SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM BASED ON TERNARY COMPOUND FORMATION

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SUMMARY.– In this review a selection has been made of the spectrophotometric methods of determining molybdenum by means of ternary compounds. They have been summarized in tables which contain the principal spectrophotometric characteriscs and other data concerning applicabillty. The parameters affecting sensitivity and selectivity are discussed as well as the nature of the compounds formed and a classification of the ternary system components is included.

RESUMEN.– En esta revisión se han seleccionado los métodos espectrofotométricos de determinación de molibdeno por medio de complejos ternarios. Se han resumido en tablas que contienen las principales características espectrofotométricas y otros datos relacionados con sus aplicaciones. Se discuten los parámetros que afectan la selectividad y la sensibilidad de las reacciones utilizadas, así como la naturaleza de los compuestos formados y se incluye también la clasificación de los componentes de los sistemas ternarios.

INTRODUCTION

The determination of molybdenum has lately attracted great attention and is specially interesting in numerous materials such as metallurgical products, geological samples, soils, fertilizers, biological materials, waters, fuels and lubricants (124).

Molybdenum at trace level introduces significant changes in the properties of a wide variety of samples types. Its importance is known in bio-and geochemical cycles in sea water and sediments (73). In lake waters it plays an important role as an active element for growth and as micronutrient in the aquatic medium (125). It is an essential element in plant nutrition since it is a metallic component of numerous enzymes and may influence several metabollic proceses in plants (126). There are considerable problems of molybdenum deficiencies of agricultural importance and animals also need low levels of this element in their diet for normal growth (127). These determinations by spectrophotometry have special importance since this technique is the most widely available.

The methods that involve the formation of blue molybdenum heteropoliacids and compounds with two metals and one ligand are not included in this review.

NATURE OF THE REAGENTS AND COMPOUNDS FORMED

A significant increase in the sensitivity of the methods based on binary complexes of metals with chelating reagents can be obtained by introducing a third component into the system. The compound formed appears in the literature with diferent denominations; the ones used more frequently are: ternary complex, mixed ligand complex, three component complex, ion association compound, ion-pair and ternary compound. Independently of the denomination, the majority of examples reported are of the ion-association type. In such a compound, the metal ion reacts with a ligand to produce a charged binary complex which then forms an ion-association compound with a specie of opposite charge (17).

Most of the work done with the ternary compounds aims at the resolution of practical problems and little information is available about theoretical foundations. However there are reasons to suspect that in numerous cases the ligand-ligand interaction plays an essential part in the properties of the ternary compuund that diferenciates it from a binary complex. Often when a third component is introduced in a binary complex a bathochromic shift of the λ_{max} and enhanced sensitivity and precision are observed (89). Some examples are reported in which the number of chelating agent molecules coordinated to molybdenum in binary complexes increases with the formation of ternary compounds (65, 89, 101, and 128).

Much of the literature concerns methods of ternary compounds formation of molybdenum which contain thiocyanate and they represent practycally half of the total. Therefore we can classify the molybdenum ternary compounds in two groups: compounds containing thiocyanate and compounds without thiocyanate.

1. Ternary compounds containing thiocyanate

Probably the oldest and most widely used reagent for molybdenum has been thiocyanate. The molybdenum-thiocyanate colour has been notorius for its lack of stabilily and reproducibility and for dificulties involved in developing its maximal intensity (129). To solve this problem, colorimetric procedures for molybdenum with thiocyanate, including also ternary compounds, frequently employ an additional reducing agent.

It is agreed that colour is due to the formation of the Mo(V)-thiocyanate complex, based on the reduction of Mo(VI) to Mo(V) (130, 131, 132 and 133) or to isomerization reaction of the $MoO_2(SCN)_2$ complex, and thus the function of the reduction agent is to catalize the isomerization reaction of the Mo(VI) (which takes place through an unstable Mo(V) intermediate) rather than to stabilize Mo(V) (130). However some modifications omit the reducing agent enterely but often longer procedures are required (1, 4, 18, 31, 36, 39 and 47).

The additional reducing agent most often used is ascorbic acid (1, 2, 4, 8, 10, 12, 13, 15, 16, 23, 24, 25, 29, 30, 32, 33, 34, 35, 36, 37, 38, 42, 46, 47, 48, 50 and 53). $SnCl_2$ has also been used (3, 7, 44 and 51) but usually reproducible results and colour are only obtained in narrow range of reductor concentration and some authors considered it too strong a reductor. Therefore in most instances ascorbic acid is preffered because it is a milder reductor and the amount to be added is not critical.

Two examples are reported in which the colour can also be developed without additional reducing agents due to the mild reductor properties of thiocyanate (37 and 38). In the case of the system Mo-thiocyanate-quinoline it is suggested that quinoline is acting as reductant (1).

In most cases the reagent used to form the ternary compound with Mo-thiocyanate contains nitrogen. We can divide the mentioned reagents as follows:

a) Nitrogenated heterocycle derivates: quinoline (1), 2 benzylaminopyridine (2), 3 benzoylaminopyridine (3), amidopyridines (4), benzylpyridine (5, 6), 2-2' bipiridilo (7), 1-10 phenanthroline (7), papaverine (8), lobeline (9), 5-pyralozone derivates (10), nitrones (11, 12) and phenothiazine derivatives (13-16).

b) Triphenyl methane derivates: rhodamine B (17), rhodamine 6G (18) and crystal violet (19-23).

c) Aromatic amines: aniline derivates (24-26), tribenzylamine (27), diphenylguanidine (28, 29), monooctylαanilinobenzylphosphonate (30).

d) Other organic bases: amidines (31-36), imidoyl derivates (37, 38), amides (39, 40), ammonium quaternary salts (42-44), and thiosemicarbazones (45).

e) Other reagents: arsonium and phosphinium quaternary salts (46, 47), triton X-100 (48), tributyl phosphate (49), carbinol derivate (50), 2 mercaptobenzo-γ-thiopyrone (51), caprolactama (52), other surfactants (53), and salsolidine (54).

2. Ternary compounds without thiocyanate

These compounds contain at least one chromogenic reagent that forms a binary complex with molybdenum. The most abundant compounds in this group are the Mo-triphenylmethane dye-surfactant, referred by some authors as surfactant sensitized reaction since the colour of the binary complex is enhanced by the addition of a surfactant. In these compounds, the surfactant micelles seem to be responsible for the ternary system formation. The most widely accepted explanation is that the positive superficial charge of the micelles induce the stuff dissociation (89 and 129) and therefore favours the ternary complex formation with a lower relationship metal: chelating agent (89, 100, 128 and 135). Consequently the critical micelle concentration must be reached. However some cases with other metals have been reported in which the ternary compound is formed below the critical micelle concentration of the surfactants (135 and 136), which could be attributed to a different reaction mechanism (135).

The chromogenic reagents described could be classified as follows:

a) -O-O ligands

1- Triphenaylmethane derivates: gallein (55-59), pyrogallol red (60-64), bromopyrogallol red (65-75), fluorones (76-85), pyrocathecol violet (86-91).

2- Poliphenols: pyrocatechol (92-100), pyrogallol (101), 4 butyrylpyrogallol (102), tiron (105-106).

3- Quinone derivates: carminic acid (104), indoferron (120), alizarin red S (121).

4- Other reagents: pyridine-2, 4 dicarboxilic acid (123), hematoxiline (103).

b) -O-N ligands

1- azo compounds: eriochrome black T (107), stilbazo (108), 4-(2-pyridylazo)-resorcinol (109-110), 2-((5-bromo-2-pyridyl)azo)-5-(diethylamino)phenol (111), Na 2-bromo-4,5 dihydroxyazobenzene-4'-sulfonate (112), other azo compounds (113, 114).

2- other reagents: hydroxamic acid derivates (115, 116), oxine (117) oxine derivates (118, 119).

The third component in these ternary compounds contains nitrogen in most cases and they can be clasified as follows:

a) Quaternary ammonium salts

1- Straight-chain alkyls: cetyltrimethylammonium, tetradecyldimethyl-ammonium, methyltriocthylammonium, dimethyldioctadecylammonium, poly (propylene oxide)-α-stearyldimethylammonium.

2- straight-chain alkyl aryls: zephiramine, dialkylmethylbenzylammonium, dimethylbenzylphenylammonium.

3- cyclicals: cetylpiridinum, triphenyltetrazolium.

b) Amines

1- cyclicals: pyridine, papaverine, antipyrine, diantipyrilmethane, 1-10 phenanthroline, α, α'dipyridyl, poly(vinylpyrrolidine), hexyldiantipyrylmethane.

2- non cyclicals: diphenilguanidine, trioctylamine, hydroxylamine, N-phenylbenzohydroxamic acid.

c) Other reagents: alkyltriphenylphosphonium, tri-n-octyl phosphine oxide, cyclohexanol, thioglicolic acid, triton X-100, dimedrol.

Other systems: sulphonitrophenol + hydroxylamine.

SENSITIVITY AND SELECTIVITY

The analysis of molybdenum traces are usually made by means of spectroscopic techniques and most of them suffer from inadequate sensitivity or selectivity. Preconcentration of the samples is therefore necessary by any one of such techniques as coprecipitation, ion-exchange, solvent extraction, chromatography or flotation prior to its analysis.

The introduction of a third component in a binary complex often leads to a drop in the pH of the complex formation and in most cases the ternary compounds are formed in a strongly acidic medium, which increases the selectivity of the methods.

Special attention has been paid to the systems Mo-triphenylmethane dye-surfactant, where the presence of the surfactant converts the dye into the reactive deprotonated form in a more acidic medium thus avoiding important interferences. The pH may also influence the stoichiometry of the compound since an increment of the pH may provoke a second dissociation of the dye which would lead to a diferent composition of the ternary compound (65). The nature of the surfactant also has some effect on the sensitivity and in numerous cases on λ_{max} of the compound. On the other hand triphenylmethane dye concentration can shift λ_{max} toward shorter wavelengths and this is the reason why different authors deduce different values of λ_{max} for the same compound (128).

The compounds with thiocyanate show the λ_{max} between 455 and 645 nm. The compounds without thiocyanate exhibit a wider range for measurements between 360 and 690 nm due to the participation in most cases of two organic reagents instead of one.

The sensitivity values are usually between 10^4 and 10^5 $l\ mol^{-1}\ cm^{-1}$ and higher values are only attained with thiocyanate-rhodamine compounds and with fluorone compounds. The high sensitivity shown by both types of ternary systems could be attributed to an increment in conjugation through meroquinoid structures together with the presence of the oxygen bridge between an aromatic ring and the quinone type ring.

The detection limits are usually of the order of part per million and part per billion levels of molybdenum can be determined with the thiocyanate-rhodamine system and with the bromopyrogallol red-cetylpyridinium system. With the fluorones the detection limits are not so low as could be expexted considering its high sensitivity.

Very often an extraction with organic solvent as preconcentration technique is used. The extraction may bring about an increase of sensitivity and/or selectivity but that is not always the case (128). Some times the extraction is applied with the sole aim of separating the ternary compound from its component (since the spectral characteristics are very similar) or solubilizing the ternary compound, allowing by this way the spectrophotometric determination in both cases. In most instances Cl_3CH has been used as solvent.

The methods gathered in this review are usually applied to molybdenum determination in ores, alloys and steels and only in some cases are applied to other materials such as waters, sediments, solid and plants. No application has been made to samples where the molybdenum content is of interest such as food, human body, animals...

The species that show interference more frequently are: Fe(III), W, V, Ti, Cu, Pd, Pt, Sn(II), Cr(VI), Zr, Bi, Al, Nb and Mn(II). These interferences may often be overcome by means of complexing or reducing agents. Thus Fe(III) is very often masked by reduction with ascorbic acid (11, 17, 25, 30, 42, 47, 65, 84, 88, 96, 104, 108, 112) or $SnCl_2$ (49) (these reductor agents sometimes are also needed to form the ternary compound). Fe(III) can also be masked by complex formation with phosphate (55, 101), pyrophosphate (119), EDTA (60, 111, 120), trilon B (78), F^- (108), $S_2O_3^{=}$ (4). W(VI) can be masked with citrate (1, 56, 26), tartrate (17, 26, 100), oxalate (10, 46) or thiocyanate (40). Other interfering cations are masked with EDTA (56, 60, 79, 84, 100, 111, 112, 120), F^- (30, 40, 56, 60, 79, 108, 112), $S_2O_3^{=}$ (4), oxalate (10, 46), thiourea (40) and citric acid (100). Sometimes a mixture of these species is used. Another way to eliminate interferences is by shaking the organic phase after separation of the aqueous phase with another aqueous solution containing a reductor agent (27, 47) or extracting the interferent species with a chelate and an organic solvent (51, 110). In some cases due to the numerous interfering species, extraction of the molybdenum with α benzoin oxime prior to its analysis, is prefered (62, 83, 101, 104, 117).

In conclusion we should say that the determination of molybdenum by means of ternary compound formation improves sensitivity in comparison with binary compounds, but selectivity is not substantially improved. Frequently preconcentration of the samples is needed when traces of molybdenum are going to be determined and prior separation of molybdenum is often convenient when it is present in complex materials.

MOLYBDENUM TERNARY COMPOUNDS CONTAINING THIOCYANATE

Ref.	Third componnent	medium	compos. Mo-SCN-X$^{a)}$	separ.	λmax	$\varepsilon^{b)}.10^{-4}$	int. or DL$^{c)}$ (µg/ml)	aplic.	interferences$^{d), h)}$
1	quinoline	2.5 M HCl	1:3:2	E$^{e)}$$PhNO_2$	470	1.8	≤ 5	steels	Cu, Fe(III), Os, Pd, Ti, V.W. No interference of Ag, Be, Bi, Cd, Co, Cr(III), Hg, Mg, Mn(II), Ni, Pb, Th, V, Cr(IV), EDTA, PO_4^{3-}, $P_2O_7^{4-}$, citrate, acetate, tartrate (50000).
2	2 benzylaminopydine	pH < 1	1:3:2	E $CHCl_3$	465	2.0	—	steels	—
3	3 benzoylaminopydine	3.6-4.8 M HCL	1:3:2$^{f)}$	—	460	1.6	—	—	—
4	amidopyridines	1.5-7 M HCl	1:2:1	E C_6H_6	470	1.9—	4.4—	steels	No interference of Cu, Co, Mn, Zn, Ni, Cd, Fe, Al, Cr, Ti, Zr, V, Nb, Ta, W, U.
5	4 benzylpyridine	2M HCl	1:4:2$^{f)}$	E $CHCl_3$	465	1.4	—	—	No interference of Ni(20), Cr(III), V(IV) (100).
6	3 benzylpyridine	1-8 M HCl	—	E $CHCl_3$	470	2.0	—	—	—
7	1,10 phenanthroline or 2,2′ bipyridyl	pH 1.5	1:3:1	E $C_2H_4Cl_2$	525	0.95 0.92	1-10	—	No interference of Fe, V(10), W, P, $SiO_3^{=}$ (100).
8	papaverine	3M HCl	—	E $CHCl_3$	470	2.4	5-60	—	—
9	lobeline	—	1:5:2	E $CHCl_3$	465	1.38	0.13-4	—	—
10	5-pyrazolones	1-5 M HCl	1:2:1	E $CHCl_3$	455	1.7-2.5	0.1-9	steel	No interference of Cu, Co, Mn(II), Fe(II, III), Al, Cr(III, VI), Ti(III), Zr, Hf, V(III, IV, V), Nb, Ta, W in excess.
11	nitron	3M HCl	2:10:3	E $CHCl_3$	465	1.52	1.2-12	steel	Mn(VII), Ti, $O_2^{=}$. No interference of W(2), Cr(VI), Cu, Fe(III), Pt, U, V(20), some alkalins, alkalinearths, heavy metals and anions (200).
12	triphenyletrazolim	—	1:6:3	E $C_2H_4Cl_2$	470	—	—	ore	—
13	phenothiazine der.	1.5-2.7 M HCl	1:4:1	E $CHCl_3$	465	—	1-10	—	Co, Cu, Bi, Fe(III), Ti, W(V), U(VI).
14	chlorpromazine	2M HCl	1:4:1	E $CHCl_3$	465	1.6	0.5-5	—	—
15	promethazine hydrochloride	0.5N H_2SO_4	1:5:2	E $CHCl_3$	465	1.5	0.5-5	steels	Co, Cu. No interference of Na, K, Mg, Ca, Ba, Zn, Mn(II), Cd, Al, Cr(III), W, UO_2^{2+} (100), Fe(III), V(50).
16	mepazine hydrochl	HCl	—	E $CHCl_3$	465	1.77	0.1-5.5	steels	—

MOLIBDENUM TERNARY COMPOUNDS CONTAINING THIOCYANATE (CONT.)

Ref.	Third component	medium	compos. MoSCN-X	separ.	λmax	$\varepsilon 10^{-4}$	int. or DL (μg/ml)	aplic.	interferences
17	rhodamine B	1.6 M H_2SO_4	1:5:2	—	600	10.9	0.004-0.4	plants, soils	W, Zn.
18	rhodamine 6G	0.55-0.8 M HCl	1:5:2	collect. $Fe(OH)_3$	570	26.3	0.04-0.24 (5ppb coll)	soils, sea w.	Zn, Co.
19	crystal violet	—	—	flotat PhMe	590	—	0.02-0.2	drinking water	—
20	crystal violet	3.5-4N H_2SO_4	1:5:2	E PhMe	595	—	0.5-4.ml	—	—
21	crystal violet	—	—	E PhMe	595	—	0.05-0.4	alloys	—
22	crystal violet	—	—	E PhMe	—	—	—	—	—
23	crystal violet	—	—	Flotat. PhMe	590	—	—	metallic Nb	—
24	N,N-dialkyl aniline der.	—	—	E $C_2H_4Cl_2$	470	—	1-10	steels	—
25	N,N-dialkil aniline	3-4 M $HClO_4$	—	E $C_2H_4Cl_2$	434	1.5	1-10	steel	—
26	N-benzylaniline	1.8 M H_2SO_4 or 2.8M HCl	—	E $CHCl_3$/ I.A	466	1.6	0-50		No interference of Pd, Pt, Rh, Au, Re, Te, PO_4^{3-}, $C_2O_4^{2-}$, BO_2^-, $A_sO_4^{3-}$, $Cr_2O_7^{2-}$, $CrO_4^{=}$, VO_3^-, citrate, tartrate.
27	tribenzylamine	2-3.5 M HCl	1:6:4	E $CHCl_3$	465	—	0-20	—	Pd, Pt, Os, acetate, oxalate, citrate.
28	diphenylguanidine	strongly acidic	1:5:2	E $CHCl_3$ $C_2H_4Cl_2$,IAg)	—	—	—	—	—
29	diphenylguanidine	0.9-3 M CHI	—	E $CHCl_3$	470	2.12	0.07-7	—	No interference of Ti, W, Re, Co (500), Cr, Mn, Ni, Cu, Zr(200), Nb(10), Bi(5).
30	monooctyl-α-anilino-benzyl-phosphonate	3M HCl	1:5:3	E $CHCl_3$	470	0.58	0.7-28	—	Zr, Th, Nb, U(VI) (100), Cu(50).
31	N-hydroxy-N-p-chlorophenyl-N'-(2-methyl-4-chlorophenyl) benzamidine hydrochloride	1.5-4.5 M HCl	—	E C_6H_6	470	0.45	2-20	ores, alloy steels	No interference of Fe(III), V, Nb Ta, W, Ti, Zr, Al, Cu, Zn, Cr(III), Mn(II), Sn, Ni, Co, Th and other metals commonly associated with Mo.
32	N^1-hidroxy-N^1-p--tolyl-N^3-(3,4-dimethylphenil) benzamidine	2-4.5 M HCl	1:2:1	—	470	0.38	—	ores, alloys	No interference of Ni, Co, Cu, Mn(II), Ti, Zr, V, Nb, Ta, W.
33	N, N' diphenylbenzamidine hydrochloride	1.2-7M HCl, 2-6 M H_2SO_4	1:2:1	E C_6H_6	465 —70	1.65-1.85	0.4-5.4	ores, alloy steels	No interference of Co, Cu, Pd, V(250), Ti(100), Nb(50).
34	p-chlorophenyl-o-chloro-benzamidine derivate	0.7-4 M HCl	—	E C_6H_6	470	0.33	3-24	ores steels	—
35	N-hydroxy-N-(p--chlorophenyl)-N'--(2,3-dimethylphenyl) p-toluamidine hydrochloride	3.4 M HCl	1:2:2	E C_6H_6	470	—	—	—	No interference of Ni, Co, Mn(II), U(VI), Zn, Cd, Pb, Cu, Al, Cr(III), PO_4^{3-}, AsO_4^{3-} (250), oxolate, citrate, tartrate, F^-, I^-, EDTA, Pd, Fe(III) (100), Zr(80), $S_2O_3^{2-}$(70), Ti(15), V(10), W(8).
36	N,N'-diphenyl-p--toluamidine	2-5 M HCl	1:2:2	E C_6H_6	470	1.77	0.4-5	—	No interference of Zr, W, U(VI)(1000), I^-, EDTA, $C_2O_4^{=}$, PO_4^{3-}, citrate, tartrate (3000), Co, Cu, Bi, Sb(III), V, F^-, $S_2O_3^{=}$(200), Ti(100).
37	imidoyl der.	1-5M HCl 0.8-6M H_2SO_4	1:2:1	E C_6H_6	645	0.8-1.4	—	ore, alloy steels	No interference of Fe(III), Bi, Sb(III), Tl(III), Th(700), Hg, F^-, $S_2O_3^{=}$(500), Pb, Zr(1000), I^-, AsO_4^{3-} (1500), Co, Pd, Nb, Ta(200), Nb, W(100).
38	imidoylphenyl-hydrazine	1.2-6.7 M HCl, 0.8-6M H_2SO_4	1:2:1	E C_6H_6	465	1.73	0.4-5	ores, alloy steels	—
39	amides	1-6.6M HCl, 1-6M H_2SO_4	1:2:1	E C_6H_6	475	1.33 —1.8	0.35 ml	ores, alloy steels	No Interference of AsO_4^{3-}(2500), Hg, Pb, Zr(1200), Fe, Bi, F^-, $S_2O_3^{=}$(600), W(350), V, Ta, Cu, Co, Pd, Ag(300), Ti(150), Nb(50).

MOLIBDENUM TERNARY COMPOUNDS CONTAINING THIOCYANATE (CONT.)

Ref.	Third component	medium	compos. MoSCN-X	separ.	λmax	$\varepsilon 10^{-4}$	int. or DL (μg/ml)	aplic.	interferences
40	hexamethyl phosphortriamide	1M HCl	—	E $CHCl_3$	460	1.76	0.5-6	alloy steels	No interference of U(VI), V, Ta, Zr(20), Re(VII) (10), $HONH_2$ (2.10^4), tartaric or ascorbic acid (10^4), F^- (9000), AEDT (3500).
41	1-carbetoxypentadecyltrimethylammonium bromide	—	—	E $CHCl_3$	460	—	—	—	—
42	carbetoxypentadecyltrimethylammonium	—	1:5:2	E $CHCl_3$	—	—	0.1-7 in org. phase	sedim.	—
43	zephiramine	—	—	E $CHCl_3$	—	—	0.48-4.8	—	Bi, Cu, Fe, IO_3^-, IO_4^-, Cr(VI), W(VI), Mn(VII) in amounts equal to that of Mo.
44	methyltrioctylammonium chloride	0.4M HCl	1:4:3	E PhMe	467	2.13	0.05-1	steels	No interference of alkalins, alkalinearths, Fe(III)(300), V, Cu, Bi, Pb, Cr(III), As(V), Sb(III), Zr, oxalate (200), Al, Zn, W, U(VI), Mn(II), Co, Hg, tartrade (100), Cd, Ni(50), Pd(10).
45	vanillin thiosemicarbazone	HCl	1:4:2	E $CHCl_3$	470	1.98	0.1-4.6	steels	—
46	tetraphenylarsonium chloride	2M H_2SO_4	—	E $CHCl_3$	470	1.7	—	steels	W(40), Nb(10).
47	tetraphenylarsonium or tetraphenylphosphonium chloride	2M HCl or 1M H_2SO_4	1:2:1 1:4:1	E $CHCl_3$	470	1.8	0.48-9.6	—	No interference UO_2^{2+}, Zr, Ta, Ga, Pd, Fe(III)(100), Nb, W(10), Fe(III) and W(1000) can be tolerated with a modified procedure.
48	triton X-100	0.22M H_2SO_4	—	—	468	1.7	0.02-4.6	steel	No interference of Ni (30); Co (12); W (2); Cu, Zn V (3) and Cr (VI) (5mg/50 ml).
49	Bu_3PO_4	—	1:5:3	E C_6H_6	480	1.8	—	steels	—
50	4-(dimethylamino) phenyl 4-(benzylmethylamino) phenyl antipyrinylcarbinol	0.7-0.8 HCl	—	—	—	—	0.04-0.3	—	Interference of Zn, Sb, Hg, W, Ga, In, NO_3^- I^-, BF_4, F^-. No interference of Be, Cu, A (500-1000), Bi, Te (100), V, Fe (50).
51	2-mercaptobenzo-γ-thiopyrone	1.4-3.6 M HCl	—	E acetophenone	470	—	0.75-8.5	steel	No interference of common ions (>1000)
52	ε-caprolactam	2-7 M HCl	1:5:4	—	475	2.0	0.5	—	No interference of Mg, Al, Ca(1000), Ba, Mn(II) (500), Ag, Zn, Co, Cr(III), Fe(II, III)(100), Ni(50), V, Zr(10).
53	ethylene glycol octyl Ph ether + Na dodecylbenzenesulfonate	H_2SO_4	—	—	470	—	0.4-2.8	Ti-Al Ti-Mo-Al alloys	No interference of Ti(20), Ni(30), Mn, Cd, Zn, Zr, Cr, Cu, Al, Pb(10), Co(2), Nb, alloys Ce, V(1).
54	salsolidine	pH 0.95 −1.15	—	E BuPh	—	2.0	0.2-16	—	W, Fe, V, Co, Re, Se, Bi, Pt, In, Cr, Ge, Os, Rh.

MOLIBDENUM TERNARY COMPOUNDS WITHOUT THIOCYANATE

Ref.	Reagents	medium	compos. Mo-Chr-T	separ.	λmax	$\varepsilon 10^{-4}$	int. or DL (μg/ml)	aplic.	interferences
55	gallein + papaverine	—	1:2:1	—	600	6.3	0.06	water	V, W.
56	gallein + zephiramine (BDTA)	pH 1-1.5	—	—	620	5:2	0-3.5	—	Sn(IV), Cr(III), Ti, Ag.
57	dibromogallein + polymeric surfactant	strong acid	1:2:1	—	642	10.8	—	steels, alloys	—
58	gallein + cetyltrimethylammonium bromide (CTA)	pH 1	—	—	618	—	< 0.5	—	Co, Fe(III), Sn, V, F^-.
59	gallein + CTA	pH 1	—	—	618	3.7	0.5-1.4	—	V, Sn, W, Sb, Fe and elements that cause precipitation.
60	pyrogallol red (PR) + cetylpyridinium chloride (CP)	pH 4.4-5.1	—	—	610	3.4	0-3	steels	—

MOLIBDENUM TERNARY COMPOUNDS WITHOUT THIOCYANATE (CONT.)

Ref.	Reagents	medium	compos. Mo-Chr-T	separ.	λmax	$\varepsilon 10^{-4}$	int. or DL (μg/ml)	aplic.	interferences
61	PR + CP	0.15-0.3 M HCl	1:2:2 1:2:4	E $CHCl_3$	610 605	5.5	–	–	No interference of Ti(250).
62	PR + CTA	pH 3.6	1:2:4	–	600	9.0	0.1-0.4	–	W, tartrate, I^-, citrate, oxalate. No interference of Bi, Th, Fe and others heavy metals(1000), Cr, Re(500), Te(300), Cu, Zr, Pd, Pt, Se(IV)(100), U(VI), Sn(IV), Hg, Ag, Ti, V, Sb(III)(10)
63	PR + CTA	–	1:2:2	–	570	5.3	0-100	ores	No interference of V, W.
64	PR + dimethylbenzylphenylammonium chlor.	pH 4	1:2:2	E BuOH	582	2.13	0.7-6	–	–
65	bromopyrogallol red (BPR) + CP	strong acid	1:2:2	–	630	–	0.08-1.4	steels, plants	W. No interference of Ca, Mg, Zn, Ni, Co, Mn.
66	BPR + CP	0.1-0.3 M HCl	1:1:1	–	630	4.3	0-1.2	–	–
67	BPR + CP	–	–	flotation	–	–	0.02	sea water	–
68	BPR + CP	1M HCl	1:2:2	E $CHCl_3$	610	5.9	0.25	sea water	–
69	BPR + CP	2M HCl	–	E $CHCl_3$	610	3.82	0.002-0.04	–	Co, Se(IV), Bi, Cr(III), Hg, Pb, Ni, Mn(II) (1000).
		2M HCl	–	E $CHCl_3$	620	6.2	0.004-0.04	–	Mn(VII), Cr(VI), W, V, Zr, Ti(5).
70	BPR + CTA	0.02-0.3 M HCl	–	absorbed on alumina	624	6.1	–	–	miligram amts. of ClO_4^-, Fe(III) and microgram amts. of V, Sn(IV), Ti, Zr, Nb, W.
71	BPR + zephiramine	0.16-0.24 M HCl	–	–	629	5.56	0.08-1	iron, steels	W.
72	BPR + some surfactants	pH 1	1:2:2	anion exchan	630	6.5-8.4	–	sea water, steels	–
73	BPR + tri-n-octyl phosphosphine oxide (TOPO)	–	–	E $PhNO_2$	–	–	–	part. matter, sea water, sediments	–
74	BPR + red-poly (vinylpyrrolidine	weak acid	–	–	600	7.4	–	enzyme sample	–
75	BPR + 1,10-phenantroline	pH 4	1:2:2	–	610	–	0.4-1	–	–
76	phenylfluorone + CTA	0.39N H_2SO_4	–	–	530	–	0.1-80	uranium solns	W(≥ 0.5). No interference of Fe.
77	phenylfluorone + triton-X 100	–	1:1:0.3	–	520	11,1	–		–
78	p-nitrophenylfluorone + antipyrine	HCl	–	E $CHCl_3$ -PrOH	530	–	–	steels, alloys	V, W, Ti, Sb(V), Sn(IV). No interference of Zn, Co, Ni, Mn.
79	4,5-dibromophenylfluorone + CTA	1.2-2.1 M HCl	–	–	538	12	0-0.55	alloys, steels, ores	–
80	o-nitrophenylfluorone + diantipyrylmethane	–	–	–	490 530	13.1	0.07-0.5	magnet. films	No interference of Ti, Zr(1400), Zn (1000), Fe(600), Ni(250), V(20).
81	propyltrihydroxyfluorone + antipyrine	pH 2-2.7	1:1:2	E $CHCl_3$	515	–	–	–	–
82	salicyifluorone + antipyrine	acid	–	E $CHCl_3$	–	13	0.03 0.5-1	NaOH, KOH, metallic Ti.	–
83	phneylfluorone + CTA	–	–	–	–	10.3	–	–	W, Sn, Ge, Nb, Ta, Ti, Zr, Ga, Sb.
84	salicylfluorone + CTA	–	1:2:2	–	530	14	0-0.3	steels	W, Ti.
85	phenylfluorone + N-phenyl-benzohydroxamic	HCl	1:1:2	E $CHCl_3$	518	7.4	0.6	std steel	–

MOLIBDENUM TERNARY COMPOUNDS WITHOUT THIOCYANATE (CONT.)

Ref.	Reagents	medium	compos. Mo-Chr-T	separ.	λmax	$\varepsilon 10^{-4}$	int. or DL (μg/ml)	aplic.	interferences
86	pyrocatechol violet (PCV) + CTA	pH 3-5	1:1:2	–	675	4.6	9.6-96	–	Pb, Cr(VI), Ti, V and ions which form complex with catechol violet.
87	PCV + CTA	pH 4-6	1:1:2	–	660	4.7	–	–	No interference of Mg, Cd, Mn(400), Cl^- (500), Zn(600), Ca, Sr(100), Ni(140), Pb, Cr, Co(20), Y(10), La(5).
88	PCV + benzyltetradecyl dimethylammonium chloride	–	1:1:1	–	690	4.24	0-0.5	–	–
89	PCV + PC	pH 2-4	–	–	–	15	–	–	Sc, Y, Cd, rare earths.
90	PCV + dialkylmethylbenzylammonium chloride	pH 0.2 -0.6	–	E $CHCl_3$	560	6.25	0.009-0.9	–	Sn(IV), W.
91	PCV + trioctylamine	pH 0.6	–	E PhMe	545	–	–	–	–
92	pyrocatechol(PC) + triphenyltetrazolium chloride	pH 0.5	–	E $Cl_2C_2H_4$	640	–	2.5-15ml	Mo conc.	Au, Os, Pt, Hg(6).
93	PC + papaverine	pH 1	1:2:1	E $CHCl_3$	400	–	0.5-6	–	No interference of Ni, Zn(200), Ti, V, Cu, U, Th(100), Nb, Cr(50), Ta(20).
94	PC + alkyltriphenylphosphonium	pH 2	1:2:1	E $CHCl_3$ CH_2Cl_2	400 620	–	–	–	$H_2C_2O_4$, HCl. No interference of W, Nb, Fe(III), Ti, V(IV), U(VI).
95	PC + $BuPh_3P^+$	acid	–	E $CHCl_3$	370	–	–	steels	–
96	PC + $BuPh_3P^+$	1-1.5M H_2SO_4	–	E $CHCl_3$	660-700	–	10-150ml	steels ores	No interference of Ni, Co, Cr, Mn, V.
97	PC+α-α', -dipyridyl	–	–	E $CHCl_3$	420	–	–	ores	–
98	PC + hexyldiantipyrylmethane	pH 2	1:1:1	E various	410 610	–	0.48-19	–	Al, Ti, Sn, Bi, Fe. Slight interference of Hg, Pb, Cr, Mn, Co.
99	PC + diantipyrinylmethane	1-2M HCl	1:2:1	E $CHCl_3$	440 640	–	–	steels	Ti, Ta, Ge, W but W($\leqslant$ 20μg) and Ti ($\leqslant$50μg) do not interfere of Al, Pb, Zn, Bi, Cd, As, Mn, Co, Cu, Ni, Cr.
100	PC + dimedrol	pH 1.3 -1.8	1:1:1	E $CHCl_3$	400	0.5	0.5-6	–	No interference of Co, U, Ni, Mn, Al, Cd, Zn, Re, Fe, Ga, Ge, Ca, Zr, Ce, Th, $P_4O_7^{4-}$, PO_4^{3-}, $H_2C_2O_4$.
101	pyrogallol + dimethyldioctadecyl ammonium	pH $\leqslant$ 1.5	1:2:2	–	600	4.2	–	natural waters	V, W(1). No interference of Pb, Mn, Al, Zn, Ni, Co, (100), Cr, Cu, Th, U, Sn, Sc(10).
102	4-butyrylpyrogallol + hydroxylamine	–	–	–	360	0.36	0.4-40	ferromolybdenum	–
103	hematoxyline + CTA	pH 5.6 -6.8	1:1:2	–	415	0.58	3-11	–	Al, Bi, Pb, Th, U, Zr.
		pH 4.7 -5.1	1:3:3	–	610	5.2	–	–	–
104	carminic acid + surfactants	pH 4.8	–	–	579	1.72	0.44-8.7	steels	No interference of Fe(III), Cu(0.01), Al(0.25), As(III), Sb(III), Pb, Zn(0.2), $C_2O_4^{=}$, NO_3^-, PO_4^{3-}, V(0.5), I^-, SCN^-, Sr(1), Br^-(2), Ni, Mn(II), ClO_4^-, IO_3^-(5), Co, Cl^-(10), ClO_3^-(30), $SO_4^{=}$(200).
105	tiron + zephiramine	pH 8	–	E $CHCl_3$	390	–	–	iron, steels	W.
106	tiron + papaverine	pH 1.2 -2.2	1:1:4	E $CHCl_3$	400	0.63	5-50	ore, ferro-fosforous	
	tiron + dimedrol	pH 2.8 -4.2	1:2:4	E $CHCl_3$	370	0.91	5-50		
107	eriochrome black T + trioctylamine	pH 2	–	E MePh	610	–	–	alloys	–
108	stilbazo + zephiramine	pH 3.6 -4.2	–	–	535	6.3	0.64	iron, steel	Al, Ga, V(IV, V), Ti, Zr, W, Pd, Pb, ClO_4^-
109	[4-(2 pyridylazo)-resorcinol} + hydroxylamine	pH 6	–	–	530	–	2	WO_3, W metal	–
110	{4-(2 pyridylazo)-resorcinol] + hydroxylamine	pH 6-7	1:1:1	–	530	2.74	0.013	–	Fe(52)

MOLIBDENUM TERNARY COMPOUNDS WITHOUT THIOCYANATE (CONT.)

Ref.	**Reagents**	**medium**	**compos. Mo-Chr-T**	**separ.**	**λmax**	**$\varepsilon 10^{-4}$**	**int. or DL (μg/ml)**	**aplic.**	**interferences**
111	2-(5-bromo-2-pyridilazo-5-(diethylamino) phenol + hydroxylamine	—	1:1:1	—	600-605	4.8	3	—	No interference of W.
112	Na 2-bromo-4,5 dihydroxyazobenzene-4'-sulfonate + CTA	pH 1.6	—	—	525	6.1	0-1.1	—	—
113	o.o'-dihydroxyazo compounds + hydrolamine	pH 3	—	—	650	5	—	—	Bi, Ti, citrate, oxalate. No interference of Mg(100), Ni, Al(20), Fe(II, III), Sn(II), Nb(2), Cu, Zr(1).
114	KTADF (azo compd.) + hydroxylamine	slight. acid	—	E benzyl alcohol	530-40	3.6	0.5-3.3	—	No interference of W, Ca, Al(20), Fe (III)(7), Cu(3).
115	salicylhydroxamic acid + methyltrioctylammonium (adogen)	pH 0.9	1:2:2	E MePh	315	1.1	0.7-5	—	V, Bi, Ti(3). No interference of Cu, Sn(II)(15), Ag, Zr, Fe(III), ClO_4^-(3).
116	benzohydroxamic acid + trioctilmethylammonium (adogen 464)	pH 0.7-10	1:1:1	E MePh	300	0.11	0.7-7	steel, pharm. pr.	No interference of Ag, Cu, Cd, Be, Cr(VI), PO_4^{3-}(17), Sn(II), Pb, Sb(III), (1.7), V, Fe(III), Ti, Bi, Zr, W(0.03).
117	oxine + pyridine	H_2SO_4	—	—	405	0.44	0.8-24	ores	No interference of W but at 450 nm.
118	8-hydroxy-5-quinolinesulfonic acid + methyl trioctylammonium chlor.	pH 4.6	2:3:5	E $CHCl_3$	570	—	3.8-29	—	Zn(10) Al, W(2), V(0.5), Ni, Cu(0.2), Fe(III), (0.1).
119	ferron + cyclohexanol	0.1-0.3N HCl or H_2SO_4	1:2:3	E cyclo hexanol	395-405	0.55	3.5-15	—	No interference of Cu(1), V(1), W(4).
120	indoferron + diphenyl-guanidine	pH 1.5-2.1	1:2:1	E $CHCl_3$	555	1.0	6.7	—	—
121	alizarin red S + tetra decyldimethylammonium chloride	pH 4.5-5.5	—	E $Cl_2C_2H_4$	525	—	0.1-2.5	—	—
122	sulfonitrophenol M + hydroxylamine	—	—	—	650	—	—	—	—
123	pyridine-2,4 dicarboxylic acid + thioglycolic acid.	pH 3	—	—	482	—	1-15	—	Be, Ca, Sr, Ba, Zn, Cd, Ce, In, Ge, Ni, W, U.

a) X and T are the third compents
b) in liter.mole^{-1}.cm^{-1}
c) int. or DL. = determination interval or detection limit
d) The number between brackets indicates fold amount of interferent relative to molybdenum
e) E = extraction
f) Chloride appears as fourth component
g) I A = isoamyl alcohol
h) The overcome interferences are not included in the tables but are described in the text

REFERENCES

1. **RAO, V.P.R.; ANJANEYULU, Y. and MURTY, A.S.R.K.,** *Mikrochimica Acta* 1975, **2-3**, 265.
2. **PILIPENKO, A.T. and SOLOMEINA, Z.G.,** *Ukr. Khim. Zh.* (Russ. Ed.) 1973, **39**(11), 1169.
3. **PILIPENKO, A.T. and SAFRONOVA, V.G.** *Ukr. Khim. Zh.* (Russ. Ed.) 1977, **43**(2), 184.
4. **PATEL, K.S. and MISHRA, R.K.,** *Talanta* 1982, **29(9)**, 791.
5. **PILIPENKO, A.T. and SAFRANOVA, V.G.,** *Ukr. Khim. Zh.* (Russ. Ed.) 1974, **40**(9), 971.
6. **PILIPENKO, A.T. and SAFRANOVA, V.G.,** *Ukr. Khim. Zh.* (Russ Ed.) 1976, **42**(6), 636.
7. **BHADRA, A.K. and BANERJEE, S.,** *Talanta,* 1973, **20**(3), 342.
8. **TALIPOV, S.T.; DZHIYANBAEVA, R.K SHAMAEV, M.; SHESTEROVA, I.P. and ZHANABAEV, B.Z.,** *Deposited Doc.* 1975, VINITI 1087, 8 pp.
9. **NYTKO, K. and SIKORSKA-TOMICKA, H.,** *Microchem. J.* 1980, **25**(4), 548.
10. **AHMAD, A.; NWABUE, F.I. and EZEIFE, G.E.,** *Talanta* 1984, **31**(4), 265.
11. **KORALEWSKI, T.J.; PARKER, G.A.,** *Anal. Chim. Acta* 1980, **113**(2), 389.
12. **ALEKSANDROV, A. and KOSTOVA, M.** Nauchni Tr.-Plovdivski Univ. 1975, 13(3), 229.

13. **TARASIEWICZ, M. and PUZANOWSKA-TARASIEWICZ, H.,** *Chem. Anal.* (Warsaw) 1973, **18**(3), 599.
14. **PUZANOWSKA-TARASIEWICZ, H.; GRUDNIEVSKA, A. and TARASIEVICZ, M.** *Anal. Chim. Acta* 1977, **94**(2), 435.
15. **GRUDNIEVSKA, A.; TARASIEWICZ, M. and PUZANOWSKA-TARASIEWICZ, H.;** FRESENIUS' *Z., Anal. Chem.* 1983, **315**(4), 355.
16. **SANKE GOWDA, H.; RAMAPPA, P.G. and MAJAPPA, S.,** *Indian J. Chem., Sect.* A 1979, **18A**(3), 276.
17. **HADDAD, P.P.; ALEXANDER, P.W. and SMYTHE, L.E.,** *Talanta* 1975, **22**(1), 61.
18. **RAO, T.P. and RAMAKRISHNA, T.V.,** *Bull. Chem. Soc. Jpn.* 1980, **53**(8), 2380.
19. **IVANOVA, I.F.; GANAGO, L.I.; PUSHKAREVA, T.M.; EZERSKAYA, T.V. and KARTASHOVA, G.I.,** *Gig. Sanit.* 1983, (1), 57.
20. **GANAGO, L.I. and IVANOVA, I.F.,** *Zh. Anal. Khim.* 1972, **27**(4), 713.
21. **GANAGO, L.I.; IVANOVA, I.F.; BUKHTEEVA, L.N. and STRIBUK, E.K.,** *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk* 1972, (1), 89
22. **SHKROBOT, E.P. and SHEBARSHINA, N.I.;** Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1980.
23. **IVANOVA, I.F.; GANAGO, L.I. and SEMENOVICH, I.A.,** *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1977, **20**(12), 1815.
24. **BABENKO, A.S.; MINEEVA, L.A. and GODOVSKAYA, K.I.,** *Zavod. Lab.* 1976, **42**(9), 1035.
25. Ibid, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 1976, **19**(11), 1671.
26. **KHOSLA, M.M.L. and RAO, S.P.,** *Anal. Chim. Acta* 1971, **57**, 323.
27. **YATIRAJAM, V. and RAM, J.,** *Mikrochim. Acta* 1974, (4), 671.
28. **VERDIZADE, N.A.; SHIRALIEVA, S.M.; MELIKOV, S.R.; AMRAHKOV, T.I. and RAGIMOVA, Z.B.,** *Org. Reagenty Anal. Khim., Tezisy Dokl. Vses. Konf.,* 4th 1976, 2, 16.
29. **DOLGOREV, A.V. and GUSHCHINA, I.D.** *Zavod. Lab.,* 1974, **40**(1), 26.
30. **TAMHINA, B.; HERAK, M.J. and JAGODIC, V.,** *Anal. Chim. Acta* 1975, **76**(2), 417.
31. **KHARSAN, R.S.; PATEL, K.S.; DEB, K.K. and MISHRA, R.K.;** FRESENIUS'Z. *Anal. Chem.* 1979, **295**(5), 415.
32. **KHARSAN, R.S. and MISHRA, R.K.** *Bull. Chem.* Soc. Jpn. 1980, **53**(6), 1736.
33. **PATEL, K.S. and VERMA, R.M.** *Anal. Chem.,* 1982, **54**(1), 52.
34. **CHANDRAKAR, L.P. and MISHRA, R.K.,** *J. Indian Chem. Soc.* 1986, **63**(10), 920.
35. **KHARSAN, R.S.; PATEL, K.S. and MISHRA, R.K.,** *Mikrochim. Acta* 1979, **1**(5-6), 353.
36. **VERMA, R.M.; PATEL, K.S. and MISHRA, R.K.;** FRESENIUS'Z. *Anal. Chem.* 1981, 307, 128.
37. **PATEL, K.S. and MISHRA, R.K.** *Bull. Chem. Soc. Jpn.* 1983, **56**(9), 2811.
38. *Ibid, Ann. Chim.* (Rome) 1983, **73**(1-2), 91.
39. **PATEL, K.S.; KHATRI, H. and MISHRA, R.K.** *Anal. Chem.* 1983, **55**(11), 1823.
40. **MITRA, M. and MITRA, B.K.,** *Talanta* 1977, **24**(11), 698.
41. **MALAT, M.;** FRESENIUS'Z. *Anal. Chem.* 1979, **297**(5), 417.
42. **RANCICOVA, M.; CUTA, J. and MALAT, M.** *Vodni Hospod.* B 1981, **31**(1), 19.
43. **HIROSHI, M. and SHOKICHI, C.,** *Bunseki Kagaku* 1967, **16**(6), 551.
44. **SALINAS, F.; BERZAS, J.J. and ACEDO, M.I.,** *Talanta* 1985, **32**(1), 63.
45. **THIMMAIAH, K.N.; SEKHAN, V.C. and CHANDRAPPA,** *Acta Chim. Hung.* 1987, **124**(3), 491.
46. **FOGG, A.G.; KUMAR, J.L. and BURNS, D.T.** *Analyst* 1975, 100, 311.
47. **TAMHINA, B. and HERAK, M.J.;** *MIKROCHIM. Acta* 1976, **1**(6), 553.
48. **HAYASHI, K.; YAMAMOTO, A.; FUJIMURA, Y. and ITO, S.** *Bunseki Kagaku* 1980, **29**(7), T39.
49. **GORLACH, V.F. and MARCHENKO, L.M.** *Ukr. Khim. Zh.* 1974, **40**(9), 983.
50. **ZHIVOPISTSEV, V.P.; SELEZNEVA, E.A. and BRAGINA, Z.I.,** *Uch. Zap., Perm. Gos. Univ.* 1966, 159, 243.
51. **SAVARIAR, C.P.; ARUNACHALAM, M.K. and HARIHARAN, T.R.** *Anal. Chim. Acta* 1974, **69**(2), 305.
52. **EREMIN, Y.G.; RODIONOVA, T.V. and KOLPIKOVA, E.F.** *Zh. Anal. Khim.* 1979, **34**(3), 491.
53. **GUO, C. and ZHAUG, L.** *Huaxue Shijie* 1984, **25**(2), 54.
54. **ALIMUKHAMEDOVA, M.M. and BUKINA, V.K.** Fiz.-Khim. Issled. Glinistykh Miner. Silikat. Mater. 1970, 110-13.
55. **ROSSINSKAYA, E.S.; MORGEN, E.A. and VLASOV, N.A.** *Deposited Doc.* 1974, VINITI 38-74, 7 pp.
56. **SATURABA, S.** *Bunseki Kagaku* 1973, **22**(3), 270.
57. *Liu, Kunyuan, and Yu,* Rufqin, Huaxue Xuebao 1987, **45**(6), 584.
58. **Lu, L.C.;** *Malaysia Geol. Surv., Annu. Rep.* 1969, 115.
59. **LEONG, C.I.;** *Analyst* 1970, **95**, 1018.
60. **MORI, I,; FUJITA, Y.; KAMATA, Y.; MAEYAMA, M. and ENOKI, T.;** *Bunseki Kagaku* 1980, **29**(9), 638.
61. **GANAGO, L.I.; ALINOVSKAYA, L.A.; IVANOVA, I.F. and KOVALEVA, L.V.** *Zh. Anal. Khim.* 1984, **39**(2), 251.
62. **WYGANOWSKI, C.** *Microchem. J.* 1980, **25**(2), 147.
63. **LIU, S. and XU, Q.,** *Fen Hsi Hua Hsueh* 1981, **9**(3), 311.
64. **POSTORONKO, A.I. and GOLOSNITSKAYA, V.A.,** *Zh. Neorg. Khim* 1980, **25**(9), 2446.
65. **SAVVIN, S.B.; CHERNOVA, R.K. and BELOLIPTSEVA, G.M.;** *Zh. Anal. Khim.* 1980, **35**(6), 1128.
66. YUNNAN UNIVERSITY, Fen Hsi Hua Hsueh 1978, **6**(3), 170.
67. **ANDREEVA, I.Y.; LEBEDEVA, L.I. and DRAPCHINSKAYA, O.L.** *Zh. Anal. Khim.* 1985, **40**(4), 694.
68. **ANDREEVA, I.Y.; LEBEDEVA, L.I. and SHABLINA, M.Y.,** *Vestn. Leningr. Univ., Fiz., Khim.* 1985, (1), 65.
69. **GARCIA-ARENAS, J.,** Tesis de Licenciatura, Universidad de Cádiz 1985.
70. **LIN, C.,** Fen Hsi Hua Hsueh 1980, **8**(4), 345.
71. **DEGUCHI, M.; IIZUKA, M. and YASHIKI, M.** Bunseki Kagaku 1974, **23**(7), 760.
72. **ANDREEVA, I.Y.; LEBEDEVA, L.I. and KAVELINA, G.L.;** *Zh. Anal. Khim.* 1982, **37**(12), 2202.
73. **BABU, S.K.; MURTHY, M.V.K. and SATYANARAYANA, D.** *Mar. Environ. Res.* 1984, **11**(4), 305.
74. **WANG, H.; and GONG, G.,** Lanzhou Daxue Xuebao, Ziran Kexueban 1982, (1), 120-4.
75. **TANANAIKO, M.M. and GORENSHTEIN, L.I.** *Ukr. Khim. Zh.* 1979, **45**(10), 1005.
76. **LI, L.** *Youkuangye* 1983, **2**(2), 39.
77. **TIE, A.; YU, W.; L, C.; LIAO, W.; SHI, Y.; LIAO, X. and LIU, H.** *Fenxi Huaxue* 1983, **11**(11), 839.
78. **MININA, L.I.; SHCHEMELEVA, G.G. and BAGDASAROV, K.N.** *Fiz.-Khim. Metody Anal. Kontr. Proizvod., Mater. Konf. Rab. Vuzov (Vyssh. Uch. Zaded.), Zavod. Lab.* Yugo-Vostoka SSSr, 4th 1971.
79. **WANG, D.; BAI, J.; CHEN, J. and PAN, Q.** *Fenxi Huaxue* 1984, **12**(2), 140.
80. **GANAGO, L.I. and IVANOVA, I.F.** *Zh. Anal. Khim.* 1980, **35**(6), 1138.
81. **NAZARENKO, V.A.; SHELIKHINA, E.I. and ANTONOVICH, V.P.,** *Zh. Anal. Khim.* 1972, **27**(2), 307.
82. **NAZARENKO, V.A.; SHUSTOVA, M.B. and SHELIKHINA, E.I.** *Zh. Anal. Khim.* 1970, **25**(11), 2139.
83. **CHANG, T.; KO, H. TSENG, H. and HSU, H.** *Fen Hsi Hua Hsueh* 1977, 5(5), 383.
84. **SHEN, H. and WANG, Z.** *Gaodeng Xuexiao Huaxue Xuebao* 1982, 3(3), 300.
85. **GUNAWARDHANA, H.D. and FERNANDO, S.A.** *Can. J. Chem.,* 1987, **65**(5), 1124.
86. **BAILEY, B.W.; CHESTER, J.E. DAGNALL, R.M. and WEST, T.S.** *Talanta,* 1968, **15**(12), 1359.
87. **TIKHONOV, V.N.; MIKHAILIVA, A.M.; MYASNIKOVA, I.A. and BANYURKINA, V.I.** *Zh. Anal. Khim.* 1983, **38**(2), 216.
88. **CHOU, T. and CHANG, S.** *Fen Hsi Hua Hsueh* 1980, **8**(6), 527.
89. **CHERNOVA, R.K.** *Zh. Anal. Khim.* 1977, **32**, 1477.
90. **KOHARA, H.; ISHIBASHI, N.; and ABE, K.** *Bunseki Kagaku,* 1970, **19**(1), 48.
91. **PONOMAREVA, A.A. and AGRINSKAYA, N.A.** *Zadov. Lab* 1972, **38**(7), 790.
92. **ALEKSANDROV, A. and KOSTOVA, M.** *Mikrochim. Acta* 1976, **1**(4-5), 487.
93. **TALIPOV, S.T.; GOR'KOVAYA, G.P. and DZHIYANBAEVE,**

R.K., *Nauch. Tr., Tashkent. Gos. Univ.* 1967, No. 284, 83.

94. **GREBENOVA, B., and vrchlabsky, M.** *Collect. Czch. Chem. Commun.* 1973, **38**(2), 379.
95. **DOCEKALOVA-KLAPALOVA, H. and VRCHLAVSKY, M.** *Hutn. Listy* 1976, (5), 356.
96. **BENATSKY, M., NOVOSADOVA, D. and TOMIK, B.**, *Sb. Ved. Pr. Vys. Sk. Banske Ostrave,* Rada Hutn. 1977, **23**(1), 97.
97. **NIGAI, K.G. and TURSUNOV, A.A.** Sb. Nauchn. Tr.-Tashk. Gos. Univ. im. V.I. Lenina 1978, **553**, 78.
98. **SHNAIDERMAN, S.Ya. and GUMEN, A.S.**; *Zh. Anal. Khim.* 1972, **27(1)**, 2060.
99. **TANANAIKO, M.M.; GORENSHTEIN, L.I. and ZHIDIK, L.G.** *Ukr. Khim. Zh.* 1970, **36**(7), 703.
100. **DUSTOV, V.; MAKSUDOV, N.K.; DZHIYANBAEVA, R.K. and TAPILOV, S.T.** *Uzb. Khim. Zh.* 1972, **16**(2), 23.
101. **MORGEN, E.A.; ROSSINSKAYA, E.S. and VLASOV, N.A.** *Zh. Anal. Khim.* 1975, **30**(7), 1384.
102. **DUMITRESCU, V. and VEGH, B.** *Rev. Chim.* (Bucharest) 1977, **28**(3), 268.
103. **VALERO, J.** Afinidad 1981, **38**(371), 50.
104. **PEREZ RUIZ, T.; MARTINEZ LOZANO, C.; TOMAS MARTINEZ, V. and BAÑON del VALLE, J.** *Quim. Anal.* 1985, 4 n° 4, 395.
105. **NAKATANI, M.; BUNSEKI KAGAKU** 1972, **21**(12), 1624.
106. **TALIPOV, S.T.; SHESTEROVA, I.P. and SHAMAEV, M.**; *Deposited Doc.* 1975, VINITI 1088-75, 10 pp.
107. **AGRINSKAYA, N.A. KUTYREV, I.M. and DAVYDOVA, R.T.** *Zavod Lab.* 1982. **48**(7), 24.
108. **OZAWA, T.; OKUTANI, T. and UTSUMI, S.**; *Bunseki Kagaku,* 1973, **22**(12), 1592.
109. **LASSNER, E.; PUESCHEL, R. and KATZENGRUBER, K.** *Mikrochim. Acta* 1969, **(3)**, 527.
110. **LASSNER, E.; PUESCHEL, R.; KATZENGRUBER, K. and SCHEDLE, H.** *Mikrochim. Acta* 1969, **(1)**, 134.
111. **CHEN, Y.; HUANG, Z. LU, J. and ZHANG, L.** *Kao Teng Hsue Hsiao Hua Hsueh Hsueh Pao* 1981, **2**(2), 155.
112. **WAKAMATSU, Y.**; *Bunseki Kagaku* 1977, **26**(7), 470.
113. **SAVVIN, S.B.; MINEEVA, V.A.; OKHANOVA, L.A. and PACHADZHANOV, D.N.**; *Zh. Anal. Khim.* 1971, **26**(3), 532.
114. **MURADOVA, F.A.; YUSUPOV, M.; and PACHADZANOV, D.N.**; *Izv Akad. Nauk Tadzh. SSr, Otd. Fiz.-Mat. Geol.-Khim. Nauk* 1979, **(3)**, 109.
115. **SALINAS, F.; MARCH, J.G. and FORTEZA, R.** *An. Quim. Ser. B* 1984, **80** (1), 116.
116. **SALINAS, F. and MARCH, J.G.** *Quim. Anal.* 1984, **3**(1), 31.
117. **NISHIDA, H.**; *Bunseki Kagaku* 1973, **22**(6), 771.
118. **SUGAWARA, M. UTO, M. and KAMBARA, T.**, *Bull. Chem. Soc. Jpn.* 1983, **56**(10), 3179.
119. **RAO, V.P.R. and RAO, K.V.**, *J. Inorg. Nucl. Chem.* 1968, **30**(9), 2445.
120. **WAKAMATSU, Y. and OTOMO, M.** *Bunseki Kagaku* 1972, **21**(12), 1650.
121. **ISHIBASHI, N.; KOHARA, H. and ABE, K.** *Bunseki Kagaku* 1968, **17**(2), 154.
122. **MALYUTINA, T.M.; SAVVIN, S.B.; ORLOVA, V.A.; MINEEVA, V.A. and KIRILLOVA, T.I.**, *Zh. Anal. Khim.* 1974, **29**(5), 925.
123. **HARTKAMP, H.; FRESENIUS'Z.** *Anal. Chem.* 1968, **241**(1), 66.
124. **KORKISCH, J. and GROSS, H.** *Talanta* 1973, **20**, 1153.
125. **CHAU, Y.K. and LUM-SHUE-CHAN, K.** *Anal. Chim. Acta* 1969, **48**, 205.
126. **STUPAR, J.; DOLINSEK, F.; SPENKO, M. and FURLAN, J.** *Landwirtsch Forsch.* **27**, 1, 1974.
127. **STEINER, J.W. and RYAN, K.M.** *Analyst* 1984, **109**, 581.
128. **TIKHONOV, V.N.** *Zh. Anal. Khim.* 1977, **32**, 1435.
129. **LILLIE, E.G. and GREENLAND, L.P.** *Anal. Chim. Acta* 1974, **69**, 313.
130. **MCKAVENEY, J.P. and FREISER, H.** *Anal. Chem.* 1957, **29**, 290.
131. **WEISS, H.V. and LAI, M.G.** *Talanta* 1961, **8**, 72.
132. **PENG, P.J. and SANDELL, E.B.** *Anal. Chim. Acta* 1963, **29**, 325.
133. **HISKEY, C.F. and MELOCHE, V.W.** *J. Am. Chem. Soc.* 1940, **62**, 1565.
134. **GRENNLAND, L.P. and LILLIE E.G.** *Anal. Chim. Acta* 1974, **69**, 335.
135. **GARCIA ALONSO, J.I.; DIAZ GARCIA, M.E. and SANZ MEDEL, A.** *Talanta* 1984. 31, No 5, 361.
136. **SHIJO, Y. and TAKEUCHI, T.** *Japan Analyst* 1971, **20**, 980.