Spectrophotometric Determination of Copper, Cobalt, Nickel, and Tellurium after Extraction with Morpholine-4-carbodithioate into Molten Naphthalene

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Potassium morpholine-4-carbodithioate has been examined as a reagent for the spectrophotometric determination of copper, cobalt, nickel and tellurium after extraction into molten naphthalene. The extracted mixture of metal complex and naphthalene was dissolved in chloroform and the trace amounts of these metals determined spectrophotometrically. Beer's law holds in the concentration range Cu: 5.0—70.0, Co: 5.0—81.0, Ni: 6.0—90.0, and Te: 5.7—125.0 μg per 10 ml of the final solution. The molar absorptivity and sensitivity are calculated to be Cu: 1.067×10^4 mol^{-1} cm^{-1}, 0.0059 μg/cm^2 (440 nm), Co: 1.350×10^4 mol^{-1} cm^{-1}, 0.0043 μg/cm^2 (360 nm), Ni: 7.920×10^3 mol^{-1} cm^{-1}, 0.0088 μg/cm^2 (390 nm), and Te: 1.075×10^4 mol^{-1} cm^{-1}, 0.0110 μg/cm^2 (415 nm). Aliquots containing 25.0 μg of copper, 27.0 μg of cobalt, 24.0 μg of nickel and 25.5 μg of tellurium gave a mean absorbance of 0.420, 0.620, 0.270, and 0.215 with a relative standard deviation of 0.0016, 0.0024, 0.0015, and 0.0013 respectively. The interference of various ions has been studied in detail. Only cobalt interfered in the determination of nickel which was eliminated by extraction first at low pH. Methods were developed for the determination of copper, cobalt and nickel in various alloys. A method was also developed for simultaneous determination of tellurium and selenium in the pure solution, based upon the thermal instability of seleniumelided carbodithioate complex.

Morpholine-4-carbodithioate has been suggested as a possible analytical reagent by Beyer and Ott[1)] in the spectrophotometric[2,3)] and volumetric[4)] determination of some metals. Recently, it has been utilized in the gravimetric determination of tellurium, copper, bismuth, palladium and nickel.[5—8)] The reagent was used in the thin layer[9)] and paper[10)] chromatographic separation of metal complexes. A preliminary study indicated that bismuth, copper, cobalt, nickel, and tellurium formed coloured, water insoluble and thermally stable metal complexes which may be extracted with molten naphthalene. The extraction-spectrophotometric determination of bismuth has been reported.[11)] Conditions have been developed for the determination of copper, cobalt, nickel and tellurium and also for the analysis of alloys containing copper, cobalt and nickel. Based upon the thermal instability of selenium complex of this reagent, a method is suggested for the simultaneous determination of tellurium and selenium using this technique and liquid-liquid extraction at room temperature.

Experimental

Reagents. Potassium morpholine-4-carbodithioate was prepared by the method given by Macrotrigiano *et al.*,[12)] 0.01 M aqueous solution being used when necessary. Solutions of copper sulfate, cobalt nitrate, nickel nitrate and potassium tellurite were prepared from samples (analytical grade) in distilled water and standardized.[13)] Naphthalene and chloroform (analytical grade) were checked spectrophotometrically before use. 1% alkali salt and 0.1% metal salt solutions were used to study intereference. Dilute solutions of perchloric acid and ammonia were used to adjust pH.

Equipment. An Elico pH meter and a SP-700 spectrophotometer were used.

General Procedure. To an aliquot of each metal solution taken separately was added 1.0 ml of the reagent, the pH being adjusted (Fig. 2). After being transferred to round bottomed flasks with stopper and heated in a water-bath at *ca.* 60 °C, 2 g of naphthalene was added, heating being continued till naphthalene melted and formed a separate liquid-layer. This was stirred vigorously till the naphthalene separated out as a solid mass. The contents were again heated in the water-bath to remelt the naphthalene, shaken vigorously and allowed to stand. Naphthalene was separated from the aqueous phase by filteration, dried in folds of filter paper, dissolved in chloroform and made exactly 10 ml in each case. These solutions were dried by adding 2 g of anhydrous sodium sulfate, a portion being taken in a 1 cm cell and the absorbance measured against a reagent blank. This was referred to the calibration curve constructed under similar conditions in each case.

Results and Discussion

Absorption Spectra. The absorption spectra of potassium morpholine-4-carbodithioate and its copper, cobalt, nickel, and tellurium complexes were recorded in naphthalene-chloroform solution against water and reagent blank, respectively. Copper, cobalt, nickel, and tellurium morpholine-4-carbodithioates show absorptions at 440 nm, 360 nm, 385—390 nm, and 410—420 nm, respectively, the absorption of reagent being negligible at these wavelengths (Fig. 1).

Effect of pH. Extraction was carried out at different pH, other conditions being kept constant. The characteristics of all spectral curves were the same, indicating the presence of only one complex. The absorbances of the extracts were constant in the pH range of Cu: 4.5—8.0, Co: 3.5—9.5, Ni: 6.5—9.0 and Te: 4.0—6.5 respectively. The pH effect in each case is shown in Fig. 2.

Effect of Reagent. Extraction was carried out at optimum pH and varying amounts of reagent (Fig. 3). It was found to be quantitative in the volume range of Cu: 0.8—1.5 ml, Co: 1.0—2.0 ml, Ni: 1.0—2.5 ml and Te: 0.5—1.5 ml of 0.01 M reagent.

Effect of Naphthalene. Extraction was carried out by varying the amount of naphthalene from 0.25—4.5 g at optimum pH and under constant conditions. In all cases absorbance remained constant for 1.0—

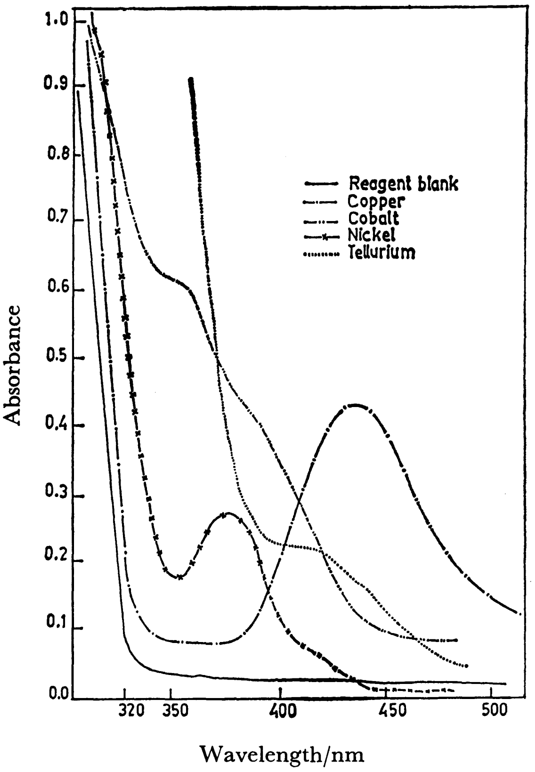


Fig. 1. Absorption spectra.
Reagent blank. Morpholine-4-carbodithioate (0.01 M): 1.5 ml, naphthalene: 2.0 g, reference: water. Cu: 25.0 μg, pH: 5.0; Co: 27.0 μg, pH: 6.5; Ni: 24.0 μg, pH: 7.5; Te: 25.5 μg, pH: 5.0; rest of the conditions were same as in reagent blank.
Reference: reagent blank.

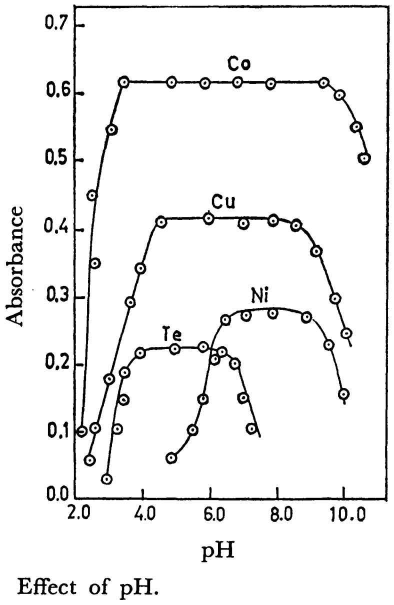


Fig. 2. Effect of pH.
Cu: 25.0 μg, wavelength: 440 nm; Co: 27.0 μg, wavelength: 360 nm; Ni: 24.0 μg, wavelength: 370 nm; Te: 25.5 μg, wavelength: 415 nm. Morpholine-4-carbodithioate (0.01 M): 1.5 ml, naphthalene: 2.0 g, reference: reagent blank.

3.5 g of naphthalene. Below 1.0 g the extraction was incomplete and above 3.5 g it was difficult to dissolve naphthalene in a limited amount of chloroform (Fig. 4).

Effect of Aqueous Phase. Since the amount of the organic phase is very small as compared to that of the aqueous phase the effect of the latter on extraction was studied. Extraction was quantitative

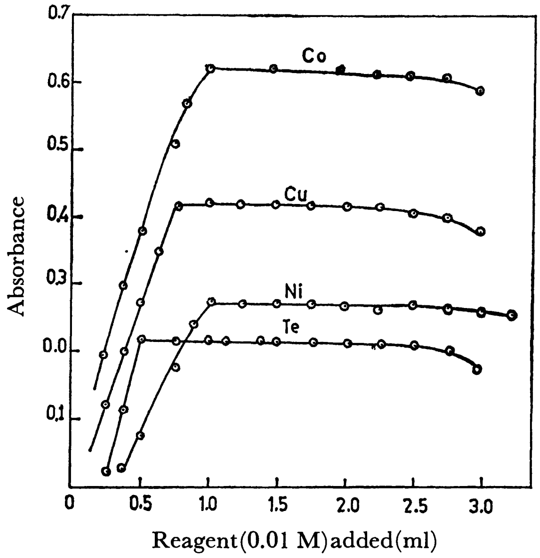


Fig. 3. Effect of reagent.
Conditions were same as in Fig. 2.

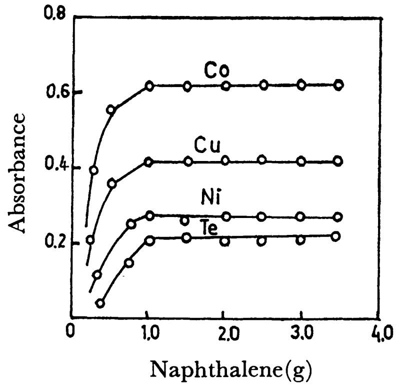


Fig. 4. Effect of naphthalene.
Conditions were same as in Fig. 2.

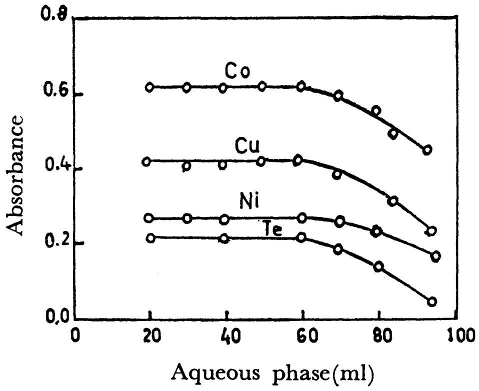


Fig. 5. Effect of the aqueous phase.
Conditions were same as in Fig. 2.

TABLE 1. EFFECT OF DIVERSE ANIONS
Cu: 25.0 μg, Co: 27.0 μg, Ni: 24.0 μg, Te: 25.5 μg.

Alkali salt added	Anion added (mg)	Absorbance at			
		440 nm	360 nm	390 nm	415 nm
—	—	0.420	0.620	0.270	0.215
Sodium acetate	40.00	0.420	0.615	0.270	0.220
Sodium oxalate	33.60	0.380	0.550	0.220	0.115
	25.20	0.420	0.620	0.270	0.215
Potassium, sodium tartrate	39.40	0.380	0.580	0.240	0.150
	29.50	0.415	0.620	0.272	0.215
Potassium bromide	33.60	0.420	0.620	0.270	0.210
Potassium chloride	23.80	0.420	0.620	0.270	0.215
Sodium citrate	31.45	0.370	0.590	0.245	0.140
	15.72	0.415	0.620	0.270	0.215
Potassium iodide	38.25	0.415	0.620	0.270	0.215
Sodium fluoride	22.60	0.380	0.580	0.245	0.150
	17.00	0.420	0.620	0.270	0.215
Sodium orthophosphate	25.00	0.420	0.615	0.270	0.220
Sodium thiosulfate	21.00	0.420	0.620	0.270	0.220
Potassium thiocyanate	29.85	0.420	0.620	0.270	0.215
Disodium EDTA	40.00	0.005	0.008	0.005	0.150
	20.00	0.008	0.008	0.005	0.210

TABLE 2. EEFECT OF DIVERSE CATIONS
Cu: 25.0 μg, Co: 27.0 μg, Ni: 24.0 μg, Te: 25.5 μg.

Metal salt added	Metal added (mg)	Absorbance at			
		440 nm	360 nm	390 nm	415 nm
—	—	0.420	0.620	0.270	0.215
Copper(II) chloride	0.431	—	0.550	0.240	0.110
	0.143	—	0.620	0.270	0.210
Manganese(II) acetate	0.480	0.420	0.620	0.270	0.210
Aluminium(III) nitrate	0.450	0.420	0.620	0.270	0.220
Lead(II) nitrate	0.616	0.415	0.620	0.270	0.210
Uranyl acetate	0.280	0.415	0.620	0.270	0.215
Zinc sulfate	0.596	0.415	0.615	0.270	0.215
Mercury(II) chloride	0.147	0.420	0.615	0.272	0.215
Zirconyl chloride	0.458	0.420	0.615	0.270	0.215
Thorium(IV) nitrate	0.160	0.420	0.620	0.270	0.210
Iron(III) chloride	0.200	0.350	0.550	0.220	0.180
	0.100	0.420	0.615	0.272	0.215
Nickel(II) chloride	0.450	0.420	0.620	—	0.215
Cobalt(II) sulfate	0.666	0.250	—	0.600	0.115
	0.111	0.415	—	0.800	0.215
Ammonium metavanadate	0.544	0.420	0.620	0.272	0.215
Sodium tungstate	0.577	0.420	0.620	0.270	0.215

when the aqueous phase did not exceed 60 ml but not quantitative, above 60 ml of the aqueous phase (Fig. 5).

Effect of Standing Time. Absorbance of the extract in naphthalene-chloroform was constant for at least 24 h for copper and cobalt, 40 h for nickel and 3 h for tellurium.

Effect of Electrolytes. Various electrolytes such as sodium chloride, sodium nitrate, and sodium acetate (0.01—0.08 M) caused no improvement in extraction, indicating that the extraction was complete.

Composition of the Complex. The composition of the copper, cobalt, nickel, and tellurium morpholine-4-carbodithioates was established by Job's method of continuous variation and the mole-ratio method. $Cu(C_4H_8ONCS_2)_2$, $Co(C_4H_8ONCS_2)_2$, $Ni(C_4H_8ONCS_2)_2$, and $Te(C_4H_8ONCS_2)_4$ have been extracted into molten naphthalene. It has been confirmed on the basis of gravimetric[5—8,14] volumetric[4,14] and conductometric[5] studies that the ligand acts as bidentate. The following tentative structures can be assigned to these metal complexes.

TABLE 3. DETERMINATION OF COPPER IN VARIOUS ALLOYS

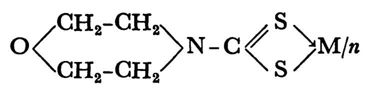
Alloy	Certified % composition	Amount of Cu taken μg	Amount of Cu found μg	Average (μg)	Error %
Mallory No. 3	Cu: 99.2, Cr: 0.8	35.70	35.50 35.50 35.80 35.50 35.50	35.56	−0.39
Monel wire	Ni: 66.24, Cu: 31.18, Fe: 1.18, Mn: 1.08, Mg: 0.093, Al: 0.093, Si: 0.083, C: 0.083, S: 0.0037	46.80	46.50 46.50 46.50 47.00 46.50	46.60	−0.42
Monel 400	Ni: 63.0, C: 0.15, S: 0.0024, Mn: 0.01, Si: 0.5, Fe: 2.5, Cu: 31.0	35.65	35.50 35.50 35.60 35.50 35.50	35.52	−0.36
Brass No. 41.2	Cu: 58.18, Pb: 2.56, Zn: 38.99, Fe: 0.09, Sn: 0.12	30.55	30.50 30.60 30.60 30.60 30.10	30.66	+0.36

TABLE 4. DETERMINATION OF COBALT IN ALLOYS

Alloy	Certified % composition	Amount of cobalt taken μg	Amount of cobalt found μg	Average (μg)	Error %
High speed steel	Co: 9.25, Mn: 0.40, Si: 0.35, S: 0.05, P: 0.05, Cr: 4.15, Mo: 5.5, W: 6—18.5	50.00	49.50 49.50 50.00 49.50 49.50	49.80	−0.40
Elgiloy (M-1712)	Co: 40.0, Cr: 20.0, Ni: 15.0, Mn: 2.0, Mo: 7.0, Fe: 15.0, Be: 0.05, C: 0.15	36.16	36.00 36.50 36.50 36.50 36.50	36.30	+0.39

TABLE 5. DETERMINATION OF NICKEL IN ALLOYS

Alloy	Certified % composition	Amount of Ni taken μg	Amount of Ni found μg	Average (μg)	Error %
Monel wire	Ni: 66.24, Cu: 31.18, Fe: 1.18, Mn: 1.08, Mg: 0.093, Al: 0.093, Si: 0.083, C: 0.083, S: 0.0037	49.65	49.50 49.50 49.20 49.40 49.40	49.40	−0.54
Stainless steel No. 304	Ni: 9.68, Cr: 18.0, Fe: 70—71	35.50	35.80 36.50 35.50 35.40 35.80	35.80	−0.55
Inconel 600	Ni: 72.0, C: 0.15, Mn: 1.0, Fe: 8.0, S: 0.5, Cu: 0.50, Cr: 15.50, S: 0.015	30.60	30.50 30.30 30.60 35.80 35.80	30.46	−0.45



where $n=2$ for Cu, Co, and Ni, 4 for Te. Crystal structure study showed that in the case of the tellurium complex all four dithiocarbamate groups are bidentate and the eight sulphur atoms are bonded around the central tellurium atom in a slightly distorted dodecahedral manner;[15] in IR studies, the C···N and C···S stretching frequencies in Te(IV) complex were observed at 1000 cm^{-1} for the latter and 1480 cm^{-1} for the former. In the free ligand these modes were observed at 990 cm^{-1} and 1440 cm^{-1}, respectively.

Beer's Law and Sensitivity. Under optimum conditions described above, calibration curves were constructed at 440, 360, 385—390, and 410—420 nm against reagent blank, respectively. Beer's Law holds in the concentration range Cu: 5.0—70.0 μg, Co: 5.0—81.0 μg, Ni: 6.0—90.0 μg and Te: 5.7—125.0 μg per 10 ml of the final solution. The molar absorptivities and sensitivities in terms of Sandell's definition were calculated to be Cu: 1.067×10^4 mol^{-1} cm^{-1}, 0.0059 μg/cm^2 (440 nm); Co: 1.350×10^4 mol^{-1} cm^{-1}, 0.0043 μg/cm^2 (360 nm); Ni: 7.920×10^3 mol^{-1} cm^{-1}, 0.0088 μg/cm^2 (390 nm), and Te: 1.075×10^4 mol^{-1} cm^{-1}, 0.0110 μg/cm^2 (415 nm) respectively. Aliquots containing 25.0 μg of copper, 27.0 μg of cobalt, 24.0 μg of nickel and 25.5 μg of tellurium gave mean absorption of 0.42, 0.62, 0.27, and 0.215 with a relative standard deviation of 0.0016, 0.0024, 0.0015, and 0.0013, respectively.

Effect of Diverse Ions. 50 mg salt of the anions and 1.0 mg salt of the cations were added separately to aliquots containing 25.0 μg of copper, 27.0 μg of cobalt, 24.0 μg of nickel and 25.5 μg of tellurium, of the anions (Table 1) fluoride, citrate, tartrate, oxalate, and EDTA interfered in the determination of the metals, minor amounts of fluoride, citrate, tartrate and oxalate giving no serious effect. The extraction was almost nil in the presence of EDTA in the case of Cu, Co, and Ni probably due to higher stability of metal–EDTA complexes. A smaller amount of EDTA is allowable in the case of tellurium.

Of the cations (Table 2), Co (II) and Fe (III) interfered in the determination of copper, Cu (II) and Fe (III) in that of cobalt, and Cu (II) and Fe (III) and Co (II) in that of nickel. In all cases the relatively small amount can be tolerated except in the determination of nickel where Co(II) seriously interfered. Its interference can be eliminated by extraction first at low pH, then nickel being determined from the aqueous phase. In the determination of tellurium relatively small amounts of Cu (II), Co (II), and Fe (III) could be tolerated, nickel not interfering at all.

Determination of Copper, Cobalt, and Nickel in Various Alloys. 0.1 g of the alloy sample was taken in a beaker to which were added 10—15 ml of concentrated hydrochloric acid and a few ml of concentrated nitric acid. This was heated over a hot plate till the mixture dissolved completely and the solution was reduced to 5 ml. The solution was cooled, 10 ml of hydrochloric acid being added, then diluted and filtered. The final volume was made exactly 500 ml.

TABLE 6. SIMULTANEOUS DETERMINATION OF NICKEL AND COBALT IN AN ALLOY

Alloy	Amount of Ni/Co taken μg	Amount of Ni/Co found μg	Average (μg)	Error %
Elgiloy (M-1712)	Ni: 33.90	33.70 34.00 33.50 33.80 33.70	33.74	−0.74
	Co: 36.16	36.00 35.90 36.00 36.00 35.00	35.98	−0.55

An aliquot containing an appropriate amount of copper, cobalt or nickel was taken separately in a beaker, 1.0 ml of the reagent being added, the pH adjusted (Fig. 2), and determined by the general procedure. Results are given in Tables 3, 4, and 5 respectively.

Simultaneous Determination of Nickel and Cobalt in Alloys. Based upon the fact that the nickel complex is decomposed by ammonia to form a more stable complex whereas the cobalt morpholine-4-carbodithioate complex remains as such in chloroform, a method has been developed for the determination of nickel and cobalt present together.

An aliquot containing nickel and cobalt was taken, 2.0 ml of the reagent being added and the pH adjusted to 7.0. The solution was then extracted with molten naphthalene. Naphthalene containing nickel and cobalt morpholine-4-carbodithioate was dissolved in chloroform, the volume being made 10 ml. 5 ml of the solution was taken, dried with sodium sulfate, the absorbance being measured at 390 nm against a reagent blank. This corresponded to total absorbance due to cobalt and nickel complexes. To the other 5 ml of the solution was added 5 ml of 1:10 ammonia solution in a separating funnel. The organic phase was separated, dried by adding anhydrous sodium sulfate and the absorbance measured at 360 and 390 nm. The cobalt complex is not affected by shaking with ammonia, the absorbance at 360 nm corresponding to the amount of cobalt present. The absorbance was referred to the calibration curve for cobalt prepared under similar conditions. The amount of nickel was determined by the difference of total absorbance at 390 nm and that due to cobalt at 360 nm and referring it to the calibration curve for nickel at 390 nm. The results of the determination of nickel and cobalt in one alloy sample are given in Table 6.

Simultaneous determination may also be carried out by the control of pH. However, this is time consuming and less accurate since two steps are involved (the relative error ≈1%).

Simultaneous Determination of Tellurium and Selenium. Preliminary investigations indicated that selenium is

Table 7. Simultaneous determination of tellurium and selenium

Tellurium
Morpholine-4-carbodithioate
(0.01 M): 1.0 ml.
Naphthalene: 2.0 g,
Wavelength: 415 nm
pH: 5.5

Selenium
Dithizone in CCl_4
(60 μmol/l): 5.0 ml.
acidity: 6 M HCl,
Wavelength: 420 nm

Amount present μg		Amount found μg		Average (μg)		Error %	
Tellurium	Selenium	Tellurium	Selenium	Tellurium	Selenium	Tellurium	Selenium
51.0	10.50	51.0	10.5	50.70	10.48	−0.58	−0.55
		50.5	10.5				
		51.0	10.4				
		50.5	10.5				
		50.5					
51.00	7.78	50.5	7.8	50.70	7.74	−0.58	−0.51
		51.0	7.7				
		51.0	7.8				
		50.5	7.7				
		50.5	7.7				
25.50	7.78	25.4	7.7	25.56	7.74	+0.55	−0.51
		25.4	7.7				
		25.5	7.8				
		25.5	7.8				
		25.0					
25.50	10.50	25.5	10.5	25.35	10.48	−0.58	−0.55
		25.4	10.5				
		25.5	10.4				
		25.2	10.5				
		25.15	10.5				

Table 8. The extraction-spectrophotometric behavior of metal morpholine-4-carbodithioates

Metal	λ_{max} / nm	Optimum pH	Morpholine-4-carbodithioate (0.01 M) (ml)	Extracted as	Concentration range from Beer's curve / μg(10 ml)$^{-1}$	Molar absorptivity / mol^{-1} cm^{-1}	Sandell's sensitivity S / μg cm^{-2}	Standard deviation
Copper	440	4.0—9.0	0.8—1.5	$Cu(C_4H_8ONCS_2)$	5.0—70.0	1.067×10^4	0.0059	0.0016
Cobalt	360	4.0—9.5	1.0—2.0	$Co(C_4H_8ONCS_2)_2$	5.0—81.0	1.350×10^4	0.0043	0.0024
Nickel	385—390	6.5—9.0	1.0—2.5	$Ni(C_4H_8ONCS_2)_2$	6.0—90.0	7.92×10^3	0.0088	0.0015
Tellurium	410—420	4.0—6.5	0.5—1.5	$Te(C_4H_8ONCS_2)_4$	5.7—125.0	1.075×10^4	0.0110	0.0013
Bismuth[a]	362—370	4.0—6.5	0.5—1.5	$Bi(C_4H_8ONCS_2)_3$	2.5—53.0	3.960×10^4	0.0052	0.0035

a) Ref.[11]

not extracted with molten naphthalene. A method has been developed for the simultaneous determination of tellurium and selenium.

An aliquot containing appropriate amounts of these two metals was taken, 1.0 ml of the reagent being added and the pH adjusted (Fig. 2). Tellurium was then determined. From the aqueous phase selenium was extracted in 6 M HCl as a dithizone complex in carbon tetrachloride.[16] The absorbance was measured at 420 nm against a reagent blank. The amount of selenium was determined by the calibration curve prepared under similar conditions (Table 7). Selenium can be extracted with a suitable organic solvent by liquid-liquid extraction as morpholine-4-carbodithioate, but not by spectrophotometry since the complex gives no absorption.

The extraction behavior of metal morpholine-4-carbodithioates is summarized in Table 8.

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References

1) W. Beyer and R. D. Ott, *Mikrochim. Ichnoanal. Acta*, **1965**, 1130.

2) W. Beyer and W. Likussar, *Mikrochim. Acta*, **4**, 721 (1967).

3) W. Likussar, W. Beyer, and O. Wawshinek, *Mikrochim. Acta*, **4**, 735 (1968).

4) W. Beyer, R. D. Ott, and G. Pokorny, *Mikrochim. Acta*, **3**, 575 (1967).

5) N. Singh, R. Kumar, and R. C. Agarwal, *Curr. Sci.*, **46**, 851 (1977).

6) N. Singh, R. Kumar, and B. D. Kansal, *J. Indian Chem. Soc.*, **55**, 240 (1978).

7) N. Singh, R. C. Agarwal, V. K. Maheshwari, and R. Kumar, *J. Indian Chem. Soc.*, **55**, 961 (1978).

8) R. Kumar, N. Singh, and H. Singh, *J. Indian Chem. Soc.*, **56**, 838 (1979).

9) N. Singh, R. Kumar, and B. D. Kansal, *Chromatographia*, **11**, 408 (1978).

10) R. Kumar and N. Singh, *Curr. Sci.*, **47**, 422 (1978).

11) B. K. Puri and M. Gautam, *Zh. Anal. Khim.*, **35**, 1024 (1980).

12) G. Macrotrigiano, G. C. Pallacani, C. Preti, and G. Tosi, *Bull. Chem. Soc. Jpn.*, **48**, 1018 (1975).

13) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Longman (1969).

14) A. B. Sakla, A. A. Helmy, W. Beyer, and F. E. Harhash, *Talanta*, **26**, 519 (1979).

15) S. Esperas and S. Hasebye, *Acta Chem. Scand.*, **29**, 185 (1975).

16) H. Mabuchi and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **36**, 151 (1965).