	0.25	4.2	1.18	3.0	93.8	8, 26
$(TT^+)[HgI_3]^-$	$CHCl_3$	1 – 9 (0.1 – 4.5 M H_2SO_4)	0.5	4.5	1.32	3.2	95.4	27
$(MTT^+)[HgI_3]^-$	$CHCl_3$	1 – 8	0.5	4.5	1.22	3.3	94.3	28
$(TV^+)I^-$	$C_2H_4Cl_2$	1 – 6 (0.25 – 1.8 M HCl)	0.25	–	–	–	–	29
$(TV^+)IO_4^-$	$CHCl_3$	broad range	3	4.3	0.97	3.3	90.3	30
$(INT^+)[La(S_2O_3)_2]^-$	$CHCl_3$	5 – 7.4	1	–	–	–	–	31
$(MTT^+)MnO_4^-$	$C_2H_4Cl_2$	5 – 8 (0.01 – 0.16 M H_2SO_4)	0.08	4.5	1.34	3.2	95.6	32
$(TT^+)MnO_4^-$	$C_2H_4Cl_2$	6 – 7 (0.01 – 0.3 M H_3PO_4)	0.033	3.3	1.25	2.1	94.7	8, 33
$(INT^+)MnO_4^-$	$C_2H_4Cl_2$	0.01 – 0.125 M HCl	0.05	3.2	1.38	1.8	96.0	34
$(TV^+)MnO_4^-$	$C_2H_4Cl_2$	0.01 – 0.03 M H_3PO_4	0.17	4.5	1.75	2.8	98.2	35
$(NBT^{2+})[MnO_4^-]_2$	$C_2H_4Cl_2$	1 – 9 (0.01 – 0.2 M H_2SO_4)	0.5	11.0	1.55	9.5	97.2	8
$(MTT^+)_3[MoO(SCN)_6]^{3-}$	$C_2H_4Cl_2$	0.9 M H_2SO_4	0.5	–	–	–	–	36
$(p\text{-}NT^+)ReO_4^-$	$CHCl_3$	1 – 10	3	3.0	0.97	2.1	90.3	37
$(TV^+)ReO_4^-$	$CHCl_3$	3 – 10	3	4.2	1.86	2.1	98.6	38
$(MTT^+)ReO_4^-$	$CHCl_3$	2 – 10	3	4.0	1.59	2.4	97.5	39, 40, 41
$(INT^+)ReO_4^-$	$CHCl_3$	3 – 10	3	4.6	1.80	2.8	98.4	39, 40, 41
$(NT^{2+})(ReO_4)_2^-$	$CHCl_3$	4 – 10	3	8.0	1.18	6.8	93.8	39, 40, 41
$(NBT^{2+})(ReO_4)_2^-$	$CHCl_3$	broad range	3	9.0	1.22	7.8	94.3	40, 41
$(INT^+)_2[ReCl_6]^{2-}$	$C_2H_4Cl_2$	2 – 7	60	–	1.38	–	96.0	42
$(NT^{2+})[ReCl_6]^{2-}$	$C_2H_4Cl_2$	3 – 7	60	4.5	0.46	4.0	74.0	43
$(MTT^+)[Sb(OH)_2Cl_4]^-$	C_6H_6 + diethyl ether (3 : 1)	> 1.65 M HCl	1	–	–	–	–	44
$(TV^+)[Sb(OH)_2Cl_4]^-$	$CHCl_3$	6 M HCl	60	–	–	–	–	5
$(TV^+)[Sb(OH)_2Cl_4]^-$	C_6H_6	> 6 M HCl	10	–	–	–	–	45
$(MTT^+)[TlCl_4]^-$	C_6H_6 + diethyl ether (3 : 1)	0.01 – 1.0 M HCl	1	5.3	1.72	3.6	98.1	41, 44
$(TV^+)[TlCl_4]^-$	C_6H_6	0.05 – 6.0 M HCl;	1	–	–	–	–	45
$(TT^+)_2[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$	broad range	3	8.3	1.05	7.3	91.8	46
$(INT^+)_2[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$	the same	3	8.3	1.02	7.2	91.2	46
$(NBT^{2+})[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$	"	3	5.1	1.68	3.4	98.0	46
$(NT^{2+})[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$	"	3	5.1	1.57	3.5	97.4	46
$(TNBT^{2+})[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$ + $(CH_3)_2O$	2 – 6	0.5	5.1	1.68	3.4	98.0	10
$(TV^+)_2[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$	2 – 8	0.02	8.5	1.03	7.5	91.4	8, 47
$(MTT^+)_2[Zn(SCN)_4]^{2-}$	$C_2H_4Cl_2$	broad range	3	8.0	1.16	6.8	93.5	13

Note. Here and in Table 3, K_{ex} is the extraction constant ($K_{ex} = K_D \times \beta$); K_D is the distribution constant of the ionic associate betweeen the phases; β is the stability constant of the associate (association constant) and R is the degree of extraction.

characterise the extraction in the system under consideration on the whole), distribution constants of the ionic associate between phases (*i.e.*, the concentration ratios in organic and aqueous phases), stability constants of ionic associates (which describe the associate formation in the aqueous phase) and the degree of extraction, *i.e.*, the percentage of the substance extracted into the organic phase.

Chloroform or dichloroethane are commonly used as an organic phase for extraction; benzene and n-butanol are used less often. Sometimes, the use of mixtures of these solvents [67, 68] or their mixtures with ethers and acetone is more preferable.[10, 44]

The extraction time varies from several seconds to several minutes. The relatively slow extraction processes of $[Sb(OH)_2Cl_4]^-$ and $[ReCl_6]^{2-}$ represent an exception, shaking for $\sim$1 h is required.[5, 42, 43] The difference between extraction

Table 3. Extraction characteristics of tetrazolium ion-associated complexes with chelate anions.

Extraction system		pH	Time of extraction /min	log K_{ex}	log K_D	log β	R(%)	Ref.
TIAC [a]	solvent							
$(MTT^+)_2[Ge(NPC)_3]^{2-}$	$CHCl_3$	2.9 – 3.5	2	11.2	1.11	9.1	92.8	48
$(TT^+)_2[Ge(NPC)_3]^{2-}$	$CHCl_3$	4.0 – 4.5	2	11.2	1.52	9.7	97.1	49
$(TV^+)_2[MoO_2(NPC)_2]^{2-}$	$C_2H_4Cl_2$	1.2 – 2.6	2	8.5	1.75	6.7	98.2	50
$(BT^{2+})[MoO_2(NPC)_2]^{2-}$	$C_2H_4Cl_2$	1.8 – 4.0	2	5.4	–	–	–	51
$(TT^+)[MoO_2(OH)\cdot(H_2O)(NPC)]^-$	$CHCl_3$	1.8 – 2.5	1	5.2	0.88	4.3	88.4	52
$(MTT^+)_2[MoO_2(NPC)_2]^{2-}$	$CHCl_3$	2.1 – 3.4	2	9.6	1.12	8.5	93.0	6
$(INT^+)_2[MoO_2(NPC)_2]^{2-}$	$C_2H_4Cl_2$	1.5 – 3.0	10	10.0	0.47	9.5	74.0	53
$(MTT^+)[MoO_2(OH)\cdot(H_2O)(DHN)]^-$	$CHCl_3$	1.6 – 3.8	2	5.3	1.17	4.2	93.7	6
$(INT^+)[MoO(OH)(DHN)_2]^-$	$CHCl_3$	0.7 – 1.9	10	5.3	1.13	4.2	93.2	53
$(TV^+)[MoO(OH)(PC)_2]^-$	$C_2H_4Cl_2$	0.3 – 1.4	1	5.0	0.76	4.3	85.2	52
$(MTT^+)_2[MoO_2(THBA)_2]^{2-}$	$C_2H_4Cl_2$	2.6 – 3.2	0.25	9.1	0.85	8.2	87.6	54
$(NBT^{2+})[MoO_2(THBA)_2]^{2-}$	$CHCl_3$	0.03 – 0.08 M HCl	0.5	5.1	1.54	3.6	97.2	55
$(INT^+)[NbO(PC)_2]^-$	$CHCl_3$	0.09 – 1.4 M H_2SO_4	15	5.2	1.74	3.4	98.0	56
$(INT^+)[NbO(DHN)_2]^-$	$CHCl_3$	0.09 – 1.2 M H_2SO_4	15	5.3	1.86	3.5	98.9	56
$(TV^+)[NbO(PG)_2]^-$	$C_2H_4Cl_2$	0.25 – 1.25 M H_2SO_4	15	4.6	1.49	3.1	96.9	57, 58
$(TV^+)[NbO(NPC)_2]^-$	$C_2H_4Cl_2$	0.25 – 1.25 M H_2SO_4	15	4.5	1.61	3.0	97.6	57, 58
$(TV^+)[NbO(PC)_2]^-$	$CHCl_3$	1 M H_2SO_4	15	5.5	1.54	3.9	97.2	58, 59
$(TV^+)[NbO(DHN)_2]^-$	$CHCl_3$	0.5 – 1 M H_2SO_4	15	5.5	1.51	4.0	97.0	58, 59
$(TT^+)[NbO(PC)_2]^-$	$CHCl_3$	0.4 – 1 M H_2SO_4	15	5.1	1.84	3.2	98.8	60
$(INT^+)[Ti(OH)\cdot(H_2O)(DHN)_2]^-$	$CHCl_3$ ($C_2H_4Cl_2$)	1.2 – 2.8	15	–	–	–	–	61
$(TT^+)_2[TiO(DHN)_2]^{2-}$	$CHCl_3$	1.7	10 – 15	–	–	–	–	62
$(TT^+)_2[TiO(PC)_2]^{2-}$	$C_2H_4Cl_2$	2.2	10 – 15	–	–	–	–	63
$(INT^+)_2[TiO(NPC)_2]^{2-}$	$CHCl_3$	1.0	15	7.4	0.74	6.6	84.0	63
$(TV^+)_2[TiO(NPC)_2]^{2-}$	$CHCl_3$	1.4 – 1.8	15	12.1	1.90	10.0	98.7	63
$(INT^+)_2[VO(NPC)_2]^{2-}$	$CHCl_3$	3.9 – 4.5	5	10.6	1.4	9.2	96.0	64
$(INT^+)_3[VO_2(NPC)_2]^{3-}$	$CHCl_3$	4.7 – 5.1	5	–	0.39	–	71.1	65, 66
$(NT^{2+})_3[VO_2(NPC)_2]_2^{3-}$	$CHCl_3$ – BuOH	4.9	20	–	–	8.9	96.1	67
$(NT^{2+})[VO(NPC)_2]^{2-}$ – $[VO(NPC)]^0$	$CHCl_3$ – BuOH	3.9 – 4.7 (4.5 – 5.5)	15	–	–	–	–	68
$(INT^+)[VO(DHN)_2]^-$	$CHCl_3$	4.6 – 5.2	3	4.8	1.03	3.7	92.0	69
$(NT^{2+})_3[VO_2(TAR)_2]_2^{3-}$	$CHCl_3$	4.5 – 5.0	2	8.2	1.21	7.0	93.8	70
$(TT^+)_3[VO_2(TAR)_2]^{3-}$	$CHCl_3$	4.3 – 5.3	2	15.1	1.13	14.0	93.0	71
$(MTT^+)_3[VO_2(TAR)_2]^{3-}$	$CHCl_3$	4.3 – 5.3	2	17.9	1.16	16.7	93.5	72
$(TV^+)_3[VO_2(TAR)_2]^{3-}$	$CHCl_3$	4.3 – 5.3	2	18.7	1.07	17.6	92.0	72
$(INT^+)_3[VO_2(TAR)_2]^{3-}$	$CHCl_3$	4.3 – 5.3	2	16.3	0.92	15.4	88.9	72
$(BT^{2+})_3[VO_2(TAR)_2]_2^{3-}$	$CHCl_3$	4.7 – 5.7	2	9.7	1.12	8.6	92.9	72
$(NBT^{2+})_3[VO_2(TAR)_2]_2^{3-}$	$CHCl_3$	5.2 – 5.7	2	8.4	0.69	7.7	83.1	72
$(TV^+)_3[VO_2(PAR)_2]^{3-}$	$C_2H_4Cl_2$	5.2 – 6.3	2	17.9	1.48	16.4	96.8	73
$(INT^+)_3[VO_2(PAR)_2]^{3-}$	$CHCl_3$	5.5 – 7.5	2	16.4	1.59	14.8	97.5	74, 75
$(MTT^+)_3[VO_2(PAR)_2]^{3-}$	$CHCl_3$	5.1 – 6.5	2	17.5	1.61	15.9	97.5	76
$(TT^+)_3[VO_2(PAR)_2]^{3-}$	$CHCl_3$	5.2 – 6.3	2	–	–	14.7	–	see [b]
$(NBT^{2+})_3[VO_2(PAR)_2]_2^{3-}$	$CHCl_3$	4.7 – 5.7	2	–	–	7.6	–	see [b]
$(TNBT^{2+})_3[VO_2(PAR)_2]_2^{3-}$	$CHCl_3$	5.7 – 6.0	2	–	–	6.7	–	see [b]
$(NT^{2+})_3[VO_2(PAR)_2]_2^{3-}$	$CHCl_3$	4.8 – 6.7	2	8.5	1.26	7.2	94.8	77
$(NT^{2+})_3[VO_2(PG)_2]_2^{3-}$	BuOH	4.8 – 5.1	0.5	–	–	–	–	78
$(INT^+)_3[VO_2(PG)_2]^{3-}$	BuOH	2.6 – 3.3	0.5	–	–	–	–	79
$(INT^+)_2[VO(PG)_2]^{2-}$ – $[VO(PG)]^0$	BuOH	2.9 – 3.5	0.5	–	1.21	8.1	94.2	80
$(NT^{2+})[VO(PG)_2]^{2-}$ – $[VO(PG)]^0$	BuOH	3.8 – 4.3	0.5	–	1.37	3.8	95.8	80
$(TT^+)[WO(OH)(DHN)_2]^-$	$CHCl_3$	0.04 – 0.09 M H_2SO_4	10	5.2	1.28	3.9	95.0	81
$(INT^+)[WO(OH)(DHN)_2]^-$	$CHCl_3$	0.10 – 1.10 M H_2SO_4	1	5.0	0.81	4.2	86.5	82
$(TV^+)[WO(OH)(DHN)_2]^-$	$CHCl_3$	0.08 – 0.35 M H_2SO_4	10	5.0	1.93	3.1	98.8	83
$(TV^+)_2[WO_2(NPC)_2]^{2-}$	$CHCl_3$	4.2 – 5.7	3	10.4	1.56	8.9	97.3	82
$(TT^+)_2[WO_2(NPC)_2]^{2-}$	$CHCl_3$	3.5 – 5.0	1	10.3	1.05	9.2	91.9	82
$(MTT^+)_2[WO_2(NPC)_2]^{2-}$	$CHCl_3$	1.2 – 3.6	2	10.3	1.03	9.3	91.5	84

Table 3 (continued).

Extraction system		pH	Time of extraction /min	log K_{ex}	log K_D	log β	R(%)	Ref.
TIAC [a]	solvent							
$(TT^+)[WO(OH)(DNC)_2]^-$	$CHCl_3$	0.25 – 0.40 M H_2SO_4	2	10.6	1.06	9.6	91.8	82
$(TT^+)[WO(OH)(PC)_2]^-$	$CHCl_3$ (C_6H_6)	0.005 – 4.0 M H_2SO_4	20	–	–	–	–	85

[a] Abbreviations: NPC is 4-nitropyrocatechol; DHN is 2,3-dihydroxynaphthalene; PC is pyrocatechol; THBA is 3,4,5-trihydroxybenzoic acid; PG is pyrogallol; TAR, 4-(2-thiazolylazo)resorcinol; PAR is 4-(2-pyridylazo)resorcinol; DNC is 3,5-dinitropyrocatechol. [b] K Gavazov, unpublished data.

times of different TIAC can be used for ion separation and identification (qualitative analysis).

The composition of the extract can differ from the composition of the aqueous phase, this depends on a number of factors, *e.g.*, the nature of the central atom of the complex, its oxidation state, concentration of the starting reagents and pH.

Contrary to amines, tetrazolium cations can be used as IAC components without preliminary protonation. Therefore, the changes in the acidity of the aqueous phase do not prevent quantitative extraction of many inorganic anions, *e.g.*, ReO_4^-, $[Zn(SCN)_4]^{2-}$, $[HgI_3]^-$, *etc.* in the form of the respective TIAC. At the same time, the control over pH is important for the extraction of complexes with metal-containing anions prone to hydrolysis (as a rule, the hydrolysed forms are not extracted) as well as complexes with organic ligands. For TIAC containing organic ligands with higher molecular masses, the pH optimum range tends to be broader (see Table 3).

The optimisation of reagent concentrations plays the key role in extraction and spectrophotometric measurements.

As TS are usually taken in a large excess, their concentrations (or changes in concentrations) have little effect on the results of analysis.[41] Moreover, in many cases TS have beneficial effects. Thus it inhibits the reduction of V(V) to V(IV) by polyphenolic compounds such that vanadium(V) is stable in ternary complexes with chelating polyphenolic ligands.[67, 79] In contrast to other cationic dyes, only in rare cases the excess of TS interfere with spectrophotometric measurements.[67] The concentration of a ligand involved in the formation of a complex anion was found to depend on its stability constant, it varies in a broad range.[41]

The results of several studies suggest [41, 75, 86, 87] that the association constant of TIAC is proportional to the molecular mass of the tetrazolium cation: the higher the molecular mass the higher the association constant. This ratio can be used for the prediction of the possibility of formation of associates [41, 86] and of the association constants of newly formed complexes in a given class of compounds.[41, 86, 87] However, this ratio is violated if the tetrazolium cation of TS-based extraction systems contains a nitrophenyl substituent (Refs 72 and 75 and Fig. 1).

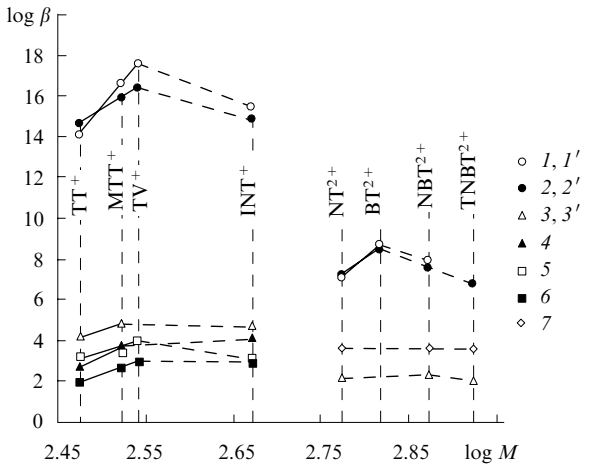


Figure 1. Dependence of the logarithm of the association constant of TIAC (β) on the logarithm of the molecular mass of the tetrazolium cation (M).
Anions: (*1*, *1′*) $[VO_2(TAR)_2]^{3-}$, (*2*, *2′*) $[VO_2(PAR)_2]^{3-}$, (*3*, *3′*) $[Cd(SCN)_4]^{2-}$, (*4*) $[TlCl_4]^-$, (*5*) $[HgI_3]^-$, (*6*) $[CrO_3Cl]^-$, (*7*) $[Zn(SCN)_4]^{2-}$.
The values of β for tetrazolium ion-associated complexes containing nitro groups (INT^+, NBT^{2+}, $TNBT^{2+}$) are lower than expected on the assumption that the association constant increases linearly with the molecular mass (solid lines).

III. Analytical applications of tetrazolium ion-associated complexes

1. 1. Extraction – photometric analysis

Some characteristics of extraction – photometric methods for determination of certain elements as TIAC are presented in Table 4. Spectrophotometric determinations with such complexes (or their decomposition products) are usually carried out by measuring absorption in the UV or visible spectral regions.

All tetrazolium complexes strongly absorb light in the UV region. However, analytical applications of UV spectra are complicated due to high absorption of the reference sample (blank experiment) and specific requirements for equipment and solvents. Therefore, very often preference is given to methods that employ compounds specially designed for spectrophotometric measurements in the visible spectral region. These include, for example, MTT complexes, TIAC containing a coloured complex anion, conversion products of TIAC (formazans formed upon reduction of tetrazolium cations in basic media),[31, 45] complexes obtained by replacement of tetrazolium cations by coloured cations (*e.g.*, rhodamine B) [4] and complexes produced in competitive reactions or their decomposition products.[10, 47, 109, 110]

The following approaches are used to increase the sensitivity of determination.

(1) Selection of an appropriate extraction system containing intensely coloured TIAC and solvents ensuring recovery close to 100%. In the context of this approach, MTT complexes containing yellow-coloured anions, *e.g.*, $[Ge(NPC)_3]^{2-}$ (Ref. 48), are especially promising, since they contain two chromophore ions absorbing in the same spectral region.

(2) Extraction of large amounts of coloured complexes by small volumes of an organic phase.

To attain the required selectivity, special attention is paid to the selection of adequate extraction-photometric conditions, *i.e.*, wavelength,[59, 62, 81, 103, 104] pH,[77, 82] reagent concentrations,[69] the order of their addition [107] and extraction time.[82, 84] Masking is also popular.

Some TIAC-based procedures are sufficiently selective to allow direct determinations without additional steps.

Table 4. Extraction-spectrophotometric methods based on TIAC.

Analyte	Reagents	Solvent	pH	Linearity range [a] /mg ml^{-1}	λ /nm (see [b])	$10^{-4}\varepsilon$ (see [c])	Samples	Ref.
Co(II)	NBT + SCN^-	$C_2H_4Cl_2$	1 – 8	0.5 – 9	625	0.76	soils	17
	TV + SCN^-	$C_2H_4Cl_2$	2.7 – 7.6	0.5 – 9	630	4.0	soils, plants	88
	MTT + SCN^-	$C_2H_4Cl_2$	2.7 – 7.6	0.5 – 10	625	0.67	soils	89
Cr(III)	MTT + SCN^-	$C_2H_4Cl_2$	1.8 – 7.2 M HCl	0.01 – 0.06	235	0.465	"	18
Cr(VI)	NBT	$C_2H_4Cl_2$	0.25 – 0.6 M HCl	0.01 – 0.4	260	8.2	soils, steels	20
	NT	$C_2H_4Cl_2$	0.36 – 1.08 M HCl	0.05 – 1.5	255	3.12	steels, soils, plants	19
	TT	$C_2H_4Cl_2$	0.1 – 1.2 M HCl	0.04 – 0.3	250	3.03	soils, plants	90, 91
	TT	$C_2H_4Cl_2$	0.3 – 1.5 M HCl	4.2 – 39.5	450	0.25	steels, plants	21, 92
	INT	$C_2H_4Cl_2$	0.1 – 1.1 M HCl	0.02 – 0.3	250	3.70, 8.8	steels, soils, vegetables	93, 94, 95, 96
	TV	$C_2H_4Cl_2$	0.07 – 1.1 M HCl	0.02 – 0.3	230	12.2	the same	94, 96
	MTT	$C_2H_4Cl_2$	0.15 – 0.42 M HCl	0.04 – 1	245	2.96	soils, steels, plants	23, 91
Ge(IV)	NPC + MTT	$CHCl_3$	2.5 – 3.9	0.15 – 1.88	410	5.11	model mixture	48
	NPC + TT	$CHCl_3$	4.0 – 4.5	0.2 – 3.0	420	2.88	the same	49
Hg(II)	TV + I^-	$CHCl_3$	0.1 – 4.5 M H_2SO_4	0.1 – 1.4	250	10.2	soils	97
	INT + I^-	$C_2H_4Cl_2$	0.2 – 5.5 M H_2SO_4	0.1 – 1.2	260	10.0	"	26
	TT + I^-	$CHCl_3$	0.2 M H_2SO_4	0.1 – 0.8	255	6.45	"	27
	MTT + I^-	$CHCl_3$	2	0.1 – 1	255	6.55	"	28
I^-	TV	$C_2H_4Cl_2$	1 – 6 (0.25 – 1.8 M HCl)	0.4 – 5	230	11.5	"	29
IO_3^-	TT + I^-	$C_2H_4Cl_2$		0.04 – 0.7		7.48	drinking water	98
	INT + I^-	$C_2H_4Cl_2$	0.1 – 2.4 M HCl	0.02 – 0.5	295	16.4	"	99
IO_4^-	TT + I^-	$C_2H_4Cl_2$		0.02 – 0.35		9.09	"	98
	INT + I^-	$C_2H_4Cl_2$	0.1 – 3.0 M HCl	0.02 – 0.5	295	16.7	"	99
Mn(VII)	MTT	$C_2H_4Cl_2$	0.01 – 0.16 M H_2SO_4	0.1 – 1.75	250	1.0	soils, plants	32
	TT	$C_2H_4Cl_2$	0.01 – 0.7 M H_2SO_4	0.5 – 12	530	0.556	soils, steels	33
	INT	$C_2H_4Cl_2$	0.01 – 0.125 M HCl	0.5 – 12	530	0.694	soils	34
	TV	$C_2H_4Cl_2$	0.01 – 0.03 M H_3PO_4	0.05 – 0.6	235	6.67	"	35
	NBT	$C_2H_4Cl_2$	0.01 – 0.2 M H_2SO_4		260	10	plants, soils	8, 100
Mo(VI)	NPC + TV	$C_2H_4Cl_2$	1.2 – 2.6	0.31 – 3.1	440	2.06	steels	50
	NPC + BT	$C_2H_4Cl_2$	1.8 – 4.0	0.2 – 6.7	445	2.38	steels, ferromolybdenum	51
	NPC + TT	$CHCl_3$	1.8 – 2.5	0.5 – 10.0	445	2.28	model mixture	52
	NPC + MTT	$CHCl_3$	2.1 – 3.4	0.2 – 7.0	440	2.41	steels, ferromolybdenum	6
	NPC + INT	$C_2H_4Cl_2$	1.5 – 3.0	0.24 – 6.9	430	1.94	the same	53
	PG + TV	$C_2H_4Cl_2$	0.3 – 1.4	0.5 – 6.0	432	0.72	the same	52
	THBA + NBT	$CHCl_3$	0.03 – 0.08 M HCl	0.5 – 5	260	15.0	soils	101
	THBA + MTT	$C_2H_4Cl_2$	2.6 – 3.2	0.15 – 3	245	1.67	soils, vegetables	54, 102
	MTT + SCN^-	$C_2H_4Cl_2$	0.9 M H_2SO_4	0.1 – 1.5	470	5.7	plants (lettuce)	36
Mo(VI), W(VI), Nb(V)	DHN + TT	$CHCl_3$	0.07 M H_2SO_4		360, 500, 625	0.81 (Mo at 360 nm)	steels	103
Nb(V)	NPC + TV	$C_2H_4Cl_2$	0.7 M H_2SO_4	0.41 – 4.54	440	1.59	"	57
	PC + TT	$CHCl_3$	0.4 – 1 M H_2SO_4	1.25 – 11.78	390	1.60	"	60
	DHN + TV	$CHCl_3$	0.5 – 1 M H_2SO_4	0.20 – 3.29	400	1.18	"	59
Re(VII)	p-NT	$CHCl_3$	1 – 10	0.2 – 16	255	2.1	copper concentrate	37
	TV	$CHCl_3$	3 – 10	0.2 – 17	280	1.32	copper ore	38
	MTT	$CHCl_3$	2 – 10	0.2 – 18	280	0.82	molybdenum concentrates	39
	INT	$CHCl_3$	3 – 10	0.5 – 24	280	1.45	the same	39
	NT	$CHCl_3$	4 – 10	0.5 – 26	280	0.73	"	39

Table 4 (continued).

Analyte	Reagents	Solvent	pH	Linearity range [a] /mg ml^{-1}	λ /nm (see [b])	$10^{-4}\varepsilon$ (see [c])	Samples	Ref.
Ti(IV)	DHN + INT	$C_2H_4Cl_2$	1.2 – 2.8	0.24 – 5.2	370	2.57	aluminium alloys	61
Ti(IV), W(VI)	DHN + TT	$CHCl_3$	1.7	0.12 – 1.66 (Ti)	380, 470	2.74 (Ti)	steels	62
Ti(IV)	PC + TT	$C_2H_4Cl_2$	2.2	0.24 – 2.6	390	1.15	aluminium alloys	62
	NPC + TV	$CHCl_3$	1.4 – 1.8	0.20 – 2.00	440	4.4	the same	63
Tl(III), Sb(V)	MTT	C_6H_6 + diethyl ether (3 : 1)	0.2 M HCl (Tl); 1.8 M HCl (Tl + Sb)	1.0 – 15.0 (Tl); 1.0 – 16.0 (Sb)	400.5		cadmium	44
	TV	C_6H_6	0.05 – 6.0 M HCl (Tl); > 6 M HCl (Sb)	1.0 – 20.0 (Tl); 0.5 – 9.5 (Sb)	520		"	45
V(V)	NPC + INT	$CHCl_3$	5.0	0.2 – 2.6	400	1.7	steels	65
V(IV)	NPC + NT	$CHCl_3$ + BuOH (7 : 3)	4.75	0.5 – 3.0	605	1.15	"	104
V(V)	TAR + TT	$CHCl_3$	4.75	0.1 – 2.5	550	2.37	catalysts	105
	TAR + MTT	$CHCl_3$	4.75	0.1 – 2.5	550	2.60	"	72
	PAR + TV	$C_2H_4Cl_2$	5.2 – 6.3	0.05 – 2.5	555	4.0	"	105
V(V), V(IV)	PAR + TV	$C_2H_4Cl_2$	5.8	0.003 – 1.45	555	3.05	"	106
	PAR + MTT	$CHCl_3$	5.8	0.21 – 1.5	560	3.30	"	76
	PAR + INT	$CHCl_3$	5.5 – 7.5	up to 1.5	560	2.4	natural waters	107
V(V)	PAR + INT	$CHCl_3$	5.5 – 7.5	up to 1.5	560	2.4	aluminium alloys	107
	PAR + NT	$CHCl_3$	4.8 – 6.7	0.15 – 3.5	560	2.95	steels	77
	PAR + TT	$CHCl_3$ + PrOH	5.8	–	560	4.7	soils	108
	DHN + INT	$CHCl_3$	4.6 – 5.2	0.1 – 0.9	340	2.5	steels	69
W(VI)	DHN + TT	$CHCl_3$	0.04 – 0.09 M H_2SO_4	0.5 – 6.0	440	1.16	"	81
	DHN + INT	$CHCl_3$	0.10 – 1.10 M H_2SO_4	0.7 – 7.4	420	0.938	"	82
	DHN + TV	$CHCl_3$	0.08 – 0.35 M H_2SO_4	0.9 – 12.9	440	0.766	"	83
	NPC + TV	$CHCl_3$	5.4	0.7 – 10.3	425 – 430	2.69	steels, ferrotungsten	82
	DNC + TT	$CHCl_3$	0.25 – 0.40 M H_2SO_4	0.5 – 7.4	400	2.12	steels	82
	NPC + MTT	$CHCl_3$	1.2 – 3.6	0.9 – 8.8	415	2.8	steels, ferrotungsten	84
Zn(II)	p-NT + SCN^- + Co(II)	$C_2H_4Cl_2$	1 – 7	1.7 – 13.3	630		cadmium	109
	MTT + SCN^- + Co(II)	$C_2H_4Cl_2$	2 – 6	3.3 – 18.3	630		"	110
	TNBT + SCN^- + Co(II)	$C_2H_4Cl_2 + Me_2O$ (1 : 1)	2 – 6	0.75 – 8.75	630		"	10
	TV + SCN^- + Co(II)	$C_2H_4Cl_2$	2 – 6	0.5 – 8	630		"	47

[a] The concentration range in which the signal is proportional to the analyte concentration enables quantitative determination. [b] Wavelength. [c] ε is the molar extinction coefficient (litre mol^{-1} cm^{-1}) (the values were taken from the cited papers). However, they were not always calculated using standard methods and different volumes of the aqueous and organic phases were employed.

a. Determination of cobalt

The extraction-photometric procedure for determination of cobalt in soils [17, 88, 89] and plants [88] is based on the formation of ion-associated complexes (NBT)[Co(SCN)$_4$],[17] (TV)$_2$[Co(SCN)$_4$] (Ref. 88) and (MTT)$_2$[Co(SCN)$_4$] (Ref. 89) and their subsequent extraction with 1,2-dichloroethane in a broad pH range. The relative standard deviation (RSD), detection limit (DL) and molar extinction coefficient (ε) for the most sensitive procedure based on the use of TV are equal to 1.15%, 1.5×10^{-3} μg ml^{-1} and 4×10^4 litre mol^{-1} cm^{-1}, respectively.[88]

b. Determination of chromium

The interactions of solutions of Cr(VI) in hydrochloric acid with NT,[19] NBT,[20] MTT,[23] TT,[90] INT [93] and TV [94] were studied by Kamburova *et al*. The complexes were efficiently extracted with 1,2-dichloroethane. Apparently, the Cr(VI) – TV complex is the most suitable for the determination of Cr(VI) in the presence of ascorbic acid and NH_4F as masking reagents in soils,[94] steels [94] and vegetables [96] [$\varepsilon_{230} = 1.22 \times 10^5$ litre mol^{-1} cm^{-1}, RSD = (0.4% – 0.7%)].

The use of a ternary chromium(III) complex with thiocyanate and MTT for the determination of chromium in soils has been described;[9] however, the sensitivity of this method is low ($\varepsilon_{235} = 4.65 \times 10^3$ litre mol^{-1} cm^{-1}).

c. Determination of germanium

Two procedures for the determination of Ge(IV) based on formation of ternary complexes with 4-nitropyrocatechol and extraction with chloroform have been described.[48, 49] The best of them [48] employs MTT ($\varepsilon_{410} \approx 5.1 \times 10^4$ litre mol^{-1} cm^{-1}). The interfering effects of Al^{3+}, Fe^{3+} and Cr^{3+} are eliminated with Na-EDTA. The presence of Mo(VI), V(IV,), W(VI), I^- and Cl^- interferes with the assay.

d. Determination of mercury

Determination of mercury in soils included extraction of mercury(II) halide complexes with chloroform.[8, 26 – 28, 97] The complexes (TV)[HgI_3] and (TV)[$HgBr_3$] manifested the highest molar extinction coefficients (1.02×10^5 litre mol^{-1} cm^{-1} and 1×10^6 litre mol^{-1} cm^{-1}, respectively).[97] Other fast and sensitive

methods for the determination of mercury(II) are based on the use of the complexes (INT)[HgI_3],[26] (TT)[HgI_3][27] and (MTT)[HgI_3].[28] Ascorbic acid and fluoride ions were used as masking reagents.

e. Determination of iodide, iodate and periodate

A sensitive method for the determination of iodide ions in soils was developed by Kamburova.[29] It is based on extraction, with 1,2-dichloroethane, of ion-associated TV complexes with iodide oxidation products. Hydrogen peroxide was found to be the oxidant of choice. The majority of ions, except for Hg^{2+}, BrO_3^- and $S_2O_3^{2-}$, do not interfere.

The optimum complexation conditions in TS – iodate – iodide – dichloroethane and TS – periodate – iodide – dichloroethane systems have been studied. Two procedures for the determination of iodates and periodates in drinking water using $(TT^+)I_3^-$ and $(INT^+)I_3^-$ have been described.[98,99] The procedure based on TT is more sensitive:[98] $\varepsilon_{295} = (1.64 \pm 0.02) \times 10^5$ litre mol^{-1} cm^{-1} (for IO_3^-), $\varepsilon_{295} = (1.67 \pm 0.05) \times 10^5$ litre mol^{-1} cm^{-1} (for IO_4^-). The presence of other ions has no interfering effect on the assay. The RSD value lies in the range from 0.8% to 1.3%.

f. Determination of manganese

Several methods were developed for the determination of manganese(VII) in natural and industrial samples.[8,32–35,100] All of them included extraction, with 1,2-dichloroethane, of tetrazolium ion-associated complexes with the permanganate anion. Complexes with TT[33] and INT[34] were used for the determination of manganese in soils[33,34] and steels[33] at $\lambda = 530$ nm; however, the sensitivity of these methods was rather low. Higher sensitivity was achieved through the use of MTT ($\varepsilon_{250} = 1.0 \times 10^4$ litre mol^{-1} cm^{-1}),[32] TV ($\varepsilon_{235} = 6.67 \times 10^4$ litre mol^{-1} cm^{-1})[35] and NBT ($\varepsilon_{260} = 1.0 \times 10^5$ litre mol^{-1} cm^{-1})[8,100] in the UV region. The NBT complex was used for the determination of manganese in diverse vegetable samples. Interfering ions were masked using saturated solutions of ascorbic acid. The RSD value did not exceed 1.8%.

g. Determination of molybdenum

A series of sensitive spectrophotometric procedures for the determination of molybdenum [$\varepsilon_{430-445} = (1.94 - 2.41) \times 10^4$ litre mol^{-1} cm^{-1}] using 4-nitropyrocatechol and various tetrazolium cations were developed by Dimitrov *et al.*[6,50–53] In particular, this method was used for the determination of molybdenum in ferrous metallurgy products. Other TIAC-forming reagents, *e.g.*, pyrogallol,[52] 2,3-dihydroxynaphthalene[103] and 3,4,5-trihydroxybenzoic acid, are also employed.[54,101,102] The use of 3,4,5-trihydroxybenzoic acid and MTT for the determination of molybdenum in soils[54] and vegetables[102] (RSD = 1.1% and 1.9%, respectively) has been described. A highly sensitive procedure for the analysis of soils[101] is based on the use of 3,4,5-trihydroxybenzoic acid and NBT ($\varepsilon_{260} = 1.5 \times 10^5$ litre mol^{-1} cm^{-1}) and does not require preliminary isolation of molybdenum.

A method based on the use of thiocyanate and MTT for the determination of molybdenum in lettuce has been described.[36] Fe(III) and V(V) ions were masked with oxalic and ascorbic acids; the RSD value did not exceed 1.2%.

A procedure for simultaneous determination of molybdenum, tungsten and niobium in steels with the use of their ternary complexes with 2,3-dihydroxynaphthalene and TT has been developed.[103] The determination of molybdenum was carried out at 625 nm; the total content of W + Mo and W + Mo + Nb was determined at 500 and 360 nm, respectively. Interfering ions were masked with EDTA. The RSD values for molybdenum, tungsten and niobium were equal to (0.5 – 1.07)%, (4.0 – 6.9)% and (5.2 – 8.0)%, respectively.

h. Determination of niobium

Several methods based on the use of Nb(V) complexes with TS and polyphenols (4-nitropyrocatechol,[57] 2,3-dihydroxynaphthalene[59,103] and pyrocatechol[60]) for the determination of niobium in steels have been developed. 4-Nitropyrocatechol – TV[57] and pyrocatechol – TT systems[60] are more suitable for the analysis of steels containing no molybdenum or tungsten. Other interfering ions are masked with EDTA or ascorbic acid. If a steel contains 0.021% Nb, its RSD value is equal to 4.7%.[57]

If a steel contains Mo(VI) or W(VI), the 2,3-dihydroxynaphthalene – TV system is used.[59] In the presence of W(VI), absorption was measured at 400 and 490 nm; in the presence of Mo(VI), at 400 and 582 nm. This approach can also be used,[103] if a steel contains simultaneously Mo and W (see Section III.1.g).

i. Determination of rhenium

ReO_4^- ions form ion-associated complexes with tetrazolium cations,[37–39] which enables reliable determination of rhenium in industrial samples, *e.g.,* copper concentrates,[37] copper ores[38] and molybdenum concentrates.[39] Extraction with chloroform is carried out in a broad pH range. The method based on *p*-NT is the most sensitive ($\varepsilon_{255} = 2.1 \times 10^4$ litre mol^{-1} cm^{-1}) and selective.[37] The assay procedure is not interfered with by Mo(VI), Ni(II), Co(II), Cu(II), Fe(II), Mg(II), Mn(II), Cd(II), V(V) or W(VI). The RSD value is 2.1% at the rhenium content of $(1.58 - 1.75) \times 10^{-3}$%.

j. Determination of titanium

Determination of titanium in aluminium alloys[61–63] and steels[62] is based on the use of its yellow-coloured TIAC involving 2,3-dihydroxynaphthalene,[61,62] pyrocatechol[62] and 4-nitropyrocatechol.[63] The 4-nitropyrocatechol – TV system[63] is the best for extraction in respect of sensitivity ($\varepsilon_{440} = 4.4 \times 10^4$ litre mol^{-1} cm^{-1}) and reproducibility (the RSD value does not exceed 1.05%). This system was used for the determination of titanium in aluminium alloys with ascorbic acid as a masking reagent.

The 2,3-dihydroxynaphthalene – TT system was used[62] for simultaneous determination of titanium and tungsten in steels. The values of molar extinction coefficients were as follows: $\varepsilon_{380} = 2.74 \times 10^4$ litre mol^{-1} cm^{-1} and $\varepsilon_{470} = 0$ litre mol^{-1} cm^{-1} for titanium and $\varepsilon_{380} = 6.33 \times 10^3$ litre mol^{-1} cm^{-1} and $\varepsilon_{470} = 4.3 \times 10^3$ litre mol^{-1} cm^{-1} for tungsten. Interfering ions were masked with ascorbic acid. The RSD values for titanium and tungten were equal to 3.5% and 2.0%, respectively.

k. Determination of thallium and antimony

Two methods for the simultaneous determination of antimony and thallium in cadmium were developed by Kostova *et al.*[44,45] They are based on extraction, with an organic solvent, *e.g.,* benzene[45] or a benzene – ether system (3 : 1),[44] of thallium(III) and antimony(V) TIAC. Both procedures imply preliminary addition of an oxidising reagent to the tested solution containing Tl(I) or Sb(III).

Only Tl(I) undergoes oxidation to Tl(III) in dilute solutions of hydrochloric acid. However, in hydrochloric acid solutions of moderate concentration both Tl(I) and Sb(III) are oxidised to Tl(III) and Sb(V). Thus, variation in solution acidity enables stepwise determination of Tl(III) and Sb(V) in the same sample.

The first procedure is more simple.[44] The use of ternary complexes with MTT allows direct determination of Tl(III) and Sb(V) in the visible spectral region (at 400.5 nm). The RSD values for Tl and Sb are equal to 1.01% and 1.45%.

The second, more sensitive procedure [45] includes reduction of TV with $NH_2OH \cdot HCl$ to formazan which absorbs at 520 nm. The detection limit is 1 μg ml^{-1} for Tl and 0.5 μg ml^{-1} for Sb.

l. Determination of vanadium

It was recommended to use ternary TIAC with 4-nitropyrocatechol,[65, 104] 2,3-dihydroxynaphthalene,[69] 4-(2-pyridylazo)resorcinol [76, 77, 105–108] and 4-(2-thiazolylazo)resorcinol [72, 105] for the determination of V(V) in the environment and in industrial samples. It was found that 4-(2-pyridylazo)resorcinol is the most sensitive and convenient reagent for the determination and identification of vanadium. If selective determination of V(V) is required, diaminocyclohexanetetraacetic acid (DCTA) [77] or DCTA + NH_4F are added to the solution as masking reagents [106, 107] as a result of which V(IV) is masked. This method is employed in indirect determination of the V(IV) content from the difference in the absorption measured in the presence and in the absence of the reagent used for the oxidation of V(IV) to V(V).[106, 107] The use of NH_4F as a secondary masking reagent results in instantaneous colouration and provides better selectivity with respect to definite ions including V(IV).[106, 107] Determination of vanadium in various natural water samples,[107] aluminium alloys,[107] catalysts,[86, 105, 106] steels [77] and soils [108] was carried out by varying detection parameters, such as the nature of TS, order of addition of the reactants, *etc*.

m. Determination of tungsten

A series of procedures for the determination of tungsten in steels and ferrotungsten have been developed. These methods are based on the formation of tungsten(VI) TIAC with 2,3-dihydroxynaphthalene,[81–83] 3,5-dinitropyrocatechol [82] and 4-nitropyrocatechol.[82, 84] The highest sensitivity ($\varepsilon_{415} = 2.80 \times 10^4$ litre mol^{-1} cm^{-1}) was achieved with 4-nitropyrocatechol and MTT.[84] The interfering effects of Fe(III), Al(III), Cr(III) and V(V) were eliminated by precipitation/coprecipitation at pH 11 in the course of sample preparation. The RSD value did not exceed 0.53%.

n. Determination of zinc

A series of spectrophotometric procedures for the determination of zinc in cadmium have been developed [10, 47, 109, 110] based on predominant formation of thiocyanate cobalt complexes with TS cations in the presence of cadmium and their selective extraction. Blue-coloured cobalt complexes are formed upon addition of a cobalt salt, an excess of thiocyanate and a small amount of a tetrazolium salt to the tested sample:

$$2TS^+ + Co^{2+} + 4SCN^- \rightleftharpoons (TS)_2[Co(SCN)_4] .$$

The presence of Zn^{2+} ions in the system makes the blue colouration of the solution less intensive due to a shift of the reaction equilibrium towards less soluble weakly coloured zinc complexes:

$$Zn^{2+} + (TS)_2[Co(SCN)_4] \rightleftharpoons (TS)_2[Zn(SCN)_4] + Co^{2+} .$$

It was found that the decrease in absorption at 630 nm is proportional to Zn^{2+} concentration in the tested solution in a rather broad range: 0.5–8 μg ml^{-1} (for a TV^+ complex),[47] 3.3–18.3 μg ml^{-1} (for a MTT^+ complex),[110] 1.7–13.3 μg ml^{-1} (for a *p*-NT^+ complex) [109] and 0.75–8.75 μg ml^{-1} (for a $TNBT^{2+}$ complex).[10] The detection limit for zinc in cadmium can be decreased to 6.9×10^{-3}% in the presence of TV.[47]

2. Application in potentiometric analysis

Two sensitive and selective potentiometric methods for the determination of Hg(II) [111] and Tl(III) [112] based on the ability of these ions to form ion-associated complexes with TT^+ have been described.

The use of the complex $TT[HgI_3]$ in the construction of a modified mercury-selective carbon paste electrode has been described.[111] The electrode shows a stable, near-Nernstian response for 1×10^{-3}–6×10^{-6} mol $litre^{-1}$ $[HgI_3]^-$ (the anionic slope in the pH range 4.0–9.0 is 55.5±0.4 mV). The lower detection limit is 4×10^{-6} mol $litre^{-1}$; the response time is 30–50 s. The interfering effects of the majority of tested ions were negligibly small. The electrode was used for direct determination of mercury in waste waters, metal amalgams and dental alloys.

The application of a membrane sensor based on $TT[Tl^{III}Cl_4]$ dispersed in a PVC matrix plasticised with dioctyl phthalate has been described.[112] The electrode shows a stable, near-Nernstian response at 1×10^{-3}–4×10^{-6} mol $litre^{-1}$ Tl(III) (the anionic slope is 56.5±0.5 mV in the pH range 3–6). The lower detection limit is 2×10^{-6} mol $litre^{-1}$; the response time is 30–60 s. The electrode was successfully employed for the determination of thallium in spiked waste waters and zinc concentrates. The RSD value at 10 μg ml^{-1} was 1.6%.

IV. Miscellaneous applications of tetrazolium salts in inorganic analysis

A method for the determination of trace amounts of selenium based on its catalytic effect on the reduction of TNBT with dithiothreitol has been described.[113] The method proved to be a simple, fast and efficient procedure for the determination of several forms of selenium. A similar procedure using the MTT–dithiothreitol system was used in the analysis of lobsters.[114]

A procedure for photometric determination of selenium in aqueous media (at the level of 10–120 μg $litre^{-1}$) with 2-(*p*-nitrophenyl)-3,5-diphenyltetrazolium chloride was developed by Moskvin *et al*.[115] The sample preparation step includes gas extraction of selenium (in the form of hydrogen selenide) followed by its liquid-adsorption extraction from the gaseous phase to an aqueous solution of reagents to yield water-insoluble formazan. A similar procedure [116] based on 5-(benzo-1,3-dioxol-5-yl)-2-(4-iodophenyl)-3-phenyl-2*H*-tetrazolium chloride was used to determine arsenic at the level of 1–120 μg $litre^{-1}$.

A method for determination of sulfur in steels, nickel alloys, chromium, tin, sodium dihydrophosphate, galena and $RbAg_4I_{5-x}S_x$ was developed by Kolesnikova *et al*.[117] Here, the determination makes use of formazans formed upon reduction of TT, INT and NBT.

Nagaraja *et al*.[118] developed a highly sensitive spectrophotometric method for the determination of silver ($\varepsilon_{510} = 4.51 \times 10^5$ litre mol^{-1} cm^{-1}) that involves silver-enhanced reduction of TT with semicarbazide hydrochloride. This procedure was used for the determination of Ag(I) in photographic process waste water.

V. Conclusion

Tetrazolium salts are popular and readily available multifunctional reagents for liquid–liquid extraction, spectrophotometric and potentiometric determination of differnt ions and elements in environmental objects and industrial samples. Each tetrazolium-containing extraction system has its own advantages and disadvantages in terms of sensitivity, selectivity, accuracy, reliability and rapidity. On the whole, these systems are efficient and enable solution of complex analytical problems. The characteristics of some of these methods are comparable with those of atomic absorption spectrometry (AAS) and inductively coupled plasma–atomic emission spectroscopy (ICP-AES). However, in contrast with the latter, these methods are inexpensive and do not require costly equipment.

Altogether, these data suggest that complexes of the monotetrazolium salts MTT, TV and INT and of the ditetrazolium salt BT hold considerable promise for further investigations. Thus MTT is a convenient reagent for extraction and spectrophoto-

metric determination of colourless anions, while TV and INT having higher molecular masses form more stable and readily extractable complexes. The properties of INT complexes are less predictable, but their application offers a significant gain in sensitivity and/or selectivity. BT complexes are the least studied; however, there are strong grounds to believe that they are more efficient in comparison with other tetrazolium salts.

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