Chemistry 311
November 22, 1996

Arrangement of Responsibility in Report Preparation
for Experiment 25: ICP-MS

Data Collection

Analysis and Manipulation of Data

Majority of Report Writing

Editing

Signed:
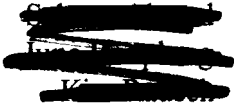
Experiment 25: ICP-MS Determination of Lead

I. Introduction

The Inductively Coupled Plasma - Mass Spectroscopy was chosen as the method for determining the amount of lead in the samples of house dust obtained by the schoolchildren. This method was decided upon for many reasons which include a low limit of detection, an instrument that is easy to use, and the little amount of time needed to analyze many samples. Because the instrument is a mass spectrometer, the system can be adjusted to measure the amounts of selected species such as the various isotopes of lead (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) along with internal standards (^{50}V, ^{51}V, ^{121}Sb, ^{123}Sb, and ^{232}Th).

II. Materials and Methods

Solutions:
70 % HNO$_3$ stock solution
1000 ppm Vanadium stock solution
1000 ppm Antimony stock solution
1000 ppm Thorium stock solution

Prepared Solutions:
1 % HNO$_3$ - wash solution
0.1 % HNO3 with 50 ppb each of V, Sb, Th - Internal standards and blank
Pb standard solutions (10, 50, 100, 200, 500, and 1000 ppb)
Sample solutions of internal controls (diluted x 5)
Samples of digested baby wipes (diluted x 5)

Materials:
18 50 ml volumetric flasks
2 1 L volumetric flasks
micropipettes
10 ml graduated cylinder
Parafilm

Instrumentation:
Inductively Coupled Plasma - Mass Spectrometer (ICP-MS)

Setup:

Element	Scanned Regions
V	50, 51
Sb	121, 123
Pb	204, 206, 207, 208
Th	232

Procedure: Pumping ➜ Standby ➜ Operating Mode

Methods: For preparing the solutions, Sabeen and Kim made up the wash solution and the solution containing the internal standards. The wash solution was made by adding 14.3 ml of the 70% HNO_3 stock solution to a 1 L volumetric flask that contained a little bit of deionized water. The solution was then diluted to 1 L with deionized water. The 0.1% HNO_3 solution was made with 1.43 ml of the HNO_3 stock solution and 50 ml each of the V, Sb, and Th stock solutions which were diluted to 1 L in a 1 L volumetric flask with deionized water. June made up the lead standard solutions by micropipetting 5, 25, 50, 100, 250, and 500 µl of 100 ppm Pb stock solution into six 50 ml volumetric flasks. Sabeen diluted all of the Pb solutions with the 0.1% HNO_3 solution while Kim covered them with parafilm and shook the flasks. June also measured out 10 ml of the lead solutions from the digestion and poured them into the remaining 50 ml volumetric flasks. Sabeen diluted them with the 0.1% HNO_3 solution, and Kim made sure that each solution was thoroughly mixed by shaking the flasks. In analyzing the solutions, Kim ran the computer while June transferred the intake tube from the wash solution to the various samples.

III. Results

The raw data obtained are contained in the appendix. Otherwise, the data are summarized in the following table (Table 1) and in Table 2 and Figure 1 which are on one of the following pages.

Table 1: The amount of lead in the samples of KimWipes and house dust using the data on ^{206}Pb.

Sample	Concentration (ppm)	Concentration ($\mu g/ft^2$)
Sabeen's internal control 1	4.350	435.0
Sabeen's internal control 2	4.530	453.0
June's internal control 1	4.710	471.0
June's internal control 2	5.025	502.5
Kim's internal control 1	4.440	444.0
Kim's internal control 2	4.470	447.0
Sabeen's Unwashed Sample	1.360	136.0
Sabeen's Washed Sample	0.1975	19.75
June's Unwashed Sample	0.4140	41.40
June's Washed Sample	0.5600	56.00
Kim's Unwashed Sample	0.0125	1.250
Kim's Washed Sample	0.0000	0.000

The internal controls are the digestions performed with 5.0 ppm of lead added to a KimWipe in a beaker. These digestions were performed twice by each student so they were given arbitrary numbers of 1 or 2 for each student.

Kim's Washed sample had counts with negative values so the concentration was assumed to be 0.0 ppm. Her Unwashed sample had negative values for ^{204}Pb and ^{207}Pb so the concentration of lead is probably near zero.

The concentrations already took the 5 times dilution into account which means that the raw data was multiplied by 5 to obtain the concentrations in ppm. The concentrations in ppm were then used to calculate the amount of lead in $\mu g/ft^2$.

IV. Summary/Discussion

According to Table 1, the children's samples are definitely below the HUD limit of 500 μg/ft². However, some error could be attributed to the children who might not have performed their part of the collection of the samples well. They might not have measured a square foot perfectly or understood the instructions concerning collecting the sample of an unwashed sample versus a washed sample particularly since June's washed sample had a higher lead content than the unwashed surface and was a noticeably dirtier baby wipe than the baby wipe for the unwashed surface before the digestions. If Sabeen's samples were acquired properly, they proved that lead content could decrease significantly with washing.

Another cause of error would be the digestions themselves which were difficult to perform. The error can be shown by the measurements of the internal standards. These internal standards originally had 5.0 ppm lead, but were analyzed with the ICP-MS to have less than this amount for everyone's samples except for June's second one which exceeded the original concentration. This may have also been caused by the digestion process which took a while and was altered. Another indication of human error is the counts per second of vanadium, antimony, and thorium in Table 2 for the controls and the samples. Each of those solutions were to contain the same amount of internal standards because they were the 5 times dilutions of the samples and thus had 10 ml each of the sample and 40 ml each of the 0.1 % HNO₃ with the internal standards. However, the counts per second of each of the elements varies significantly among the samples even though they should be the same. One reason for the inconsistency is that the 10 ml of samples were not measured accurately or the dilutions with deionized water was not done accurately. This shows the great probability of human error.

The instrument itself could also have been a cause of error which can be exemplified by the limit of detection (LOD) and the limit of quantification (LOQ) but also includes human error in the ability to make the lead standard solutions. Since none of the solutions were run repeatedly, the standard deviation of the blank would have to be taken from the regression line as being the same as the mean of the blank. From Figure 1, the mean of the blank as well as the standard deviation of the blank was determined to be 461.547 counts per second. Since LOD equals the mean of the bland plus three times its standard deviation, the LOD was calculated to be 1846.188 counts per second (461.547 + 3 x 461.547) which pertains to 14.35 ppb Pb. The LOQ is the mean of the blank plus nine times its standard deviation which would be 4615.47 counts per second. This pertains to 43.05 ppb Pb which is a very small number and means that the instrument can make very accurate measurements. Furthermore, the linear range reached 1000 ppb Pb but could extend further since the 1000 ppb was the maximum concentration that we used. Finally, the r value was determined to be 0.99982 which indicates that the regression line is a very good fit.

The relatively little background is one reason for the low LOD, and the ICP-MS has many causes for such little background noise. One of these is the use of argon plasma as an ionizing source. At the temperature of the plasma, Ar is only slightly ionized (0.002 %) so any ions of Ar will not contribute significantly to the detector and cause much background. Additionally, the mass of Ar (40) is far form any of the isotopes being analyzed so it will not interfere. Another contributor to the little background is the high vacuum behind the skimmer. The decrease in pressure increases the mean free path which means that the ions travel separately instead of colliding with one another. This allows the ions to hit the detector one at a time so they will not interfere with each other.

The primary reason why the ICP-MS has such a low LOD is the efficiency of the instrument. The instrument can make many measurements in a short amount of time. In 50 μs, about 10^7 counts can be acquired. With a coadded spectra, the signal-to-noise ratio would increase so much that any noise would be practically insignificant.

The Gaussian shape curve could be attributed to the different energies of the ions as they travel through the quadrapole. The ions cannot enter the quadrapole with the exact same velocity. In fact, the velocity at which the ions enter are random which is shown as the Gaussian curve. The curve does not mean that the ions have varying masses because they do not. In fact, each ion of the same isotope should have the same mass because they have the same composition of neutrons and protons that determine contributes to its mass. Perhaps, this would be the main instrumental error because the peaks are not perfectly narrow. Every other part of the instrument would give narrow peaks which would have a low degree of uncertainty.

Since the first ionization energy of lead is 7.4 eV and the percent ionized at a plasma temperature of 7500 K is 0.994 %, the formation of Pb⁻ would not be a problem. In fact, 97 5 of Pb is completely ionized which would mean that the singly ionized lead would not interfere significantly with the measurements.

The excellent choice for using this method to analyze the samples is supported by many reasons. First of all is the low LOD and LOQ along with the large linear range and the good r value. Another reason for making ICP-MS the primary method is the short turn around time for measuring samples which was approximately 5 minutes. This method is also ideal because of the lack of use of hazardous materials except for the lead that is analyzed. Moreover, a paper trail could be easily constructed for this procedure because it does not require much preparation. Unfortunately, one flaw is the difficulty in instructing a technician on how to use the instrument. In fact, delays were caused because a few times someone who understood the computer program were not available so the experiment could be run. However, with a knowledgeable technician nearby, the procedure was simple and accurate.

Instrument	LOD (ppb)	LOQ (ppb)
UV-Vis	2400.0	indeterminable
GFAA	169.0	508.0
Fluorescence	2290.0	2360.0
ASV	31.3	93.9
ICP-MS	14.35	43.05

V. Sample Calculations

Determination of $\mu g/ft^2$:
Sabeen's Unwashed Sample

$$1.360 \text{ ppm} = \frac{1.360 \ \mu g \ Pb}{1 \ ml \ digestion} \times \frac{100 \ ml \ digestion}{1 \ ft^2} = 136.0 \ \mu g/ft^2$$

Start Mass : 46.6
End Mass : 234.4
Mass Calibration : $y = a + bx + cx^2 ... ex^4$
-1.37E-01 4.44E-03 -4.57E-10 0.00E+00 0.00E+00

TABLE 2

Blank - 1% Nitric Acid

Mass	% Ab	Z	Int CPS
49.95	0.24	23	37.71
50.94	99.76	23	58.73
120.9	57.25	51	176.19
122.9	42.75	51	127.97
203.97	1.37	82	65.53
205.97	25.15	82	1726.77
206.98	21.11	82	2575.6
207.98	52.38	82	5299.47
232.04	100	90	34.62

Internal Standard - 0.1% Nitric Acid with 50 ppb V, Sb, Th

Mass	% Ab	Z	Int CPS
49.95	0.24	23	207.72
50.94	99.76	23	42010.35
120.9	57.25	51	15818.22
122.9	42.75	51	10547.15
203.97	1.37	82	7.42
205.97	25.15	82	24.73
206.98	21.11	82	25.96
207.98	52.38	82	55.64
232.04	100	90	52220.88

10 ppb Pb

Mass	% Ab	Z	Int CPS
49.95	0.24	23	192.26
50.94	99.76	23	40909.35
120.9	57.25	51	14946.31
122.9	42.75	51	10124.63
203.97	1.37	82	73.57
205.97	25.15	82	1354.57
206.98	21.11	82	2432.78
207.98	52.38	82	4698.43
232.04	100	90	50884.63

50 ppb Pb

Mass	% Ab	Z	Int CPS
49.95	0.24	23	152.7
50.94	99.76	23	39743.03
120.9	57.25	51	14448.8
122.9	42.75	51	9851.19
203.97	1.37	82	301.07
205.97	25.15	82	7379.8
206.98	21.11	82	12850.12
207.98	52.38	82	25146.49
232.04	100	90	48363.19

Multi-Element Calibration   Fri Nov 22 1996
Calibration graph coefficients for selected isotopes.
User Name   : STUDENT   Experiment name   : LEAD2
Analysis procedure   : LEAD STANDARD and samples

Introduction method   : 60 sec. acquire method 30up 10wash
First sample started at : Fri Nov 22 1996 11:31:03
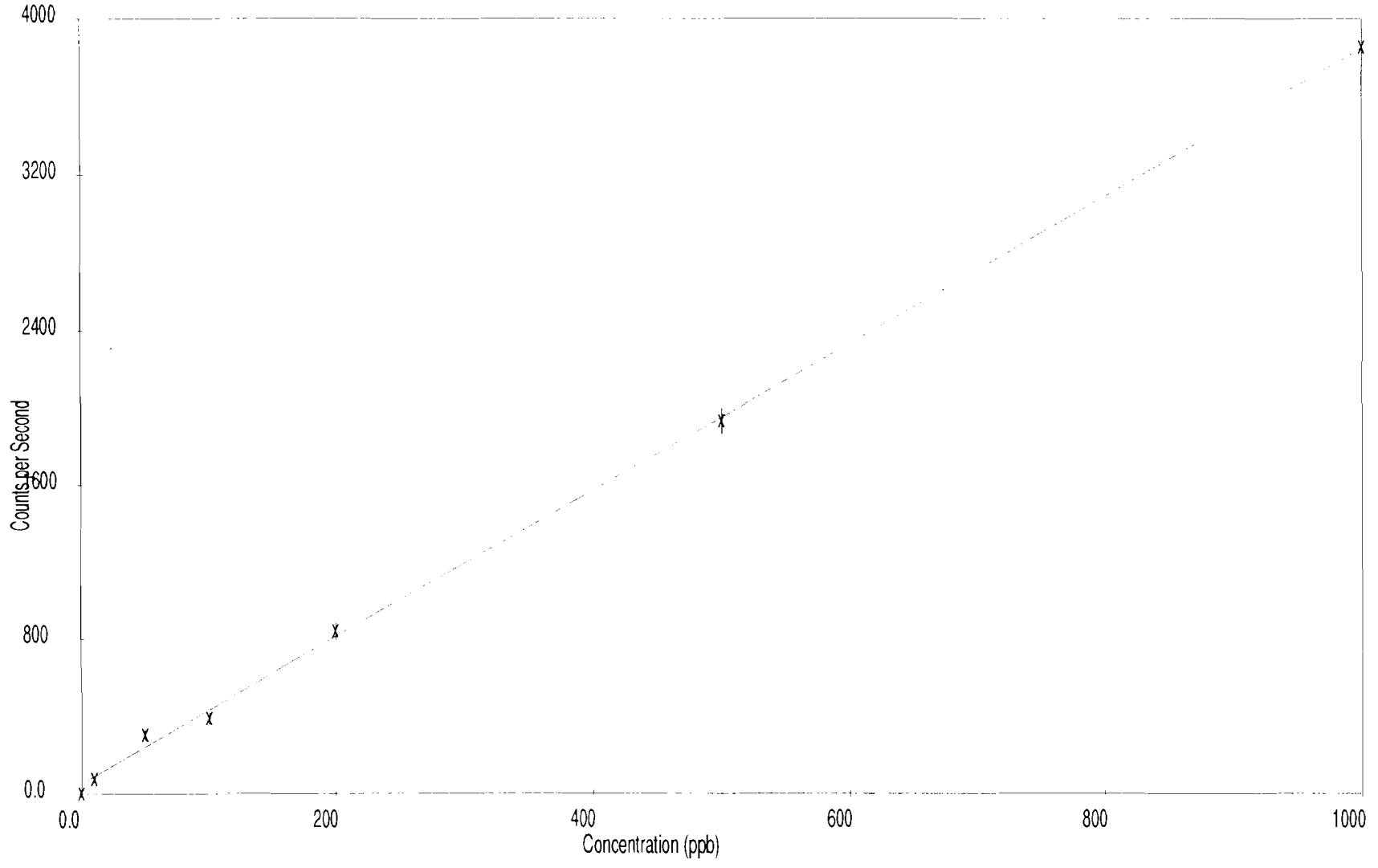Last sample started at : Fri Nov 22 1996 12:14:23

Polynomial fit   : $y = a0 + a1.x + a2.x^2$
Units of response   : y = counts per second
Units of concentration : x = ppb

Element	Symbol	Mass	a0	a1	a2	regression
Lead	Pb	204	51.6	3.80	0.0	1.000
Lead	Pb	206	462	96.5	0.0	1.000
Lead	Pb	207	1128	166	0.0	1.000
Lead	Pb	208	1614	330	0.0	1.000

Pb 204

Coefficients : Y = A0 + A1X + A2X^2 ... AnX^n

A0	A1	A2	A3	A4	Regression
5.15608E+1	3.79688E+0	0.00000E+0	0.00000E+0	0.00000E+0	9.99666E-1

sabeen washed 1

Mass

Raw Counts

3600
3200
2800
2400
2000
1600
1200
800
400
0.00

201 202 203 204 205 206 207 208 209 210
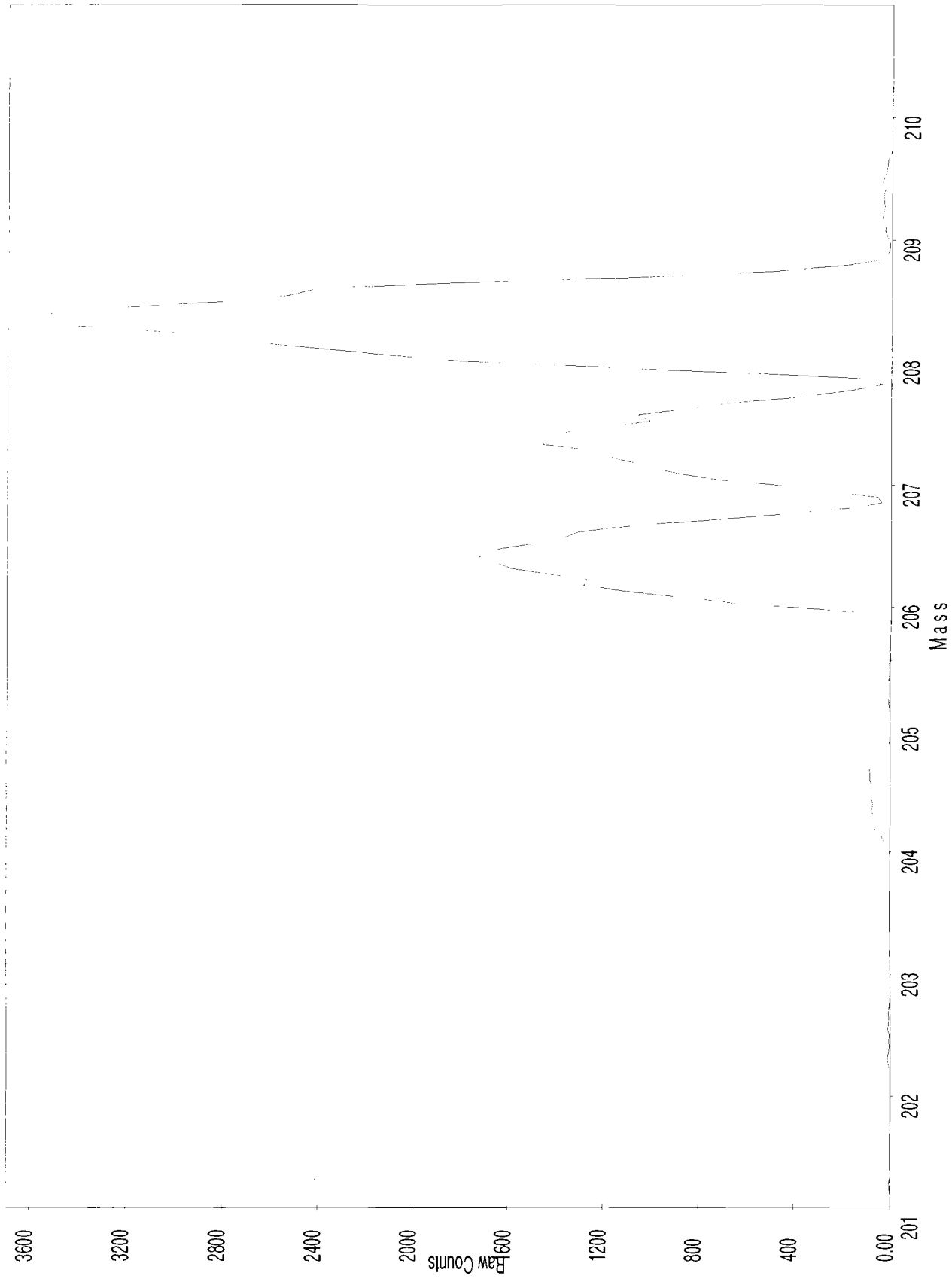
RUN AT STOLT)   Pb STANDARDS   in 50mL volumetric

Pb = 1000ppm   10 ppb   5 uL

                  50   25 uL

                  100   50 uL

                  200   100 uL

                  500   250 uL

                  1000   500 uL

INTERNAL STANDARDS   in 1 L volumetric

.1% HNO$_3$ (70%.)

$$V_1 = \frac{(.001)(1000mL)}{.7} = 143 mL$$

(1000ppm)

50 ppb   V, Sb, Th = 50 uL of each

RUNNING SAMPLES

1. Blank 1% HNO$_3$

2. 1% HNO$_3$, V, Th, Sc - INTERNAL STANDARD

3. 10 ppb Pb

4. 50 ppb Pb

5. 100 ppb Pb

6. 200 ppb Pb

7. 500 ppb Pb   16 Sabeen washed

8. 1000 ppb Pb   17. Kim unwashed

9. Kim control 1   18. Kim washed

10. Sabeen control 1   19. June unwashed

11. June control 1   20. June washed

12. Kim control 2

13. Sabeen control 2

14. June control 2

15. Sabeen unwashed

ICP MS - used to determine amount of Pu in house dust

... solutions: 70% HNO_3

1000 ppm V, Sb, Th each

100 ppm Pb

Prepared solutions:

0.1% HNO_3 with 50 ppb each of V, Sb, Th - Internal Standards

To a 1L volumetric flask containing some DI water, 1.43 ml of the 70% HNO_3 stock solution was added with a micropipette by Simon. 50 μl each of V, Sb, and Th were subsequently micropipetted. The solution was diluted and shaken by Lim.

$M_1 V_1 = M_2 V_2$

$$V_1 = \frac{M_2 V_2}{M_1} = \frac{(0.1\%)(1000\,ml)}{70\%} = 1.43\,ml$$

1.0% HNO_3 wash solution

14.3 ml of 70% HNO_3 was diluted to 1L in a 1L volumetric flask.

All of the glassware was rinsed with diluted nitric acid, then, and deionized water prior to use.

CP-993

_____ + samples : 5x dilution (10 ml in 50 ml vol flasks)

____ standards : from 100 ppm ?b stock sol'n

ppb (?b)	vol of stock sol'n (μl) to 50 ml vol flasks
10	5
50	25
100	50
200	100
500	250
1000	500

____ unstoppered. Steven diluted w/ Int. Std., Kim covered w/
parafilm + shook th__

_____

1 diff. conc. + V, Sb, Th
2 10 ppb ?b
3 50 ppb ?b
4 100 ppb Pb
5 200 ppb ?b
6 500 ppb ?b
7 1000 ppb ?b
8 ___ control 1
9 _____ control 1
10 ___ _____ 1
   Kim ____ 2
2 Steven ____ 2
_ June ____ 2
__ Steven _____
__ _____ _____
__ Kim _____
__ Kim _____
__ ____ _____

For dilutions, June measured 10 ml
with a graduated cylinder, Steven
diluted with Internal Std, Kim
covered with parafilm and shook.

ICP-MS   Second Run   11/22/

dilution of samples five fold
ex. 10mL of sample solution
brought up to 50mL with
addition of 0.1% HNO_3 w/ Interna
Standards

Data   Lead Samples
1. blank 0.1% HNO_3
2. 0.1% HNO_3 plus Internal Standar
3. 10ppb Pb
4. 50ppb Pb
5. 100ppb Pb
6. 200ppb Pb
7. 500ppb Pb
8. 1000ppb Pb
9. Kim control 1
10. June control 1
11. Saleen Control 1
12. Kim control 2
13. June Control 2
14. Saleen Control 2
15. Saleen unwashed
16. Saleen washed
17. Kim unwashed
18. Kim washed
19. June unwashed
20. June washed