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DISCLAIMER

High Gas Temperature Furnace for Species Determination of

Organometallic Compounds with HPLC-ZAA System

Hideaki Koizumi, Ralph D. McLaughlin and Tetsuo Hadeishi

Lawrence Berkeley Laboratory, University of California
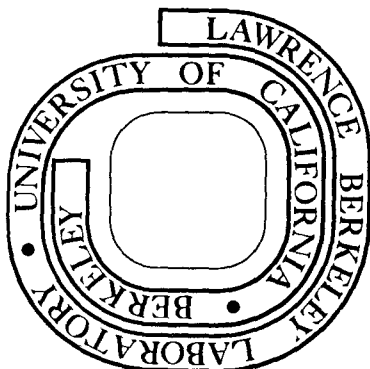
Berkeley, California 94720

Species determination of organometallic compounds is nowadays one of the most important subjects in analytical chemistry. This is because the toxicity of metals depends upon the binding conditions in the compound.[1] Data on toxic species is more important than data on total metal content, both in the analysis of food and in the determination of the impact of environmental pollution.

Speciation of organometallic compounds is also important in physiology and biology. Until now, more than 1,000 enzymes and coenzymes have been found and about one third of them are "metalloenzymes" or "metal-substrate complexes".[2] Iron in hemoglobin, Zn in carboxypeptidase and carbonic anhydrase, and Co in vitamin B12 are well known examples. With the acquisition of more knowledge, larger numbers of trace elements are found to be very important in the human body.[3,4] Even a biologically active chromium compound (glucose tolerance factor) has recently been found in yeast.[5]

It is a well known fact that commercial gasoline contains alkyl lead compounds. In the U.S.A., leaded gasoline contains around 0.1% of alkyl lead, and commercial unleaded gasoline is defined as gasoline having not more than 0.05 g Pb/gal (13.16 μg/ml).[6]

There are several techniques that can be used to separate organometallic compounds (liquid chromatography, gas chromatography, thin layer chromatography, and thermal selective vaporization).

Gas chromatography is not necessarily a suitable technique for the separation of organometallic compounds, because some of the organometallic compounds are unstable in the gas phase. Thin layer chromatography suffers from the difficulty of introducing the separated sample into a detector. The thermal selective vaporization technique is at an early stage of development.[7,8]

High performance liquid chromatography (HPLC) would be the most convenient and universal technique for non-destructive separation of organometallic compounds. HPLC utilizes various mechanisms to achieve separation, i.e., adsorption, ion exchange and molecular sieving.[9] It could be said that the only requirement is that the sample of organo-metallic species be soluble in the solvent without alteration of its chemical form.

However, various types of organic solvents are used as eluents; aromatic compounds such as benzene and toluene, alcohols, ketones and nitro-compounds. Therefore, we are obliged to determine trace amounts of metals in these organic solvents. With conventional techniques of trace element detection, including atomic emission and absorption spectroscopy and mass spectroscopy, it is very difficult to avoid interferences caused by the large amount of organic solvent. In many cases, the organic solvent cannot be eliminated by vaporization before the measurement, because many organometallic compounds have boiling points below 200°C and a considerable part of the organometallic compound escapes with the vaporization of the solvent.

For example, the mercury signal from methylmercuric chloride in benzene solution cannot be obtained by mass spectrometry, because this compound evaporates at around 100°C.[10]

Several researchers have used atomic absorption methods as the detector for HPLC.[8,11,12] These methods generally have many advantages over other techniques. However, interference caused by the eluent was still a problem, because ashing temperatures had to be kept as low as possible to avoid the evaporation of organometallic compounds. Strictly speaking, furnace ashing should not be used for organometallic compounds because of their volatile nature.

The Zeeman atomic absorption (ZAA) technique has features that make it attractive for determinations of this kind.[13] ZAA can measure accurate values of atomic absorption signals with 500-1,000 times larger background absorption.[14,15,16] The stability of the base line is also a desirable feature for long time measurement with HPLC.[17]

However, at times, there is a problem in the determination of organo-metallic compounds, even though the ZAA technique provides excellent back-ground correction. For example, the absorption signal of Pb in alkyl lead compounds cannot be observed with the conventional graphite furnace because highly volatile alkyl lead escapes from the cuvette before atomization.

There are also problems that arise when the flame is used for atomiza-tion of alkyl lead in gasoline which require special treatment of the sample to obtain accurate results. These problems arise because tetramethyllead (TML) produces a different absorbance value than does the same amount of tetraethyllead (TEL).[18] Special solvents, special burner design,[19,20] and the "halogen effect" were employed to minimize the difference of absorption between these organometallic species.[21,22] If an unknown Pb species is con-tained in the gasoline sample, digestion using wet chemical methods is neces-sary before aspirating into the flame. It is much more difficult to get the same absorbance response from the various species in conventional furnace AA than in flame AA. Therefore, a different furnace is necessary to atomize the metal in organometallic compounds and for speciation studies in conjunction with HPLC.

There are two ways to minimize the different response of different species. One way is to dissociate the metalorganic compound as completely as possible into individual atoms by heating to high temperatures. Conventional furnaces are not very effective at this because the gas temperatures of the furnace is

much lower than the wall temperature and the sample vapor easily diffuses out of the hot part of the cuvette before reaching a high temperature.[23,24] The other is to convert the various kind of species into a single species. The authors have employed the latter way to determine total mercury in various kinds of biological and geological samples using the ZAA technique.[14,25,26] In this case, the sample was inserted into a T-shaped furnace that contained an oxygen atmosphere at high temperature and the various species of mercury were converted into mercuric oxide. As the temperature of the mercuric oxide molecules increased, dissociation occured and, finally, mercury atoms flowed into the absorption cell. The area of the absorption peak was then proportional to the total mercury in the sample. Methyl mercuric chloride in benzene solution showed the same absorption as mercury nitrate in HNO_3(0.5N). This furnace, combined with HPLC, could be used for the speciation of mercury compounds. However, the maximum operating temperature is $1200^{o}C$.

The latter method is difficult to apply to elements other than mercury because of the higher temperatures required to dissociate the oxides of other metals. Hence, the former approach was chosen, which attempts to raise the temperature of the vaporized species as high as possible before introduction into the optical path.

Figure 1 shows various possible furnace designs to achieve high gas temperatures. Figure 1a shows the type of furnace used in this work. Figure 1b shows a double chamber furnace[15] cuvette which can be used in commercially available Massmann type furnaces. The same high temperature can be obtained as with the conventional graphite tube cuvettes because the surface area of the cuvette is kept small to minimize radiation loss. The recovery of the element in a sample with a complex matrix is highly improved compared with conventional cuvettes. However, this cuvette cannot achieve 100% recovery for highly volatile organometallic compounds such as TML and TEL.

Figure 1C shows a closed system furnace. A sample is atomized in a closed space and kept there for a while to achieve complete dissociation. The piston is moved with the thermal expansion of the sample vapor, and just after the piston passes by the windows an absorption measurement is made. The properties of this cuvette are now being investigated. The circular cavity furnace,[27] which was recently developed by L'vov, is also a kind of the high gas temperature furnace. Since dissociation of all metalorganic compounds occur if the temperature is high enough, the signal will be independent of species. In this paper, we will report the species determination of organometallic lead compounds by utilizing a HPLC-ZAA system with a new furnace that can efficiently atomize these highly volatile compounds.

Experimental

Table 1 lists the experimental apparatus and parameters. The same ZAA spectrophotometer as reported before was used through this experiment.

Figure 2 shows the cross section of the present furnace, which is called the high gas temperature (HGT) furnace. This furnace consists of several separate parts; the sample cup, the thermal convertor and reactor of porous graphite, a narrow hole (which at high temperatures also acts as a thermal convertor), and the absorption cell. The sample vapor is flowed through the thermal convertor and its temperature is raised sufficiently to decompose the compound and to atomize the metal. After that, the sample vapor is carried to the absorption cell for ZAA measurement.

In the case of the present furnace, the center portion of the cuvette is heated to a high temperature first because of the small heat capacity and the large electrical resistance. Conductive heating causes the porous graphite to be heated next and, finally, the tantalum cup is heated. A few seconds after the current is turned on, the temperature difference between

the three sections begins to decrease. Vaporized sample in the cup follows the flowing argon gas through the porous graphite where its temperature is raised by coming into intimate contact. It then passes through a small hole, the walls of which have the highest temperature. Because of intimate contact with these surfaces, the gas temperature becomes equal to the wall temperature before passing into the absorption cell.

Figure 3 shows the relationship between the temperature of the regions just above the absorption cell and the supplied current to the cuvette. The surface area and the heat capacity of this cuvette are as small as the Massmann furnace.[30] It is easy to raise the temperature of the cuvette to 2,800°C by supplying about 5 kW of electric power. This high temperature makes it possible to atomize various types of elements that are not possible with the Woodriff type furnace.[31,32] This furnace is small enough to fit between the poles of a permanent magnet if the polarized Zeeman AA technique is utilized.[17] The system used to separate alkyl lead compounds is described in Table 1. Methyl alcohol was used as the eluent. The pressure was about 30 kg/cm^2, and the flow rate was 0.67 ml/min. A sample of 10 μl was injected into the HPLC while the flow was stopped. A 10 μl aliquot from each 250 μl portion of column effluent was intermittently introduced into the HGT furnace.

Results and Discussion

Table 2 shows the properties of lead and some lead compounds.[33] Usually, $Pb(NO_3)_2$ is used for the lead standard in atomic absorption spectrometry. $Pb(NO_3)_2$ decomposes into PbO around 470° C, and atomic Pb is produced from the dissociation of PbO. In the graphite furnace, the following reduction process also proceeds on the surface of graphite.

$$C + PbO = Pb + CO_2.$$
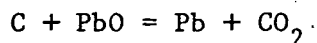
Atomic lead appears at around 770° C, and the change of free energy, ΔG,

for this reaction is -22 kcal/mol at this temperature. Usually, the ashing

temperature for Pb is chosen to be below 600° C, and the atomizing temperature

is around 1,500° C.[34]

TML and TEL are liquid at room temperature with boiling points at 91°C

and 110° C, respectively. They are easily vaporized, even at the drying

temperature. With the conventional furnace, if we try to atomize these

organometallic compounds without drying, they vaporize before the gas

temperature becomes high enough to produce lead atoms.

The organometallic lead compounds listed in Table 2 were introduced

into the present furnace and the signals were compared with those from an

inorganic lead standard; $(Pb(NO_3)_2$ 0.1 µg/ml in HNO_3 (0.5N). The alkyl

lead compounds were dissolved in benzene, such that the final concentra-

tion was 0.1 µg/ml, 10 µl aliquots were directly atomized without drying

and ashing. The strong background absorption interference was corrected

by using ZAA technique. The same peak height of lead atomic absorption

was observed for each sample. Examples of the signal shape for organic

and inorganic lead compounds are presented in Figure 4. The similarity

in peak shape supports the idea that the metal organic compound is totality

atomized in the furnace.

The concentration of Pb was determined in the NBS standard fuel

SRM-1636 which contains the lead in the TML and TEL forms in 91-octane-

number reference fuel (a mixture of about 91% 2,2,4-trimethylpentane and

9% n-heptane). This NBS standard was diluted by a factor of 1/200 with

MIBK, and 10 µl of the sample was directly atomized using the HGT furnace.

Both inorganic and organic lead solutions were employed as standards;

$Pb(NO_3)_2$ in HNO_3 (0.5N), and tetraphenyllead (TPL) in benzene. The reason

TPL was used as the organic lead standard is that TPL is crystaline at

room temperature and is comparatively stable. This aids in the preparation

of an accurate standard solution. Table 3 shows the results of the analysis.

Good agreement was obtained with the certified NBS value, both when the

inorganic and organic lead standard solutions were used. From these results,

we can safely conclude that both the same accuracy and the same sensitivity

is obtained for the inorganic lead and organic lead compounds in spite of

a big difference in vaporization temperatures. Now, the determination of

the concentration of various organometallic species is possible with the

HGT furnace because the sensitivity is independent of species.

Figure 5a shows the histogram of lead concentration in various portions

of the eluent. The peaks of TML and TEL appear at retention times at 5.5

min and 10 min, respectively. The histogram in Figure 5a shows that

TML and TEL can be separated without overlap. The recovery (the ratio

of the amount of injected lead to the total amount of the observed lead

in the elutent from the column) was 97% for TEL, and 25% for TML. 75%

of TML might be dissociated and trapped in the resin. In the GC-Flame

AA system, several TML peaks were observed.[35] This shows that TML is

very unstable. When the inorganic lead solution $Pb(NO_3)_2$ was introduced

into the HPLC containing Hitachi No. 3010 resin, almost no lead was recov-

ered (Fig. 6). In order to separate organic lead from inorganic lead,

the Hitachi ion exchange column no. 2611 should be used. We have already

reported on the use of this column to separate Co bound to vitamin B12

from inorganic Co.[13]

Next, the determination of TML and TEL in the NBS standard was per-

formed using the HPLC-ZAA system. 10 µl of NBS 1636-A (19.15 µg Pb/ml)

was introduced into the system. A clear peak (Figure 5b) was obtained

at the retention time at 10 min. The concentration of lead in the eluent

is also shown in this Figure. The content of lead integrated over this peak is 187 ng, which is 97.6% of the lead in the injected NBS standard (191.5 ng). No peak could be observed at the retention time corresponding to TML at 5.5 min. A higher concentration standard (NBS 1636-B, 535 μg Pb/ml) was introduced into the system to check the existence of TML. However, a peak for TML could not be observed as shown in Figure 5c. We also confirmed that inorganic lead and TPL do not cause a peak near the TEL position (Figure 6). Therefore, we can conclude that the NBS standards which were used in this experiment contain only one lead species (TEL). (These NBS standard Pb in gasoline samples were purchased in 1975 and the unopened ampules were stored in a dark box until used.)

Decrease of chemical interferences caused by large quantities of salts.

Chemical interference caused by metal halides causes serious problems in conventional furnace AA.[36-43] The use of the HGT furnace greatly reduces this type of interference. A typical case of this kind of interference occurs when $MgCl_2$ is present during the determination of Pb. Sometimes only 50 μg/ml of $MgCl_2$ causes a 30% depression of the Pb signal. Molecular absorption and scattering by $MgCl_2$ is not large at 283.3 nm (the wavelength of the Pb resonance line). Therefore, this phenomenon is totally due to chemical interference. Figure 7 shows the effect of $MgCl_2$ upon the Pb signal using the HGT furnace. Table 4 lists the magnitude of signal suppression for several salts. It can be seen that $MgCl_2$ is the strongest suppressing agent.

This ability of the HGT furnace to prevent signal suppression cannot be explained by the high temperature of the sample vapor. The change of free energy, ΔG, for the dissociation of PbCl is still large at a temperature of 2,500° C. Hence, thermal dissociation would not be expected to

occur. A possible explanation would be that a reduction process is accelerated because of the large surface area of the porous graphite.

Other applications of high gas temperature furnace

The lead concentration in exhaust gases can be measured by using the HGT furnace. Automobile exhaust gas was collected in a polyethylene bag and was forced to flow through the HGT furnace carrier gas inlet port at a flow rate of 90 cm^3/min. The lead concentration in the exhaust gas was determined from the peak area of the absorption signal to be 0.3 ng/cm^3. Hence, this furnace is capable of on line monitoring of trace elements in gas or ambient air.

Another important area of application is to the direct analysis of solid samples. Because this furnace tends to prevent molecular form-ation, solids can be volatized and the elements in that sample can be atomized, and the sensitivity will be largely independent of metalorganic species. This will be true, even for highly volatile compounds. Prelim-inary work on metal organic lead compounds in oil have indicated complete recovery when the oil is injected directly into the furnace.

In this paper, the problems that cause difficulties in species deter-mination of organometallic compounds have been discussed. HPLC is a very powerful technique for the nondestructive separation of organometallic compounds. However, if this technique is used, the problems of inter-ference caused by the organic eluent and losses of highly volatile organometallic compounds, still remain. It is very difficult to separate the eluent from volatile organometallic compounds. Our approach is to vaporize the sample in a quasi closed space and to raise the temperature of the sample vapor as high as possible in order to highly dissociate the molecules. The interference caused by background absorption is avoided

by utilizing the Zeeman AA technique. When more complete dissociation of molecules is necessary a DC or RF discharge in the furnace might be effective.

Acknowledgement

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Table 1

Instrumentation for HPLC-ZAA System

HPLC

High Performance Liquid Chromatograph - Hitach M633,

0-350 kg/cm^2, 0.36∿3.6 ml/min

Column - Hitachi, 2.5 x 500 mm

Resin - Hitachi Gel No. 3010

Furnace

Graphite - Ultra carbon 0.5" dia.

Porous graphite - RVC 100 PPI Porosity Grade

Furnace power supply - Reactor controlled, 20V, 700A

ZAA spectrophotometer

Light source - Magnetically Confined Lamp.[28]   (DC + RF (50 MHz)).

Magnet - Permanent, 12 KG

Variable retardation plate[29] - 0∿$\frac{\lambda}{2}$, 30 Hz

Polarizer - Rochon prism (Quartz, Optical contact)

Monochromator - Hitachi M100 Spectrophotometer

Photomultiplier - Hamamatsu T.V., YA 7122

Chopper - Bulova L2C, 1.0 KHz

Electronics

Lock-In amplifier (including log convertor, AGC)

Recorder - Honeywell Electronik 17

Table 2

Properties of selected Pb compounds[33]

Compound	Formula	Critical temperatures, °C		
		Melting	Boiling	Dissociation
Lead nitrate	$Pb(NO_3)_2$			470
Lead chloride	$PbCl_2$	501	950	
Lead monoxide	PbO	888	1740	
Lead chloride	$PbCl_2$	501	950	
Tetramethyllead	$Pb(CH_3)_4$	-27.5	110	
Tetraethyllead	$Pb(C_2H_5)_4$	-136.8	91	200
Tetraphenyllead	$Pb(C_6H_5)_4$	227.7		270

Table 3.

Results of direct determination of Pb in NBS gasoline standard by ZAA with High Gas Temperature Furnace

Standard Used	Solvent	Pb in NBS, SRM 1636, µg/mL[a]	
		Result,[b]	Certified value
$Pb(NO_3)_2$	HNO_3 [0.5N]	19.1 ± 0.5	
$Pb(C_6H_5)_4$	C_6H_6	19.3 ± 0.5	19.15

[a] At 20°C.

[b] Solvent: MIBK

Number of determinations: 6

Table 4

Comparison of Chemical Interferent Levels between High Gas Temperature

Furnace and Conventional Furnaces

Element	Interferent	Concentration of interferent, μg/ml	Recovery, %		
			Conventional Furnace	Ref.	High Gas Temperature Furnace
Pb	$MgCl_2$	100	63 (95)[a]	34, 35	
		1,000	6 (29)[a]	34	
		5,000	18	36	93
		10,000			68
	$CaCl_2$	100	74 (98)[a]	34	
		1,000	0 (45)[a]	34	
		5,000	48	32	
		10,000			100
	$CuCl_2$	100	0	33	
		10,000			82
Cd	$CaCl_2$	10,000	0	32	97

a: CTA

Ref. 32: HGA70, HGA2000

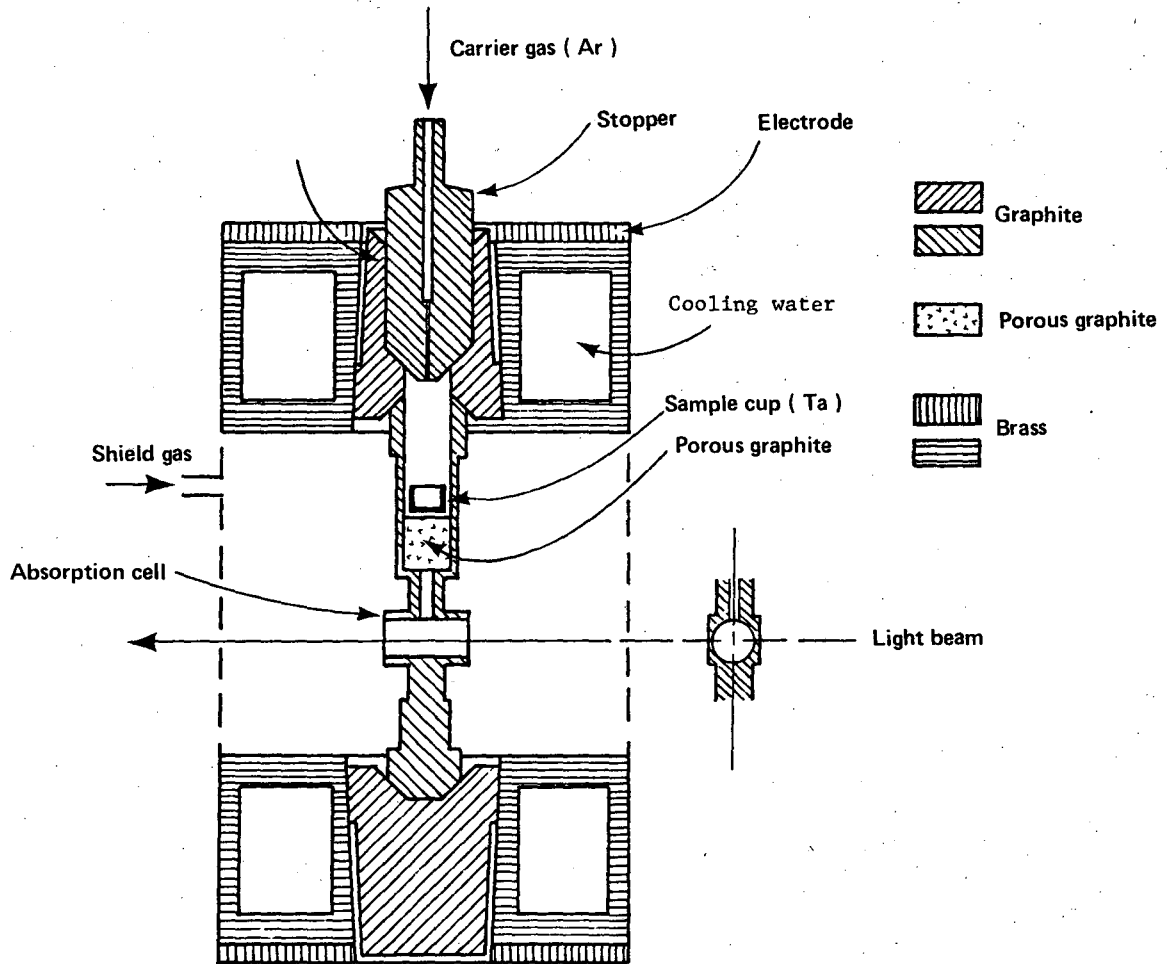Ref. 33: CRA63

Ref. 34: CRA53 (a.CTA)
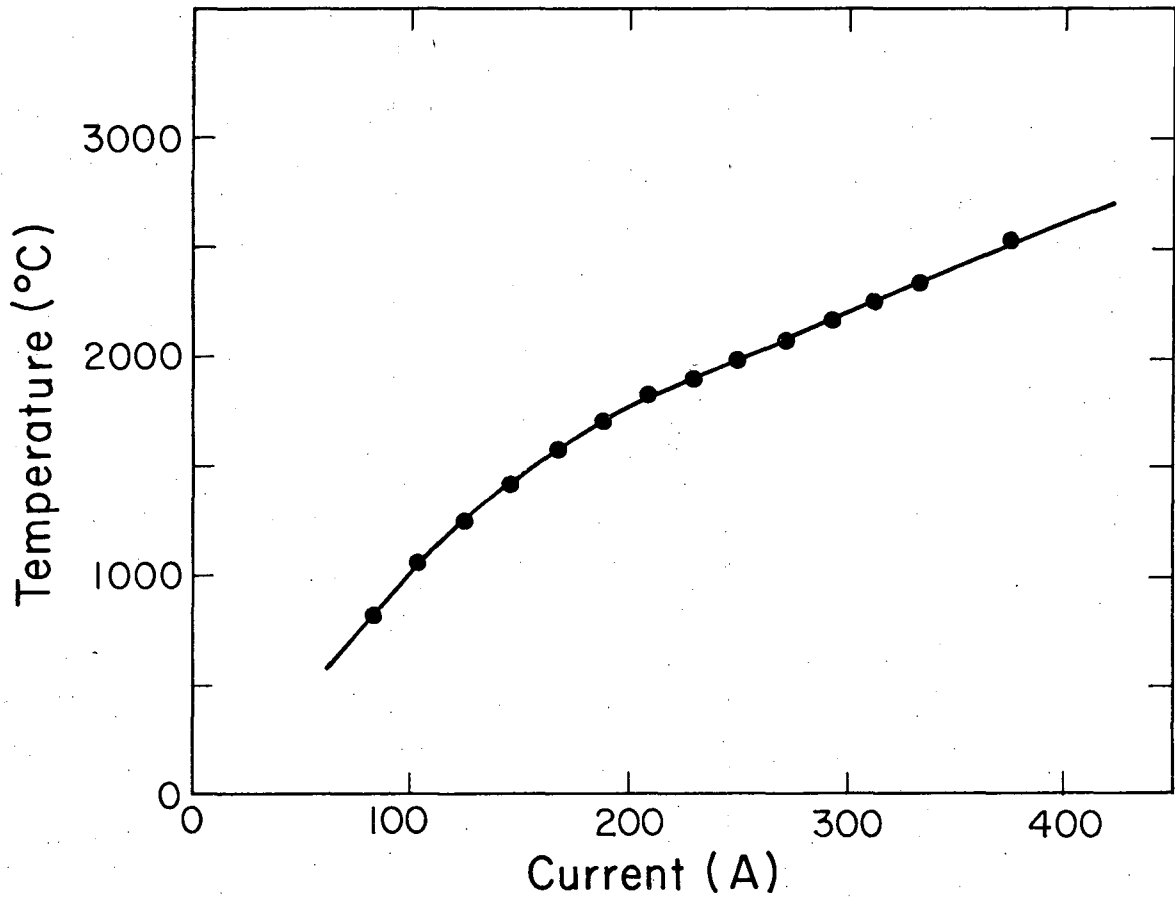
Ref. 35: HGA.70

Ref. 36: HGA2200

Figure Captions

Fig. 1   Various types of HGT furnaces.

Fig. 2   Cross section of high gas temperature (HGT) furnace.

Fig. 3   Relationship between current and temperature of hottest
         region of HGT furnace.

Fig. 4   a)   ZAA signals of tetraethyllead peak from HPLC
               column showing distribution in 1.5 ml of eluent;

         b)   signal from standard lead solution (0.5 N HNO$_3$).

Fig. 5   Elution chromatograms for alkyl lead compounds:

         a)   80 µg/mL tetramethyl lead and 20 µg/mL tetraethyl lead;

         b) and c)   NBS standard lead in gasoline samples.

Fig. 6   Chromatogram showing spreading of Pb(NO$_3$)$_2$ by the Hitachi
         Gel No. 3010 column.

Fig. 7   Lessening of suppressions of Pb signal by MgCl$_2$ through the
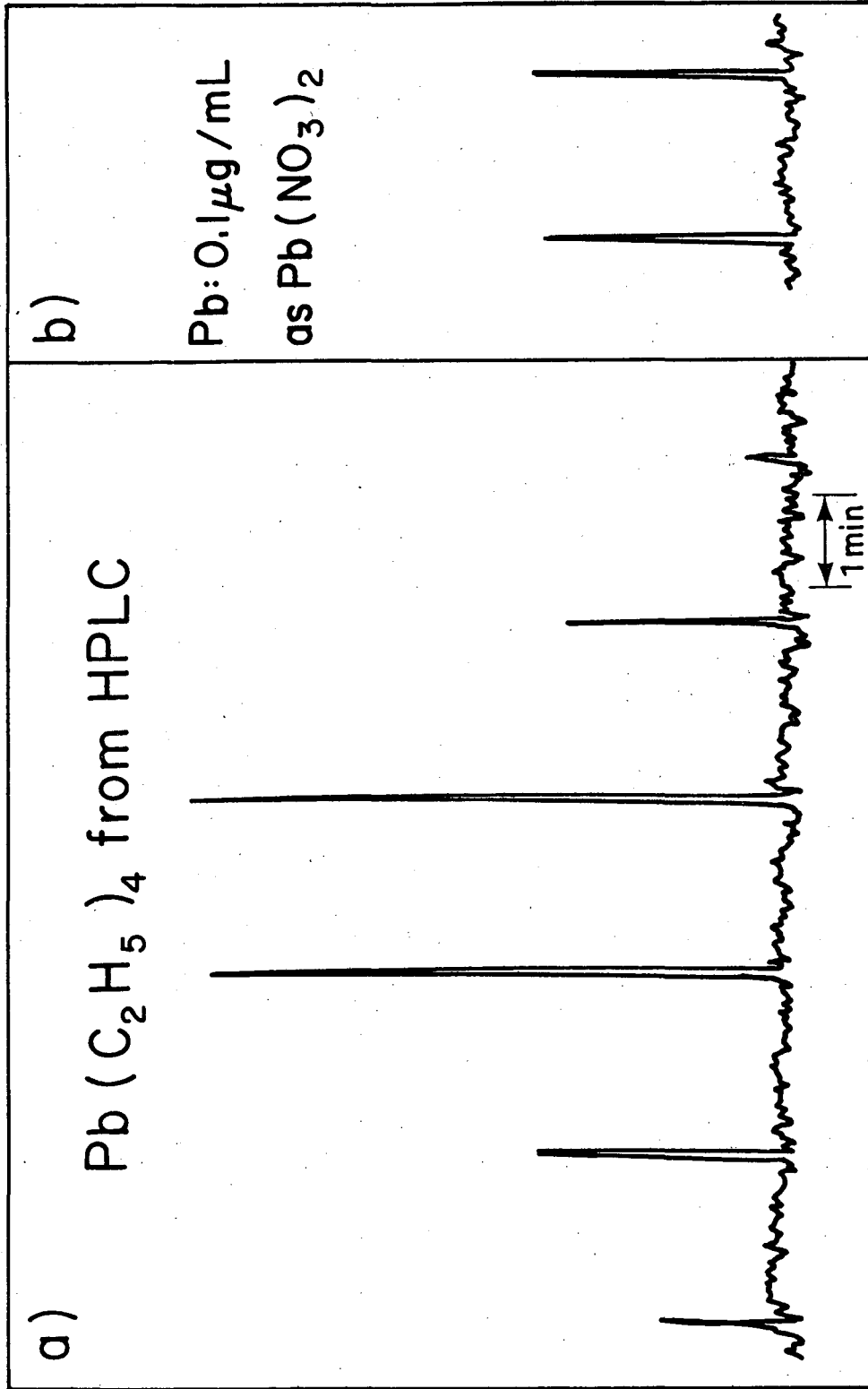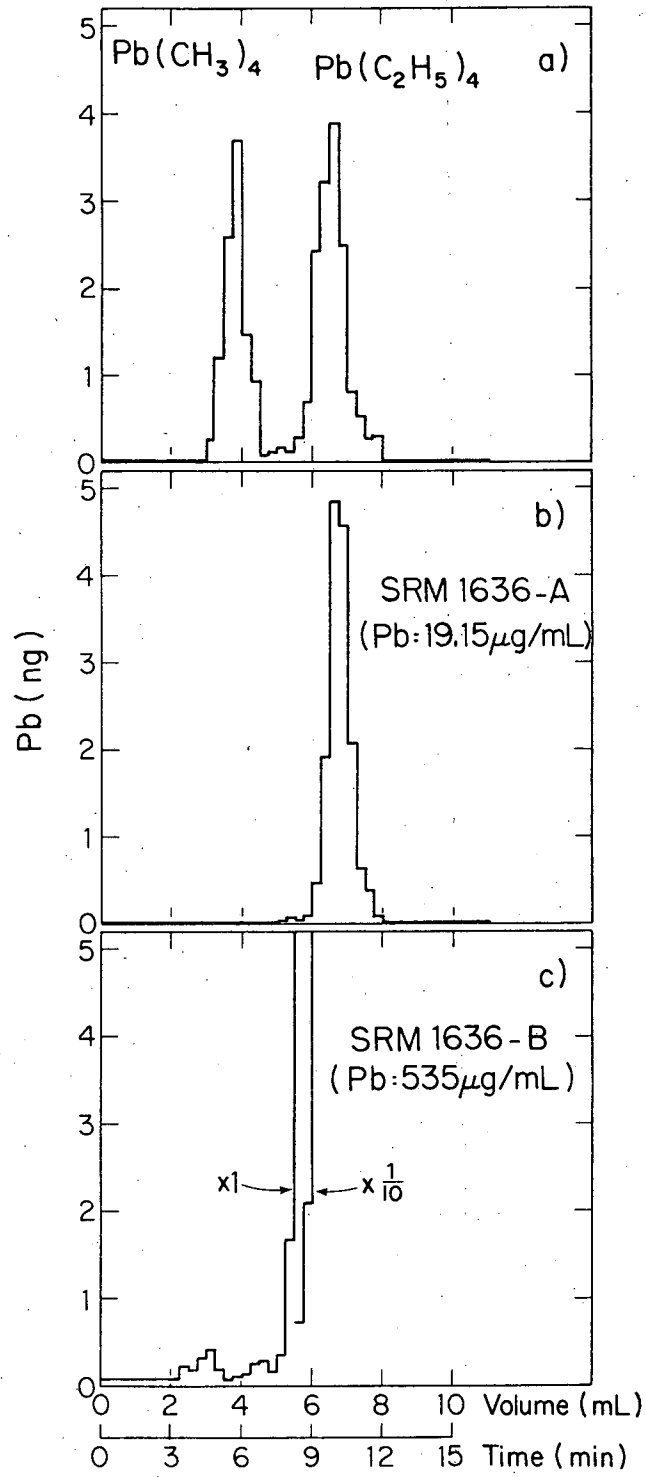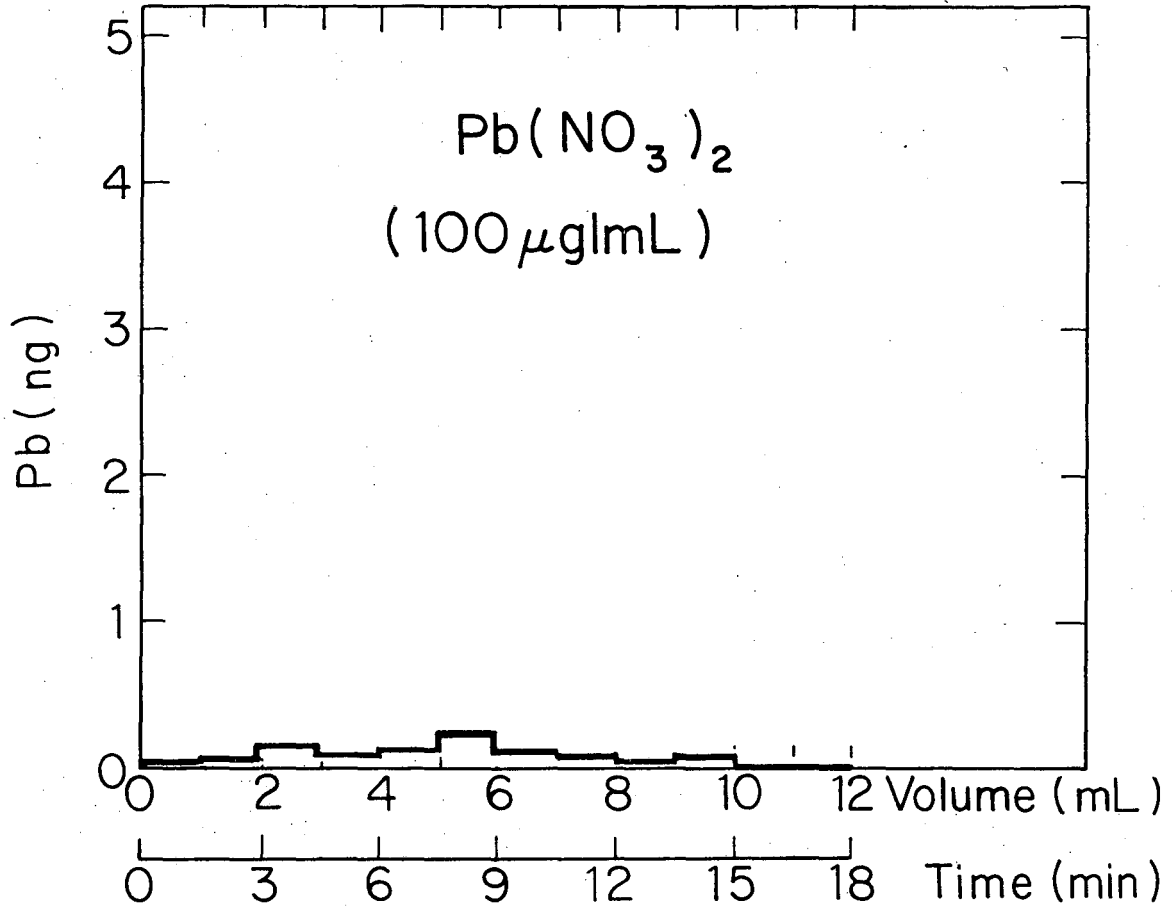   use of the HGT furnace.

Carrier gas
or sample gas

Light

(a)

Carrier gas

Light

Graphite tube   Inner chamber

(b)

Piston (movable)

Light

(c)

10 mm

XBL 787 - 1213

Carrier gas (Ar)

Stopper

Electrode

Cooling water

Sample cup (Ta)

Porous graphite

Shield gas

Absorption cell

Light beam

Graphite

Porous graphite

Brass

XBL 785-930

a) Pb(C₂H₅)₄ from HPLC

b) Pb: 0.1 μg/mL as Pb(NO₃)₂

Time

1 min

XBL 785-931

Pb(NO$_3$)$_2$
(100 μg/mL)

XBL 785-929

XBL 785-932