
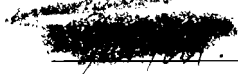



ICP-MS


 -- experiment



 -- experiment, results, materials, methods



D  -- experiment, results, discussion



I. Purpose:

1. To familiarize ourselves with ICP-MS.
2. To calibrate the instrument.
3. To calculate limit of detection.
4. To measure the lead content in samples obtained from digestion of baby wipes.

II. Materials:

Instruments:

1. ICP-MS
2. pump
3. Pentium computer.

Solutions:

50 μL of 1000 ppm Thorium, 50 μL of 1000 ppm Vanadium, 50 μL of 1000 ppm Antimony and 1.43 mL of 70% Nitric acid in 1L of deionized water

Standard solutions:

Concentration of Lead (ppb)	Volume of Pb (μL)	Total volume (mL)
1	2.5	250
10	10.0	100
50	25.0	50
100	50.0	50
200	100.0	50
500	250.0	50

Samples obtained from digestion of baby wipes:

Dilution factor = 5		
Sarah	Dmitriy	Maggie
Pb standard	Pb standard	Pb standard
Clean baby wipe		Pb standard
Unwashed surface	Unwashed surface	Unwashed surface
Washed surface	Washed surface	Washed surface

III. Methods:

The solvent solution was prepared first. 50 μL of Th, 50 μL of V, and 50 μL of Sb were pipetted into 1 L volumetric flask. Then 1.34 mL of 70% nitric acid was pipetted into the same flask in order to obtain 0.1% solution of nitric acid. Water was added to obtain 1L of that solution. This solution is used as the solvent for all other solutions.

The standard lead solutions were prepared by pipetting appropriate amount of 100 ppm Pb solution and diluting it with solution prepared above. The solutions for samples were prepared in the way that for 5 times dilution 10 mL of digest was pipetted into the 50 mL volumetric flask and diluted with solvent to 50 mL.

The solutions were moved to the cart and the experiment was started. ICP-MS instrument was turned on. Then it was moved from stand by mode to running mode. The torch was lit. The plastic hose which was connected to pump was placed into each solution. After each solution, the hose was placed into the washing solution to make sure that each reading belongs to the particular solution. After all solutions were ran, the instrument was turned down to stand by mode, and the data was looked at.

IV. Results:

Table 1. Results of the analysis for lead 208.

Analyst	Samples provider	Concentration, ppb			
		Standard	Clean wipe	Unwashed surface	Washed surface
Sarah		4594.80	48.32	221.48	60.28
Maggie	Charlie	3785.82 4019.56		1129.87	267.30
Dmitriy	Dewayne	5626.99		133.86	301.33

Table 2. Results of the analysis for lead 208 in the units used by HUD.

Analyst	Samples provider	Concentration ($\mu\text{g}/\text{ft}^2$)	
		Unwashed surface	Washed surface
Sarah		22.15	6.03
Maggie	Charlie	112.99	26.73
Dmitriy	Dewayne	13.39	30.13

Table 3. Isotopes.

Sample	Ratio		
	Pb 207 to Pb 208	Pb 206 to Pb 208	Pb 204 to Pb 208
Standard	0.485992959	0.310851269	0.013075049
Maggie	0.47812858	0.314212761	0.013539299
Sarah	0.480013526	0.315888915	0.01264392
Dmitriy	0.472066862	0.322810648	0.014574818
Mean	0.479050481	0.315940898	0.013458271
Standard deviation	0.005737197	0.005036101	0.00082931
RSD	0.011976184	0.01594001	0.061620902

Table 4. Regression Information.

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.997066
R Square	0.994141
Adjusted R Square	0.992969
Standard Error	8982.891
Observations	7

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	6.85E+10	6.85E+10	848.3997	8.94E-07
Residual	5	4.03E+08	80692335		
Total	6	6.89E+10			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-4129.96	4211.166	-0.98072	0.371771	-14955.1	6695.166	-14955.1	6695.166
X Variable 1	589.9516	20.25425	29.1273	8.94E-07	537.8865	642.0168	537.8865	642.0168

Table 5.

Linear regression:

$$y = 589.95 x - 4129.96$$

LOD:

$$\text{LOD} = x_{bl} + 3 s_{bl}$$

Signal at LOD:

$$\text{Signal at LOD} = y \text{ constant} + 3(\text{standard error } y \text{ constant})$$

$$\text{Signal at LOD} = 8503.538$$

$$8503.538 = 589.95 x - 4129.96$$

$$x = 21.41 \text{ ppb}$$

$$\text{LOD} = 21.41 \text{ ppb}$$

LOQ:

$$\text{Signal at LOQ} = y \text{ constant} + 9 (\text{standard error } y \text{ constant})$$

$$\text{Signal at LOQ} = 33,770.534$$

$$\text{LOQ} = 64.23 \text{ ppb}$$

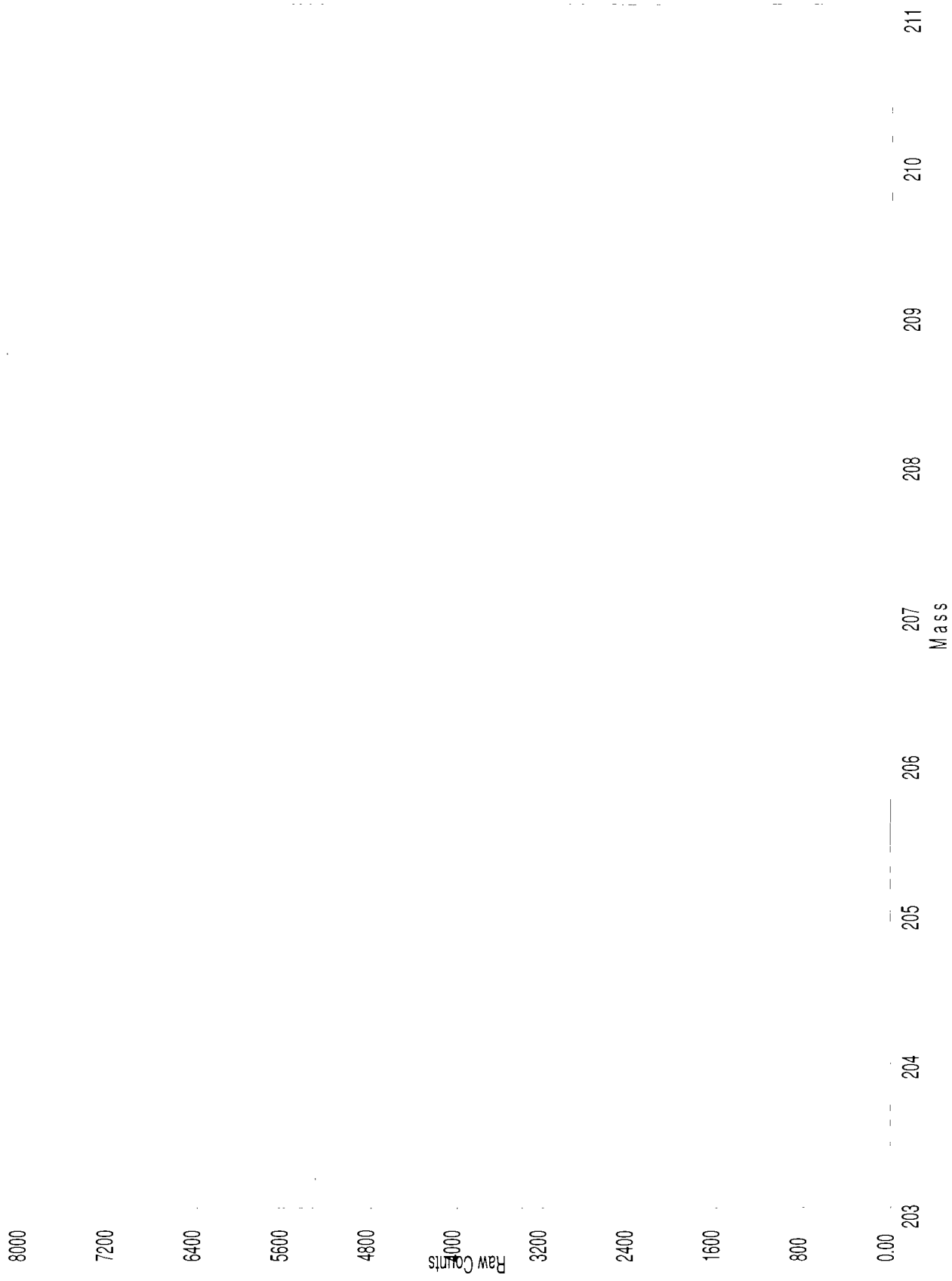
$$R = 0.997$$

Table 6.

	GFFA	UV-Vis	FTIR	Fluorimeter	ASV DT=225sec	ICP-MS
LOD	92.8 ppb	454.7 ppb		468 ppb	701.6 ppb	21.41 ppb
LOQ	278.5 ppb	1364.1 ppb		1400 ppb	2104.8 ppb	64.23 ppb
R	0.99533	0.96120		0.9997	0.985	0.997
Linear range		1.3641 to 2.5 ppm		1.4 to 16 ppm	2.1 to 4 ppm	64 to at least 500 ppb
Turn around in samples	2 min.	5 min.	12 min.	3 min.	1.5 min.	1.5 min

DATA HEADER FILE							
Filename :	maggie stand * 1						
About file :							
Version No. :	2						
Date :	Mon Nov 18 1996						
Time :	12:53:46						
Original Date :	Mon Nov 18 1996						
Original Time :	11:42:09						
Element Menu used :	INTERNAL STANDARD						
Version No. :	0						
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		
Regression coeff :	1.00E+00						
Scan parameters :	On File						
Peak Jump parameters	None						
Peak Data :	On File						
(s16.6H							
PEAK LIST DATA							
Mass	% Ab	Z	Int CPS	Dwell (æ)s	Detector	Peak Cycle	Channels
49.95	0.24	23	226.88	10240	PC	1	3
50.94	99.76	23	38348.32	10240	PC	1	3
120.9	57.25	51	13530.81	10240	PC	1	3
122.9	42.75	51	9203.34	10240	PC	1	3
203.97	1.37	82	5863.56	10240	PC	1	3
205.97	25.15	82	136134	10240	PC	1	3
206.98	21.11	82	210553.2	10240	PC	1	3
207.98	52.38	82	442559.4	10240	PC	1	3
232.04	100	90	50538.59	10240	PC	1	3
(s10H							
SCAN PARAMETERS							
Detector modes used :	PC						
Number of Channels :	3872						
Channels per AMU :	19						
DAC Step :	11						
Start DAC :	10538						
End DAC :	53119						
Background :	30						
Integration range :	0.8						
INTEGRATED DATA							
	0						
	0						
	0						
	0						
	0						
	0						
	0						
	0						
	0						

dmitry washed 1



V. Discussion:

Certain spectroscopic methods can reach extremely high temperatures capable of ionizing most of the elements. They are based on the more energetic atomization (ionization) sources, such as the inductively coupled plasma (ICP), the direct current plasma (DCP), the electric arc, and the electric spark. In this study we investigate the properties of the ICP in the combination with the mass spectroscopy, an instrument called ICP-MS. Temperatures in such an instrument can easily exceed 5000 K. As usual, our interest lies in the limiting characteristics of the ICP-MS, such as LOQ, LOD, and LOL. We calculate them based on our analysis of standard lead samples as well as samples obtained in the environmental setting.

The samples were obtained by elementary school students by wiping window sills in their homes with baby wipes. In this way, three types of samples were obtained: dirty surface, washed surface, and the control baby wipe. Occasionally, the control baby wipes were not given to us, and such is the case with the samples analyzed by Dmitriy and Maggie. The baby wipes were digested according to the EPA method #200.2 with certain necessary variations outlined in separate reports.

The analysis of the samples yielded the results presented in Table 1. The standard solutions were prepared by the individual analysts, and this explains the great variation in the concentration values. The values of concentration in parts per billion were converted to the units used by the City of Chicago Department of Housing and Urban Development in order to determine whether the results of the analysis indicate excessive amount of lead in the housing units. These results are presented in Table 2. From comparing the values in Table 2 with the allowable limits ($500 \mu\text{g Pb}/\text{ft}^2$ on window sill and $800 \mu\text{g Pb}/\text{ft}^2$ on exterior window sill), it is

clear that none of the experimental results exceed the allowable limits: the highest concentration of lead obtained in the analysis was 112.99 $\mu\text{g Pb}/\text{ft}^2$. Therefore, we conclude that none of the elementary school students involved in the analysis are in danger of lead poisoning from window sills residing in their households.

The concentrations of the sample solutions were determined on the basis of the graphed calibration curve (Chart 1). This calibration curve was plotted on the basis of the analysis of the standard solutions prepared by us prior to the analysis. The data points were analyzed by the regression technique, and the best-fit line with r^2 of 0.9941 was obtained (Table 4). The curve was also used to calculate the limiting characteristics of the ICP-MS analyzer. The process of calculation is outlined in Table 5, and the results are presented in Table 6. We see that the ICP-MS instrument can detect 21.41 ppb of lead, quantify 64.23 ppb, and its LOL exceeds 500 ppb. The value of R is 0.997. The limiting characteristics of the ICP-MS instrument are the best in the array of the values obtained for the various instruments in the course of our investigation. Its LOD and LOQ are clearly lower than those of the other instruments, and its turn around time (2 minutes and 20 seconds) is well comparable to those of other instruments and certainly much better than that of the FTIR spectrometer (Table 6).

Generally, the value for LOD for the ICP-MS should be much lower than that experimentally obtained by us. Usually it is reported to be on the order of parts per trillion, yet our analysis yielded parts per billion only. We think that this is due to the specific chemistry of the analytical procedure.

Such low detection limits are possible because the scan in the ICP-MS takes tenth of a second which allows for co-spectra addition and S/N enhancement. Another aspect that

decreases amount of noise and improves detection is minimization of matrix effects. High temperatures in the ICP-MS analyzer atomize most of the refractory species that produce noise in the graphite furnace spectrometer. In addition, the ICP-MS features inert environment which reduces the chance of formation of oxides. Consequently, improved detection limits appear to be the result of increased measurement speed, virtually complete atomization of the sample, and reduction of matrix effects.

Indeed, the peaks appear to be extremely well resolved in the ICP-MS. The only background peaks that we have encountered were at 49.95, 50.94, 120.9, 122.9, and 232.04. The first two are due to the isotopes of vanadium, the third and the fourth peaks represent the isotopes of antimony, and the last peak is the one of thorium. These are the elements commonly encountered in the analysis of lead by the variety of methods, and one of the techniques that resolves them the best is the ICP-MS.

Besides the background isotopes, we certainly obtained the peaks for the four isotopes of lead. These are Pb^{204} , Pb^{206} , Pb^{207} , and Pb^{208} . We are interested in Pb^{207} , for it is the most abundant isotope. Yet, it is instructive to find the ratio of isotopes and plot the data points. Theoretically, they would group together based on the ratio forming clusters. If there is a number of samples, the clusters of points will be spread apart, each sample occupying its own niche. If later on, a second set of samples is run, the newly obtained values can be correlated with the niches. Unfortunately, in our investigation we did not plot the data points, yet the obtained ratios with their means and standard deviations are summarized in Table 3.

Consequently, we think that the ICP-MS technique is greatly superior to all other methods we have evaluated up to date in terms of the limiting characteristics. Besides, the ICP-MS technique is simpler in chemistry of sample preparation than most of the other methods. It

does not require either complexing of lead with dithizone, or addition of any other chemicals.

This greatly reduces the amount of hazardous materials used, and thus simplifies the problem of disposal. The only hazardous material used in the course of analysis is lead, and even its concentration is usually below the hazardous level, as it was determined in our analysis. In addition, the ICP-MS method is very simple, and the use of the apparatus requires little training if it is well calibrated and programmed. We did not go into calibration and programming, so we can not comment on the degree of difficultness of these procedures.

ICP-MS

November 18, 1996

Procedures

I Preparation of solutions:

- ① Pipetting 50 μ l of Th, 50 μ l of Sb, and 50 μ l of V (all solutions are 1000 ppm) into 1L volumetric flask
- ② Pipetting 1.43 mL of 70% Nitric acid into 1L volumetric flask
- ③ Fill it up with ~~de~~ deionized water and mix.
- ④ Preparation of standard Pb solutions:
pipetting appropriate amounts of Pb stock solution of 100 ppm and diluting it with the solution prepared above.
- ⑤ Preparation of samples from digestion:
pipetting 10 mL of digest into 50 mL volumetric flask; rest of the flask was filled with matrix solution.

II Turning on the instrument:

- ① The instrument was set to ~~scanning~~ stand-by mode.
- ② Changed to run mode
- ③ Lighting torch

III Running the experiment:

Plastic hose from pump was placed into the solution. The pump was pumping the solution into ICP-MS. Then the hose was placed into washing solution and sample again.

IV The order in which samples were run:

Lucht's clean rope
standard
unwashed
washed

Meggo's standard *
standard
unwashed

Smithy
washed
standard
unwashed
washed

I (4)

concentration

1 ppb
10 ppb
50 ppb
100 ppb
250 ppb
500 ppb

volume of Pb stock solution

2.5 μ l / 250 ml
10 μ l / 100 ml
25 μ l } / 50 ml
50 μ l
100 μ l
250 μ l

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~~XXXXXXXXXXXXXXXXXXXX~~

Procedure:

1. Preparation of solutions:

- pipette 50 μl of each: Th, Sb, V (from 1000 ppm soln) into 1L volumetric flask
- pipette 1.43 ml of 70% nitric acid into 1L volumetric flask
- fill with DI water. Mix
- Digested Samples:
30 ml of sample into 50ml vol. flask, then fill to the line with matrix soln.

2. Turn on the instrument

- Put in "Run" mode from "Stand-by" mode
- Light the torch

3. Run the experiment

Follow directions on the computer screen

Order of run:

- standards
- Sarah:
 - Standard
 - unwashed
 - washed
- Maggie:
 - Standard
 - Standard
 - unwashed
 - washed
- Dmitriy
 - Standard
 - unwashed
 - washed.

1 ppb	\rightarrow	2.5 μl / 250ml	
10 ppb	\rightarrow	10 μl / 100ml	
50 ppb	\rightarrow	25 μl] / 50ml
100 ppb	\rightarrow	50 μl	
200 ppb	\rightarrow	100 μl	
500 ppb	\rightarrow	250 μl	

Concentrations & dilutions.