

STUDIES IN HYDRIDE GENERATION FOR THE DETERMINATION OF TRACE LEVELS OF LEAD BY ATOMIC FLUORESCENCE SPECTROMETRY

Beltrán Blanca¹, Miranda Silvia¹, Leal Luz^{1*}

¹Environment and Energy Department

Advanced Materials Research Center

Miguel de Cervantes 120

Chihuahua, Chihuahua, 31109

*corresponding author: leal.luz@cimav.edu.mx

Abstract: Two methods were used for the determination of lead at ng L^{-1} levels by Flow Injection- Hydride Generation- Atomic Fluorescence Spectrometry (FI-HG-AFS). Lead hydride was generated using hydrogen peroxide and potassium hexacyanoferrate (III), both as oxidants agents. A reducing KBH_4 solution, HCl solution and the sample were dispensed into a gas-liquid-separator. An argon flow delivered the lead hydride (PbH_4) and the hydrogen gas into the flame of an atomic fluorescence spectrometer. Instrument parameters and chemical variables were optimized. A study of interference of the most common ions was also carried out. Analytical curves were obtained for lead determination with hydrogen peroxide between 1 and $80 \mu\text{g L}^{-1}$, whereas using hexacyanoferrate (III) between 0.5 and $80 \mu\text{g L}^{-1}$. The detection limit of the proposed technique was $0.42 \mu\text{g L}^{-1}$ y $0.03 \mu\text{g L}^{-1}$, respectively. The better results were observed with the hexacyanoferrate (III) as oxidant agent due its accuracy and sensitivity.

1. INTRODUCTION.

Lead (Pb) is an accumulative poisonous substance (Fang et al, 1999). It is widely known for its toxic properties and they are well documented (Nielsen et al, 1975). An excess of ingested lead is a real health hazard affecting both the nervous system and the biosynthesis of hemoglobin (Elçi et al, 2009). Thus the determination of lead is increasingly important. Hydride Generation (HG) or Chemical Vapor Generation (CVG) is one of the most popular analytical methods for the determination of trace or ultratrace levels of several hydride-forming elements (Dedina et al, 1995). This process in presence of tetrahydroborate (III) (THB) (sodium or potassium salt), converts ionic species of Ge, Sn, Pb, As, Sb, Bi, Se, Te, in the corresponding volatile hydrides or in the volatile element as in the case of inorganic Hg (II) (D'Ulivo et al 2008) and more recently, to many transition and noble metals (Phol and Prusisz, 2007).

Exists a variety of techniques and methods for lead measurement such as Hydride Generation with Atomic Absorption Spectrometry (HG-AAS) (Baraguan et al, 2002), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Zheng et al, 2009), Hydride Generation with Atomic Fluorescence Spectrometry (HG-AFS) (Xiaohua et al 2006; Yuxiu and Haolinhua, 2000; Zheng et al 2009), Analysis Flow Injection System (FIA-System) (Mingshu and Pacey, 1995). In the determination of lead by FI-HG-AFS, the effect of the oxidizing agent on the lead hydride generation plays an important role.

The lead hydride is called plumbane (PbH_4), and is one of the most interesting and controversial case (D'Ulivo et al, 2008). Little work has been done on lead hydride generation in comparison with other hydride forming elements: most likely due to the low yield and thermal instability of plumbane (Dedina et al 1995; Madrid and Cámara, 1994).

Pollock and West (1973) investigated the determination of lead for the first time by a hydride generation method, but they failed to obtain absorbance signals even at concentration of $100 \mu\text{g L}^{-1}$. Thompson and Thomerson (1974), using a similar approach, were the first to achieve the generation of lead hydride for analytical purposes.

The generation efficiency of plumbane is greatly enhanced in presence of additives such as H_2O_2 (Vijan and Wood, 1976), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Jin and Taga, 1982), $\text{K}_2\text{Cr}_2\text{O}_7$ (Fleming and Ide, 1976), KMnO_4 , CeSO_4 (Castillo et al, 1985), KBrO_3 (Nakahara and wasa, 1985), $\text{K}_3\text{Fe}(\text{CN})_6$ (Tao and Zhou, 1985); with inorganic acids, HNO_3 (Cabrera et al, 1994), HCl (Ebdon et al, 1994), organic acids such as malic, tartaric, lactic acids (Maleki et al, 1994). Masking agents such as potassium thiocyanate/oxalic acid/1,10 phenantroline can be also used (Zheng et al, 2009).

Lead hydride generation process is considered very complex. The plumbane generation is more efficient for Pb (IV) than Pb (II); this hypothesis was supported by Castillo et al (1985). However, Nerin et al (1989) were in disagreement with the hypothesis mentioned above, because they found that the presence of oxidant was always necessary to achieve improved plumbane generation, independently of the oxidation state of lead. D'Ulivo et al (2008) gave further evidence about the strong enhancement produced by the hexacyanoferrate (III), known as potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), in the generation efficiency of plumbane by formation of borano complex intermediates.

The coupling of HG with AFS has provided a powerful tool for the determination of hydride-forming elements including lead (Zheng et al, 2009). The use of hydride generation (HG) can separate analytes from sample matrices, thereby reducing or eliminating potential chemical and spectral interferences. Atomic Fluorescence Spectrometry (AFS) has been employed because of its high sensitivity, wide linear range, ease of use and low cost (Gong et al, 2002). This technique uses much simpler and cheaper equipment, and therefore is more practical in laboratory use (Xiaohua et al, 2006; Leal et al, 2006).

The efficient generation of lead hydride usually requires large amounts of tetrahydroborate and oxidant, increasing the cost of analysis (Dedina et al, 1995). In addition, a vigorous reaction is produced when the reagents are mixed, with formation of aerosols and foams. These drawbacks can be avoided in a FIA-system (Baraguan et al, 2002). The flow injection analysis has proved to be a suitable technique for on-line analysis because of its low reagents and sample consumption, high sampling frequency and ease of automation. Furthermore, it allows the reduction of transition metal interferences in comparison with the batch systems. It is due to a shorter period of sample-reagents interaction (Leal et al, 2006).

The aim of this study was to evaluate the efficiency of $K_3[Fe(CN)_6]$ (Ferricyanide Method, FeM) and H_2O_2 (Peroxide Method, PM) as additives for plumbane generation. Several variables such as sample and reagents volumes, flow rates and reagent concentrations were investigated in detail for each method. A study of interference of the most common ions was also carried out.

2. EXPERIMENTAL.

2.1. Apparatus.

A non-dispersive atomic fluorescence spectrometer, AFS-640 (manufactured by Beijing Raleygh Analytical Instrument Corp., China) with a continuous flow-interval sampling vapor generation was employed as detector. It consists of a peristaltic pump with two channels, one of them for aspirating the reducing solution, whereas the other one for sample/carrier solution (HCl). In addition, the instrument has a storage sample ring, a Mixed Module and two argon flows. The light source, a Pb hollow-cathode lamp, was operated at 80 mA in a double-modulated pulsed mode at 283.3 nm. Plumbane and co-generated hydrogen gas were transported by a carrier gas (argon) through the gas-liquid separator to the atomizer. The quartz tube atomizer is ignited to form the argon-hydrogen flame and makes an effective atomization. The photomultiplier R166 was employed as detection system. All functions of AFS-640 are controlled by computer and data processing and RS232 standard interface are communicated with the main unit. Windows 98/2000/XP operation system is provided with the software.

2.2. Reagents.

All chemicals used were of analytical reagent grade. For preparation of all solutions Millipore-purified water was used. Glassware needed for lead determination was soaked in 10% (v/v) nitric acid and rinsed with Millipore water.

Series of Pb (II) standard solutions were prepared by gradually diluting 1000 mg L⁻¹ standard stock solutions (high-purity standars). 5% (v/v) H_2O_2 (J.T.Baker 30%) and 1.5% (m/v) $[Fe(CN)_6]$ (J.T.Baker 99.7%) were used as additives. The 1.5 % (m/v) reducing solution was prepared from KBH_4 (aldrich 98%) in a basic media of KOH (J.T.Baker 87%). The carrier solution was made of HCl 1.5 % (v/v) (Baker intrad-analyzed 37.6%).

For peroxide method (PM), series of Pb(II) standard solutions were prepared by gradually diluting 1000 mg L⁻¹ standard stock solutions in 50 ml of 1.5% HCl and adding 2.5 ml de H_2O_2 . KBH_4 was used as a reducing agent at a concentration of 15 g L⁻¹ in a 2 g L⁻¹ KOH solution.

In the case of Ferricyanide method (FeM), the standard solution was prepared as the same (PM) but without H_2O_2 , and $KBH_4/K_3 [Fe(CN)_6]$ solution was prepared by dissolving 7.5 g $K_3 [Fe(CN)_6]$ and 5 g KBH_4 in 500 mL 2 g L⁻¹ KOH solution.

2.3. Procedure.

In the measurement, the reducer solution (KBH_4) through the peristaltic pump directly enters into the mixed module. The carrier current will pass through the peristaltic pump and enter into the storage ring, when the pump stops running, the

sample collection is complete. Then the peristaltic pump runs again and the carrier current will push the sample into the mixed module (reaction ring) to process the reaction. During this procedure, the volatile hydride and excess hydrogen gas are formed and delivered to the quartz furnace atomizer by an argon flow. The co-generated H_2 supports the flame of an atomic fluorescence spectrometer. Meanwhile the fluorescence real time signal is recorded and displayed on the screen.

3. RESULTS AND DISCUSSION.

In order to achieve the most efficient performance in terms of highest analytical sensitivity and lowest deviation of signal (measure precision), some parameters were investigated for both methods and summarized in Table 1. The optimization of the variables was carried out by the univariate method.

3.1. The AFS system

The temperature of atomizer, carrier and auxiliary argon flow, delay time and reading time were optimized (Table 1). Lamp current, auxiliary cathode current, height of atomizer, were established as recommended by the AFS-640 manual. Negative high voltage was optimized. It has been found that at 290 mV is obtained the highest fluorescence intensity. However, the manual recommends to use 270 mV for better equipment performance and to extend the life time of the lamp.

Table 1. Operation parameters AFS and FI system.

	^a PM	^b FeM
<u>AFS</u>		
Lamp Current	80 mA	80 mA
Negative high voltage	270 mV	270 mV
Auxiliary cathode current	0 mA	0 mA
Height of atomizer	7 mm	7 mm
Temperature of atomizer	100 °C	0 °C
Carrier argon flow	300 ml L ⁻¹	400 ml L ⁻¹
Auxiliary argon flow	0 ml L ⁻¹	0 ml L ⁻¹
Delay time	6 seg	4 seg
Reading time	24 seg	22 seg
<u>FI system.</u>		
Load sample time	10 s	8 s
Load sample volume	1.6 mL	1.3 mL
Flow injection to the detector(PMT)	10 mL min ⁻¹	8 mL min ⁻¹

Conditions for ^a Peroxide Method: 20 $\mu\text{g L}^{-1}$ Pb solution, 1.5 % (v/v) HCl, 1.5 % (m/v) KBH_4 , 5%(v/v) H_2O_2 .

Conditions for ^b Ferricyanide Method: 10 $\mu\text{g L}^{-1}$ Pb solution, 1.5 % (v/v) HCl, 1.5 % (m/v) KBH_4 , 1.5%(m/v) $\text{K}_3\text{Fe}(\text{CN})_6$.

3.2. Load volume and speed.

The sample load time and injection speed were optimized for achieving adequate sample load volume and pushing speed to the detector. When sample load time increasing (2,4,6,8,10,12,14 seconds), the signal increased at a constant injection speed (10 ml min⁻¹), although the concentration of reagents increases at the same time (Hong et al, 2007) For these reasons, the sample load time was set at 10 seconds and load volume calculated was 1.6 ml for PM (Fig. 1) and in FeM (Fig. 2), 8 seconds and 1.3, in addition those values had lower deviation between their measurements.

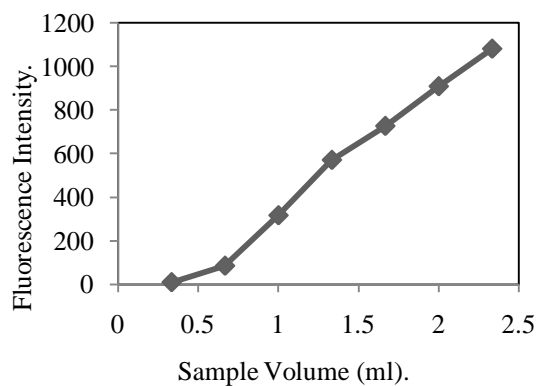


Figure 1. Sample load volume optimization for PM method. Conditions: $20 \mu\text{g L}^{-1}$ Pb solution, 1.5 % (v/v) KBH_4 , 1.5% (v/v) HCl, 5% (v/v) H_2O_2 , sample injection speed 10 ml min^{-1} .

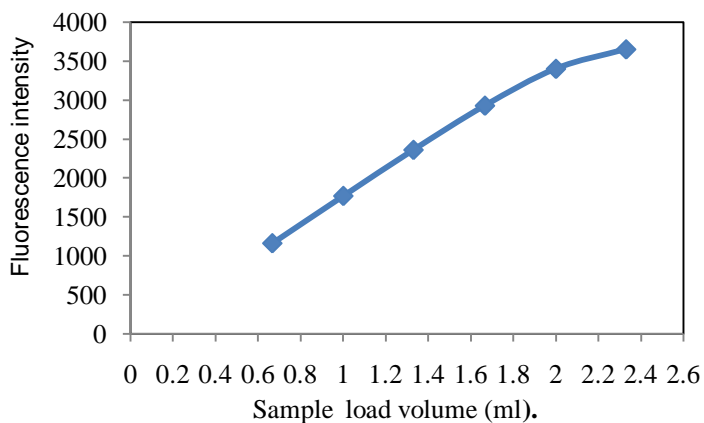


Figure 2. Sample load volume optimization for FeM method. Conditions: $10 \mu\text{g L}^{-1}$ Pb solution, 1 % (v/v) KBH_4 , 1.5% (v/v) HCl, 1.5% (m/v) $\text{K}_3 [\text{Fe}(\text{CN})_6]$, sample injection speed 10 ml min^{-1} .

The optimal sample injection speed was obtained varying the injection flows at 8, 10, 11.5, 13 ml min^{-1} in PM, and at 6, 8, 10, 12, 14, 16 ml min^{-1} in FeM. Figure 3 shows the obtained results. The optimal value was of 10 ml min^{-1} in both methods.

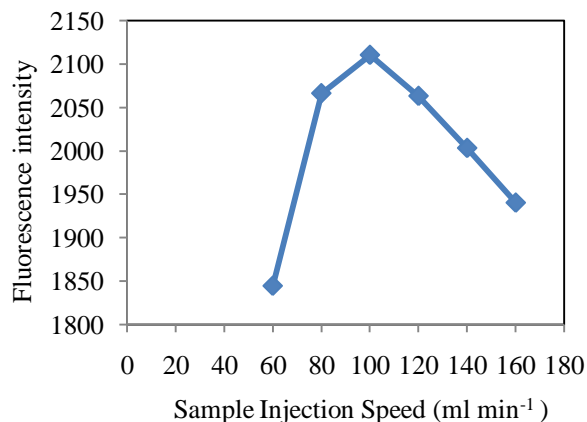


Figure 3. Sample injection speed optimization. Conditions: 10 $\mu\text{g L}^{-1}$ Pb solution, 1 % (v/v) KBH_4 , 1.5% (v/v) HCl, 1.5% (m/v) $\text{K}_3[\text{Fe}(\text{CN})_6]$, sample load volume 1.3 ml.

3.3. Optimization of the chemical variables.

The KBH_4 solution was used as both reductant and hydrogen supplier, which was necessary to support the argon-hydrogen flame (Hong et al, 2007). As shown in figure 4, a low concentrations of KBH_4 could not effectively reduce the analyte to hydride, or can not support the argon-hydrogen flame, while higher concentrations (>2.5 % m/v) increasing the signal, but there is a excessive foaming and aerosol formation as well as reactive spending, therefore a KBH_4 concentration of 1.5 and 1 % (m/v), were chosen for PM and FeM respectively.

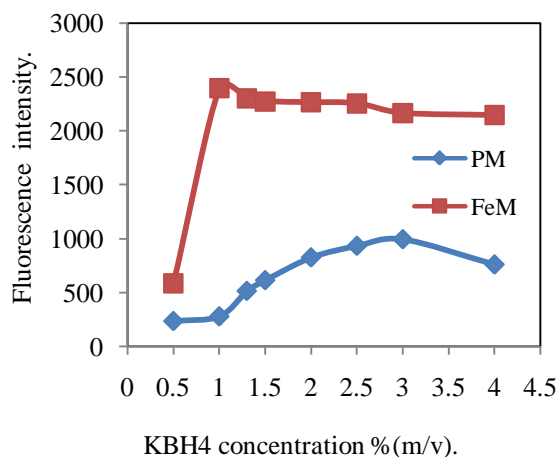


Figure 4. Effect of tetrahydroborate (KBH_4) concentrations on the analytical signal of lead. Conditions: Peroxide Method using 20 $\mu\text{g L}^{-1}$ Pb solution, 1.5 % (v/v) HCl, 5% (v/v) H_2O_2 . Sample load volume 1.6 ml, sample injection speed of 10 ml min⁻¹. Ferricyanide Method: 10 $\mu\text{g L}^{-1}$ Pb solution, 1.5 % (v/v) HCl, 1.5% (m/v) $\text{K}_3\text{Fe}(\text{CN})_6$.

In more than half of 90 papers published, hydrogen peroxide was employed as the oxidant for lead hydride generation (Braguan et al, 2002). In the presented method, a solution of 5% (v/v) hydrogen peroxide was chosen as the optimal value. On the other hand, $\text{K}_3[\text{Fe}(\text{CN})_6]$ is one of the most used additives due its enhancing the generation efficiency of lead hydride (D'ulivo, 2008). The optimization of this oxidant was carried out. The obtained results showed that with concentration of 1% (m/v) of $\text{K}_3[\text{Fe}(\text{CN})_6]$, the fluorescence intensity is maintained almost linear. Then 1.5% (m/v) was selected as the optimal value, since it provides a smaller standard deviation between theirs measurements.

The influence of the HCl concentration on the analytical signal has been evaluated (Figure 5). The sensitivity of lead was higher in 1.5% HCl for both PM and FeM methods. The acidities of samples and standards solutions were also tested. The values of them should be similar to the HCl solution in order to achieve a high sensitivity (Xiaohua et al, 2006).

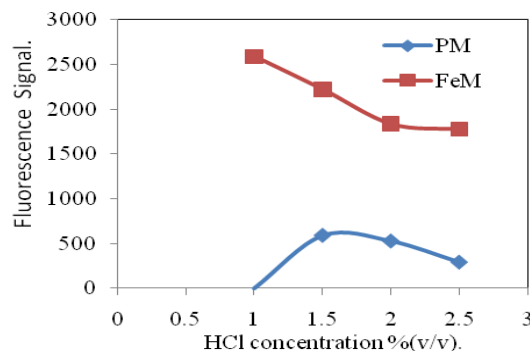


Figure 5. Effect of HCl concentration. Peroxide Method Conditions: $20 \mu\text{g L}^{-1}$ Pb solution, 1.5% (m/v) KBH_4 , 5% (v/v) H_2O_2 . Sample load volume 1.6 ml, sample injection speed of 10 ml min^{-1} . Ferricyanide Method: Conditions: $10 \mu\text{g L}^{-1}$ Pb solution, 1% (m/v) KBH_4 , 1.5% (m/v) $\text{K}_3\text{Fe}(\text{CN})_6$. Sample load volume 1.3 ml, sample injection speed of 10 ml min^{-1} .

3.4. Analytical parameters.

The calibration curve of lead was constructed to obtain linearity of the method, that is the relationship between the response of the instrument at the known concentrations of analyte (Daneshtalab et al 2001). The detection limit corresponds to the least amount of the analyte in a sample that can be detect but not necessarily quantify exactitude (Food and Drug Administration (FDA), 2001); the relative standard deviation was also calculated. All this values are showed in Table 2.

Table 2. Analytical parameters of FI-HG-AFS system for lead determination.

	^a PM		^b FeM	
Calibration graph	1-11 $\mu\text{g L}^{-1}$	10-80 $\mu\text{g L}^{-1}$	0.5-2 $\mu\text{g L}^{-1}$	8-80 $\mu\text{g L}^{-1}$
Regression graph	$Y=43.83x+0.175$	$Y=28.96x+53.63$	$Y=360.07x+20.474$	$Y=192.1x+676.61$
Correlation coefficient	0.9994	0.9999	0.9975	0.9986
Detection limit (3σ).(n=10)	0.42 ng L^{-1}	0.83	0.03	.062
Relative standard deviation(n=15)	7.15 (std 3 $\mu\text{g L}^{-1}$)	2.29 (std 40 $\mu\text{g L}^{-1}$)	1.14 (std 1.2 $\mu\text{g L}^{-1}$)	0.830 (std 50 $\mu\text{g L}^{-1}$)
Sampling frequency	53 injection h^{-1}		70 injection h^{-1}	

^aConditions for PM: $20 \mu\text{g L}^{-1}$ Pb solution, 1.5% (v/v) HCl, 1.5% (m/v) KBH_4 , 5%(v/v) H_2O_2 . Sample load volume 1.6 ml, sample injection speed of 10 ml min^{-1} . ^bConditions for FeM: $10 \mu\text{g L}^{-1}$ Pb solution, 1.5% (v/v) HCl, 1.5% (m/v) KBH_4 , 1.5%(m/v) $\text{K}_3\text{Fe}(\text{CN})_6$. Sample load volume 1.3 ml, sample injection speed of 10 ml min^{-1} .

3.5. Interferences

The selectivity of the proposed technique has been evaluated by studying the effect of adding foreign ions in the determination of $10 \mu\text{g L}^{-1}$ and $1 \mu\text{g L}^{-1}$ of lead for PM (Table 3) and FeM (Table 4) methods, respectively. The study of the

interferences was carried out in presence of transitions metals such as zinc, iron, cobalt, nickel, chromium and hydride forming elements like arsenic, antimony, cadmium and aluminum. An element was considered not to interfere when the maximum peak variation is three times less than the standard deviation (Leal et al, 2006).

Table 3. Tolerance level of metal ions in the determination of $10 \mu\text{g L}^{-1}$ Pb (II) with H_2O_2 as oxidizing agent.

Ion added	As	Cd	Cr	Fe	Zn	Al	Ni	Co
Tolerated concentration ($\mu\text{g L}^{-1}$)	10	100	10	10	1000	10	50	10

Table 4. Tolerance level of metal ions in the determination of $1 \mu\text{g L}^{-1}$ Pb (II) with $\text{K}_3[\text{Fe}(\text{CN})_6]$ as oxidizing agent.

Ion added	Sb	Cd	Cr	Co	Al
Tolerated concentration ($\mu\text{g L}^{-1}$)	10	1000	5	50	10

In all cases these interferences decreased the signal for concentrations higher than those mentioned in Table 3 and 4. The main problem with the determination of lead by the HG technique arises from its high susceptibility to suffer interferences, which severely restricts the analysis of complex sample matrices (Zheng et al, 2009).

As can be seen in Tables 3 and 4, elements that form volatile hydrides produced the highest suppression of the signal. It is due their competition for the reducing agent, since they react faster than lead (Ramesh and Riyazuddin, 2010). Therefore, As, Cr, Fe, Al and Co can suppress the signal by affecting the generation of plumbane even if its concentration is as low as that of the analyte. Zn and Cd were well tolerated.

4, CONCLUSIONS.

The FI-HG-AFS system proposed for trace levels of lead using two different methods has been developed. The parameters of the system, that includes chemical and instrumental variables, were optimized and selected. The use of potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ as oxidizing agent showed more advantages, such as higher sensitivity (detection limit of $0.03 \mu\text{g L}^{-1}$) and better reproducibility, whereas with hydrogen peroxide as additive was obtained a detection limit of $0.42 \mu\text{g L}^{-1}$. The study of interferences showed that both methods presented low tolerance to foreign ions, indicating the need of a detailed interference study with several masking agents. It will be developed in a second part of this investigation work. The proposed methods offer some advantages in front of conventional laboratory techniques, such as optimum sensitivity, higher sample throughput and decreasing of reagents and sample consumption, which leads to a lower waste generation.

5. ACKNOWLEDGEMENTS

This work was funded by FOMIX CHIH-2008-C02-92172. B. Beltrán acknowledge to CONACYT for the scholarship given to support this work.

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