Rapid Solvent Extraction and Direct Spectrophotometric Determination of Lead(II) with 1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one

S. B. Akki and S. M. Khopkar

Department of Chemistry, Indian Institute of Technology, Bombay-76, India

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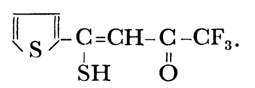
The thio derivative of 2-thenoyltrifluoroacetone 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA) is used for the simultaneous extraction and direct colorimetric determination of lead. About 100 μg of lead is quantitatively extracted, at pH 6.5, with 10 m*l* of 0.0020M STTA-CCl_4 as a bright orange colored complex, which can be measured spectrophotometrically at 480 nm. The system conforms to Beer's law over the concentration range of 1—40 μg/m*l* of lead(II). The color of the complex is stable for 60 hr. Lead can be quantitatively extracted and determined in the presence of a number of ions. The method is made selective by using some sequestering agents and carrying out selective extractions with mesityl oxide. The procedure is found to be suitable for the analysis of lead in gun metal and solder.

Thiothenoyltrifluoroacetone (1,1,1-trifluoro-4-(2-thienyl)-4-meracptobut-3-en-2-one) was used for the solvent extraction of several transition elements.[1] Lead also forms bright orange colored complex with this reagent around pH 6.5 which can be measured spectrophotometrically at 480 nm. The above reagent shall for the sake of brevity be assigned the symbol STTA indicating that it is a monosulphur substituted derivative of thenoyltrifluoroacetone commonly known as TTA. It has structural formula as:



The various β-diketones used as extractants for lead are acetylacetone,[2] benzoylacetone, dibenzoylmethane,[3] and thenoyltrifluoroacetone.[4] Extraction with acetylacetone was not quantitative, while that with dibenzoylmethane or benzoylacetone was possible only in alkaline media. Extraction with thenoyltrifluoroacetone needed high reagent anion concentration. Several other chelating agents[5] such as oxine, oximes, cupferron, azonaphthols, dithizone, neutral organophosphorus compounds were used for the extraction of lead to little advantage.

The method proposed by us is simple and rapid, and it affords clean-cut separation of lead from other ions. The method is sensitive and applicable at tracer concentrations. It is also found to be applicable to the analysis of lead in alloys such as gun metal or solder.

Experimental

Apparatus and Reagents. A type Cϕ4 quartz spectrophotometer with 10 mm matched cells; Cambridge pH meter; Wrist action flask shaker. 1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA) was synthesised from 2-thenoyltrifluoroacetone (Fluka, A. G.) by the procedure of Berg and Reed.[6] About 0.0020M reagent in carbon tetrachloride was utilised. The reagent was always preserved in a refrigerator.

A stock solution of lead nitrate was prepared by dissolving about 1.6 g of lead nitrate (May and Baker, England) in 1 *l* of distilled water containing 0.01% nitric acid. The solution was standardised gravimetrically as the chromate[7] and was found to contain 1 mg of lead per m*l*. The dilute solution containing 100 μg/m*l* of lead was prepared by ten fold dilution.

A buffer solution of pH 6.5 was prepared by dissolving 77 g of ammonium acetate in water, acidified with acetic acid to pH 6.5, and diluted to 1 *l*.

General Procedure. An aliquot of lead nitrate solution (containing about 100 μg of lead) was taken. It was treated with 10 m*l* of buffer solution of pH 6.5 and then diluted with water to 25 m*l*. For the study of extraction as a function of pH, the buffer solution was not added except when pH 6.5 was required. In such cases the pH of lead nitrate solution was adjusted to the desired value with 0.01N nitric acid and 0.01N ammonium hydroxide, the pH meter being used and then the solution was diluted as above. For the study of the effect of diverse ions, the solution containing the foreign ion under investigation was added prior to the buffer solution. The aqueous solution was then transferred into a 250 m*l* separatory funnel. It was extracted for 10 min, on a wrist action flask shaker, with 10 m*l* of 0.0020M STTA solution in carbon tetrachloride. The solution was allowed to settle and separate into two layers. The bright orange colored organic phase was withdrawn in a 10 m*l* volumetric flask. It was then measured at 480 nm against the reagent blank. The amount of lead was then computed from the calibration curve.

Results and Discussion

Absorption Curve. The absorption spectrum of a solution of lead(II)-STTA complex (lead $= 4.33 \times 10^{-4}$M) extracted at pH 6.5 is illustrated in Fig. 1; the reagent blank being used as a reference solution. The spectrum of the reagent blank against carbon tetrachloride is also given. The bright orange lead(II) chelate solution shows maximum difference in absorbance, between itself and the reagent blank at 480 nm.

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[2] A. Krishen and H. Freiser, *Anal. Chem.*, **29**, 288 (1957).

[3] J. Stary and E. Hladky, *Anal. Chim. Acta*, **28**, 227 (1963).

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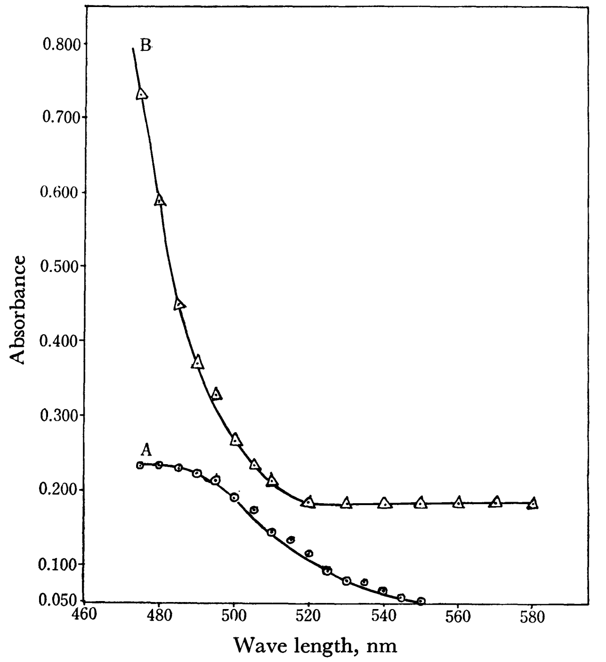

Fig. 1. Absorption spectra of (A) lead(II) thiothenoyltrifluoroacetone in carbon tetrachloride *vs.* reagent blank and (B) reagent blank *vs.* carbon tetrachloride.
Pb(II) 4.83×10^{-4}M, STTA$=1\times10^{-3}$M, pH$=6.5$.

TABLE 1. EXTRACTION OF LEAD(II)-STTA COMPLEX AS A FUNCTION OF pH
Pb(II)$=100$ μg; 0.0020M STTA-CCl_4

pH	Extraction (%*E*)	Distribution ratio (*D*)
0.5	10.6	0.30
1.0	10.6	0.30
1.5	10.6	0.30
2.0	14.8	0.44
2.5	19.1	0.59
3.0	23.4	0.76
3.5	23.4	0.76
4.0	29.8	1.06
4.5	29.8	1.06
5.0	63.8	4.41
5.5	74.5	7.31
6.0	93.6	36.56
6.1	95.0	47.50
6.2	97.9	116.50
6.3	97.9	116.50
6.4	100.0	∞
6.5	100.0	∞
6.6	100.0	∞
6.7	97.9	116.50
6.8	85.1	14.17
6.9	85.1	14.17
7.0	85.1	14.17
7.5	85.1	14.17
8.0	85.1	14.17
8.5	63.8	4.41
9.0	48.9	2.40

The curve steadily falls and the absorbance of the complex becomes negligible beyond 600 nm. The reagent blank itself has strong absorbance till 460 nm and falls beyond this wavelength. Thus all the absorbance measurements were performed at 480 nm. The absorptivity at 480 nm is 4.803×10^2, calculated on the basis of lead content of 4.83×10^{-4}M, with an absorbance of 0.235 at 480 nm, when 1 cm cell was used.

Extraction as a Function of pH. The liquid-liquid extraction behaviour of lead(II)-STTA system was studied in the pH range of 0.5—9.0. The extraction is quantitative at pH of 6.4—6.6 (Table 1, Fig. 3). Beyond this pH the extraction decreases and becomes negligible at pH 9.0. Therefore, all extractions were carried out at pH 6.5 using the acetate buffer to facilitate rapid quantitative extractions.

TABLE 2. APPLICABILITY OF BEER'S LAW

Lead (II) taken, μg	Absorbance		
	475 nm	480 nm	490 nm
10	0.055	0.065	0.060
25	0.110	0.110	0.095
50	0.135	0.135	0.120
100	0.235	0.235	0.225
150	0.300	0.310	0.275
200	0.375	0.375	0.350
250	0.460	0.460	0.420
300	0.550	0.560	0.510
400	0.650	0.650	0.600

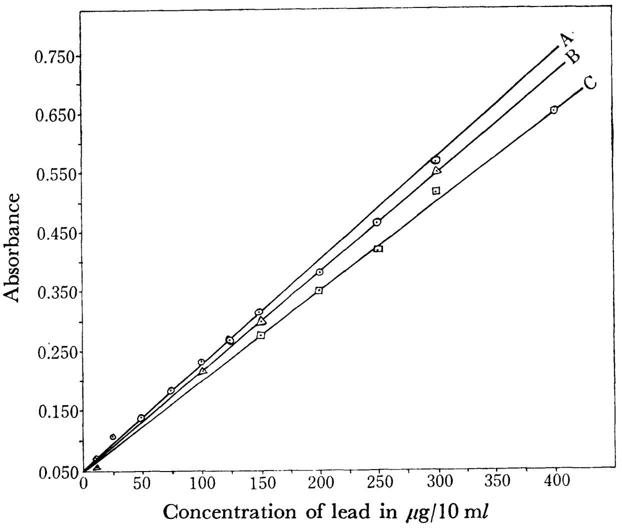

Fig. 2. Beer's law curve. pH$=6.5$
A$=480$ nm, B$=475$ nm, C$=490$ nm

Beer's Law Curve. Different amounts of lead(II) were taken and extracted at pH 6.5 as above. Their corresponding absorbances were measured at various wavelengths, *viz.* 475, 480, and 490 nm, to observe how colored system holds in the Beer's law (Table 2, Fig. 2). The Pb(II)-STTA system conforms to Beer's law over the concentration range of 1—40 μg of lead per m*l* at 480 nm.

Stability of Coloration. The absorbance of Pb(II)-STTA complex was measured at intervals of 0, 0.5, 1, 2, 3, 6, 12, 24, 48, 60, 72, and 96 hr. The absorbance is stable up to 60 hr, beyond which it undergoes about

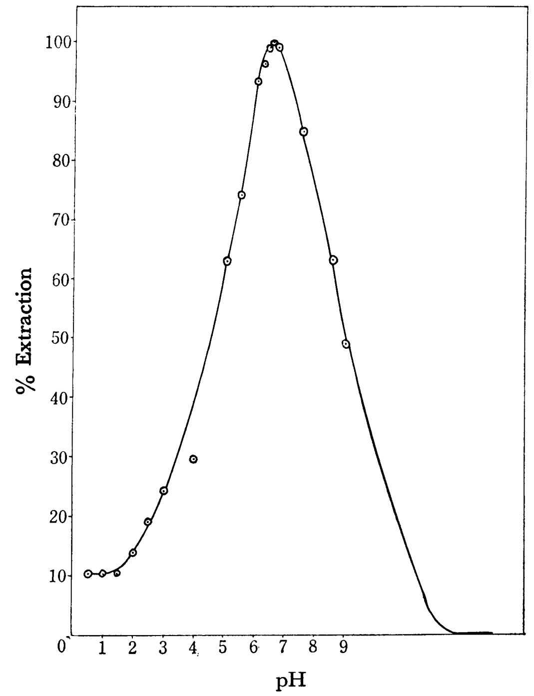

Fig. 3. Extraction as the function of pH.

4% decomposition. It is recommended therefore to measure the absorbance of the complex within 60 hr of extraction.

Reagent Concentration. With other factors being constant, the concentration of STTA was varied from 5.0×10^{-4}M to 2.0×10^{-3}M. The results in Table 3 indicate that the optimum reagent concentration is 10 m*l* of 2.0×10^{-3}M. Similarly, the absorbance is essentially constant with higher reagent concentration *e.g.* 3.0×10^{-3}M or 4.0×10^{-3}M. Extraction is incomplete with dilute solution of the reagent *viz.* 5.0×10^{-4}M, 1.0×10^{-3}M. The variation in volume of 2.0×10^{-3}M reagent showed that 10 m*l* of this reagent is quite adequate for quantitative extraction of lead.

Table 3. Effect of reagent concentration

(100 μg of Pb(II) after extraction with 0.0020 M STTA-CCl_4 at pH 6.5 gives an absorbance of 0.235±0.010 in 10 m*l* of solution.)

STTA concentration (M) × 10^{-3}	STTA added (m*l*)	Absorbance at 480 nm
0.5	10	0.120
1.0	10	0.180
1.5	10	0.230
2.0	10	0.235
3.0	10	0.245
4.0	10	0.245
2.0	15	0.190
2.0	7.5	0.185
2.0	5.0	0.185

Diverse Ions. The effect of the presence of several ions on the extraction behaviour of lead was studied (Table 4). The tolerance limit was set at the amount required to cause ±2.0% error in the lead recovery. It was observed that the alkaline earths, alkali metals, fluoride, tartrate, ascorbate etc. are tolerated in the ratio of 1: 50; while thallium(III), aluminium, beryllium, arsenite, cyanide, sulphite, thiocyanate, malonate, citrate are tolerated in the ratio of 1: 10. Some elements form characteristic colored complexes with the reagent and show interferences. They are mercury, cadmium, palladium, noble metals, cobalt, nickel, and

Table 4. Effect of diverse ions

Pb(II) = 100 μg; pH = 6.5; STTA = 0.0020M

Foreign ions	Added as	Tolerance limit μg
Tl^{3+}	$Tl(NO_3)_3$	1000
Cu^{2+}	$CuSO_4\cdot5H_2O$	250
Sb^{3+}	$SbCl_3\cdot3H_2O$	250^a
Bi^{3+}	$Bi(NO_3)_3\cdot5H_2O$	None
Sn^{2+}	$SnCl_2\cdot2H_2O$	None
Pt^{4+}	$H_2PtCl_6\cdot xH_2O$	75
Rh^{3+}	$RhCl_3\cdot3H_2O$	250^a
Fe^{3+}	$FeCl_3\cdot6H_2O$	250^c
Cr^{3+}	$Cr_2(SO_4)_3\cdot18H_2O$	100^c
Al^{3+}	$Al(NO_3)_3\cdot9H_2O$	1000^b
Zn^{2+}	$Zn(NO_3)_2\cdot4H_2O$	250^c
Mn^{2+}	$MnCl_2\cdot4H_2O$	100^b
Th^{4+}	$Th(NO_3)_4\cdot4H_2O$	250^a
Zr^{4+}	$Zr(NO_3)_4$	100^a
$Mo_7O_{24}{}^{6-}$	$(NH_4)_6Mo_7O_{24}\cdot12H_2O$	100^c
U^{6+}	$UO_2(NO_3)_6\cdot6H_2O$	100
$VO_3{}^-$	NH_4VO_3	250^c
Be^{2+}	$Be(NO_3)_2$	1000
Ti^{4+}	$Ti(SO_4)_2$	None
Re^{7+}	$KReO_4$	100^c
Ge^{4+}	$GeCl_4$	100^b
Ca^{2+}	$Ca(NO_3)_2\cdot4H_2O$	5000
Sr^{2+}	$SrCl_2\cdot6H_2O$	5000
Ba^{2+}	$BaCl_2\cdot2H_2O$	5000
Mg^{2+}	$MgSO_4\cdot7H_2O$	5000
Li^+	LiCl	5000
Rb^+	RbCl	5000
Cs^+	CsCl	5000
$WO_4{}^{2-}$	Na_2WO_4	100
$AsO_3{}^{2-}$	Na_2AsO_3	1000
$TeO_3{}^{2-}$	Na_2TeO_3	None
$SeO_3{}^{2-}$	Na_2SeO_3	200
F^-	NaF	5000
CN^-	KCN	1000
$EDTA^{4-}$	EDTA (disodium salt)	None
$S_2O_3{}^{2-}$	$Na_2S_2O_3\cdot5H_2O$	250
Br^-	NaBr	500
$SO_3{}^{2-}$	Na_2SO_3	2500
$NO_2{}^-$	$NaNO_2$	5000
SCN^-	KSCN	2500
$C_2O_4{}^{2-}$	$H_2C_2O_4\cdot2H_2O$	None
$Malon^{2-}$	Malonic acid	2500
$Tart^{3-}$	Tartaric acid	5000
Cit^{3-}	Citric acid	1000
$Ascorb^-$	Ascorbic acid	5000

Masked with (a) citric acid; (b) sodium fluoride; (c) selective extraction with pure mesityl oxide for Fe, at 3.5M HCl; Cr, from 1M HCl containing 2.5M KCl; Mo, form 1M HCl and 8M LiCl; V, from 6M HCl and Re, from 1M HCl and KCl.[5)] cerium. However, the interference of ions such as antimony, rhodium, and thorium can be eliminated by using masking agents, while alkali fluoride can mask interferences due to aluminium, manganese and germanium. In addition, the process of selective extraction[5] with mesityl oxide (4-methyl-3-pentene-2-one) can eliminate interferences due to iron(III), chromium(III), molybdenum(VI), vanadium(V), and rhenium(VI), (Table 4). The interference due to copper or zinc can be similarly removed by prior extraction with acetylacetone,[3,8] or with 8-hydroxyquinoline-chloroform,[9,10] respectively.

Separation of Lead from Gun Metal. 0.692 g of gun metal was dissolved in concentrated nitric acid. Tin was removed as metastannic acid and it was determined gravimetrically. The filtrate was evaporated to dryness. The residue was dissolved in water and made up to 1 *l*. One milliliter of the diluted solution was then taken and adjusted to pH 2.5, and extracted with (10 ×5) m*l* of 0.1 M acetylacetone-benzene solution to remove copper.[3,8] The aqueous phase was then adjusted to pH 4.5 and extracted with (10×3) m*l* of 0.01 M oxine-chloroform to remove zinc.[9,10] Finally the aqueous phase containing lead was taken and mixed with 10 m*l* of acetate buffer of pH 6.5, and extracted with 10 m*l* of 0.0020M STTA in carbon tetrachloride. The bright orange colored Pb(II)-STTA complex was measured spectrophotometrically at 480 nm. The percentage of lead was found to be 4.90, 4.98, and 4.96 as against 5.0%.

Separation of Lead from Solder. About 0.5 g of the solder was dissolved in minimum volume of concentrated nitric acid. Tin was then removed as the insoluble residue of metastannic acid. The filtrate was evaporated to dryness, extracted with water and made up to 1 *l*. Two milliliters of this diluted solution was taken and mixed with 5% citric acid to complex antimony. Then 10 m*l* of buffer solution (pH 6.5) was added, and lead was extracted with 10 m*l* of 0.0020M STTA-carbon tetrachloride and measured at 480 nm. The percentage of lead was found to be 58.2, 59.3, and 60% as against 59.5%.

Recommended Procedure and Precision. Take an aliquot of the solution containing 10—400 μg of lead in a separatory funnel. Add 10 m*l* of buffer solution of pH 6.5 to and shake it for 10 min with 10 m*l* of 0.0020M STTA-carbon tetrachloride solution. Allow the layers to settle. Separate the aqueous layer into the beaker and organic layer into 10 m*l* volumetric flask. Then measure the absorbance of bright orange colored lead(II)-STTA complex at 480 nm against the reagent blank. Calculate the lead concentration from the calibration curve.

In six runs with 100 μg of lead(II) the absorbance found was 0.235±0.010. The standard deviation was ±1.2%.

Table 5. Accuracy data

Lead taken μg	Absorbance at 480 mμ	Lead found μg	% Error
30	0.115	30	0
40	0.125	41	2.0
60	0.170	62	3.3
110	0.250	112	2.0
175	0.360	175	0
275	0.525	273	3.5
		Av. Error=±1.8%	

Different amounts of lead(II) were taken and determined by the recommended procedure. The results (Table 5) are accurate to within ±1.8%. Thus the proposed method has fairly good precision and accuracy within ±1.8%. The total operation for each run requires only 25—30 min. The sensitivity of the method by Sandell's definition is 0.5 μg/cm^2 per m*l* of solution.

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9) J. Stary, *Anal. Chim. Acta*, **28**, 132 (1963).

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