

## Synthesis of a new reagent 4-(2'-thiazolylazo)-6-formyl-resorcinol and spectrophotometric determination of lead (II) in waste water

Zhu Yurui\*, Jiang Wanquan, Jing Gu & Liu Wei

Department of Applied Chemistry, University of Science and  
Technology of China, Hefei, Anhui, P R China 230026

Received 17 November 1995; revised 3 June 1996

Synthesis and characteristics of a new chromogenic reagent, 4-(2'-thiazolylazo)-6-formyl-resorcinol (TAFR) has been reported. The optimum conditions for spectrophotometric determination of lead (II) using TAFR is present. At pH 7.5-8.0, TAFR forms a 1:1 red complex with lead (II) with molar absorptivity  $1.62 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  at 565 nm. Beer's law is obeyed in the range of 0-8  $\mu\text{g}/25 \text{ ml}$  Pb (II). The method has been applied for the direct determination of lead (II) in water samples.

Although lead is toxic to human beings, analytical methods for spectrophotometric determination of lead (II) are relatively rare. Some of recently reported methods<sup>1-4</sup> for determination of lead (II) involve reagents such as hexaoxacyclicazo compound, porphyrin derivative, ethyl violet and 4(2-pyridylazo)-resorcinol. 4-(2'-thiazolylazo)-resorcinol (TAR) is one of thiazolylazonol reagents which forms coloured complex and can be used for estimation of metal ions. However, it is not very selective<sup>5</sup>. In order to improve the analytical properties of such reagents, we have synthesized a new reagent, substituting 2,4-dihydroxybenzaldehyde for resorcinol in TAR. The new reagent 4-(2'-thiazolylazo)-6-formyl-resorcinol (TAFR), is highly selective for the determination of lead (II). The synthesis and characteristics of TAFR and the optimum condition of colour reaction with Pb(II) are reported for the first time. The proposed method has been successfully applied to the determination of lead (II) in environmental waste water samples.

### Experimental

A UV-240 spectrophotometer (Shimadzu, Japan) and PHS-2 model pH-meter (Shanghai, China) were used.

Standard solution of lead(II) (10.0  $\mu\text{g}/\text{ml}$ ) was prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  (0.1599 g) in

15 ml distilled water containing 1 ml of  $\text{HNO}_3$  (1:1) in a 100 ml standard flask and diluting to the mark. Stock solution 1.0 mg/ml Pb, working solution 10.0  $\mu\text{g}/\text{ml}$ . Working solution (10.0  $\mu\text{g}/\text{ml}$ ) was prepared by suitable dilution.

### Synthesis of 4-(2'-thiazolylazo)-6-formyl-resorcinol

Concentrated  $\text{H}_2\text{SO}_4$  (9 ml) was added slowly to distilled water (40 ml), and cooled. To this 2-aminothiazole (5.0 g) was added and the mixture was cooled to below 5°C in ice-water. Then aqueous sodium nitrite solution (35 ml, 10%) was added with stirring over 30 min. 2,4-Dihydroxybenzaldehyde (6.9 g) was dissolved in 20 ml ethanol in a 500-ml beaker and cooled to 0°C. Then the diazonium salt was added to the beaker with constant stirring. After 30 min, the mixture was added to 170 ml water. The precipitated crystals were filtered off, washed with water and dissolved in ethanol. The orange reddish crystals were recrystallized from water. [Found: C, 50.3%; H, 3.07%; N, 18.8%.  $\text{C}_{10}\text{H}_7\text{N}_3\text{O}_3\text{S}$  requires: C, 48.18%; H, 2.84%; N, 16.84%]. The purity was tested by thin-layer chromatography using petroleum ether-ethyl ether-ethanol (10:10:1) as solvent. The orange reddish crystals were recrystallised from ethanol.

Infrared spectrum (KBr pellets) showed stretching vibration bands at  $3430 \text{ cm}^{-1}$  (-OH associated with -CHO),  $1622 \text{ cm}^{-1}$  (C=O),  $1492 \text{ cm}^{-1}$  (C=C),  $1238 \text{ cm}^{-1}$  (-OH).

The NMR spectrum in deuterated chloroform showed bands at  $\delta = 6.55, 7.42-7.92, 8.17-8.19$  and 9.87 ppm.

Based on the above observations, structure is proposed for the reagent as follows:

The dissociation constants are  $pK_{a1} = 4.80$ ;  $pK_{a2} = 9.00$ .

### General procedure for estimation of Pb(II)

To 4 ml of standard solution of Pb(II) (10  $\mu\text{g}/\text{ml}$ ), were added 1 ml of TAFR-ethanol solution (0.02%) and 5 ml of sodium tetraborate buffer solution (pH = 7.7). The volume was made up to the mark with distilled water and mixed well. The absorbance was measured at 565 nm after 5 min against reagent blank.

### Results and discussion

The absorption of TAFR and the complex are

Table 1—Determination of Pb(II) in water samples

Sample	Pb(II), ppm		Error (%)	Coeff. of var.(%)
	Cert. value	Found <sup>†</sup>		
1	1.34 ± 0.07	1.38	3.0	2.83
2	1.20 ± 0.06	1.25	4.2	4.87

<sup>†</sup>mean of seven determinations.

maximal at 480 and 565 nm respectively. The absorbance of the complex was found to be maximum and constant in the pH range 7.5-8.0, therefore, pH 7.7 was selected for all further experiments.

It was found that surfactants like cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB), sodium dodecylbenzene sulphate (SDS), sodium dodecylbenzene sulphate. Triton X-100, Tween-20 did not enhance the colour of the complex or improve the solubility of TAFR or the complex.

For complete complex formation, 0.6-1.4 ml of 0.02% TAFR was required. For further studies, 1.0 ml of 0.02% TAFR was used. The colour development was maximum in 5 min at room temperature. The complex was stable for at least 2 h. Beer's law was obeyed in the range 0-80  $\mu\text{g}/25\text{ ml}$  Pb(II). The molar absorptivity is  $1.62 \times 10^4\text{ l mol}^{-1}\text{ cm}^{-1}$ . The linear correlation and absorbance were 0.9990 and 0.01002 respectively. The molar-ratio and slope-ratio methods showed ratio of TAFR : Pb to be 1 : 1 in the complex.

### Effect of diverse ions

The effect of nearly 35 diverse ions on the determination of 40  $\mu\text{g}$  Pb(II) was studied. A change of 5% in absorbance was set as the tolerance limit. The following metal ions (amounts given in mg) interfered seriously:  $\text{K}^+$  (30),  $\text{Na}^+$  (30),  $\text{Mg}^{2+}$  (5),  $\text{Ba}^{2+}$  (5),  $\text{Sn(II)}$  (5),  $\text{Mo(VI)}$  (3),  $\text{Ca}^{2+}$  (1),  $\text{Al(III)}$  (1),  $\text{Cr(III)}$  (1),  $\text{V(V)}$  (0.7),  $\text{Cr(VI)}$  (0.4),  $\text{Zr(IV)}$  (0.2),  $\text{Fe(III)}$  (0.03),  $\text{In(III)}$  (0.03),  $\text{NH}_4^+$  (160),  $\text{Cl}^-$  (300),  $\text{SO}_4^{2-}$  (100),  $\text{NO}_3^-$  (80),  $\text{SCN}^-$  (29),  $\text{SO}_3^{2-}$  (10),  $\text{Br}^-$  (10),  $\text{F}^-$  (10),  $\text{CN}^-$  (4),  $\text{C}_2\text{O}_4^{2-}$  (2), thiourea (100), tartrate (10), citrate (10), phenanthroline (10),  $\text{Cu(II)}$ ,  $\text{Co(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Hg(II)}$ ,  $\text{Ni(II)}$  and  $\text{Cd(II)}$ . When 50 mg thiourea and 2 mg phenanthroline were added to the solution,  $\text{Co(II)}$  (0.03),  $\text{Zn(II)}$  (0.03),  $\text{Mn(II)}$  (0.03),  $\text{Hg(II)}$  (0.03),  $\text{Cu(II)}$  (0.02),  $\text{Ni(II)}$  (0.01) and  $\text{Cd(II)}$  (0.01) did not interfere.

### Analysis of Pb(II) in the waste water

The proposed procedure was applied for the determination of Pb(II) in the environmental water samples. The results are in agreement with certified values (Table 1).

### Acknowledgement

This study was financially supported by National Science Fund, P.R. China.

### References

- Savvin S B, Petrova T V & Dzherayan T G, *Fr J anal Chem*, 34G (1991) 217.
- Pan J M, Li Z J & Xu Z J, *Fenxi Shiyanshi*, 13 (1994) 29.
- Hou M & Bai W H, *Fenxi Shiyanshi*, 12 (1993) 75.
- Barve A D & Shinde V M, *Indian J Chem*, 32A (1993) 1102.
- Hnilickova M & Sommer L, *Talanta*, 13 (1966) 667.