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Understanding the effects of potassium ferricyanide on lead hydride formation in tetrahydroborate system and its application for determination of lead in milk using hydride generation inductively coupled plasma optical emission spectrometry

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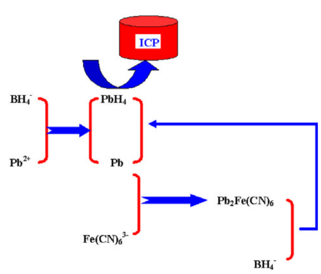
HIGHLIGHTS

- Proposed a novel explanation for plumbane generation.
- Expounded the role of $K_3Fe(CN)_6$ in plumbane generation.
- Clarified the controversial aspects in the mechanism of $K_3Fe(CN)_6$ enhancement.
- Used X-ray diffractometry to analyze the intermediates.
- Developed a method to analyze lead in milk using $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ as new additives.

GRAPHICAL ABSTRACT



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ABSRACT

To understand the formation of plumbane in the Pb^{II}-$NaBH_4$-$K_3Fe(CN)_6$ system, the intermediate products produced in the reaction of lead(II) and $NaBH_4$ in the presence of $K_3Fe(CN)_6$ were studied. The produced plumbane and elemental lead were measured through continuous flow hydride generation (HG)-inductively coupled plasma optical emission spectrometry (ICP OES) and X-ray diffraction spectrometry techniques, respectively. Based on the experimental results, the explanations can be depicted in the following steps: (1) plumbane and black lead sediment (black Pb) are formed in the reaction of lead(II) and $NaBH_4$; (2) the black Pb is oxidized by $K_3Fe(CN)_6$ to form $Pb_2[Fe(CN)_6]$, which further reacts with $NaBH_4$ to form more plumbane and black Pb; and (3) another round starts in which the produced black Pb from the step 2 is then oxidized continuously by $K_3Fe(CN)_6$ to form more $Pb_2[Fe(CN)_6]$ complex, which would produce more plumbane. In short, the black Pb and $Pb_2[Fe(CN)_6]$ complex are the key intermediate products for the formation of plumbane in the Pb^{II}-$NaBH_4$-$K_3Fe(CN)_6$ system. Based on the enhancement effect of potassium ferricyanide and potassium ferrocyanide, a method was developed to analyze lead in milk with HG-ICP OES technique. The detection limit of the method was observed as 0.081 $\mu g\,L^{-1}$. The linearity range of lead was found between 0.3 and 50,000 $\mu g\,L^{-1}$ with correlation coefficient of 0.9993. The recovery of lead was determined as 97.6% ($n = 5$) for adding 10 $\mu g\,L^{-1}$ lead into the milk sample.

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1. Introduction

Lead is a ubiquitous and nonessential toxic heavy metal that has cumulative effects and a relatively long biological half-life [1]. Ingested lead is a real healthy hazard affecting both the nervous system and the biosynthesis of hemoglobin [2]. Therefore, the studies on the analytical methods of lead are always important topics in environment and medicine sectors. Due to the ability of lead to produce volatile covalent hydride (PbH_4), chemical vapor generation is presently considered as one of the most popular derivatization procedures for the analysis of trace and ultra trace amounts of lead in combination with various atomic spectrometric techniques [3,4]. Thus, since the mid-1970s, researchers have always been committed to the study of atomic spectrometry on the hydride generation (HG) of lead. At present, there are various experimental methods; for example, continuous generation [5–10], flow injection generation [11–13], and acidic and alkaline reactions modes [14,15], which have made considerable progress in the analysis of lead HG. However, potassium ferricyanide system has shown the best sensitivity and most convenient operation for all of lead HG types, so it has been widely applied for the determination of lead in various samples.

Nascent hydride mechanism has usually been used for the explanation of hydride generation [16]. D'Ulivo reported that hydroborate decomposes to produce borane and nascent hydride [17]. It has also been observed that the generation efficiency of plumbane greatly enhances in the presence of oxidants [18,19]. Subsequently, some systems with oxidants for example, $K_2Cr_2O_7$ [20], $K_3Fe(CN)_6$ [21], nitroso-R salt (2-nitroso-1-naphtol-3,6-disulfonic acid; disodium salt) system [22], $(NH_4)_2Ce(NO_3)_6$ [23], and PAN-S (1-(2-pyridilazo)-2-naphtol-6-disulfonic acid) can strongly enhance the lead signal [24] and the efficiency of plumbane formation. A series of research works and reviews about the mechanisms involved in the chemical vapor generation (CVG) were published by D'Ulivo et al. [25–32].

The additives perform important actions in the efficiencies enhancement of plumbane formation. From literatures concerning the determination of lead, the mechanisms for discussion could be reduced to the following cases: (a) oxidation action, conversion of the oxidants oxides Pb^{II} to metastable Pb^{IV} [19,33,34]; (b) complex role in which PAN-S does not provide oxidation or catalytic character and the role of enhancing plumbane formation efficiency is only the chelation of PAN-S and Pb^{II} [24,35,36]; (c) nascent hydride mechanism [16,17]; (d) non-nascent hydride mechanism [37]; and (e) other mechanism: BH_4^- and Pb^{II} generated “atomic (groups) transfer reaction” [38]. The key role of $K_3Fe(CN)_6$ is recognized as its reaction with $NaBH_4$ to give “special” borane complex intermediates, which are highly effective in the production of plumbane from Pb^{II} [30].

From the above mechanisms, there have been different opinions to explain the mechanisms of plumbane formation, which some of them are full of contradictions. However, a few systematic investigation or dedicated experiments were performed on the mechanism of oxidants enhancement of plumbane generation efficiency and thus few reasonable theoretical explanations were proposed.

In this research, the X-ray diffractometry technique was applied to study the intermediates produced in the plumbane formation reaction. The intermediates in the lead hydride production were obtained when various potassium ferricyanide(III) concentrations were added to the plumbane generation system. The enhancement effect of potassium ferricyanide on lead hydride generation in tetrahydroborate system is discussed. The explanation could be used to understand the plumbane formation and the reasons for its enhancement efficiency by $K_3Fe(CN)_6$. The analytical method of lead in milk was developed using continuous flow hydride generation inductively coupled plasma optical emission spectrometry technique using $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ as additives. The effects of influencing parameters were examined in detail.

2. Experimental

2.1. Apparatus and operating conditions

An inductively coupled plasma-optical emission spectrometer, model Optima 2000DV (PerkinElmer, USA), an X-radial diffraction spectrometer (Rigaku D/max 2500 V pc^{-1}, Rigaku, Japan), TU-190 double-beam UV–vis spectrophotometer (Beijing Purkinje General Instrument Co., Beijing, China), WR-3TA system of microwave digestion (Beijing Ying An Meicheng Scientific Co., Beijing, China), and the self-made device of hydride generator (Fig. 1) were used in the present work. Operating conditions for examinations with HG-ICP OES are presented in Table 1.

2.2. Reagents

Stock standard solution of 1 g L^{-1} lead (atomic spectroscopy standard, PerkinElemer, USA) was used to prepare Pb^{II} working solution. Sodium borohydride (Shanghai Tianlian Fine Chemical Co., Shanghai, China), sodium hydroxide (Guangdong Xinning

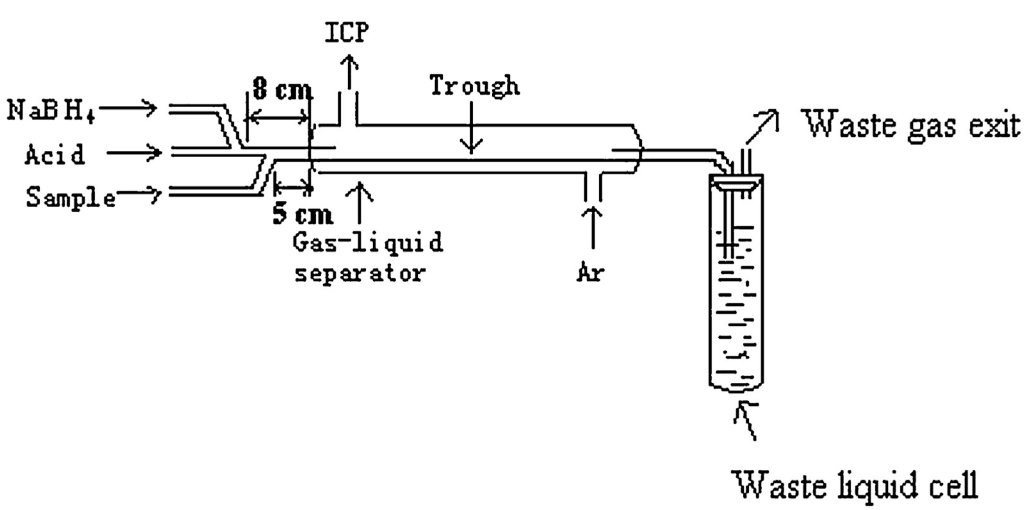

Fig. 1. A self-made device used as hydride generator.