

A Potential Method for Determination of Gaseous and Particulate Lead in Exhaust Gas by Microwave-Induced Air-Plasma Emission Spectrometry and Zeeman Furnace Atomic Absorption Spectrometry

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Résumé

Une méthode de dosage du plomb gazeux et particulaire présent dans les gaz d'échappement est décrite. Un système à plasma d'air induit par rayonnement micro-onde à la pression atmosphérique a été utilisé pour le dosage direct du plomb gazeux et le dosage du plomb particulaire a été effectué par spectrométrie d'absorption atomique utilisant un four Zeeman. Le plomb particulaire a été recueilli sur papier-filtre et digéré à l'aide d'un mélange d'acide nitrique et d'acide chlorhydrique. Dans cette étude, les gaz d'échappement provenaient d'un moteur de tondeuse à gazon. La concentration de plomb particulaire a été estimée à environ 4% du plomb total présent dans les gaz d'échappement.

Abstract

A method for the determination of gaseous and particulate lead in exhaust gas is described. An atmospheric pressure microwave-induced air-plasma system was used for direct determination of gaseous lead and Zeeman furnace atomic absorption spectrometry was used for the determination of particulate lead. The particulate lead is collected on filter paper and digested with a nitric acid and hydrochloric acid mixture. In this study, lawn mower gasoline engine exhaust has been used. The concentration of particulate lead was found to be about 4% of the total lead in the exhaust gas.

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Introduction

Lead emission constitutes a serious problem for the environment. Leaded gasoline used for automobiles is a major source of airborne lead pollution. In exhaust gas from automobiles, lead is present as gaseous compounds as well as particulates. At present, the determination of lead in air is often limited to the particulate form of lead. Atomic absorption spectrometry, polarography, emission spectrometry, and colorimetry are widely used measurement techniques for the determination of lead in airborne dust. Atomic fluorescence spectrometry has been used to monitor stacks continuously, although unacceptable results were obtained (1). Long path atomic absorption spectrometry has also been used for continuous monitoring of airborne lead (2,3).

In this work, total lead in exhaust gas is determined by microwave induced air plasma emission spectrometry. The single electrode microwave induced plasma can be operated with several gases and their mixtures (including air) (4-9) for the continuous measurement of lead. The particulates containing lead were collected on filter paper, were completely digested, and the resulting solution was then measured by Zeeman furnace atomic absorption spectrometry.

Experimental

Instrumentation

The single electrode air plasma torch system has been previously described by two of the authors (4,7). The schematic diagram of the direct lead monitoring system is shown in Figure 1. A glass chimney and a water-cooled metal covered plasma torch (9) were used to minimize contamination by lead which could diffuse

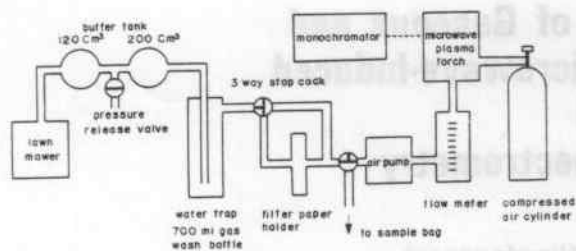


Figure 1. Schematic diagram of the direct lead monitoring system.

from the surrounding room air into the plasma. Compressed cylinder air was used as the plasma gas because cylinder air contained less water and hydrocarbon impurities than laboratory room air. The latter indeed was found to produce intense bands of OH, CN, etc. (see Figure 2).

A small gasoline engine of a lawn mower was used as the source of exhaust gas; the exhaust gas was transported to the plasma torch through tygon tubing, (I.D. 0.25 in., length 9 m), with the assistance of an air pump. The exhaust gas flow rate introduced into the microwave plasma was adjusted to either 4 or 5 $L \cdot \text{min}^{-1}$. The compressed air flow rate was adjusted to 12 $L \cdot \text{min}^{-1}$. These two gases comprised the plasma gas of the microwave plasma.

Buffer tanks were provided to minimize fluctuations of the exhaust gas flow rate; the pressure in the sampling line was controlled by a pressure release valve. A water trap was placed just after the second buffer tank to remove condensed water and organic impuri-

ties. For collecting the particulate lead, a filter holder was placed just before the plasma torch. The filter paper (4 in. OD, TFA 41, Staplex, 777 Fifth Avenue, NY 11232) for the high volume air sampler had a collection efficiency of 95% for particles with a size of 1 μm or larger.

The instrumental components, including types and manufacturers are listed in Table I and operating characteristics of the experimental system are given in Table II.

Reagents

The nitric acid and the 50% hydrochloric acid were purified by sub-boiling distillation in a laboratory-constructed quartz apparatus. Fisher ACS grade nitric acid and hydrochloric acid were used. The lead concentration in nitric acid was expected to decrease from 0.2 ppb(ACS) to 0.02 ppb, and the concentration in hydrochloric acid was expected to decrease from 0.5 ppb (ACS) to 0.07 ppb (12) by use of the sub-boiling technique. The sulfuric acid was Baker Instra-Analyzed Grade.

The lead standard solutions for the Zeeman furnace atomic absorption spectrometer were prepared from high purity lead metal.

Table I. Equipment Used in Microwave Plasma Emission Spectrometry and Zeeman Furnace Atomic Absorption Spectrometry.

1) Microwave plasma emission spectrometry	
magnetron (Hitachi)	model R3032L (for microwave oven) output frequency 2450 MHz
power supply for magnetron (Hiptronics)	model 803-330, constant current
monochromator (Jarrell-Ash)	model 82,000, 0.5 m with 1180 grooves/mm grating reciprocal linear dispersion to exit slit 1.6 nm/mm resolution 0.2 nm in the first order
photomultiplier tube (Hamamatsu)	model R-955
lock-in amplifier (Princeton Applied Research)	model JB-4
temperature indicator (Omega)	model 411A
strip chart recorder (Fisher Scientific)	model 5000
air pump (Universal Electric)	model 4K Neptune Dyna pump
tubing material	Tygon [®] R-3603 (1/4 in. i.d.)
gas sampling bag (AeroVironment)	5 L Tedlar [®] bag
2) Zeeman furnace atomic absorption spectrometry	
Zeeman atomic absorption spectrometer (Hitachi)	model 180-80
data processing unit (Hitachi)	model 180-0205
Pb hollow cathode lamp (Hamamatsu)	

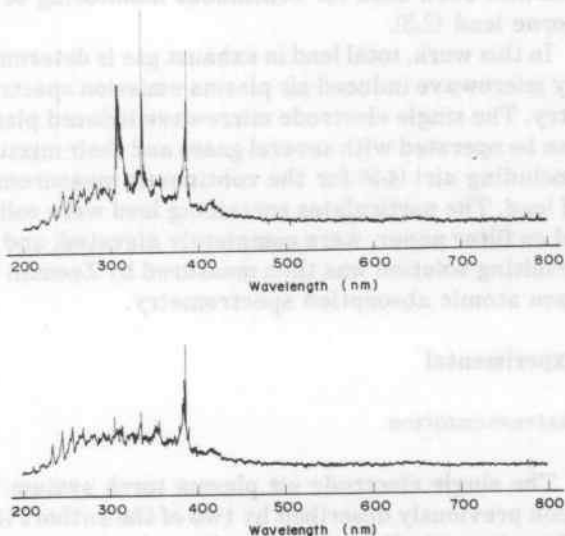


Figure 2. Background emission spectrum of air plasma, from 200 nm to 800 nm.
A: room air.
B: dried cylinder air.

Table II. Operating Characteristics of Experimental Systems.

1) Microwave Plasma emission spectrometry	
air plasma	
plasma gas	12 L/min
carrier gas	4 L/min
monochromator	
slit width	0.05 mm (spectral bandpass 0.08 nm)
slit height	2 mm
magnetron	
current	280 mA
supply voltage	2150 V
photomultiplier tube	
supply voltage	-700 V
2) Zeeman furnace absorption spectrometry	
hollow cathode lamp current	7.5 mA
wavelength	283.3 nm
spectral bandpass	1.3 nm
ramp drying temperature	80° C-120° C
time	30 s
ramp ashing temperature	400° C-600° C
time	30 s
ramp atomization temperature	2000° C-2400° C
time	7 s
cleaning temperature	2600° C
time	3 s
measurement mode	peak height
solution volume	10 μ L
Ar carrier gas (off at atomization stage)	0.21 L/min

Calibration of Total Lead in Exhaust Gas

Preanalyzed leaded gasoline was used as a standard for calibration. The standard gasoline was evaporated and introduced into the plasma torch with the carrier gas. In this study, two introduction techniques were used. In the first technique, a sampling bag (6) system was used to introduce gasoline vapor into the microwave plasma. In the sampling bag (5 L) case, a sample (10 μ L of standard gasoline) was diluted with 5 L of air in the sampling bag at room temperature while reducing the plasma gas flow rate by the same amount and introduced into the plasma with a 3.3 L \cdot min⁻¹ flow rate of air. After the sample bag was emptied (took about 5 min) into the plasma, the bag was filled with clean air and emptied again into the plasma, and the latter procedure was repeated once more. The second (and other) introduction accounted for less than 2% of the total signal. To minimize the memory effect of the transport line between the sample vapor generation section and the plasma torch, it was heated by a heating tape. The second technique consisting of an electro-thermal furnace gave results which agreed to within 5% of the sampling bag technique.

Calibration of Lead in Gasoline

Aliquots of 0.5 mL of leaded gasoline were digested with 20 mL of concentrated nitric acid and 1 mL of concentrated sulfuric acid in a laboratory-constructed reflux condenser and nitric acid reservoir. Nitric acid was trapped in the reservoir during refluxing and the sample solution was heated until sulfuric acid fumed. At that time, the sample solution mainly contained the sample and sulfuric acid and therefore the temperature of the solution rose to about 300° C carbonizing the sample. After cooling, the collected nitric acid was added back to the solution, and the solution was refluxed again. This procedure was repeated two times. After complete decomposition of the sample, the solution was transferred to a beaker and heated until sulfuric acid fumed. The sample solution was then diluted to 50 mL with 4% (v:v) nitric acid solution. Standard solutions which contained the same concentration of nitric acid and sulfuric acid were used to prepare the calibration curves. The lead concentration in leaded gasoline was then measured by Zeeman furnace atomic absorption spectrometry. A lead concentration of 268 μ g \cdot mL⁻¹ (%RSD, 1.5%) was found for the gasoline using lead metal in nitric acid as the standard.

Determination of Particulate Lead in Exhaust Gas

After collecting particulates from the exhaust gas (see Figure 1) for 5 min., the filter paper was removed and was cut in half; 20 mL of concentrated nitric acid and 14 mL of 50% (v:v) hydrochloric acid was added to each half, and the resulting solutions were heated in two round bottom flasks with a condenser until the solutions were totally clear (4 to 6 hours). The solutions were then evaporated to dryness, and the residue was dissolved in an appropriate volume of 5% (v:v) nitric acid.

Digestion in an open beaker was found to give no sample losses as compared to work in a flask with a condenser.

The lead in the resulting solution was measured by Zeeman atomic absorption flame spectrometry at 405.8 nm.

Direct Determination of Total Lead and Gaseous Lead in Exhaust Gas

The lawn mower exhaust gas (4-5 L \cdot min⁻¹) and cylinder compressed air (12 L \cdot min⁻¹) were used as the plasma gas for the microwave plasma as shown in Figure 1. The lead emission at 405.8 nm was measured without the particulate filter in place (total lead) and with the filter in place (gaseous lead). The lead

signals were quantitated by comparing with preanalyzed leaded gasoline (see calibration method above). The difference in the two lead results corresponded to the gaseous lead.

Results and Discussion

Selection of Wavelength

The relative intensities and signal-to-background ratios found for Pb at different wavelengths in the air plasma are given in Table III. The background emission spectrum of the air plasma is shown in Figure 2. The background intensity at the lead emission lines 283.3 nm and 280.2 nm is substantially higher than at the other three lines mentioned in Table III. The background emission spectrum around the most sensitive lead emission line (405.8 nm) is shown in more detail in Figure 3. The spectrum shows a background emission peak (not due to impurity lead) near 405.8 nm. This peak is probably due to molecular emission of NO_x or N_2 species. Large changes ($\geq 20\%$) in the nitrogen and oxygen content of the plasma gas changed the emission intensity; however, changes in air composition and humidity had no influence.

In order to minimize lead contamination, in the plasma gas, the plasma gas air was bubbled through 10% nitric and subsequently through a cold trap and a droplet remover. However, the background spectra around 405.8 nm of washed and of unwashed air showed no difference. Accordingly, it was concluded that the peak recorded in the background spectrum around 405.8 nm was not due to lead impurities in the plasma gas and so the amount of lead in the air, used as the plasma gas, was smaller than the detection limit of our system.

The background spectra around 405.8 nm with and without introducing exhaust gas were also compared so as to determine whether species in the exhaust gas, other than lead, interfered with the lead determination. It was found that the intensities of the background emission were slightly changed when exhaust gas was introduced but the spectral structure remained unchanged. As a result of these experi-

Table III. Relative Intensity of Pb Atomic Emission Lines in Air Plasma.

wavelength (nm)	relative background emission intensity	relative signal intensity	signal/background
405.8	1.0	100	100
368.3	1.8	65	36
364.0	1.6	30	19
283.3	5.5	43	8
280.2	3.7	22	6

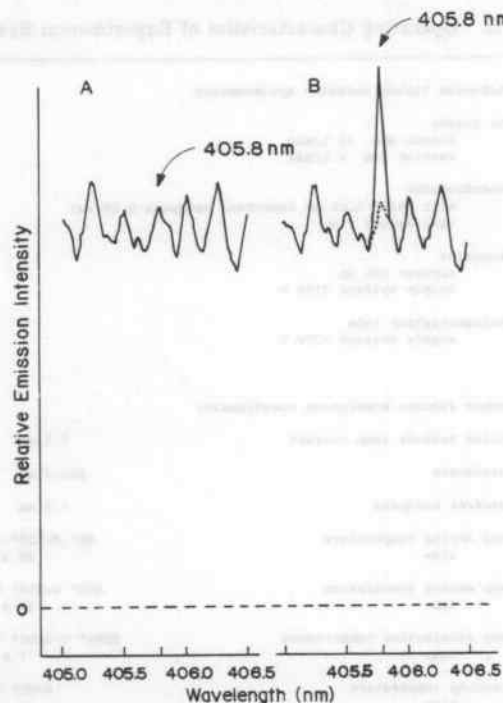


Figure 3. Background emission spectrum of around 405.8 nm. A: background emission spectrum of air plasma. B: emission spectrum of air with leaded gasoline vapor, $0.37 \mu\text{g}\cdot\text{L}^{-1}$.

ments, it was concluded that the lead 405.8 nm was a suitable wavelength for lead determination in air by microwave induced plasma emission spectrometry.

Influence of Input Power on Lead Emission Intensity

As the input power was increased from 270 W to 660 W, the lead 405.8 nm line intensity increased in signal-to-background ratio. When the power exceeded 600 W, erosion of the plasma torch electrode took place. Therefore, 600 W was chosen in the present study.

Detection Limit for Lead in Gases as Determined by Air Plasma Spectrometry

The lead calibration curve obtained using preanalyzed leaded gasolines was found to go through the origin and was found to be linear between 5 and 500 $\mu\text{g}\cdot\text{m}^{-3}$. The detection limit, defined as the concentration which produced 3 times the standard deviation of the baseline fluctuation, was 5 $\mu\text{g}\cdot\text{m}^{-3}$.

Recovery of Pb From Filters and Pb In Laboratory Air

The recovery was measured by adding 100 μL of

100 $\mu\text{g}\cdot\text{mL}^{-3}$ lead nitrate solution to three blank particulate filters. Measurements by Zeeman atomic absorption showed an average recovery of 100.9% and an % RSD of 0.9%. The particulate lead concentration in laboratory air was estimated by depositing two filter samples collected by the high volume sampler for 6 hours. The lead concentrations in two samples were 0.07 and 0.11 $\mu\text{g}\cdot\text{m}^{-3}$; such concentrations are common for rural areas (13).

Table IV. Mass Balance of Lead in Engine Exhaust.

Day ^a	Amount of Pb (μg) ^b			
	Gaseous Pb ^c	Particulate Pb ^d	Total (Gaseous + Particulate) Pb ^e	Total Measured Pb ^f
1-M	1.52 \pm 0.22	0.45	1.97	1.88 \pm 0.14
3-M	0.60 \pm 0.15	0.43	1.03	0.96 \pm 0.11
3-A	0.77 \pm 0.06	0.29	1.06	1.10 \pm 0.10
9-M	1.04 \pm 0.22	0.20	1.34	1.31 \pm 0.17
9-A	1.18 \pm 0.14	0.37	1.55	1.49 \pm 0.15
\bar{x}	1.02	0.35	1.39	1.35

- N means day number - X = M, morning or A, afternoon.
- Amount of Pb (μg) per 1 L of exhaust gas.
- Gaseous Pb measured by microwave plasma but with filter in place results are average of 6 measurements. The \pm represents the standard deviation.
- Particulate Pb measured by collecting particulates with filter and using Zeeman AA.
- Total (Gaseous + Particulate) = sum of Gaseous Pb (item c) and Particulate Pb (item d).
- Total Measured Pb is measured by microwave plasma with no filter. Results are average of 6 measurements. The \pm x represents the standard deviation.
- \bar{x} = average of 5 day results.

Determination of Pb in Lawn Mower Exhaust

In Table IV, the results obtained for gaseous lead, particulate lead, and total measured lead are given. In Table V, the results obtained for particulate lead by two approaches are given. Although there is substantial variation of lead in any of the forms (gaseous, particulate, or total) from day-to-day, there is excellent agreement between the total lead measurement (with no filter present and microwave plasma emission) and the total lead obtained by summing the gaseous lead (with filter present and microwave plasma emission) and the particulate lead (collected on the filter and Zeeman AA). It was not possible to compare these results with the total lead in the combusted gasoline due to the inaccuracy of measuring the combusted gasoline and losses in the more than 20-foot tubing leading from the lawn mower exhaust (on the roof) and the microwave plasma in the laboratory.

Table V. Comparison of Particulate Lead Measured Directly By Zeeman AA and by Difference Between Total and Gaseous Lead.

Day ^a	Particulate Lead ^b		Particulate Lead ^c	
	(μg)	(%)	(μg)	(%)
1-M	0.36	19	0.45	24
3-M	0.36	38	0.43	45
3A	0.33	30	0.29	26
9M	0.27	21	0.20	15
9A	0.31	21	0.37	25
	\bar{x} = 26%		\bar{x} = 27	

- See Table IV.
- Particulate lead obtained by difference between total and gaseous.
- Particulate lead obtained by Zeeman AA.

Conclusions

The goal in this study was to develop a method to measure gaseous lead and particulate lead in engine exhaust. The method worked out can be used for monitoring total lead as well as the gaseous and particulate forms on a continuous basis. Excellent mass balances were obtained between the sum of the gaseous and particulate lead and the total lead measured directly. It was not possible to compare the total measured lead with the combusted lead because of poor accuracy of measuring the "burnt" gasoline and because of losses of gaseous and particulate lead in the tubing connecting the engine exhaust to the collection system (or to the microwave plasma). Nevertheless, the approach appears to be viable for continuously monitoring lead (or other metals) in exhaust gases, atmospheric environments, etc. The sampling problems may be solvable by expertise from environmental scientists.

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