Liquid-Liquid Extraction of Zinc with Thiothenoyltrifluoroacetone Direct Photometric Determination in the Organic Phase

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The thioderivative of 2-thenoyltrifluoroacetone [1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA)] is used for the simultaneous extraction and direct photometric determination of zinc. About 68 μg of zinc was quantitatively extracted at pH 7—7.5 with 10 ml of 0.001 M STTA in carbon tetrachloride as yellow green colored complex. It was measured spectrophotometrically at 450 nm. The system conformed to Beer's law over the concentration range of 0.4 to 30 μg of zinc per ml. The color of the complex was stable for more than 96 hr. Zinc was extracted quantitatively and was determined in the presence of large excess of (1: 300) ions which are associated with it. The method was made selective by using sequestering agents like ascorbic, oxalic, citric acids or alkali cyanide to form unextractable negatively charged complexes. The selective extraction with mesityl oxide was used to eliminate the interferences due to iron and chromium. The procedure was found to be applicable for the analysis of zinc in gun metal and brass. The proposed method is comparable with the standard methods for the extraction of zinc.

Thiothenoyltrifluoroacetone (1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA) has been used as the extracting and colorimetric reagent for the number of transition elements.[1] It was observed that zinc can be quantitatively extracted at pH 7.0—7.5 with 0.001 M STTA in carbon tetrachloride. The yellow green complex can be measured spectrophotometrically at 450 nm.

The method proposed in this paper with thiothenoyltrifluoroacetone as the extracting and colorimetric reagent is simple, rapid and selective. It is possible to accomplish clean cut separation of zinc at micro gram concentrations. It was found to be applicable to analysis of zinc in alloys such as gun metal and brass.

Experimental

Apparatus and Reagents. Type SF-4 quartz spectrophotometer with 10 mm matched cells. Type FEK-57 photoelectric filter photometer with 10 mm Corex glass cells. Cambridge pH meter with glass electrode; wrist action flask shaker.

Thiothenoyltrifluoroacetone (1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA) was synthesised from 2-thenoyltrifluoroacetone (Koch-light England) as per the method indicated in earlier paper[2] with all the necessary precautions to get the best yield as described by Kiba.[3] About 0.001 M reagent in carbon tetrachloride was used. The reagent was always preserved in the refrigerator.

A stock solution of zinc was prepared by dissolving about 1.2 gm of zinc sulphate hexahydrate in 100 ml of distilled water containing 0.001% of sulphuric acid. The solution was standardized complexometrically[4] with EDTA, and was found to contain 2.7 mg of zinc per ml. The dilute solution containing 67.5 μg per ml of zinc was prepared by appropriate dilution.

General Procedure. An aliquot of solution containing about 67.5 μg of zinc was taken. After addition of 10 ml of water, the pH of the solution was adjusted to 7—7.5 with 0.01 M sulphuric acid or ammonium hydroxide. The solution was diluted to 25 ml with water. It was then transferred into a 250 ml separating funnel. Then 10 ml of 0.001 M STTA in carbon tetrachloride was added. The solution was then extracted on the wrist action flask shaker for about ten minutes. The solution was allowed to settle and separate. The yellow green colored organic phase was withdrawn in a ten ml volumetric flask. It was then measured spectrophotometrically at 450 nm against the reagent blank prepared similarly. The amount of zinc was then calculated from the calibration curve.

For interference studies the solution containing desired ion was added before the pH adjustment.

Results and Discussion

Absorption Spectra. The absorption spectra of Zn–STTA complex ($Zn=9.333\times10^{-3}$ M) extracted at pH 7 against the reagent blank (A) and that of complex against carbon tetrachloride (B) is shown in Fig. 1. The spectrum of reagent blank against carbon tetrachloride (C) is also shown. The yellow green Zn–STTA chelate solution showed the maximum absorption at 450 nm. The cruve steadily fell until absorbance became negligible beyond 500 nm. The reagent blank had strong absorbance at 410 nm. This became insignificant compared to chelate solution from 450 nm onwards. Therefore, all the absorbance measurements were taken at 450 nm. The molar absorptivity was 6.697×10^3 calculated on the basis of zinc contents (9.3×10^{-3} M) with the absorbance of 0.300 at 450 nm when 1 cm cells were used. The sensitivity (as per Sandell's definition) is 0.0022 μg/cm^2.

Extraction as the Function of pH. The solvent extraction behaviour of Zn–STTA system was studied over the pH region of 0.5—10.0 (Fig. 2). It was observed that there is no extraction in the pH region of 0—3.5. The extraction commenced at pH 4.0 and half of the zinc was extracted at pH 6. The extraction was quantitative at pH 7.0—7.5. Beyond this pH region the extraction had decreased. It became insignificant at pH 9.0. Therefore the optimum pH of extraction is 7.0—7.5.

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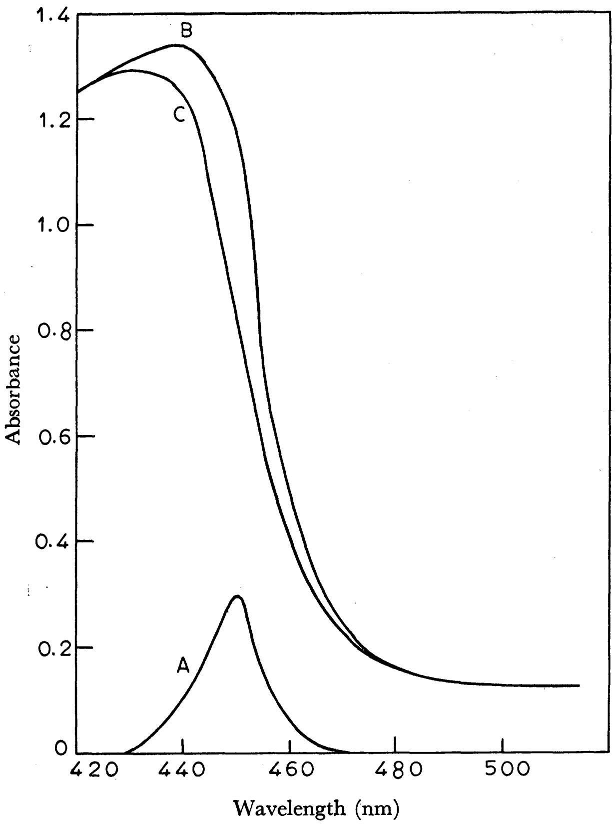

Fig. 1. Absorption spectra of Zn–STTA complex.
Zn=9.33×10^{-3} mM pH=7.0 1×10^{-3} M STTA–CCl_4
A) Zinc–thiothenoyltrifluoroacetone in carbon tetrachloride *vs.* reagent blank.
B) Reagent blank *vs.* carbon tetrachloride.
C) Complex *vs.* carbon tetarchloride.

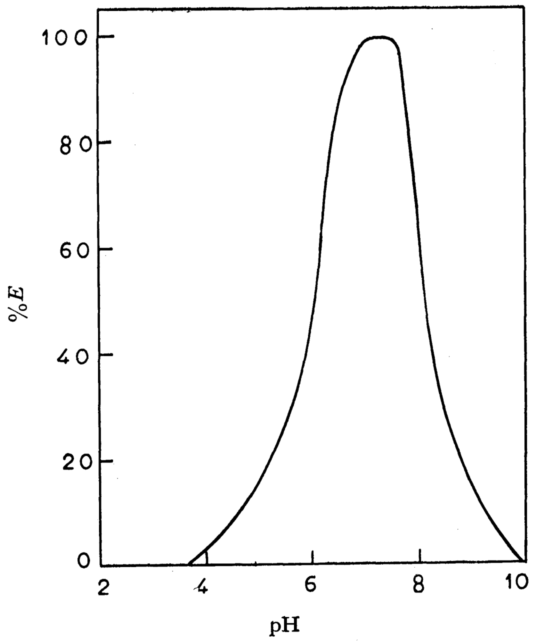

Fig. 2. Extraction as the function of pH.
Zn=9.333×10^{-3} M STTA=1×10^{-3} M in CCl_4

Adherence to Beer's Law. The varying amounts of zinc ranging from 4.25 to 303.75 μg per ml were taken. They were extracted at pH 7.0 with 0.001 M STTA in carbon tetrachloride as described earlier. To observe the adherence of the system to Beer's law, their absorbances were measured at three different wave lengths namely 440, 450, 460 nm (Table 1). The yellow green zinc–STTA system conformed to Beer's law at 450 nm over the concentration range of 0.4 to 30.3 μg/ml of zinc.

Table 1. Applicability of Beer's law
pH=7, 0.001 M STTA in carbon tetrachloride

Zinc taken μg	Absorbance		
	440 nm	450 nm	460 nm
4.25	0.015	0.030	0.020
8.5	0.025	0.060	0.035
17.0	0.040	0.100	0.070
33.75	0.080	0.180	0.160
67.5	0.120	0.300	0.250
84.5	0.125	0.390	0.270
118.25	0.130	0.410	0.290
168.75	0.170	0.640	0.470
236.25	0.200	0.860	0.610
303.75	0.290	1.100	0.890

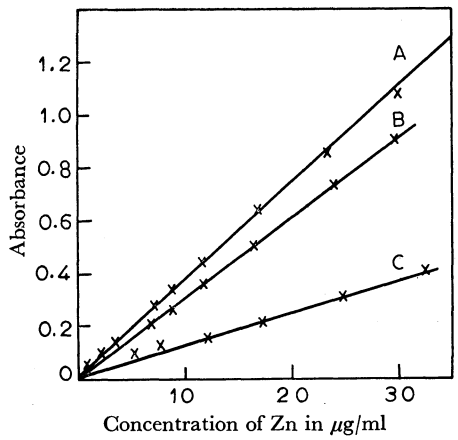

Fig. 3. Beer's law.
A) 450 nm B) 460 nm C) 440 nm

Stability of Colour of the Complex. The absorbance of the colored complex was measured at elapsed interval of 0.5, 8, 16, 24, 48, 96, and 120 hr. The value of the absorbance was found to be constant *viz.* 0.300 until 96 hr. The absorbance after 120 hr was about 0.280. This showed that the complex was stable for at least 96 hr.

Period of Equilibration. With all other factors constant the period of shaking was varied from 3—30 min, on wrist action flask shaker. It was seen that the extraction was quantitative if period of equilibration was 7.5 min. Hence in all measurements, extraction was carried out for at least 10 min.

Effect of Reagent Concentration. The concentration of the reagent was varied from 1×10^{-4} M to 2×10^{-3} M. Similarly the volume of 1.0×10^{-3} M reagent was varied from 2.5 to 20 ml. It was seen (Table 2) that the extraction was quantitative with the reagent concentration of 1×10^{-3} M. It was incomplete with low concentration of the reagent. The extractions did not improve substantially at the higher reagent concen-

Table 2. Effect of reagent concentration
$Zn = 67.5\ \mu g$ pH=7.00

STTA concetration (M) $\times 10^{-3}$	STTA added	Absorbance at 450 nm
0.10	10	0.240
0.25	10	0.290
0.50	10	0.300
0.75	10	0.300
1.00	10	0.300
1.5	10	0.300
2.0	10	0.290
1.0	2.5	0.170
1.0	5	0.230
1.0	7.5	0.300
1.0	10	0.300
1.0	15	0.210
1.0	20	0.150

Table 3. Effect of salting-out agent
$Zn = 67.5\ \mu g$ pH=7.0 0.001 M STTA-CCl_4

Salting-out agent	Molarity (M)	Absorbance at 460 nm
Li_2SO_4	0.5—3.0	0.300
Na_2SO_4	0.5—2.0	0.300
K_2SO_4	0.5—2.0	0.300
$(NH_4)_2SO_4$	1.0—3.0	0.320
$MgSO_4$	0.5—1.0	0.300
	2.0	0.280
$CaSO_4$	0.5—1.0	0.300
	2.0	0.270

tration. The variation in volume of the reagent showed that the extraction was quantitative with 10 ml of 1.0×10^{-3} M of the reagent in carbon tetrachloride.

Effect of the Salting-out Agents. Various salting-out agents such as sulfates of sodium, lithium, potassium, ammonium, magnesium and calcium were tried as the salting-out agents. The extraction of zinc was carried out in the presence of the salting-out agents, with 0.001 M STTA in carbon tetrachloride. It was observed from values of absorbance that the extraction remained constant with the use of 0.2—2 M of lithium, sodium, potassium and ammonium sulfates (Table 3). There was insignificant decrease in the extractability of zinc with 2 M calcium or magnesium sulfate. There was some enhancement in extraction if 1—3 M ammonium sulfate was used as the salting-out agent. On the whole the results revealed that the salting-out agents did not materially enhance the extraction.

Effect of Diverse Ions. The effect of presence of several ions on the extraction behaviour of zinc was studied (Table 4). The tolerance limit was set as the amount required to cause ±2% error in zinc recovery.

It was observed that complexing anions like oxalate, citrate, tartrate are tolerated in the ratio 1 : 300. While thalium, alkali and alkaline earths and anions such as molybdate, selenite, phosphate, thiosulfate *etc.* are tolerated in the ratio of 1 : 150. Other ions were

Table 4. Effect of diverse ions
$Zn = 67.5\ \mu g$ pH=7.5 STTA=0.001 M

Foreign ions	Added as	Tolerance limit, μg	Foreign ions	Added as	Tolerance limit, μg
Tl^{+}	$TlNO_3$	10000	Ba^{2+}	$BaCl_2 \cdot 2H_2O$	10000
In^{3+}	$InCl_3 \cdot 3H_2O$	100[a]	Sr^{2+}	$SrCl_2 \cdot 6H_2O$	10000
Ag^{+}	$AgNO_3$	None	Ge^{4+}	$GeCl_4$	20000
Pb^{2+}	$Pb(NO_3)_2 \cdot 2H_2O$	None	Rb^{+}	$RbCl$	10000
Hg^{2+}	$Hg(NO_3)_2$	200[b]	Cs^{+}	$CsCl$	10000
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	1000[b]	ReO^{4-}	$KReO_4$	1000
Cd^{2+}	$CdCl_2$	None	VO_3^{-}	NH_4VO_3	5000
Sn^{2+}	$SnCl_2 \cdot 2H_2O$	None	$Mo_7O_{24}^{6-}$	$(NH_4)_6 \cdot Mo_7O_{24}$	10000
Sb^{3+}	$SbCl_3 \cdot 3H_2O$	1000[c]	WO_4^{2-}	Na_2WO_4	5000
As^{3+}	$AsCl_3$	20000	SeO_3^{2-}	Na_2SeO_3	10000
Au^{3+}	$HAuCl_4 \cdot XH_2O$	1000[b]	TeO_3^{2-}	Na_2TeO_3	500
Pt^{4+}	$H_2PtCl_6 \cdot XH_2O$	1000	NO_2^{-}	$NaNO_2$	10000
Os^{8+}	OsO_4	500	F^{-}	NaF	5000
Ti^{4+}	$TiCl_4 \cdot 4H_2O$	1000[a]	Br^{-}	$NaBr$	1000
Fe^{3+}	$Fe(NO_3)_3 \cdot 6H_2O$	100[e]	I^{-}	NaI	1000
Cr^{3+}	$Cr(NO_3)_3$	100[e]	CN^{-}	KCN	2500
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	1000[d]	SCN^{-}	$KSCN$	1000
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	1000[b]	$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	10000
UO_2^{2+}	$UO_2(NO_3)_2 \cdot 6H_2O$	5000	PO_4^{3-}	Na_3PO_4	5000
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	1000	$C_2O_4^{2-}$	$H_2C_2O_4 \cdot 2H_2O$	20000
Ce^{4+}	$Ce(SO_4)_2 \cdot 4H_2O$	500[d]	CH_3COO^{-}	CH_3COOH	20000
Be^{2+}	$BeSO_4 \cdot 4H_2O$	100	Malonate^{2-}	$(COOH)_2CH_2$	20000
Zr^{4+}	$Zr(SO_4)_2$	500	Ascorb^{-}	Ascorbic acid	20000
			Cit^{3-}	Citric acid	20000
			Tart^{3-}	Tartaric acid	20000
			EDTA^{4-}	EDTA(disodium salt)	None

Masked with a) ascorbic, b) alkali cyanide, c)oxalic, d) citric acid, e) selective extraction with pure mesityl oxide for Fe at 3.5M HCl, Cr from 1M HCl+2.5M KCl (2) tolerated in the ratios exceeding 1: 15. Some ions such as lead, silver, cadmium, tin formed characteristic colored complex with reagent and showed strong interference. The interference of some of the ions could be removed by complexing with sequestering agents. As a matter of fact sequestering agents are tolerated in larger amounts (*viz.* 20000 μg) and hence can be used for masking number of metals. Further some of the ions which might hydrolyse at very high concentrations can be successfully complexed with sequestering agents to prevent hydrolytic precipitation. Thus sequestering agents play two fold role to eliminate interference and mitigate hydrolysis of certain ions. Hence antimony was complexed with oxalic acid; aluminium, cerium and zirconium with citric acid and silver, copper and gold were complexed with alkali cyanide. The process of selective extraction (2) with mesityl oxide (4-methyl-3-pentane-2-one) was also used to eliminate the interferences due to iron(III) and chromium(III).

Separation of Zinc from Gun Metal. About one gm of gun metal was dissolved in concentrated nitric acid. Tin was removed as metastannic acid and was determined gravimetrically. The filtrate was evaporated to dryness. The residue was dissolved in water, and made up to 1 litre. One ml of the diluted solution was taken. It was adjusted to pH 2.5 to extract copper with 0.1 M acetylacetone in benzene as described in earlier2) paper. The aqueous solution was taken. To this solution 3 M hydrochloric acid and 2 M lithium chloride was added. It was extracted with a 10 ml of tributyl phosphate in MIBK to quantitatively remove lead.6) The aqueous phase containing zinc was taken. Its pH was adjusted to 7.0. Then zinc was extracted with 10 ml of 0.001 M STTA in carbon tetrachloride. The yellow green colored complex was measured spectrophotometrically at 450 nm. Another aliquot of solution containing zinc after removal of copper and lead as described earlier was taken. The acidity was adjusted to 3 M with hydrochloric acid. Then it was extracted twice with 10 ml of 8% tribenzoylamine.7) Zinc from the combined organic phase was stripped with 10 ml of 0.1 M hydrochloric acid and was determined as usual.8) It was found that the percentage of zinc found by STTA method was 4.6, 4.9, 4.8 while percentage of zinc by TBA method was 4.5, 4.4, 4.3 as against 4.5% actually present.

Separation of Zinc from Brass. About 0.885 gm of brass sample was dissolved in concentrated nitric acid. Tin was which was present in traces was removed as insoluble residue of metastannic acid. The filtrate was evaporated to dryness and extracted with water. The solution was made up to 1 litre. Then 2 ml of diluted solution was taken and copper from it was removed by extraction as described earlier.2) The aqueous phase was then taken. The pH was adjusted to 7.0. Then it was extracted with 10 ml of 0.001 M STTA in carbon tetrachloride. The yellow green colored complex was measured at 450 nm. The percentage of zinc was found to be 35.9, 35.4, 36.2 as against 36%. Another aliquot of solution containing zinc after removing tin and copper was taken. It was then extracted with 8% tribenzylamine7) from 3 M hydrochloric acid. It was stripped to the aqueous phase with 0.1 M hydrochloric acid and was determined as usual.8) The percentage of zinc was found to be 35.8, 35.2, 36.0 as against 36%. This shows the method proposed by us for the extractive separation and colorimetric determination of zinc compares favourably well with standard method.7)

Comparison with Other Methods. Four sets of five samples containing varying amounts of zinc were taken. Then zinc from each sample was determined by extraction with thiothenoyltrifluoroacetone (STTA); tribenzoylamine (TBA);7) triisooctylamine (TIOA)9) and dithizone10) methods (Table 5). It was interesting to observe that the amount of zinc found by STTA method compares favourably well with other methods for the extraction of zinc. This further shows that the proposed method is rapid, simple, selective as well as sensitive. Total operation of each run requires only 30 min. It is possible to accomplish clean-cut separation of zinc from cadmium, mercury, copper, silver, gold, aluminium and iron with which it is usually associated.

TABLE 5. COMPARISON WITH OTHER METHODS

Zinc taken μg	Zinc found (%) by			
	STTA method	TBA method (7)	TIOA method (9)	Dithizone method (10)
6.35	6.30	6.0	6.4	6.4
12.75	12.5	12.2	12.70	12.5
48.0	48.0	47.9	48.4	48.2
101.25	102.0	100.00	101.3	103.0
202.5	200.5	198.7	202.6	204.0

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