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Non-Extractive Spectrophotometric determination of lead in water samples using Salicylaldehyde isonicotinoylhydrazone

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Abstract: A very simple, highly selective and non - extractive spectrophotometric method for the trace amounts of lead (II) has been developed. Salicylaldehyde isonicotinoylhydrazone (SAINH) has been proposed as a new analytical reagent for the direct non- extractive spectrophotometric determination of lead(II). The reagent reacts with lead in an basic medium (pH 8.25, ammonium hydroxide and ammonium chloride buffer) to form a yellow coloured 1: 1(M : L) complex. The reaction is instantaneous and the maximum absorption was obtained at 390 nm and remains stable for 3h. The molar absorptivity and sandell's sensitivity were found to be 1.197 x 10^4 L mol^{-1} cm^{-1} and 0.173 µg cm^{-2} respectively. Linear calibration graphs were obtained for 1.0 -9.0 µg/ml of lead(II). The method is highly selective for lead and successfully used for the determination of lead in various water samples.

Key words: Spectrophotometric determination, salicylaldehyde isonicotinoylhydrazone, alloy and steel samples, molar absorptivity and sandell's sensitivity.

1.INTRODUCTION

The lead is not necessary for living and consider as very important pollutant for vital systems[1-2]. Lead supply to the environment in different ways[3-5]. The single most commercial use of the lead is in the manufacture of lead – acid storage batteries, antifriction metals, solders and type metal. Lead is used for covering cables and as a lining for laboratory sinks, tanks and the " chambers " in the lead chamber process for the manufacture of sulphuric acid. It is extensively used in plumbing. Lead is also employed as protective shielding against X – rays and radiation from nuclear reactors. Unlike other chemicals lead does not vapourise (or) break down over time. As a result lead poisoning occurs very easily through inhalation and ingestion.

Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidney's, reproductive and nervous systems. Although lead and most of its compounds are only soluble in water , the use of lead pipe to carry drinking water is dangerous since lead is a cumulative poison that is not excreted from body.

This paper describes the non - extractive spectrophotometric determination of lead(II) using salicylaldehyde isonicotinoylylhydrazone (SAINH) in aqueous medium. In continuation of our ongoing work, we report here the spectrophotometric determination of lead in various water samples. A close literature survey reveals that SAINH is so for not been employed for the spectrophotometric determination of lead (II). This method is far more selective, simple and rapid than the existing spectrophotometric methods. Various spectrophotometric used for the determination of lead are summarized in Table 1. [6-12]

Table 1. Spectrophotometric methods for the determination of lead (II) with different reagents

Name of the reagent	λ_{max} (nm)	pH	Beers law(ppm)	Molar absorptivity (ε) L mol^{-1} cm^{-1}	M:L	Ref
Molybdophosphoric acid	490	4.3	0.0-5.0	$0.13x10^4$	1:1	6
4-(5-utiro-2-thiozolylazu resorcinol)	540	6.5	4.0	$1.0x10^4$	1:1	7
Pthalaldehyde dithiosemicarbazone(PADT)	400	7.5-9.0	Upto4.5	$0.81x10^4$	1:1	8
Salycilaldehyde thiosemicarbazone(SAT)	370	6.5-7.0	0.5-5.0	$0.98x10^4$	1:1	9
Acenapthaquinone thiosemicarbazone(ANQT)	420	6.3-8.4	Upto14.7	$0.28x10^4$	1:2	10
2-hydroxy-4-isopropoxy acetophenone thiosemicarbazone (HIAT)	400	9.0	1.6-4.4	$0.08x10^4$	1:2	11
2-(2-Furanylmethylene)hydrazine carbothioamide (FMHC)	440	5.8	0.36-6.0	$0.72x10^4$	1:2	12
Salicylaldehyde isonicotinoylhydrazone(SAINH)	378	1.0-10.0	7.5	$1.197x10^4$	1:1	Present method

2.MATERIALS AND METHODS

Preparation of SAINH : Salicylaldehyde (1.05 ml, 0.01 mol) and isoniazid (0.69g, 0.01 mol dissolved in 3 ml of ethanol) were mixed in a clean round bottom flask. Suitable quantity of (~10ml) of ethanol was added to the reaction mixture and refluxed with stirring for 2 hrs. A pale yellow coloured product was separated out on cooling. It was collected by filtration, washed several times with hot water. This compound was recrystallized from methanol and dried in vacuuo. Yield 2.8 gm, melting point is 250 – 252°C.

Preparation of SAINH solution: It was prepared by taking 0.060 gm of SAINH reagent substance in a 25–ml standard flask. The reagent substance was dissolved in 10 ml of DMF and diluted up to the mark with the same solvent.

Preparation of lead (II) ion solution *:* Stock solution (0.01 M) of lead was prepared by dissolving 0.33 g of lead nitrate in doubly distilled water and made up to the mark in a 100- ml volumetric flask. A few drops of concentrated sulphuric acid was added before dilution of stock solution. The resulting solution was standardised gravimetrically[13]. Dilute solutions were prepared from this stock solution.

Recommended procedure *:* An aliquot of the solution containing lead in optimum concentration range , 10 ml of buffer solution (pH 8.25) and 1 ml of 0.01M reagent solution were combined in 25 – ml volumetric standard flask and resulting solution was diluted to the mark with distilled water. The absorbance of the solution was measured at 390 nm against reagent (SAINH) blank. The measured absorbance was used to compute the amount of lead from predetermined calibration plot.

Preparation of water sample : Each filtered (with whattman No.40) water sample (250 ml) was mixed with 10 ml of concentrated nitric acid in a 500 ml distillation flask. The sample was digested in the presence of an excess potassium permanganate solution according to the method recommended by Fifield et al [14]. The solution was cooled and neutralized with a dilute NH_4OH solution. The digest was transferred into a 25-ml calibrated flask and diluted up to the mark with deionised water.

Instrumentation: Perkin – Elmer (Lamda 25), UV – Visible spectrophotometer equipped with 1.0 cm (path lenth) quartz cell and Elico model LI- 610 pH meter were used in the present study.

3.RESULTS AND DISCUSSIONS

The reagent (SAINH) are easily obtained by condensation reaction and is shown in Fig 1.

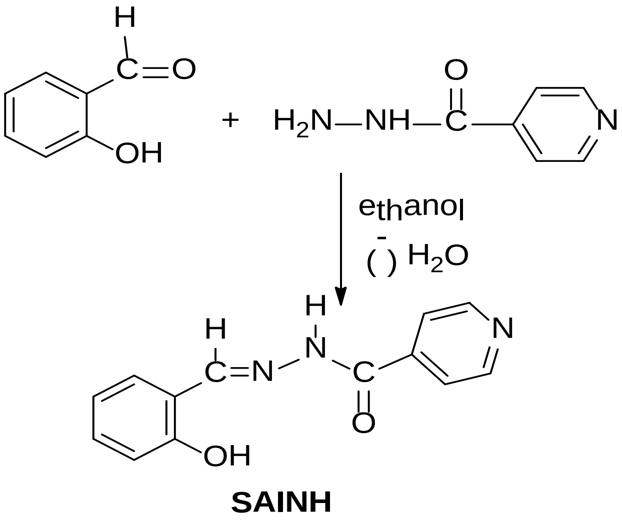

Fig 1. Condensation reaction of SAINH

It has been characterized using IR, NMR and Mass spectral data. The infrared spectrum of SAINH showed bands (cm^{-1}) at 3271(m), 3120(m), 3051(m), 1649(s), 1619(s), 1535(m),1473(s),1290(s), 768(s), 711(s) and 682(m), are respectively assigned to ν (NH) secondary stretching, ν (C-H) stretching, (isoniazid), ν (C-H) aromatic stretching (salicylaldehyde), ν (C=0) isonicotinoyl stretching , ν (N-H) plane bending, ν (C- C) aromatic ring stretching, ν (C-H) asssymetric bending, ν (C-N) streching vibrations, ν (C-H) aromatic oop bend(salicylaldehyde), and ν (N-N)strech and ν (C-H) aromatic oop bending respectively. This spectrum is given in Fig 2.

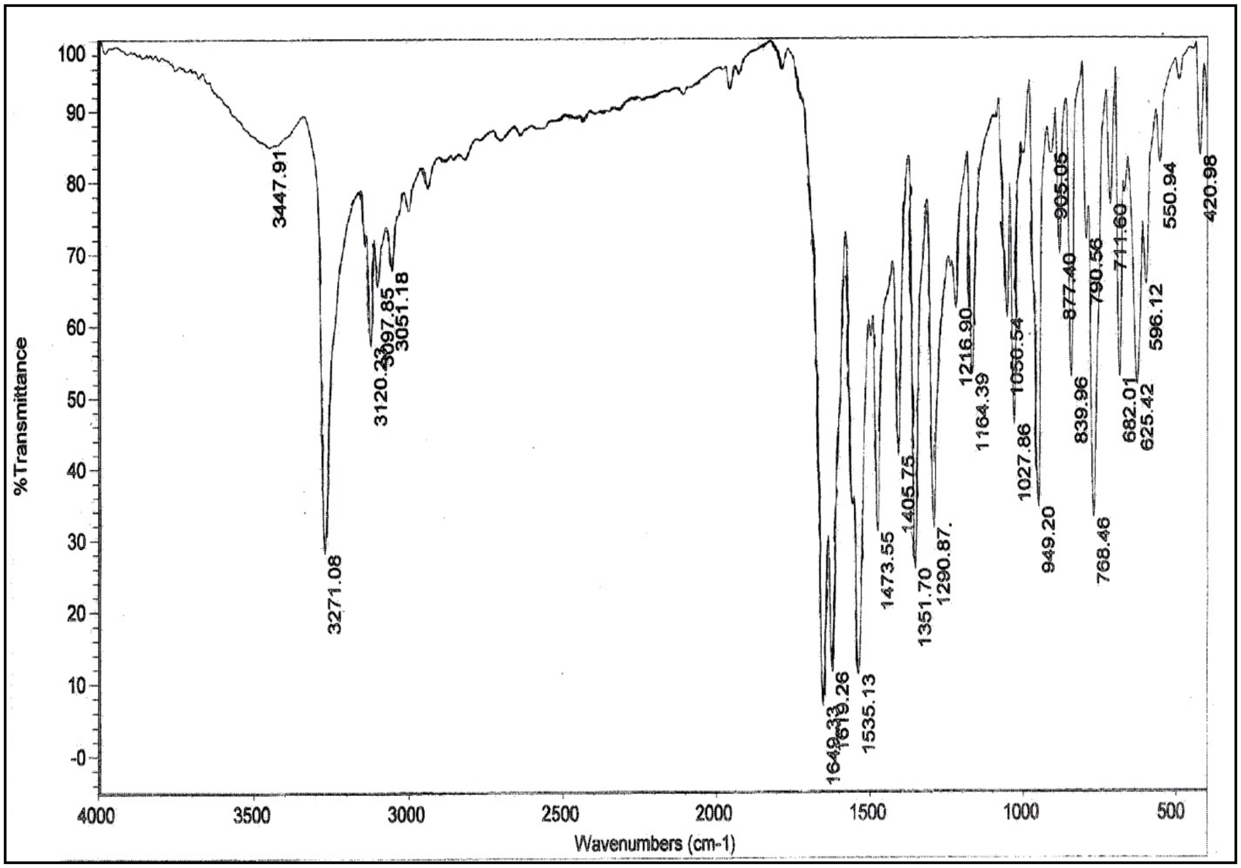

Fig 2. Infrared Spectrum of SAINH in KBr disc

^{1}H – NMR spectra (DMSO –d^6) showed signals (δ ppm) at 6.65, 7.786-7.801 and 8.33 due to - CH$_3$, - OH (aliphatic), phenolic and - NH$_2$ protons of SAINH respectively. NMR spectrum is given Fig 3.

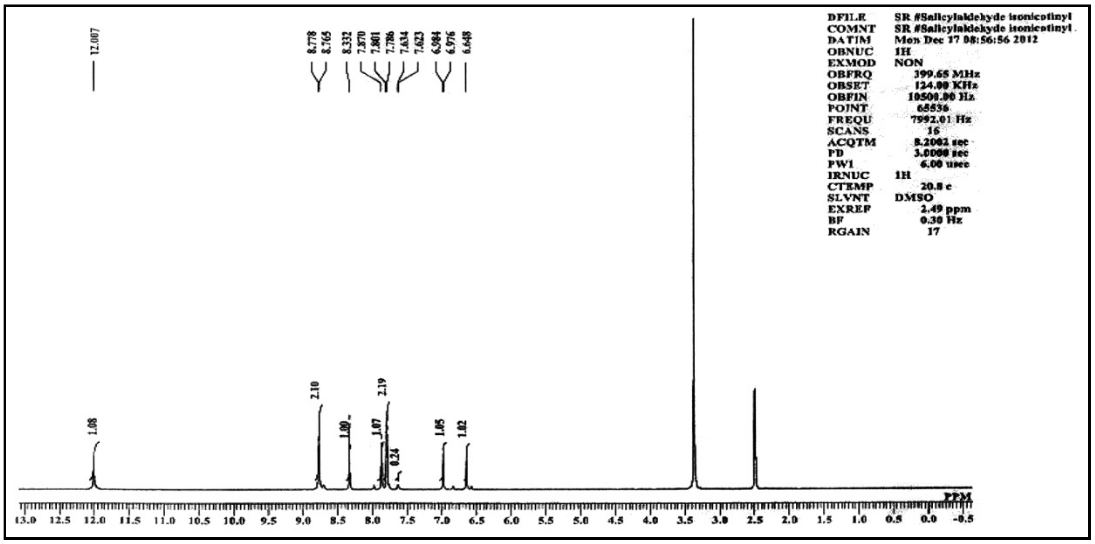

Fig 3. ^{1}H-NMR Spectrum of SAINH in DMSO – d_6 medium

Massspectra shows molecular ion signal at m/z 241. Other peaks are observed at m/z values of 240 and 163 respectively due to the loss of -H and -C_5H_4N radicals. Based on above spectral data the structure of the reagent is given in Fig 4.

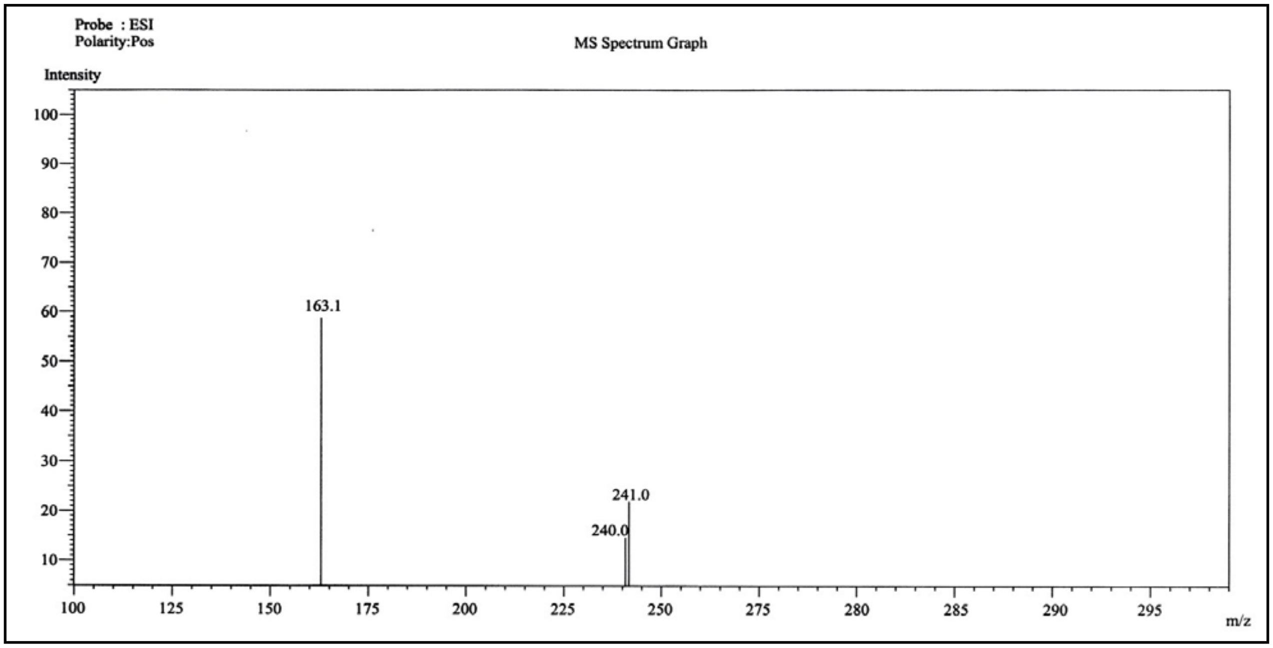

Fig 4. Mass Spectrum of SAINH in DMSO – d_6 medium

Absorption spectra of 2×10^{-5} solution of SAINH at different pH values were recorded and pKa values were determined spectrophotometrically using Phillip and Merrit method [15]. The bathochromic shift from 295 – 365 nm indicates that in solution on increasing pH the >C=0 group of the reagent (SAINH) is enolised and dissociated. The values of

SAINH are 4.2(pK_1) and 9.0 (pK_2) respectively. The pK_1 and pK_2 values are presumably due to keto – enol tautomerism and deprotonation of - NH group respectively.

A 0.01M solution of reagent is stable for 1h. The colour reactions of reagent with lead (II) are instantaneous at room temperature. The order of addition of lead ion, reagent and buffer has no effect on the absorbance of the complex. Various physico – chemical and analytical characteristics of lead complex are summarized in Table 2.

Table 2.Physico – chemical and analytical characteristics of Pb(II) – SAINH complex

S. No.	Characteristics	Results
1	λ_{max} (nm)	390
2	pH range (optimum)	8.0 – 8.5
3	Mean absorbance	0.219 ± 0.0002
4	Mole of reagent required per mole of metal ion for full colour development	5 fold
5	Time stability of the complex (in minutes)	3 hrs
6	Beer's law validity range (µg/ML)	1.0 – 10.0
7	Molar absorptivity (L. $mol^{-1}cm^{-1}$)	1.197×10^4
8	Specific absorptivity (ML. $g^{-1}cm^{-1}$)	0.060
9	Sandell’s sensitivity my of Pb(II) cm^{-2}	0.173
10	Composition of the complex as obtained in Job's and molar ratio methods	1 : 1
11	Stability constant of the complex	3.15×10^4
12	Standard deviation in the determination of 8.28µg/ml of Pb(II) for ten determinations	0.0050
13	Relative Standard deviation (RSD) %	2.28
14	Y–intercept	–0.0002
15	Angular co–efficient	0.0503
16	Detection limit (µg/ml)	0.068
17	Determination limit (µg/ML)	0.2040

Stoichiometry of the complex (M : L = 1 : 1) was determined by Job's continuous variation method and molar ratio method. Ammonium hydroxide (2M) –ammonium chloride (2M) buffer (pH 8.25) is used in these studies. The dissociation constant (α) and concentration (c) of the reagent at intersecting point were used in the calculation of stability constant of the complex. Stability constant of the complex 1: 1 (M : L) complex is given by $1-\alpha/\alpha^2c$. The predicted structure of Ni(II) – SAINH is given in Fig 5.

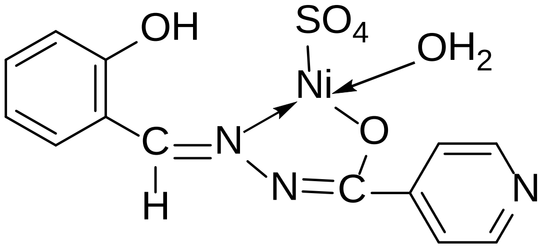

Fig 5. Predicted structure of Ni – SAINH complex

Tolerance limits of foreign ions *:* The effect of foreign ions which often accompany nickel has been studied by adding different amounts of foreign ions to fixed amount of lead (II) in solution. The colour reaction was studied as described in the standard procedure. An error of ±2% in the absorbance of the reaction mixture was considered tolerable. The results are given in Table 3.

Table 3.Tolerance limit of foreign ions in the determination of 6.21 μg/ml of lead.

Ion added	Tolerance limit μg/ml	Ion added	Tolerance limit μg/ml
Citrate	653.04	Ag(I)	129.04
Tartrate	592.20	Hg(II)	32.09
Sulphate	384	Cu(II)	1.77
Bromide	319.6	Mo(II)	1.51
Thiourea	304.00	Co(II)	1.17
Oxalate	281.6	Mn(II)	1.07
Iodide	253.80	Fe(III)	0.66
Nitrate	248	Al(III)	0.53
Chloride	141.80	Zn(II)	0.523
Fluoride	76		
Phosphate	15.20		
EDTA	3.72		

4.APPLICATIONS

The present method was successfully applied for the determination of lead in various environmental water samples and the results were presented in Table 4.

Table 4. Determination of lead in various water samples.

S. No	Sample	Amount of Lead* found (µg/ml)	
		SAINH method	Dithiozone method
1.	Tap water[a]	2.1983	2.1896
2.	Pond water[b]	2.1118	2.1019
3.	Tank water[c]	2.0945	2.1132
4.	Drain water[d]	2.1464	2.1925
5.	River water[e]	2.0945	2.1138

* Average of five determinations

a = Akuthotapalli tap water
b. = Madanapalle pond water
c = Madanapalle tank water
d = Madanapalle drain water
e = Pennahobilam river water (Anantapur)

5. CONCLUSION

The synthesized reagent salicylaldehyde isonicotinoyl hydrazone (SAINH) is characterized by analytical and spectral studies. The reagent forms a yellow coloured complex with lead(II). The Pb(II)-SAINH complex structure is predicted and various physic-chemical and analytical characteristics are determined.This reagent SAINH is successfully used for the determination of lead(II) in various environmental samples.

6.ACKNOWLEDGEMENT

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REFERENCES

[1] Adachi K., and Toinosho Y., Single particle characterization of size fractioned rood sediments, *J. Applied geochemistry,* 20, 849-859, 2005.

[2] Elmer E., Jose H., and Jose R., Using a Feather – Modified carbon paste Electrode by Anodic Stripping Voltammetry, *World Applied Sci. j.,* 2(5), 512-518, 2007.

[3] Hossein T., Elham A., Abodlmohammad. And Mahaboobeh T., Sensitive determination of Lead in Soil and Water Samples by Cloud Point Extraction – Flame Atomic Absorption Spectrometry Method. *J. of Chem Tech Res.*, 2(3), 1731-1737, 2001.

[4] Berthelesen B., Steiness E., Solberg W. and Jingsen L., Heavy metal concentration in plant in relation to atmospheric metal deposition., *j. Environ. Qual.*, 24, 1018-1026, 1995.

[5] Lanphere B.P., Burgoon D.A., Rnst S.W., Eberly, and Galke W., Environmental exposure to Lead and Urban children's blood lead levels, *Environm*, Res., 76, 120-130**,(1998).**

[6] R.L. Heller, J.C.Guyon ., *Talanta*, , 17(9), 865-7,1970.
[7] A.K. Alikhodzheer, D.N. Pachadzha, M.Yusuprov, Z.Yu ., Ana. Khim, , 40(1), 2021,1985.

[8] H. Sanke Gouda, K.N. Thimmaiah and S. Maqbool Ahmed., India.j.chem, , 2, 327, 1982.

[9] M. Subbarami Reddy, Ph.D. Thesis, S.K. University, Anantapur, India, 1982.

[10] S. K. Singh, M. Kamini and S. K. Sindhwani., J. Chinese. Chem.,soc., , 29, 131, 1982.

[11] V.K,Desai, K.K. Desai., Orient. J. chem.., 12, 203,1996.
[12] F. Salinas, J.C. Jiminez Sanchez and J.L. Lemus., Bull.Soc.Chim. Beig, ,95,293, 1986.

[13] Vogel, A.I., *"A Text Book of Quantitative Inorganic Analysis"*, 3rd edn., ELBS and Longman p.325,1975.
[14] Kamburova, M., *Talanta*, 40(5), pp.719-723, 1993.

[15] J.P. Phillips and L.L. Merrit., J. Ame. Chim.Soc., ,70, 410. 1978.