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Lead Analysis of Ambient Air Particulates: Interlaboratory Evaluation of EPA Lead Reference Method

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Lead Analysis of Ambient Air Particulates: Interlaboratory Evaluation of EPA Lead Reference Method

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The evaluation of the U. S. Environmental Protection Agency's "Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air" among four laboratories and the quantitation by additional techniques are summarized. Coefficients of variation of 10% for the lead reference method were obtained. Optical emission spectrometry produced data that are statistically indistinguishable from data obtained from the reference atomic absorption spectrometry technique.

The U. S. Environmental Protection Agency (EPA) was required to set a standard for the lead content of ambient air and, consequently, to select suitable collection and analysis techniques for lead.[1,2] Since it has been estimated that nearly 90% of the ambient atmospheric Pb burden results from particulate emissions from mobile sources,[3] the utilization of already existing particulate sampling devices (hi-volume samplers with glass-fiber filters)[4] and analysis of the collected total suspended particulate (TSP) by acid extraction and atomic absorption spectrophotometry were selected as the reference methods.[1] Alternative procedures will eventually be identified as equivalent methods after passing specific tests. Those equivalency tests have recently been proposed.[5]

The purpose of this paper is to present a summary of the important results to date of those investigations surrounding the reference method as well as some alternative quantitation techniques.

Preliminary Studies of the Reference Method

A procedural write-up was prepared by EPA which combined the experiences of two laboratories gained through thousands of Pb analyses of TSP. The procedure consisted of an acid extraction of the particulate, conducted with either boiling nitric acid or with cold nitric acid and ultrasonic energy, and quantitation of the resulting extract from either procedure by flame atomic absorption spectrometry.

The write-up was sent to approximately 100 laboratories engaged in work with air particulate for comments. Slightly less than half of the laboratories responded. Comments received and some limited additional work in one laboratory led to modifications of the original write-up, most importantly the inclusion of an ultrasonic extraction procedure using mixed nitric-hydrochloric acids.

EPA activities to date have not included an evaluation of the sensitivity of parameter variations. Rather, it has consisted of a limited interlaboratory comparison of the HNO_3 write-up applied by several laboratories to split samples of real atmospheric particulate with which they were provided. These data, when subjected to an analysis of variance, provide a reasonable basis for expectations about the performance of this method when it is applied on a large scale. In addition, all four of the laboratories in this interlaboratory comparison analyzed the same HNO_3 extracts using optical emission spectrometers having different excitation sources. One of the laboratories went further subjecting these same extracts to other analytical methods of anodic stripping voltammetry (ASV), flameless atomic absorption (FAA), and spark excitation optical emission spectrometry (SE OES). Finally, in a more limited evaluation, two laboratories tested the application of ultrasonic energy with a mixed HNO_3-HCl extraction medium, quantitating by the same techniques utilized for the HNO_3 extract. The procedures used, the results obtained, and the statistical analyses of these various activities constitute the remainder of this paper.

Interlaboratory Comparison of the Reference Method and Alternative Analytical Techniques

Four laboratories who commented on the write-up volunteered to participate in this portion of the study. All four laboratories received the same materials and instructions which requested their application of the proposed reference procedure using the nitric acid extractions to the material supplied with quantitation via the reference atomic absorption and optical emission spectrometry techniques. Two of these laboratories had previously participated in studies that included blind quality control strips provided by the Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Environmental Protection Agency, Research Triangle Park, NC. These strips had been processed by methods identical to the boiling and ultrasonic HNO_3 reference methods and had shown an average bias from the expected value of

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Table I. Lead data from nitric acid extraction reference procedure: flame atomic absorption spectrometry quantitation. (mg Pb/l)

Extraction	Lab No. (λ[a])	Filter number 1	2	3	4	5	6	7
Boiling Nitric Acid (H)	1 (283 nm)	0.116	10.88	1.42	2.20	0.251	15.08	6.36
		0.154	10.94	1.44	2.16	0.266	15.08	6.40
		0.131	10.93	1.43	2.14	0.258	15.09	6.40
	2 (283 nm)	<0.20	12.90	1.50	2.00	<0.200	14.30	6.00
		<0.20	11.40	1.30	1.50	<0.200	14.30	6.00
		<0.20	11.30	.60	2.20	<0.200	6.00	6.00
	3 (283 nm)	0.20	11.30	1.53	2.21	0.36	15.00	6.96
		0.27	11.32	1.64	2.32	0.44	15.07	7.09
		0.36	11.29	1.72	2.42	0 51	15.18	7.17
	4 (217 nm)	0.20	10.80	1.40	2.10	0.26	15.20	6.50
		0.20	11.00	1.40	2.10	0.29	15.20	6.50
		0.18	10.80	1.40	2.10	0.29	15.10	6.50
Ultrasonified Nitric Acid (R)	1 (283 nm)	0.110	10.40	1.36	2.03	0.221	14.77	6.38
		0.086	10.45	1.37	2.01	0.229	14.65	6.39
		0.094	10.45	1.38	2.05	0.236	14.72	6.37
	2 (283 nm)	0.30	10.00	2.00	2.50	0.50	15.00	< .20
		0.30	10.00	1.70	2.00	0.50	14.00	< .20
		0.50	9.60	1.30	1.90	<0.20	14.00	< .20
	3 (283 nm)	0.21	11.45	1.54	2.25	0.29	15.04	6.78
		0.23	11.58	1.62	2.37	0.37	15.02	6.91
		0.37	11.55	1.69	2.39	0.47	15.16	6.90
	4 (217 nm)	0.20	11.20	1.40	2.20	0.26	15.20	6.5
		0.20	11.30	1.40	2.20	0.26	15.30	6.5
		0.20	11.50	1.40	2.20	0.26	15.10	6.6

[a] λ = wavelength utilized

−1.5% (for 284 strips) and −3.0% (for 40 strips), respectively, over the concentration range of 0 to 2000 μg lead/strip.

All laboratories were provided with portions of exposed glass-fiber filters containing real ambient particulate which had been collected by hi-vol samplers over 24 hr periods. Seven such filters were cut into 8 strips each with physically adjacent strips being paired in order on each filter. Thus, 4 pairs of strips were available from each filter. Pairs were randomly assigned to each of the laboratories to ensure that strip bias was negligible. Each laboratory was requested to extract one strip of each pair with the boiling HNO_3 procedure and the other with the ultrasonic HNO_3 procedure. All extracts were to be analyzed three times in random order by both the reference atomic absorption and optical emission spectrometry techniques. As analyses were to be performed using the laboratory's routine analytical procedures, no instructions were given nor requirements made on the instrument parameters to be utilized in quantitation of the extracts other than those outlined in the reference procedure. The data which resulted from this effort are shown in Tables I and II.

Reference Method

Using analysis of variance techniques,[6] estimates of precision were derived from the data under the assumption that the four participating laboratories were a sample from a larger group of equally competent laboratories.

Precision of a measurement method generally refers to the closeness of repeated measurements when the method is applied to the same chemical sample or different specimens from the same chemically homogeneous material. The two terms used here to describe precision are "*within-laboratory* standard deviation," denoted by σ_r, and "*between-laboratory* standard deviation," denoted by σ_L. The within-laboratory standard deviation is a measure characterizing a single laboratory or operator and is based on repeated observations. On the average, two observations will not differ by more than $\pm 2.77\ \sigma_r$ more than 5% of the time due to chance alone. The between-laboratory standard deviation is a measure of laboratory bias. When combined with the within-laboratory standard deviation, a value is obtained such that on the average, two observations should not differ by more than ±2.77 times this value more than 5% of the time due to chance alone regardless from which laboratory the two observations are taken. All the estimates of precision may be expressed as a percent of the average concentration.

The results of these computations for the HNO_3 reference procedure and optical emission procedures are shown in Tables III and IV. The indicated values were excluded due to analytical difficulties. The tables of precision estimates demonstrate the usual behavior of techniques of this kind where, at concentrations less than approximately 10 times the limiting noise, the noise

Table II. Lead data from nitric acid extraction reference procedure: optical emission spectrometry quantitation. (mg Pb/l)

Extraction	Lab No. (λ)[a]	Filter number 1	2	3	4	5	6	7
Boiling Nitric Acid (H)	1 (405 nm)	0.16	10.76	1.42	2.19	0.26	14.94	6.49
		0.17	10.72	1.43	2.16	0.25	14.97	6.12
		0.12	10.70	1.43	2.09	0.21	14.86	6.23
	2 (220 nm)	0.15	10.81	1.49	2.20	0.26	14.40	6.36
		0.15	10.76	1.48	2.20	0.23	14.30	6.36
		0.15	10.75	1.48	2.21	0.26	14.30	6.36
	2 (220 nm)	0.137	11.40	1.49	2.14	0.264	15.60	7.23
		0.111	11.50	1.50	2.17	0.207	15.70	7.14
		0.134	11.60	1.44	2.15	0.215	15.30	7.31
	4 (283 nm)	0.33	10.00	1.70	2.10	0.32	16.00	6.6
		0.30	10.10	1.70	2.00	0.32	15.80	6.6
Ultrasonified Nitric Acid (R)	1 (405 nm)	0.14	10.31	1.35	2.01	0.27	15.00	6.41
		0.16	10.31	1.35	2.06	0.26	14.93	6.43
		0.15	10.08	1.35	1.96	0.23	14.46	6.40
	2 (220 nm)	0.130	10.36	1.45	2.18	0.26	14.84	6.38
		0.230	10.36	1.45	2.18	0.26	14.87	6.37
		0.120	10.33	1.45	2.20	0.26	14.78	6.36
	3 (220 nm)	0.128	11.80	1.41	2.16	0.207	15.40	6.94
		0.158	11.50	1.40	2.16	0.205	15.60	6.92
		0.150	12.00	1.50	2.15	0.205	15.60	7.09
	4 (283 nm)	0.20	10.40	1.60	1.90	0.32	15.50	6.6
		0.20	10.50	1.60	1.80	0.33	15.70	6.5

[a] λ = wavelength utilized

Table III. Precision estimates of nitric acid extraction reference procedure and flame atomic absorption spectrometry quantitation. (Numbers in parentheses are ratios of the precision estimates expressed as a percent of the average.)

Filter number	Concentration average (mg Pb/l)	Boiling Nitric Acid							Ultrasonic				
		$\hat{\sigma}_L$[a]	(%CV_L)	$\hat{\sigma}_e$[a]	(%CV_e)	$\hat{\sigma}_y$[a]	(%CV_y)	$\hat{\sigma}_L$	(%CV_L)	$\hat{\sigma}_e$	(%CV_e)	$\hat{\sigma}_y$	(%CV_y)
1	0.218	0.06	(28)	0.04	(18)	0.07	(32)	0.10	(46)	0.07	(32)	0.13	(60)
5	0.305	0.10	(33)	0.04	(13)	0.11	(36)	0.06	(20)	0.09	(30)	0.11	(36)
3	1.456	0.15	(10)	0.24	(16)	0.28	(19)	0.11	(7)	0.18	(12)	0.21	(14)
4	2.148	0.13	(6)	0.19	(9)	0.23	(11)	0.08	(4)	0.16	(8)	0.18	(8)
7	6.550	0.44	(7)	0.05	(1)	0.45	(7)	0.25	(4)	0.06[b]	(1)	0.25	(4)
2	11.011	0.38	(3)	0.45	(4)	0.59	(5)	0.77	(7)	0.14	(1)	0.78	(7)
6	14.897	0.36	(2)	0.06[c]	(.4)	0.37	(2)	0.35	(2)	0.30	(2)	0.46	(3)

[a] $\hat{\sigma}_L$ = Between-laboratory standard deviation.
$\hat{\sigma}_e$ = Within-laboratory standard deviation.
$\hat{\sigma}_y = (\hat{\sigma}_L^2 + \hat{\sigma}_e^2)^{1/2}$
[b] Laboratory 2 was excluded from the analysis.
[c] The value 6.0 μg/ml reported by laboratory 2 was excluded.

becomes an ever increasing part of the determination. This nearly constant limit can be estimated by determining the standard deviation of repeated measurements on a given solution for a series of solutions increasingly more dilute in the constituent of interest. In both of these tables it can be seen that the limiting noise is on the order of 0.1 mg/l, implying that limiting noise is an important part of the lowest two filter concentrations. Discarding the two lowest concentrations and averaging the coefficients of variation over the remaining five concentration levels gives a rough idea of the degree of precision which could be anticipated from using the reference HNO_3 method. In comparing individual results from a single laboratory, one can anticipate that, on the average, two observations will not differ by more than 17% of the concentration level more than 5% of the time due to chance alone. In dealing with averages, this value is decreased by a factor of $1/\sqrt{n}$. For example, two averages, each based on 16 observations, will not differ by more than ±4.25% of the concentration level. When comparing individual observations between laboratories, this value is increased to 28%. Average coefficients of variation from the optical emission techniques are similar though slightly smaller. Statistical tests based on the analysis of variance indicate that differences between the methods used to extract the Pb and differences between the methods used to quantitate the Pb are not significant.

Alternative Analytical and Mixed Acid Extraction Techniques

Two laboratories participated in this study. Each laboratory received strips from two different hi-volume filters, with nominal Pb concentrations of 7.5 mg/l and 2.0 mg/l, to assess whether or not the addition of hydrochloric acid to the ultrasonic extraction medium would alter the amount of Pb extracted. The HNO_3 was replaced by a mixed acid of similar nitric acid concentration and a HNO_3-HCl ratio of two.[5] Though more limited in scope and materials, the procedure was carried out in a fashion analogous to the original study and with similar conclusions. Based on an analysis of variance, the addition of HCl does not alter the amount of Pb extracted when compared to the results of the reference method. This is concluded with reference to a large body of laboratories of which the two participants are a sample. On the average it was determined that no two individual extracts should differ by more than 6% of the concentration level about 5% of the time, regardless of which laboratory makes the measurements and independent of the extraction method used.

One laboratory analyzed the extracts from both interlaboratory studies via three other techniques whose parameters are outlined in Table V. The instruments were calibrated using solutions whose acid composition matched those of the extracted samples.

The results from the reference atomic absorption procedure were not statistically different from this laboratory's results of the inductively coupled argon plasma optical emission spectroscopy (ICAP OES) for all extraction medium and filters tested. The other techniques in this laboratory's hands, however, were distinguishable from the above in that they were all less precise than the flame AA and the ICAP OES. Typical coefficients of variation for repeating a single measurement were 2% for ICAP OES, 3% for flame AA, 6% for flameless AA, 10% for ASV and 15% for spark excited OES.

Overall Conclusions

Results from this study indicate the

Table IV. Precision estimates of nitric acid extraction reference procedure and optical emission spectroscopy quantitation. (Numbers in parentheses are ratios of the precision estimates expressed as a percent of the average.)

Filter number	Concentration average (mg Pb/l)	Boiling Nitric Acid						Ultrasonic					
		$\hat{\sigma}_L$[a]	(%CV_L)	$\hat{\sigma}_e$[a]	(%CV_e)	$\hat{\sigma}_y$[a]	(%CV_y)	$\hat{\sigma}_L$[a]	(%CV_L)	$\hat{\sigma}_e$[a]	(%CV_e)	$\hat{\sigma}_y$[a]	(%CV_y)
1	0.175	0.08	(46)	0.02	(11)	0.07	(40)	0.01	(6)	0.03	(17)	0.04	(23)
5	0.263	0.03	(11)	0.02	(8)	0.04	(15)	0.04	(15)	0.03	(11)	0.06	(23)
3	1.485	0.11	(7)	0.02	(1)	0.11	(7)	0.09	(6)	0.03	(2)	0.10	(7)
4	2.095	0.05	(2)	0.03	(1)	0.06	(3)	0.14	(7)	0.04	(2)	0.15	(7)
7	6.598	0.44	(7)	0.11	(2)	0.46	(7)	0.29	(4)	0.05	(1)	0.30	(4)
2	10.732	0.56	(5)	0.06	(1)	0.57	(5)	0.74	(7)	0.15	(1)	0.76	(7)
6	15.156	0.67	(4)	0.13	(1)	0.68	(4)	0.35	(2)	0.23	(2)	0.42	(3)

[a] $\hat{\sigma}_L$ = Between-laboratory standard deviation.
$\hat{\sigma}_e$ = Within-laboratory standard deviation.
$\hat{\sigma}_y = (\hat{\sigma}_L^2 + \hat{\sigma}_e^2)^{1/2}$

Table V. Analytical conditions of candidate methods.

Heated vaporization (flameless) atomic absorption spectroscopy			
Spectrophotometer	Perkin-Elmer Model 403 atomic absorption[a]	Lamp	Pb EDL at 9 watts
Analytical Line	283.3 nm	Slit width	0.7 nm
Atomizer	Perkin-Elmer Heated Atomizer Model 2100	Purge gas	Ar at 50 units and 20 psig
Dry	100°C for 30 sec	Atomization tube	Graphite
Char	500°C for 20 sec	Cooling water	1.5 l/min
Atomize	2500°C for 10 sec		
Injection	Perkin-Elmer Automatic Sampler-1	Aliquot	20 µl
Sample Matrix	0.225 M HNO_3		
Spark excitation optical emission spectroscopy			
Spectrometer	Applied Research Laboratory Model 9500 Production Control Quantometer[a]	Source	High Voltage Spark
Analytical Line	283.3 nm	Amperage	4.0
Entrance Slit	25 µm	Upper electrode	ASTM C 1
Exit Slit	75 µm	Lower rotrode	ASTM D 5
Soaking Time	30 sec	Electrode gap	3 mm
Pre-sparking Time	12 sec	Integration time	36 sec
Sample Matrix	4.5 M HNO_3, 2% LiCl, 100 mg In/l		
Anodic stripping voltammetry			
Analyzer	Environmental Sciences Associates Model 2014 Multiple Anodic Stripping Analyzer[a]	Plating Time	15 min
Sweep Rate	+ 82.5 and + 60 mV/sec	Plating Potential	−900 mV
Sweep Hold	−20 mV		
Purge Gas	N_2 at 5 psig	Initial Potential	−900 mV
Sample Matrix	1 M $NaC_2H_3O_2$ or 1 M $NaC_2H_3O_2$ and 0.2 M NaCl at pH 5.4	Sample Aliquot	50 µl

[a] Mention of commercial or trade names does not constitute an endorsement or recommendation for use.

following: extraction of lead from atmospheric particulate occurs equally well under mild and severe oxidizing conditions in nitric acid or mixed nitric–hydrochloric acids; that from all the laboratories which may use the method as written, the effect due to extraction technique is not significant with regard to bias and precision; the precision of data generated by any given laboratory utilizing the reference flame atomic absorption method is such that two measurements are expected to differ by more than ±17% only 5% of the time due to chance alone, and ±28% when measurements are compared between laboratories. Modern optical emission spectrometry produces results of similar quality to flame atomic absorption. For samples collected and prepared by the lead reference procedure, it is expected that no two measurements should differ by more than 28% even if the measurements are from different laboratories using different analytical techniques as long as the concentrations are larger than 0.5 µg Pb/m^3 air sampled.

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