

Particulate Pb in low volume Metro Manila air samples

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Metro Manila air particulate samples were collected with a low volume pump and membrane filters. Pb particulate pollution levels were determined by graphite furnace AAS (GFAAS). Experimental parameters were optimized to minimize GFAAS interference effects and low volume air samples' susceptibility to contamination. Majority of the samples had Pb levels way above the World Health Organization (WHO) allowable level.

Key Words: air particulate Pb, low volume sampling, GFAAS, matrix effects

LEAD IS THE MOST ABUNDANT HEAVY METAL IN THE EARTH'S CRUST and is very useful for manufacturing a whole range of products from batteries to circuit boards. Its use, however, has caused serious environmental and health problems. Even low level exposures to lead can have health effects, especially in children (1).

One of the main pathways for lead entrance into the human system is via inhalation of lead containing air particulates which are prevalent in areas with motor vehicles powered by fuel with lead additives, as in Metro Manila.

Concentrations of Pb in ambient air range from ng/m³ to µg/m³. Thus, flame AAS Pb analysis uses high volume air sampling which involves long sampling hours (usually 24 hours and up to 7 days). Powerful pumps, with flow rates of 500 - 2000 LPM (liters per minute), at heights of 10 to 50 m above ground collect air particulates through large (500 cm²) glass fiber filters (2).

Low volume sampling (30 min-8 hr at 2-4 LPM using 40 to 70 cm² membrane filters) needs more sensitive instrumentation (graphite furnace AAS or anodic stripping voltammetry) and greater care must be exercised to avoid contamination. Lower sampling heights (1 to 2 m above ground) are used which better approximate inhalable Pb levels, compared to high volume sampling.

Forty Metro Manila low volume air particulate samples were collected and analyzed for Pb in this study. The samples were divided into 'indoor', 'beside street traffic' and 'inside moving public vehicles' categories.

Experimental

Air Particulate Sampling. Air was drawn through a Gelman GN-4 cassette filter unit (consisting of a 37 mm

diameter, 0.8 µm pore size cellulose ester membrane filter in a plastic cassette filter holder) by an SKC 224-PCXR3 personal sampling pump at 2 to 4 LPM. This is the NIOSH (National Institute of Occupational Safety and Hygiene) recommended sampling method for determination of trace metals in industrial and ambient airborne materials (3).

Air sampling was done at about 1.6 m from the floor (for indoor samples) or from the ground (for street samples). For samples inside moving vehicles, the air filter cassette was attached to the shoulder of the person carrying the pump. Sampling times were 30-60 min (for outdoor samples) and 1-4 hrs (for indoor samples).

Pb Extraction. Five different methods of Pb extraction from air particulates in filters were done and examined for contamination effects. Standard additions was used to determine blank values using a clean air filter subjected to the same extraction procedure as the air samples. The extraction methods are described in Table 1.

Extracted air sample and blank filters were recovered intact for most of the methods and were subjected to a repeated extraction procedure to ascertain complete extraction of particulate Pb.

Analysis of Pb in Extracts. An improvised higher sensitivity AAS instrument system was used, consisting of a Perkin Elmer HGA 2200 graphite furnace interfaced with a Varian AA6 atomic absorption spectrophotometer.

Continuum source and adjacent non-resonance line manual background correction was used to correct for spectral interferences. Standard additions method was used to correct for non-spectral interferences (matrix effects). Both aqueous standardization and standard addi-

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Table 1. Pb extraction methods

Method 1	Heat filter gently with 2 mL conc. HNO_3 for a few minutes until filter dissolves completely. Dilute to volume with deionized H_2O .
Method 2	Ultrasonicate filter with 0.1M HNO_3 for 5 min three times (with 5 min rest in between extractions) in 100 ml pyrex beaker covered with a watchglass. Filter remains intact but partially disintegrates.
Method 3	Completely digest filter with 4 mL conc. HNO_3 by heating with 1 mL portions until almost complete evaporation. Dissolve residue in 0.1 HNO_3 .
Method 4	Ultrasonicate with 0.1M HNO_3 (same as Method 2) but use Teflon beakers with Teflon covers. Filter remains intact with no disintegration.
Method 5	Add 1 mL conc. HNO_3 to filter in Teflon beaker. Tightly cover with Teflon watchglass by wrapping with Saran wrap and Al foil. Leave overnight at room temperature. Filter dissolves completely. Dilute to volume with deionized H_2O .

tions method were done to examine matrix differences among the air particulate samples. The optimized analytical methods and parameters are summarized in Table 2.

A Standard Reference Material (NBS-SRM 2676c metals on air filter) was analyzed using the optimized conditions to ascertain analytical accuracy.

Results and Discussion

Particulate Pb Levels. Pb levels of Metro Manila air particulate samples collected in filters are shown in Table 3 and in Figs. 1 to 4. The sampling objective was not for an extensive survey but only to get an idea of typical particulate Pb levels in indoor air, in street spots where commuters wait for a ride and inside moving public vehicles.

As seen in Fig. 1, all indoor air samples except one were below the World Health Organization (WHO) maximum allowable Pb air level of $1.5 \mu\text{g}/\text{m}^3$. Sample 33 was taken at a bedroom of a residence in Project 1 (Roxas District, Quezon City), 2nd floor, with the door and all windows closed, during the 1992 New Year's Eve celebration. The very high lead level ($6.21 \mu\text{g}/\text{m}^3$) was attributed to particulates from fireworks and firecrackers. Pb compounds are common constituents of low explosives. Examples of lead compounds used in explosives and pyrotechnics are lead thiocyanate, lead styphanate, (2,4,6-trinitroresorcinatate compound), lead azide ($\text{Pb}(\text{N}_3)_2$), lead dinitroresorcinatate (2,4 dinitro compound), and lead dinitroresorcinatate (the 4,6 isomer). Typical priming compositions may contain from 5 to 45% of one or two of the above lead compounds. Upon explosion, these compounds are transformed to lead oxides (4).

Most of the indoor air samples were from the same room in Project 1 where the New Year's Eve sample was taken, with Pb level average of $0.42 \mu\text{g}/\text{m}^3$ air. (The New Year sample was not included in the averaging.)

Lowest Pb levels for indoor samples were for those taken inside Ateneo de Manila University's (ADMU) Chemistry rooms (Samples 3 to 7) averaging $0.11 \mu\text{g}/\text{m}^3$ Pb in air. The ADMU Chemistry rooms from which the samples were taken were on the third floor of the Chemistry building inside the ADMU campus and far from street traffic. The Proj. 1 samples were taken in the second floor of a house situated in a populated residential area near busy thoroughfares. Among the ADMU samples, the highest level was for Sample 5 taken inside a hood (hood not running). The hood was not cleaned when Sample 5 was collected. Since air is drawn from other parts of the room whenever the hood is used, accumulated dust and residues from digestion procedures could cause the comparatively high Pb level for Sample 5.

The outdoor air samples had two categories. The first (Fig. 2) was sampled along or near busy streets, mostly in places where commuters wait for a ride. The second (Fig. 3) was sampled inside moving passenger vehicles (mostly jeepneys and some inside buses).

The majority of the street samples exceeded the WHO allowable level of $1.5 \mu\text{g}/\text{m}^3$ air as shown in Fig. 2. If only street samples taken from sites where commuters wait for a ride were considered, the average Pb level was $3.25 \mu\text{g}/\text{m}^3$ air. The lowest levels (0.11 and $0.35 \mu\text{g}/\text{m}^3$) were for samples 8 and 9 which were taken near Gate 2 inside the ADMU campus, under very windy conditions. Two other street samples had Pb levels lower than or very close to $1.5 \mu\text{g}/\text{m}^3$ (Samples 23 and 24 taken in Quiapo, also on a windy day). Durando and Aragon (5) have shown good negative correlation between wind speed and lead levels in air.

Samples 31 and 32 had the highest Pb levels among the street samples, with Sample 31 having the highest level ($8.67 \mu\text{g}/\text{m}^3$) taken at the junction of K-Mart Road (Katipunan Ave.) and Aurora Blvd., where traffic density is very high. Sample 32 had windier conditions compared to Sample 31, although traffic volume was almost the

same. This may account for the lower value of Sample 32 compared to Sample 31. Samples 31 and 33 (the New Year's Eve indoor sample) were the dirtiest among the filter samples.

The samples inside moving vehicles had generally higher Pb levels compared to the street samples, as seen in Fig. 4. All were above the allowable WHO level of 1.5 $\mu\text{g}/\text{m}^3$ air. None of the samples in this category were taken under heavy traffic situations. The levels would expectedly be higher under heavy traffic or rush hour conditions.

Analytical Accuracy. Interferences in graphite furnace absorption analysis are due to radiation detected by the instrument which are extraneous or different from that absorbed by the analyte (called spectral interferences), and non-spectral interferences which affect the analyte signal itself.

The most common spectral interferences are due to light scattering and molecular absorbance which are termed background absorption. Based on the results of background correction studies (0.000 absorbance or same absorbance as graphite tube blanks), the extracts of the Metro Manila air samples exhibit little or no background.

Most non-spectral interferences are detected by checking the effect of the sample matrix on an added standard of the analyte (standard additions method). If the matrix does not affect the analytical signal, the standard additions curve and the aqueous standardization curve will be parallel (have the same slope), in which case aqueous standardization is sufficiently accurate (assuming background correction is adequate or not needed).

Fig. 5 compares slopes of air particulate filter extracts using aqueous standardization (AQS) and standard additions methods (SAM). Many of the samples exhibit signal suppression by the matrix (below the [SAM slope]/[AQS

Table 2. Analysis of Pb in Metro Manila filter air samples

Pb Hollow Cathode Lamp (HCL)	4 mA
wavelength	283.3 nm
spectral bandpass	0.5 nm
background correction , nm (manual)	280.2 (Pb HCL), 283.3 (H_2 HCL)
graphite tube	pyrolytic coated, no platform
sample volume	10 μl (Eppendorf pipette)
internal gas flow (nitrogen)	300 mL/min
dry temperature	100°C, (10-20 sec)
char temperature	500-550°C, (20 sec)
atomization temperature (10 sec, maximum power heating rate, 50 mL per min internal gas flow)	1900°C
sensitivity (pg/.0044 A. peak ht.)	15
detection limit (based on 3x blank std. deviation)	0.53 ppb (or .044 $\mu\text{g}/\text{m}^3$ air for 30 min sampling at 4 LPM)
Apparatus	Varian AA6 Spectrophotometer interfaced with Perkin Elmer HGA 2200
Reagents	1000 $\mu\text{g}/\text{mL}$ stock solution of Pb (Titrisol) deionized water HNO_3 (Merck, A.R.)
Sample Preparation	Filter air samples ultrasonicated with 0.1M HNO_3 in Teflon beakers for three 5 min periods (with 5 min rest in between) in a windowless, air-conditioned room
Calibration	Aqueous standardization (0.1M HNO_3 Pb standard solutions) and standard additions method

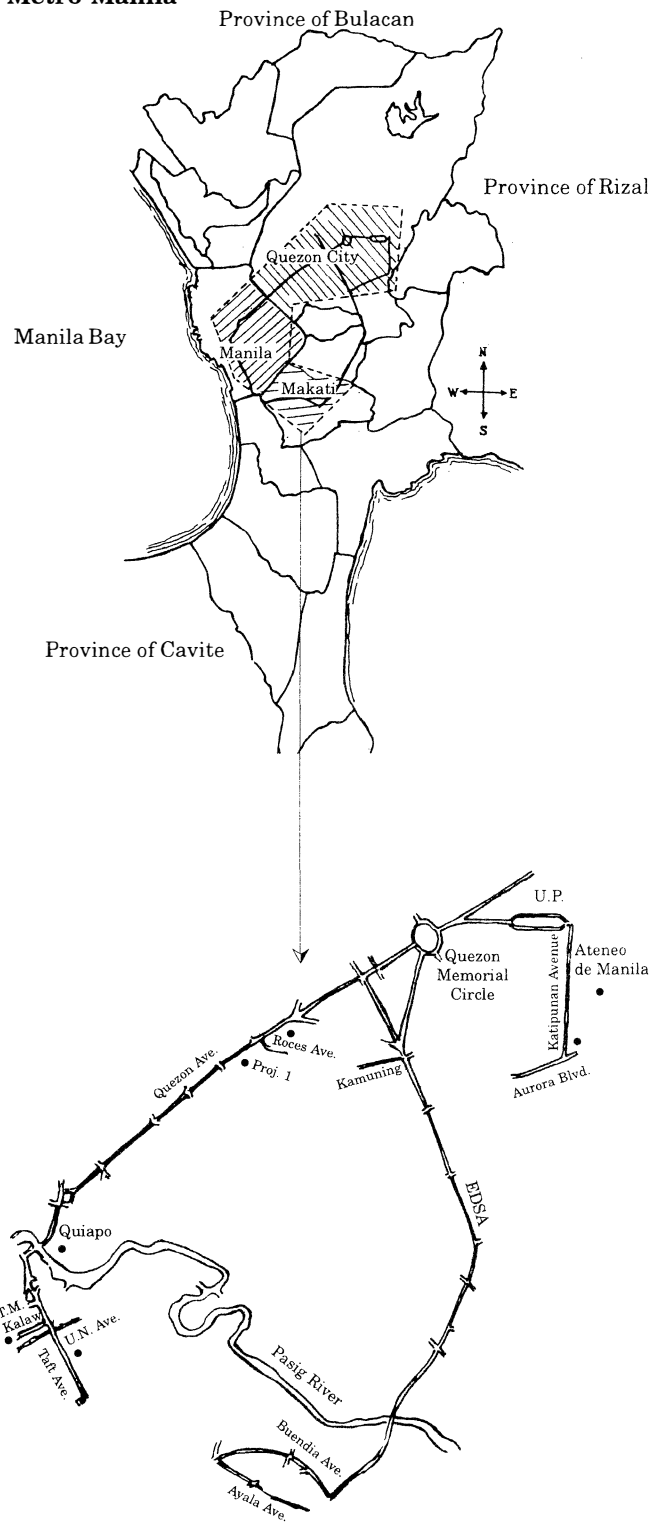
Table 3. Metro Manila air samples

Sample No.	Location	Sampling Date	Pbair ($\mu\text{g}/\text{m}^3$)
Indoor			
1	Proj. 1 house	12/16/91	0.61
2	"	12/21/91	1.02
22	"	8/10 & 8/14/92	0.45
25	"	9/19/92	0.31
30	"	10/17 & 10/31/92	0.56
33	"	12/31/92	6.21
38	"	1/09/93	0.74
3	ADMU CH308	1/17 & 1/18/92	0.09
5	ADMU CH307	3/26 & 3/28/92	0.35
6	ADMU CH309	4/08/92	0.08
7	"	"	0.07
Street			
8	ADMU Campus (near Gate 2)	4/04/91	0.11
9	"	5/05/92	0.35
10	Q. Blvd.-Roces	5/08/92	1.99
11	"	"	2.59
18	Kalaw-Taft Ave.	5/18/92	2.58
19	UN Avenue.-Taft	"	3.30
23	Quiapo sidewalk	9/14/92	1.44
24	"	"	0.96
31	Corner Katipunan -Aurora Blvd	10/22/92	8.67
32	"	"	4.44
In vehicles			
26	Proj. 1-Kalaw St.	9/29/92	4.60
27	Kalaw St.- Proj. 1	"	4.17
28	Proj. 1-ADMU	10/01/92	3.58
29	ADMU-Proj. 1	"	4.58
34	Proj. 1-ADMU	1/05/93	4.00
35	ADMU-Roces	"	3.62
36	Kamuning-Buendia	1/09/93	4.93
37	Ayala-Cubao	"	2.97
39	Proj. 1-ADMU	1/13/93	3.32
40	ADMU-Roces	"	2.64

Pb levels are standard additions method values.
 WHO (World Health Organization) allowable Pb air
 level: $1.5 \mu\text{g}/\text{m}^3$

Sampling Sites

Metro Manila



• Sampling sites

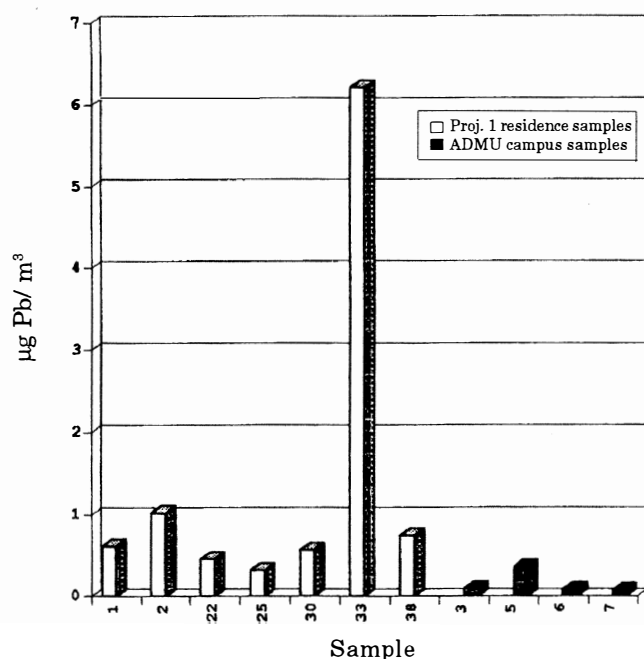


Figure 1. Metro Manila indoor air samples

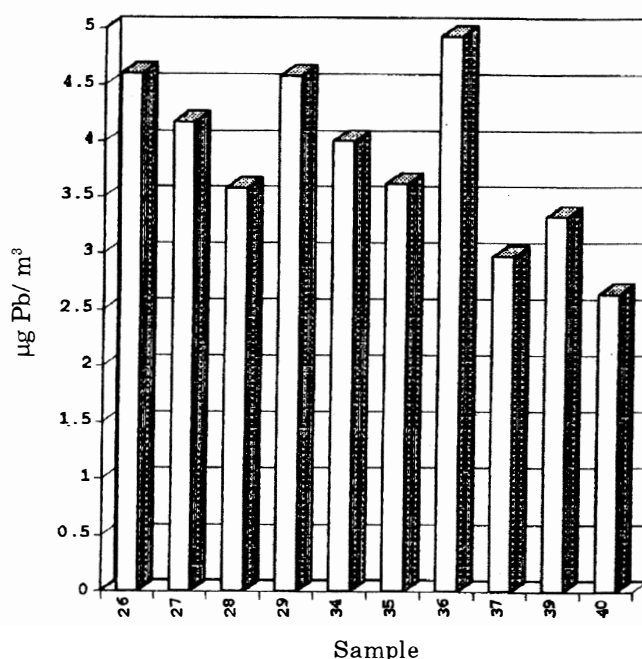


Figure 3. Inside moving vehicle air samples

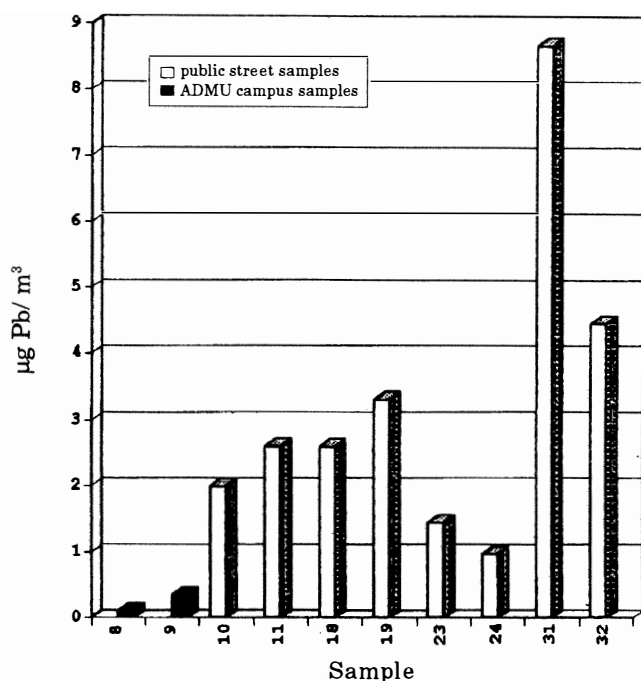


Figure 2. Metro Manila street air samples

slope] = 1 line and some exhibit matrix signal enhancement. Non-spectral interferences have a greater effect on the Pb signal accuracy of the air samples. The SAM results were therefore used as the basis for calculating and reporting Pb levels in Metro Manila urban aerosols.

Aside from standard additions, another method for correcting matrix interferences is the use of matrix modifiers. This was not done in this study to avoid increased contamination risks and additional manual pipetting.

One of the factors that most often affect accuracy is contamination, which in turn is determined to a large extent by the method of sample preparation. Blank values for five different methods of Pb extraction from air particulates in filters (see Table 1) are tabulated in Table 4.

Method 4 gave consistently low blanks and was used for the majority of the air samples. The highest blank levels were those for Method 3, which required at least 30 minutes of heating in the hood. Since the hood draws air from other parts of the room, the risk of contamination is higher for this method and is reflected in the high blank values. Although Method 1 and Method 5 also use the hood, the time spent in the hood is considerably shorter than for Method 3.

For Method 4, the whole procedure was done in a windowless air conditioned room (weighing room of ADMU Chemistry Department) for most of the samples. The Teflon beakers were thicker walled and heavier compared to pyrex beakers, so filters were kept intact (unlike in Method 2 where pyrex beakers were used and there was partial filter disintegration).

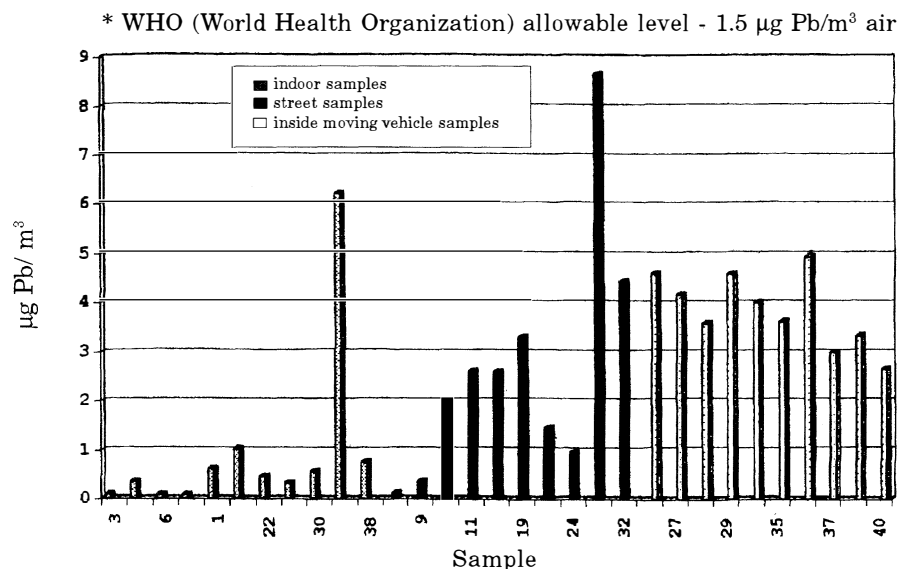


Figure 4. Metro Manila air samples

Table 4. Blank levels for Metro Manila air filter samples

Air Sample No.	Method of Pb Extraction	Volume of Extract (mL)	Blank (ppb Pb)
1	1	50.0	5.4
3	2	10.0	9.7
2	3	50.0	10.3
5	3	10.0	25.0
18, 19	2	10.0	7.1
8, 9, 10, 11	4	10.0	5.1
14, 15	4	20.0	3.4
6, 7	4	10.0	5.0
29	5	100.0	1.8
Standard Reference Air Filter Blank	4	100.0	3.0
Standard Reference Air Filter Blank (diluted 4x)	4	400.0 (actually 10.0 ml of orig. extract diluted to 40.0 ml)	2.7
26, 27	4	50.0	2.2
22, 23, 24	4	10.0	3.5
33, 34, 35	4	30.0	1.7
36, 37, 38, 40	4	20.0	2.4
31, 32	4	30.0	2.2
35, 38, 30, 39	4	10.0	2.6

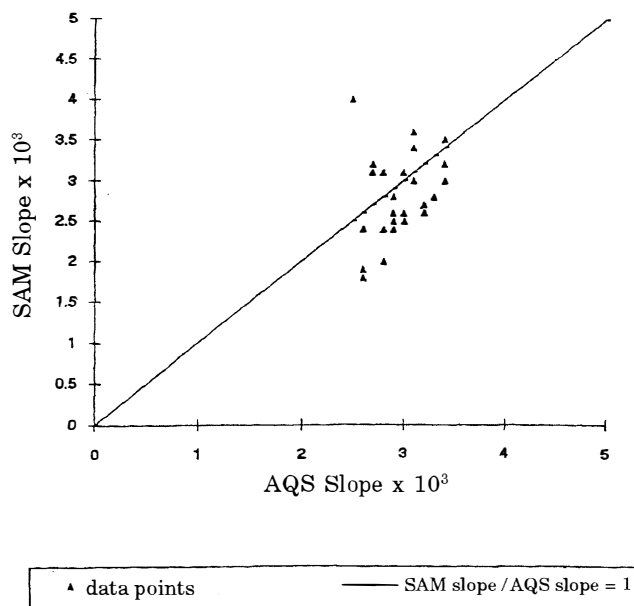


Figure 5. Comparison of aqueous standardization (AQS) and standard additions method (SAM) slopes

The cold digestion method (Method 5) holds promise for convenience and low contamination (although an extra precaution of thoroughly cleaning the hood and the room was first done for this method). The main inconvenience was the longer sampling time needed to collect enough air particulates for quantifiable Pb, since the minimum extract volume was 100 ml for optimum HNO_3 concentration. Higher HNO_3 concentrations attack the graphite surface and lowers sensitivity (6).

Contamination caused by the different components that go into the filter blank extract can be partially assessed by looking at the results for the Standard Reference Material (SRM) filter blank. The original extract contained 3.0 ppb Pb. When diluted four times with 0.01M HNO_3 , the Pb level was almost the same at 2.7 ppb.

Based on the certified value for Pb of the SRM filter blank ($< 0.01 \mu\text{g}/\text{filter}$) and on the Pb content printed on the label of the A.R. concentrated HNO_3 bottle ($< 0.000005\%$ Pb), the Pb level contribution of the filter and the HNO_3 to the SRM filter blank extract is only 0.1003 ppb Pb. The de-ionized (DI) water used to prepare the 0.1M HNO_3 solution is always tested for every fresh batch (about 20 L/batch) procured from the source (Philippine Institute of Pure and Applied Chemistry or PIPAC laboratory), and consistently gives 0.000 absorbance when 10 μL is analyzed in the graphite furnace. Labware (beakers, vol. flasks and pipettes) used are always soaked for at least 24 hours in 20% HNO_3 and rinsed with deionized H_2O before use. So the most probable source of the blank lead level is atmospheric dust absorbed while solutions are being prepared and transferred from one vessel to another. Pb levels are almost the same for original and diluted blank filter extracts, showing that almost all of the blank Pb is in the 0.1 M HNO_3 solvent.

A very important accuracy consideration for the sample preparation method is whether all particulate Pb has been extracted from the filter. Residual Pb in the air filters, after ultrasonication, were found to have the same level as residual Pb in ultrasonicated blank filters. This supports the findings of previous studies which show complete removal of pollution Pb from the filters (7).

A standard reference material (NBS - SRM 2676c metals on air filter) from the U.S. National Bureau of Standards was subjected to the ultrasonication method of extraction (Method 4). The analyzed Pb content ($7.49 \pm 0.16 \mu\text{g Pb}/\text{filter}$) agreed closely with the NBS certified value ($7.47 \pm 0.11 \mu\text{g Pb}/\text{filter}$). However, this standard reference material does not exactly match the air particulate samples collected in Metro Manila. An exactly matched standard would be difficult to prepare since, as shown in Fig. 5, the matrix of the air samples vary significantly. In terms of instrument performance and extraction procedure for air filter Pb soluble in dilute acid, the above results show the absence of significant systematic error.

Matrix Effects. To explain signal suppression or enhancement by the matrix (shown in Fig. 5), the composition of typical urban particulates where the particulate

Pb source is predominantly automobile exhaust was studied in the literature.

Lead alkyls (i.e., tetraethyl lead) are added to internal combustion engine fuel to improve the fuel octane number and prevent engine 'knock'. Lead additives also act as lubricants for valve guides seats. Many engines will quickly seize up if run on lead-free petrol, unless properly modified (8).

After combustion, the lead residues are scavenged by adding ethylene dichloride and ethylene dibromide to the fuel. Consequently, Pb compounds in vehicle exhausts have been identified by x-ray diffraction as principally lead bromochlorides (PbBrCl), often associated with ammonium chloride ($\text{PbBrCl} \cdot 2\text{NH}_4\text{Cl}$ and $\alpha\text{-2PbBrCl} \cdot \text{NH}_4\text{Cl}$), and $2\text{PbO} \cdot \text{PbBrCl}$ (9).

Biggins and Harrison (10) used x-ray powder diffraction to identify lead compounds present in ambient air polluted by vehicle exhaust. Aside from the lead bromochloride compounds, PbSO_4 and $\text{PbSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ were found to be predominant lead forms in most of the sampling sites. These were postulated to be formed by coagulation and reaction of lead bromochlorides with neutral and acid sulfates of ambient aerosol. Results of experiments involving PbBrCl and an aerosol mist of sulfates supported this proposed mechanism.

Sulfates are formed by the atmospheric oxidation of sulfur dioxide. In Metro Manila, diesel fuel is widely used and emits considerable amounts of sulfur dioxide to the atmosphere. There is therefore a good probability that ambient Metro Manila aerosols also contain lead sulfate compounds together with the lead bromochloride compounds plus an abundance of sulfate ions in the particulate matrix.

With the above suggested composition of Metro Manila air particulates, an explanation for matrix differences among the air samples can be attempted.

Atomization characteristics of the lead bromochlorides in the graphite furnace can be approximated by PbCl_2 . When lead is atomized as a chloride, it has a lower atomization efficiency than the nitrate (which is the form of the aqueous standards). Atomization efficiency is the fraction of the analyte mass present in the atomizer surface that becomes atomic vapor. The PbCl_2 atomization peak is smaller, shorter and appears at an earlier time than the $\text{Pb}(\text{NO}_3)_2$ atomization peak (11).

Sulfates cause serious suppression of lead graphite furnace signals even in samples digested with concentrated HNO_3 (12). The bromochlorides and sulfates are thus postulated to cause lead signal suppression which is shown in Fig. 5 to occur in majority of the samples.

For the Project 1 (indoor) area, Sample 33 (the New Year's Eve sample) showed signal enhancement, with a SAM to AQS slope ratio of 1.16. Assuming that most of the Pb in this particular sample came from fireworks and firecrackers, the lead combustion product would predominantly be the oxide, which is postulated to be the main lead species atomized by thermal dissociation of the vapor in the furnace (13,14). Atomization would be more efficient than and would have the same mechanism as the $\text{Pb}(\text{NO}_3)_2$ aqueous standards (13). The dissolution of

PbO would also decrease the acidity of the extract, causing signal enhancement. Absorbance increases with decreasing HNO_3 concentration (15) for GFAAS. This is the most likely reason for the large signal enhancement of Sample 1 (SAM to AQS slope ratio of 1.60) since the digesting acid was allowed to evaporate, followed by dilution with deionized water.

For the outdoor air samples, significant signal suppressions are seen in most of the samples taken in loading/unloading areas for passengers which were most exposed to vehicle exhaust. These are Samples 10, 18, 19, 23 and 24 with SAM/AQS slope ratios from 0.71 to 0.86.

Samples 31 and 32 had very high Pb in air levels (8.67 and 4.44 $\mu\text{g}/\text{m}^3$ respectively) and were also taken in a loading/unloading area (corner Aurora Blvd. and the road where K-Mart is situated). Matrix effects for these two samples, however, were smaller (SAM/AQS slope ratios of 0.92 and 1.03 respectively) compared to the other samples taken in loading/unloading areas. Visual comparison of particulate content of the filters show Samples 31 and 32 to be much dirtier than other loading/unloading area samples. This was because a lot more buses and trucks pass through the K-Mart/Aurora Blvd. corner, belching huge quantities of black smoke, compared to the other loading/unloading sites. However, extracts for Samples 31 and 32 were three times more dilute than the extracts for the other loading / unloading site samples. Dilution significantly decreases matrix effects.

For air samples inside moving vehicles, majority exhibited signal suppression, but to a generally lesser extent (SAM/AQS slope ratios of 0.88 to 0.97) compared to the street samples.

Conclusion

Majority of Metro Manila Pb particulate air levels were way above the WHO allowable Pb level of 1.5 $\mu\text{g}/\text{m}^3$. This was expected as all gasoline fuel in the Philippines uses tetraethyl lead as the anti-knock additive. An interesting observation is the generally higher Pb levels in air inside moving public vehicles compared to outside on the streets, at least for the limited data gathered in this study. Another striking observation is the very high Pb air level during the New Year firecracker and pyrotechnics spree.

It would be interesting to do similar studies after the hopefully successful production and use of low lead or unleaded gasoline in the Philippines, and the improvement of diesel powered vehicle exhaust particulate levels.

Extraction of air particulate Pb from the air filter samples was optimized. Least blank Pb levels and contamination was obtained by ultrasonication of the filters in

a windowless, air-conditioned room. The extraction procedure, however, has been proven efficient only for particulate Pb. Other trace metals may necessitate the use of the hood, in which case clean room conditions are necessary for the sensitive analytical methods used for low volume air samples.

Non-spectral interferences (matrix effects) were detected when standard additions method slopes were compared with aqueous standardization slopes. These were attributed to acidity effects, particulate composition, and atomization mechanisms in the graphite furnace.

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